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Membrane Separations, Extractions and Precipitations in Aqueous Solutions for CO$_2$ Mineralisation

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Preface

I would like to start by expressing my deepest gratitude to my supervisor, Prof. Ron Zevenhoven at the Thermal and Flow Engineering Laboratory at Åbo Akademi University. Without him, this Thesis would never have been completed in time. He has always supported, answered to questions, commented drafts and being a supervisor standing there when needed. It has for sure been a pleasure to work with and for him. Together, we also managed to financially arrange for this thesis going on by writing quite many applications for funding - and receiving sufficiently many. This leads me to express my deepest gratitude to all the foundations and projects that have supported and financed this thesis; K. H. Renlund foundation in 2013, Åbo Akademi and CLEEN/CLIC Oy CCSP project with specific support from Nordkalk Oy AB in 2014-2016, Ella and Georg Ehrnrooth foundation in 2015-2019, Åbo Akademi Foundation in 2017, the Society of Swedish Literature in Finland with funding from Ingrid, Margit och Henrik Höijers donationsfond II in 2019 and Walter and Lisi Wahl foundation in 2017-2019. Finally, the work was also supported by the Åbo Akademi University Rector's scholarship in 2019 to bring this work to the end.

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Turku in September 2019

Evelina Koivisto

Svensk sammanfattning

De globala koldioxidutsläppen har ökat snabbt sedan den industriella revolutionens inledning på 1700-talet. Detta har lett till ökade koldioxidkoncentrationer i atmosfären, vilket i sin tur värmer upp atmosfären som ett resultat av att koldioxid (CO_2) kan absorbera värme. Uppvärmning av atmosfären har skett genom tiderna många gånger, så det är inte ett nytt fenomen på jorden. Problemet med den globala uppvärmningen idag är emellertid att det nu går mycket snabbare. Den årliga ökningen av koldioxid i atmosfären är cirka 100 gånger snabbare idag än det var senast när naturlig uppvärmning inträffade för ungefär 300 000 år sedan.

Olika åtaganden, såsom Kyotoprotokollet, syftar till att minska växthusgaserna till specifika nivåer under olika åtagandeperioder. Målet för EU är att minska utsläppen med 20% jämfört med utsläppen av CO_2-ekv. under 1990. På längre sikt har Finland målet att nå ett kolneutralt samhälle. Finland är på väg dit, men målet är utmanande att nå. Att hitta alternativ för att minska utsläppen ytterligare eller utveckla alternativ för koldioxidlagring är dock av största vikt i detta sammanhang.

Det enda alternativet för avskiljning och lagring av koldioxid, CCS, i Finland är genom CO_2-mineralisering. Ett alternativ for detta har utvecklats vid Åbo Akademi under de senaste åren, den så kallade *ÅA-route*. I processen extraheras magnesium från magnesiumsilikater genom en termisk reaktion vid ≈ 400 °C, i närvaro av ammoniumsulfat som tjänar som flussalt. Det extraherade magnesiumet fälls därefter ut som magnesiumhydroxid genom tillsats av ammoniak, vilket frigörs i den termiska reaktionen. Magnesiumhydroxid kommer slutligen att reagera med rökgas i en trycksatt fluidiserad bäddreaktor vid 500 °C och ett tryck på 20 bar för att erhålla magnesiumkarbonat, en stabil förening som kan lagra CO_2 på ett säkert sätt. Ett alternativ till den konventionella ÅA *route* är att processen sker i vattenlösningar med ett initialt extraktionssteg med

ammoniumvätesulfat och/eller ammoniumsulfat närvarande. Den slutliga karboneringen sker också i vattenlösning under tillsats av koldioxidgas och ammoniak.

Konceptet för *ÅA route* har studerats i stor utsträckning men effektiviseringen och återvinningen av ingående kemikalier måste fortfarande utvecklas. Denna avhandling fokuserar på flera olika metoder, bl.a. separering av överskott av vatten efter upplösning (omvänd osmos), utfällning och separation av utfällda produkter i en enhet (lutande sedimentationstankar), extraktion av magnesium från sidostenar från gruvdrift (termisk extraktion eller extraktion i vattenlösning), separering av två salter från varandra (elektrodialys med monovalenta jonselektiva membran) eller produktion av syror och baser från ingående kemikalier, vilka sedan kan användas igen i processen (elektrodialys med bipolära membran).

Två av de undersökta bergarterna, vilka båda innehöll signifikanta mängder av serpentin, resulterade i bindningskapaciteter av 292 respektive 260 kg CO_2 /ton berg vid extraktion i vattenlösning. Kapaciteten hos samma bergarter var något lägre vid applicering av ett termiskt extraktionssteg; 240 respektive 207 kg CO_2 /ton berg, för serpentinit från Hitura och Vammala. Dessa resultat indikerar att extraktion i vattenlösning verkar ha bättre potential än det termiska extraktionssteget, åtminstone under de undersökta betingelserna.

Försök att separera magnesium- och järnfällningar i en lutande sedimentationstank gjordes för att göra *ÅA route* mer kontinuerlig. Magnesium och järn måste fällas ut stegvis och separeras från processflödet i den konventionella ÅA route. Partikelstorleken hos båda fällningarna visade sig vara mycket liten enligt SEM-analyser, vilket påverkade sedimenteringshastigheten negativt. Sedimenteringshastigheten för magnesiumhydrokarbonat var emellertid snabbare. Detta bekräftades också av SEM-bilder som visade att magnesiumhydrokarbonaterna hade större partikelstorlek, vilket också påverkade sedimenteringshastigheten positivt. Kontinuerlig sedimentering och separering var fortfarande svår att uppnå med den valda uppställningen, även vid låg pumphastighet som användes för att minimera turbulens.

Ett omvänt osmos-membran användes för att försöka separera vatten från processflödet. Den vattenmängd som måste användas för att få all reagerad bergart sköljd ur ugnens reagenskärl vid termisk extraktion kan vara något för stor för senare processteg. Därför skulle omvänd osmos kunna vara ett alternativ

för att kontrollera vattenmängden. Det osmotiska trycket är typiskt 23 bar i en lösning efter utvinningssteget där magnesium extraheras. Detta måste övervinnas innan någon separation kan äga rum. Inga signifikanta separationer uppnåddes, även om justeringar av permeatströmmen som ersattes av nedströms vattenhaltiga lösningar gjordes. Med det studerade membranet kommer RO inte att vara ett alternativ för att styra vattenmängderna i *ÅA route*.

En uppställning av monovalent jonselektiv membranelektrodialys byggdes upp vid laboratoriet och användes för att se om separationen av ammoniumsulfat från ammoniumvätesulfat kunde uppnås. Från början var de respektive avdelningarnas bredd 40 mm. Jonselektiva elektroder (ISE) användes för att mäta förändringen i ammoniumjoner under provningarna. Dessa mätningar visar att nästan 100% av ammoniaken transporterades från avdelningen för inloppet till avdelningen där ammoniumsulfat uppsamlades. Genom att jämföra blandningsexergin med ingående exergi visades det emellertid att den ingående exergin (dvs elektriciteten) som behövdes jämfört med i vilken utsträckning jonerna separerades var i storleksordningen flera tusen gånger större. En förändring i uppställningen blev därför att begränsa avståndet mellan avdelningarna till 18 mm för att övervinna en del av det elektriska motståndet i lösningarna. Detta avstånd användes för fyra olika uppställningar med användning av bipolära membran. De bipolära membranen anordnades på olika sätt tillsammans med monovalenta membran, med syftet att producera sura och alkaliska lösningar som kan användas för ytterligare extraktions- respektive karboneringssteg.

Energibehovet för olika typer av test varierade från 1,7 till 350 MJ/kg separerad NH_4^+. De två bästa fallen, antingen en uppställning placerad efter extraktionssteget eller efter karboneringssteget, bör studeras ytterligare. Behovet av att köra experiment i en kommersiell uppställning i laboratorieskala med tillräckligt smalt avstånd mellan avdelningarna och fler cellpar än vad som användes här, är nu väsentlig. Finansiering för inköp av en kommersiell uppsättning kunde inte göras vid tidpunkten för arbetet med denna avhandling. Användning av en kommersiell uppställning i laboratorieskala kan ge bättre indikationer på lämpligheten för de enskilda uppställningarna och kan också ge mer exakta siffror av den exergi (el) som behövs för elektrodialyssteget. Separationen i smalare avdelningar med fler cellpar kommer fortfarande att använda två elektroder så den energi som används för elektrolys av vatten ökar

inte. En signifikant lägre exergiingång kommer sannolikt att vara fallet där flera upprepande enheter används.

Resultaten från alla metoder som används i denna avhandling tyder på att det alternativ för *ÅA route* där processtegen hålls i vattenlösning verkar vara mer gynnsam även när det gäller effektivisering av processen och regenerering av det använda flussaltet.

Abstract

The global carbon dioxide (CO_2) emissions have been growing rapidly since the industrial revolution starting in the 18th century. This has led to increasing CO_2 concentrations in the atmosphere, which in turn heats up the atmosphere as a result of CO_2 being able to absorb heat. Heating of the atmosphere has naturally taken place many times, so it is not a new feature on Earth. The problem with the global heating today, however, is that it apparently goes much faster. The annual increase of CO_2 in the atmosphere is about 100 times faster today than it was the last time when natural heating occurred, around 300 000 years ago.

Different commitments, like the Kyoto Protocol, have the aim to decrease the greenhouse gases to certain levels in different commitment periods. The target for EU by 2020 is to reduce the emissions by 20%, compared to the CO_2-eq. emissions measured in 1990. On a longer-term basis, Finland has the target to reach a carbon neutral society. Finland is on its way, but this target will be challenging to reach. However, finding options to decrease emissions further or develop options for CO_2 storage is of highest importance in this context.

The only option for carbon capture and storage, CCS, in Finland is through CO_2 mineralisation. An option has been developed at Åbo Akademi University during the last years, often referred to as the ÅA route. The process extracts magnesium from magnesium silicates through a thermal reaction at ≈ 400 °C, in the presence of ammonium sulphate serving as flux salt. The extracted magnesium is thereafter precipitated as magnesium hydroxide by the addition of ammonia, which is released in the thermal reaction. Magnesium hydroxide will finally react with flue gas in a pressurized fluidized bed reactor at 500 °C and a pressure of 20 bar to obtain magnesium carbonate, a stable compound that enables storing CO_2 safely. As an alternative ÅA route, the process could take place in aqueous solutions with an initial extraction step where ammonium bisulphate and/or ammonium

sulphate are present. The final carbonation would also take place in aqueous solution inserting CO_2 gas and ammonia.

The concept for the ÅA route is extensively studied but the streamlining and the generation of input chemicals must still be established. This thesis focused on several different methods, i.e. the removal of excess water after dissolution (reverse osmosis), precipitation and separation of precipitated products in one unit (inclined settlers), extraction of magnesium from overburden rock from mining activities (thermal solid/solid or aqueous extraction), separation of two salts from each other (electrodialysis with monovalent ion selective membranes), or producing acid and bases from input chemicals used, which could be used in the process again (bipolar membrane electrodialysis).

Two of the studied rocks, both containing significant amounts of serpentinite, resulted in CO_2 binding capacities of 292 and 260 kg CO_2/ton rock, respectively, in aqueous solution extraction. The capacities for the same rock types were somewhat lower when applying the thermal solid/solid extraction step; 240 and 207 kg CO_2/ton rock, for Hitura serpentinite and Vammala serpentinite, respectively. This indicates that the aqueous extraction route seems to have a better potential than the thermal solid/solid extraction step, at least under the studied conditions.

Attempts to separate magnesium and iron precipitates in an inclined tube settler were made in order to make the ÅA route more continuous. Magnesium and iron must be stepwise precipitated and separated from the process stream in the conventional ÅA route. The particle size of both precipitates was found to be very small according to SEM analyses, which affected the settling rate negatively. The settling rate for magnesium hydrocarbonates, however, was more rapid. This was confirmed by SEM images showing that the magnesium hydrocarbonates had a larger particle size, which also affected the settling rate positively. Continuous sedimentation and separation was still hard to achieve with the chosen set-up, even at low pump speed as to avoid too turbulent conditions.

A reverse osmosis membrane was used in order to try to separate water from the process stream. Some excess water must be used in order get all reacted rock washed out from the kiln as the thermal solid/solid route is applied. Reverse osmosis might therefore be an option to control the water volumes. The osmotic pressure of typically 23 bar in a solution after the magnesium extraction step must be overcome before any separation can take place. No significant separations

were achieved, even with adjustments of the permeate stream composition replaced by downstream aqueous solutions. At least with the available membrane, RO will not be an option for controlling the amount of water used in the ÅA route.

An in-house built set-up of monovalent ion selective membrane electrodialysis was used to see if the separation of ammonium sulphate from ammonium bisulphate could be achieved. Initially, the compartment width was 40 mm. Ion selective electrode analyses (ISE) were done to measure the change in ammonium ions during the tests. These measurements show that almost 100% of the ammonia was transported from the feed compartment to the compartment where ammonium sulphate was collected. By comparing the exergy of mixing with the input exergy, however, it was shown that the input exergy (i.e. electricity) needed compared to what extent the ions were separated was in a magnitude of several thousand larger. One change in the set-up was therefore to narrow the compartment distance to 18 mm to overcome part of the electrical resistance in the solutions. This distance was used for four different set-ups using bipolar membranes. The bipolar membranes were arranged in different ways together with monovalent membranes, with the aim to produce acidic and alkaline solutions that may be used for further extraction and carbonation steps, respectively.

The energy demands for different type of tests were ranging from 1.7 to 350 MJ/kg separated NH_4^+. The two best cases, either a set-up placed after the extraction step or after the carbonation step, respectively, should be further studied. The need for running experiments in a commercial lab-scale set-up with sufficiently narrow compartment width and more repeating units than was used here is now substantial. No funding could do far be made available for purchase of a commercial set-up at the time of writing this thesis. Using a commercial lab-scale set-up will give better indications of the suitability of the individual set-ups and could also give more accurate numbers of the exergy (electricity) input needed for the electrodialysis step. The separation in more and more narrow repeating units will still use two electrodes so the energy used for the water electrolysis will not increase. A significantly lower exergy input will most likely be the case where more repeating units are used.

The results from all methods used in this thesis indicate that the all-aqueous variety of the ÅA route seems to be more favorable also when it comes to the streamlining of the process and the regeneration of the flux salt used.

ABSTRACT

Contribution of the Author and List of Publications

This section presents the articles of this thesis. The introduction will give a background to the topic and put the work made in this thesis into a wider context. The author of this thesis performed and developed the experimental work as well as the theoretical parts of all the articles and wrote the first draft of them, except for paper III that was mainly written and produced by R. Erlund.

I. **KOIVISTO, E**. and ZEVENHOVEN, R. (2014). Inclined Settlers for Separation of Magnesium Hydroxide and Iron Oxides for Mineral Carbonation. In *Proceedings of 27th international conference on efficiency, cost, optimization, simulation and environmental impact of energy systems (ECOS2014)*, Turku, Finland, June 2014, Paper 309 (peer-reviewed).

II. **KOIVISTO, E.**, ERLUND, R. FAGERHOLM, M. and ZEVENHOVEN, R. (2016). Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 1: Thermal solid/solid extraction. *Hydrometallurgy,* 166, 222-228.

III. ERLUND, R., **KOIVISTO, E.**, FAGERHOLM, M. and ZEVENHOVEN, R. (2016). Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 2: Aqueous solution extraction. *Hydrometallurgy,* 166, 229-236.

IV. **KOIVISTO, E.** and ZEVENHOVEN, R. (2017). Methods for recovery and re-use of additive chemicals during CO_2 mineralisation. *Journal of Water Process Engineering,* 20, 61-70. Originally; Poster presentation at the 1st International Conference on Sustainable Water Processing, Sitges, Spain, September 11-14, 2016.

V.   **KOIVISTO, E**. and ZEVENHOVEN, R. (2018). Membrane separation of ammonium bisulfate from ammonium sulfate in aqueous solutions for CO_2 mineralisation. *Geosciences,* 8(4), 123 (open access). Originally; In Proceedings of 30th international conference on efficiency, cost, optimization, simulation and environmental impact of energy systems (ECOS2017), San Diego, USA, July 2017, Paper 331 (peer-reviewed).

VI.   **KOIVISTO, E**. and ZEVENHOVEN, R. (2019). Energy use of flux salt recovery using bipolar membrane electrodialysis for a CO_2 mineralisation process. *Entropy* (Special issue Thermodynamics of Sustainability), 21, 395 (open access).

Related Publications

ZEVENHOVEN, R., SLOTTE, M., **KOIVISTO, E.** and ERLUND, R. (2018). Serpentinite carbonation using the Åbo Akademi routes – status update. *Presented (by RZ) at ACEME2018,* Newcastle NSW, Australia, March 10-14, 2018.

ZEVENHOVEN, R., SLOTTE, M., **KOIVISTO, E.** and ERLUND, R. (2017). Serpentinite carbonation process routes and integration in industry. *Energy Technology* 5(6), 945-954 (open access).

KOIVISTO, E. (2013). *Utilization Potential of Iron Oxide By-product from Serpentinite Carbonation.* MSc Thesis. Åbo Akademi University, Turku, Finland/Luleå University of Technology, Luleå, Sweden.

CLEEN/CLIC Oy CCSP Deliverables

ZEVENHOVEN, R., **KOIVISTO, E.,** ERLUND, R., SLOTTE, M. AND FAGERHOLM, M. (2016). *Updated cost evaluation including a feasible plant design for large-scale magnesium silicate carbonation at a lime kiln.* Deliverable D556; CLIC Innovation Oy Carbon Capture and Storage Program (CCSP).

KOIVISTO, E., ERLUND, R., ZEVENHOVEN, R. AND FAGERHOLM, M. (2016). *Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation.* Deliverable D555; CLIC Innovation Oy Carbon Capture and Storage Program (CCSP).

ERLUND, R., **KOIVISTO, E.,** MATTILA, H.-P., ZEVENHOVEN, R. AND FAGERHOLM, M. (2015). *Process for upgrading diopside-based rock for lime kiln gas CO_2 carbonation.* Deliverable D548; CLEEN CCSP WP 5.2.2.

List of Abbreviations and Symbols

Abbreviations

AAS	Atomic Absorption Spectrometry
AS	ammonium sulphate
ABS	ammonium bisulphate
ACE	average current efficiency
AMS	monovalent anionic selective membrane
BECCS	bioenergy with carbon capture and storage
BPM	bipolar membrane
BPMED	bipolar membrane electrodialysis
CCS	carbon capture and storage
CCSM	carbon capture and storage by mineralisation
CCSP	carbon capture and storage program
CCU	carbon capture and utilisation
CE	current efficiency
CMS	monovalent cationic selective membrane
ED	electrodialysis
FO	forward osmosis
GHG	greenhouse gas
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISE	Ion-Selective Electrode
IPCC	Intergovernmental Panel on Climate Change
LCA	life cycle analysis
NET	negative emissions technology
PCC	precipitated calcium carbonate
PFBR	pressurised fluidised bed reactor
RO	reverse osmosis
S	serpentinite
SEM/EDX	Scanning Electron Microscopy/Energy-Dispersive X-ray
UNFCCC	United Nations Framework Convention on Climate Change

XRD	X-Ray Diffraction
ÅA	Åbo Akademi University

Chemical compounds and minerals

Ammonia	NH_3
Ammonium	NH_4^+
Ammonium bisulphate	NH_4HSO_4
Ammonium nitrate	NH_4NO_3
Ammonium sulphate	$(NH_4)_2SO_4$
Bisulphate	HSO_4^-
Calcium carbonate, calcite	$CaCO_3$
Carbon dioxide	CO_2
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Iron (oxy)hydroxide	$FeOOH, Fe(OH)_2, Fe(OH)_3$
Lansfordite	$MgCO_3 \cdot 5H_2O$
Magnesium carbonate, magnesite	$MgCO_3$
Magnesium hydroxide	$Mg(OH)_2$
Magnetite	Fe_3O_4
Nesquehonite	$MgCO_3 \cdot 3H_2O$
Olivine	Mg_2SiO_4
Serpentinite	$(Fe,Mg)_3Si_2O_5(OH)_4$
Sulphate	SO_4^{2-}
Sulphuric acid	H_2SO_4

Symbols

c	concentration, mol/dm^3
Ex_{in}	exergy input, J
ΔEx_{mix}	exergy of mixing, J
I	electric current, A (C/s)
M	molarity, mol/dm^3
n_{if}	molar amount of i in feed
n_{ip}	molar amount of i in product
$\prod$	osmotic pressure, atm
P_{in}	power input, J
R	gas constant
$\sum p$	sum of products
$\sum f$	sum of feed
T_0	temperature of surroundings, K
T	temperature, K
U	voltage, V (J/s)
x_i	molar fraction of species i

Table of Contents

1. Introduction

1.1. Atmospheric CO_2 Concentrations Over Time

Global CO_2 emissions have been growing rapidly since the onset of the industrial revolution in the 18th century. This has led to increasing CO_2 concentrations in the atmosphere, which in turn causes heating of the atmosphere and hydrosphere as a result of the heat absorbing capacity of CO_2. The heat absorbed from radiation while the sun warms up the land and oceans will gradually be released making the Earth's atmosphere warmer (Ritchie & Roser, 2017).

Increased CO_2 concentrations in the atmosphere will affect both land and marine biodiversity. The pH of the oceans has decreased from 8.2 to 8.1 since the start of the industrial revolution. This acidification has effects on the marine life, since the ability of building shell and skeleton is reliant on the ability to extract calcium from seawater (Lindsay, 2018).

Heating of the atmosphere has naturally taken place many times, so it is not a new feature on Earth. The problem with the global heating today, however, is that it apparently goes much faster. The annual increase of CO_2 in the atmosphere is about 100 times faster today than it was the last time when natural heating occurred, around 300 000 years ago (Lindsay, 2018). The rapid change is mainly a result of fossil fuels burnt to give energy, which releases carbon and leads to the increase in CO_2 concentrations in the atmosphere. Figure 1 illustrates the rapid increase of CO_2 in the atmosphere the last years, also showing the natural occurring changes in CO_2 concentrations during the last 800 000 years.
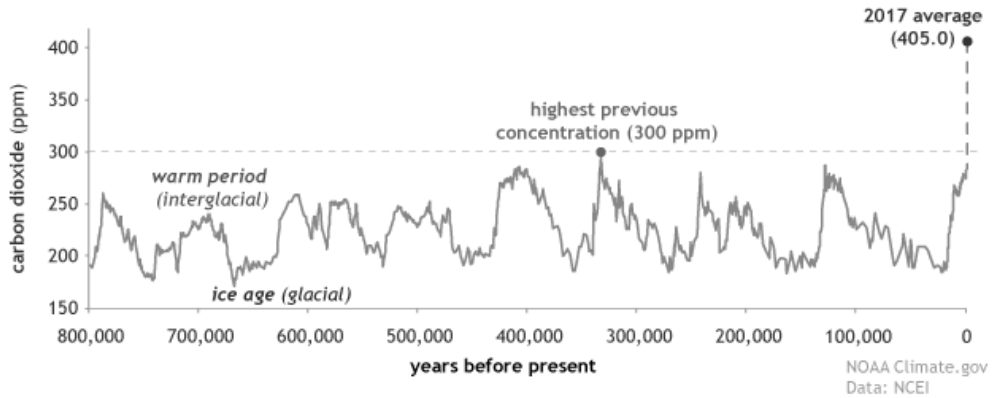
Figure 1.CO_2 concentration in ppm in the atmosphere during the past 800 000 years (Lindsay, 2018).

CO_2, being the largest contributor of the greenhouse gases (GHG), will thus contribute most to the global warming (IPCC, 2005). CO_2, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride are the six main greenhouse gases (UNFCCC, 2019). In order to curb and reverse the trend of human activities contributing to the global warming there is a need for all countries to deal urgently and actively with the impacts of climate change. This thesis presents the results of practical studies designed to contribute, if only in a small way, to the huge task of finding sustainable ways to help control CO_2 emissions.

1.2.   The Paris Agreement and Kyoto Protocol

The Paris Agreement came into force in late 2016 with the aim of keeping the global temperature rise well below 2 degrees Celsius above pre-industrial levels. Further efforts should also be made to limit the temperature increase to 1.5 degrees Celsius. This should be done by a binding commitment from all nations together to reach this target and by providing enhanced support to assist developing countries (UNFCCC, 2018). Figure 2 illustrates different temperature scenarios if the aim of 1.5 °C or 2 °C is kept as a target, or if current pledges, current policies or *no* climate policies are followed, respectively (Ritchie & Roser, 2017).
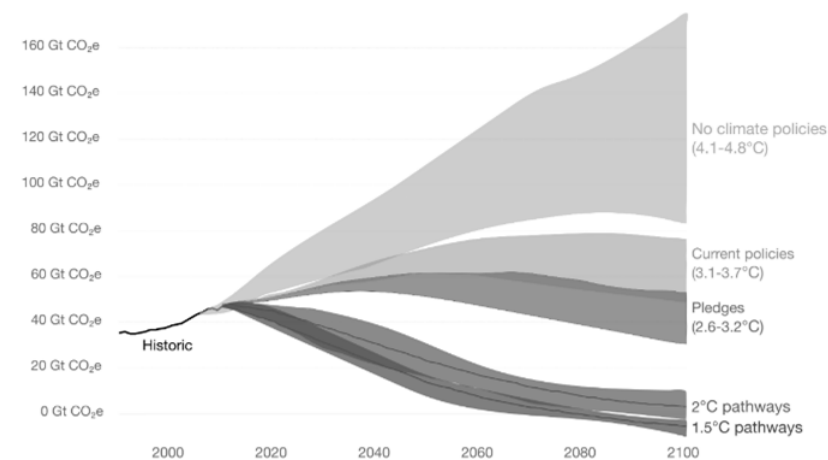
Figure 2. Scenarios for the greenhouse gas emission for five different policy regimes (Ritchie & Roser, 2017).

The Kyoto Protocol was adopted in 1997 for which the first phase of commitments started in 2008 and ended in 2012. The second period started in 2013 and will end in 2020. The aim of the protocol is to set emission reduction targets and commit the parties of the United Nations Framework Convention on Climate Change (UNFCCC) to follow these. Targets have been set higher for the developed industrialised countries, since they have already contributed with GHG emissions from industrial activities for over 150 years. In short, the first commitment period aimed at reducing GHG emissions to levels of 5 % less compared to emission levels in 1990. During the second commitment period, the target is to reduce the emissions by 18 % below levels in 1990. These values are average values and the numbers and compositions of countries are different from the first to the second period. Canada withdrew from the agreement in 2012 (UNFCCC, 2019).

1.3. CO_2 Emissions and Targets in Finland

Finland realised its stated objectives for the first commitment of the Kyoto protocol, which required that the CO_2-eq. emissions should be lowered to the 1990 levels. The second commitment implies compliance with a general EU target for 2020 of reducing emissions by 20% compared to the levels in 1990. Figure 3 shows how the CO_2-eq. emissions have decreased in Finland since 1990.
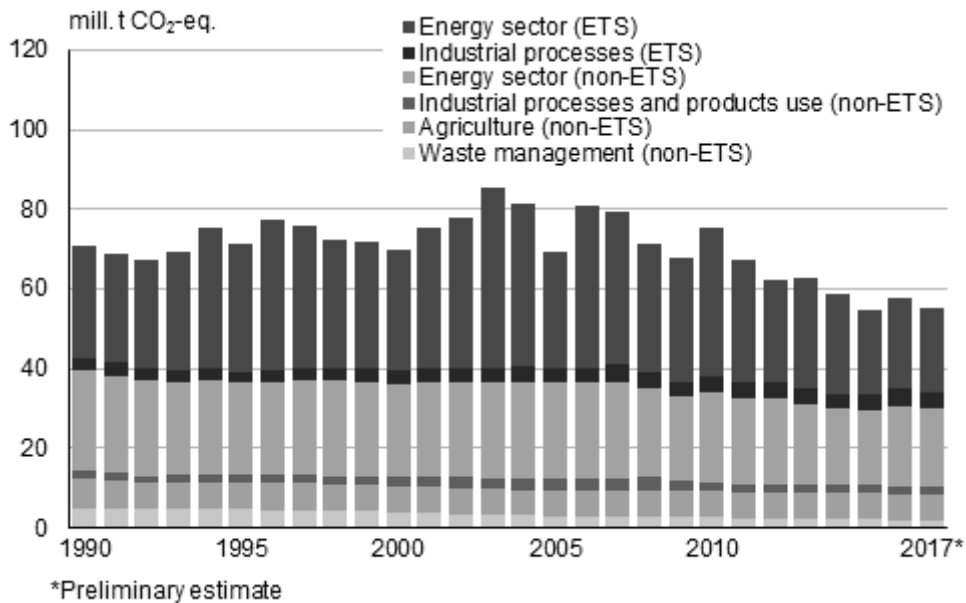
Figure 3. CO- eq emissions from 1990 to 2017 (OSF, 2018).

The total emissions in CO_2-eq. were 55.4 million tons in Finland in 2017. This is 15.9 million tons, or approximately 22%, less than the emissions in 1990. The decrease from 2016 to 2017, for example was almost 5 %. The decrease was mainly the result of the increased share of biofuels while the fossil fuels consumption decreased in the traffic sector. The target of the second commitment in the Kyoto Protocol has thus also been reached in Finland. Although this represents a good start, there are still possibilities and opportunities for further actions in decreasing CO_2 emissions, as well as those from other GHGs. From Figure 3 it can be seen that emissions have decreased in all sectors from 2016 to 2017, indicating that effective action has been implemented in several areas in order to reduce Finnish CO_2 emissions. However, it should be noted that data for 2017 concerning land use, land-use change and forestry sector are incomplete and therefore not published at the date of writing (OSF, 2018).

The second commitment period of the Kyoto protocol will, as mentioned above, end in 2020. On a longer-term basis, the target for Finland is a carbon neutral society. Finland is at present progressing towards this goal, but attaining it will be challenging. However, finding options to decrease emissions further or develop solutions for CO_2 storage in cases where emissions cannot be reduced, will represent alternative mechanisms for promoting a carbon neutral society. A

parliamentary committee on energy and climate issues in Finland was established in 2013 with the task to prepare a strategy for how a carbon neutral society could be reached until the year 2050 (MEE, 2014). 80% of the GHG emissions come from producing or consuming energy, including energy involved in the transport sector. In order to achieve an 80-95% decrease in GHG emissions by 2050 compared to 1990, it is important that all sectors and activities take action. Many industrial sectors will need to apply carbon capture and storage (CCS) or utilisation (CCU), since for many industries, this is the only effective way to reduce emissions. Focus in this thesis has therefore been to try to develop an energy and material effective process for carbon capture and storage by mineralisation (CCSM), which is one option for CCS/CCU in Finland. It is clearly stated in the report by the Ministry of Employment and the Economy that the commercialisation of CCS is essential in order to reach the target of an 80-95% reduction by 2050 (MEE, 2014).

Finland lacks the appropriate porous sedimentary basins that are pre-requisites for more conventional underground storage of CO_2, which places demands on finding options for other CO_2 storage methods (Koljonen et al., 2004). Regarding underground storage, the ultimate option would be to achieve in situ mineralisation, but this process takes very long time and the fraction of CO_2 mineralised will be minor during the first few hundred years (Romanov, 2015). Bioenergy carbon capture and storage (BECCS) could be a viable pathway to developing carbon-neutral industries in Finland, as the report from the Ministry of the Environment states, and CCSM could therefore be an important part of this (MEE, 2014). BECCS is a method for replacing fossil fuels with biomass derived from trees and crops. When they grow they will extract CO_2 from the atmosphere and if that CO_2 is captured and stored after combustion/gasification it can be regarded as CO_2 emission negative (Möllersten et al., 2003). A general descriptive review of CCSM will be presented below, followed by more detailed descriptions of the CCSM routes that form the focus of this thesis (MEE, 2014). However, according to more recent reports, it is questioned if BECCS actually should be seen as a negative energy technology (NET) or not (EASAC, 2019).

1.3.1. Carbon Capture and Storage by Mineralisation (CCSM)

Seifritz (1990) first presented the concept of engineered rather than natural passive CO_2 mineralisation. The aim of the concept is to make the naturally occurring "weathering" process, i.e. the conversion of silicates to carbonates, accelerated. Lackner et al. (1995) presented a proposal for CO_2 sequestration by

mineral carbonation using two different routes over two decades ago. The raw material for combining CO_2 into stable carbonates must be abundant and free of already carbonated magnesium or calcium. Once suitable minerals are found, either a high temperature direct carbonation method could be used in order to enhance the slow natural carbonation process, or an aqueous route could be applied, involving the separate extraction of calcium or magnesium in acidic solutions. Lackner et al. (1995) proposed that extraction could take place in hydrochloric acid, sulphuric acid or steam. The carbonation would then take place in a separate step after the extraction.

Common for all routes is the fact that the overall mineral carbonation equation

$$Mg\text{-silicate} + CO_2 \rightarrow MgCO_3 + SiO_2 + (H_2O) \tag{R1}$$
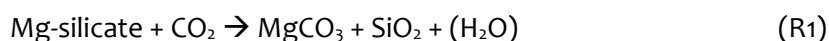
is an exothermic reaction (Mg-silicate as forsteritic olivine Mg_2SiO_4 (ΔH= -95 kJ/mol) or $Mg_3Si_2O_5(OH)_4$ (ΔH= -64 kJ/mol) meaning that the reaction will release energy. The challenge, however, is that the reaction itself is very slow. The different routes defined above are therefore designed to speed up the reaction (Lackner et al., 1995).

O'Connor et al. (1999) presented the idea of direct CO_2 sequestration in a slurry with magnesium silicate rock and subcritical CO_2. Elevated temperatures and pressures of 185 °C and 11.6 MPa, respectively, were needed to speed up the process and to reach a conversion of 90% after 24 h.

Currently, research into CO_2 mineralisation by CCSM appears to go in two major directions; either focusing on heat activated serpentinites, or using leaching salts such as ammonium sulfate (AS) and/or ammonium bisulfate (ABS). CO_2 sequestration using heat activated serpentinites has been reported in recent publications by Benhelal et al. (2018) and Farhang et al. (2016, 2019). Several different acids, bases and salts have been used in order to optimise the extraction of magnesium from magnesium silicates (Maroto-Valer et al., 2005; Mäkelä, 2011; Park et al., 2003; Teir et al., 2007; Wang & Maroto-Valer, 2011). 2 M solutions of H_2SO_4, HCl, and HNO_3 at 70 °C with test times varying between 1-2 h, respectively, were able to dissolve all magnesium from serpentinite rock (Teir, et al., 2007). Wang & Maroto-Valer (2011) reported a 100% magnesium extraction from serpentinite as well, using a 1.4 M NH_4HSO_4 solution with a test time of 3 h. The recyclability and the efficiency of mineral dissolution are mentioned as two

parameters in need of development for finding an efficient CO_2 mineralisation process (Wang &Maroto-Valer, 2011).

1.3.2. Dry vs Wet Mineral Carbonation Process Routes

The different steps in mineral carbonation using salts can be accomplished in various ways. The so-called *ÅA route* was developed and described at Åbo Akademi University almost a decade ago (Fagerlund, 2012; Nduagu, 2012). The process utilises magnesium silicate rock, preferably serpentinite ($Mg_3Si_2O_5(H_2O)_4$) to sequester CO_2 from flue gas. The process is stepwise including an extraction step with the addition of AS to the rock at high temperature (approx. 400ºC), followed by dissolution of sulphates and separation of insoluble matter and thereafter precipitation and separation of iron(hydr)oxides and magnesium hydroxide, respectively. The magnesium hydroxide is finally carbonated by flue gas in a pressurised fluidised bed reactor (PFBR) at 20 bar CO_2 and 500 ºC. The integration of this process to a steel plant was studied from an energy efficiency point of view by Romão et al. (2011). The publication concludes that 1 kg of CO_2 is sequestrered by 3.1 kg of serpentinite and 3.04 MJ (of which approximately 25% is power and 75% heat) and takes the use of heat released in the carbonation step into account, serving for 31 kJ/kg CO_2. Work has also been done on the possibilities to extract other metals from serpentinites, which could serve as feedstock for the steel industry or any Ni production industry (Koivisto, 2013; Romão, 2015).

An *alternative* ÅA route process involves replacing the carbonation step in PFBR with carbonation in an aqueous solution, adding ammonia and flue gas to the solution. The differences between the conventional ÅA route and the alternative wet route are shown in Figure 4. The alternative route eliminates the need for altering the process conditions from dry/hot conditions to wet/cold conditions and again back to a dry/hot state before carbonation is accomplished. Process simulations showed that rates and conversions are approximately the same for both options, but that excess NH_3 might be needed in order to increase pH to the desired level in the wet route. pH control is an important parameter for the precipitation of hydromagnesite, which is the end product in the wet route (Zevenhoven et al., 2016). It should also be pointed out that the product is magnesium carbonate ($MgCO_3$) in the conventional ÅA route, while hydromagnesite ($MgCO_3 \cdot 3H_2O$), lansfordite ($MgCO_3 \cdot 5H_2O$) or nesquehonite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) precipitate in the wet route, from an aqueous solution at lower temperatures. The formation of hydromagnesite is favoured at

temperatures above 50 °C, while hydromagnesite and lansfordite are favoured at temperatures below 50 °C. Kinetics are, however, slow at these low temperatures and the reaction kinetics are favoured by maintaining somewhat higher temperatures in the carbonation solutions. Only 80% of the CO_2 molecules could theoretically be captured in the wet route when hydromagnesite is formed ($Mg:CO_2=5:4$), compared to 100% when $MgCO_3$ is the product (Zevenhoven et al., 2017; Åbacka, 2014).
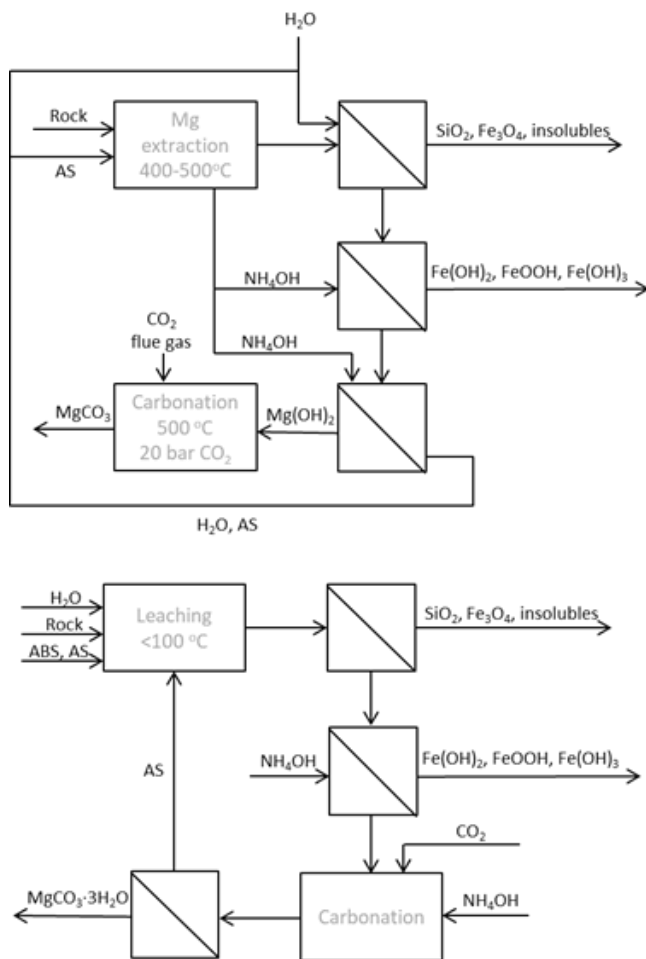

Figure 4. Upper: ÅA route (dry-wet-dry); Lower: Alternative carbonation route (wet-wet-wet). Figures adopted from Paper VI.

Ammonium sulfate (AS) is the flux salt used in both processes and flue gas can be directly used in the carbonation step without need for a pre-separation step of CO_2 from the flue gas. It was earlier shown by Zevenhoven et al. (2013) that the

carbonation results were practically the same at a given (wet) CO_2 pressure when using a diluted gas stream at higher pressures, at the same CO_2 partial pressure. The CO_2 depleted gas can be vented to the atmosphere after the carbonation step.

A third option was presented by Wang & Maroto-Valer (2011) where AS is replaced by ABS and the extraction step takes place in aqueous solution at low temperatures, i.e. <100 °C. The aqueous extraction efficiency using different kinds of salts was also studied, amongst these AS, ABS and ammonium chloride, NH_4Cl. ABS, however, was found to be most efficient when it came to extraction of Mg. The process route developed has sometimes been referred to as the *UK route* (Zevenhoven et al., 2016). The aqueous solution left after carbonation contains mainly AS, which must be transferred back to ABS to achieve proper regeneration of the input flux salt. Wang & Maroto-Valer (2011) suggests that this can be done by evaporation and heating, which would regenerate NH_3 needed for the carbonation step and ABS for the aqueous magnesium extraction from the rock. This would, however, have a significant energy penalty.

One challenge with all these process options is to find ways to recycle input flux salts and to make the processes more streamlined. The challenge concerning the regeneration of AS and/or ABS has been mentioned by several authors (Wang & Maroto-Valer, 2011). Three different ways of recycling AS or ABS were also briefly addressed by Romão et al. (2014). Crystallisation at approximately 120 °C through mechanical vapor recompression with compressed steam leaving the crystalliser was suggested for AS recovery. In the case where ABS is used, it could be according to the authors possible to convert AS to ABS by thermal decomposition close to 400 °C according to the reaction

$$(NH_4)_2SO_4 \text{ (s)} \rightarrow NH_4HSO_4 \text{ (s)} + NH_3 \text{ (g)} \tag{R2}$$
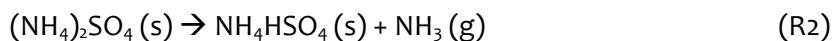
According to (Romão et al., 2014), however, it does not seem to be feasible to decompose AS, since AS will form a sticky grey melt at temperatures close to 300 °C, which will be hard to handle and slow to dissolve in water. The economic feasibility for thermal recovery of ABS has also been questioned (Wilhamson & Puschaver, 1977). Thus, the final preferred option according to Romão et al. (2014) would be to recover ABS by adding sulphuric acid to AS according to (R3). In this case, however, a large amount of ABS will accumulate since the addition of sulphuric acid will result in twice the necessary amount of ABS

$$(NH_4)_2SO_4 \text{ (aq)} + H_2SO_4 \text{ (l)} \rightarrow 2NH_4HSO_4 \text{ (aq)}, \Delta H_r\text{=-70,6 kJ/mol} \tag{R3}$$

To compensate for this, it was suggested that the exact amount of ABS needed for the extraction could be regenerated, while the remaining AS could serve as an input chemical for agriculture, pharmaceutical or cosmetics industries (Romão et al., 2014). The reaction is exothermic and the heat might be used elsewhere in the process, but since the balance does not make up properly, this option has not been investigated any further.

The separation of AS from ABS using alcohol was studied by Sanna et al. (2016).[1] The idea was to separate AS by a liquid/liquid separation instead of evaporation of water and subsequent crystallisation of AS. However, ABS is used as flux salt for the extraction in the presented pH swing process, which still will require the transformation from AS to ABS that is obtained by thermal decomposition, as will be shown below. Acetone, methanol and ethanol were compared and over 90% conversion was achieved with 70% methanol and a solid to liquid ratio of 200 g/L. Calculations were also made showing that 2908 kWh of heating was needed to extract AS enough to sequester 1 ton of CO_2 with a solid to liquid ratio of ammonium sulfate and water of 200 g/L. Applying a water evaporation step instead would according to Sanna et al. (2016) require 35% more, i.e. 4465 kWh. Virtanen (2015) studied the possibilities of separating ammonium sulphate with reverse osmosis (RO) and concluded that RO requires << 1/10 of the energy needs as electricity, compared to the studies by Sanna et al. (2016).

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[1] It should be mentioned that the article by Sanna et al. (2016) was published at around the same time as paper IV in this thesis, which briefly tested a similar approach.

2. Methods and Theoretical Background

Many chemical processing and unit operations steps involve the separation of particulates or dissolved species from water. This is done either to recover or obtain a valuable chemical or marketable product, or to remove contaminants from water that is to be disposed of. Many of the most commonly used conventional methods are quite energy intensive (for example crystallisation by water evaporation), or negatively affect the quality of the solid product (filter presses). Increasing costs related to energy use and more sustainable use of water are drivers for the development and implementation of more advanced technologies. Several options for separation and regeneration of solid material and chemicals in aqueous solutions (as encountered during CO_2 mineralisation) are available and some of them have been studied in this thesis. The separation methods used in this thesis project will be described here and the concept of exergy calculations is also presented, which is a convenient tool for obtaining information about the energy input demand and efficiency of different process, extraction and recovery routes.

2.1. Inclined Settlers

The possibilities for separating precipitated iron and magnesium hydroxides in the ÅA route, respectively, were studied using inclined settlers. Many mineral separation processes involve substantial handling of water, which in turn will require separation of solids from water. The first stage of dewatering is usually sedimentation (Napier-Munn & Wills, 2005). Sedimentation can take place in several different ways, e.g. through gravity sedimentation, which is the most widely used sedimentation technique in mineral processing, or by centrifugal sedimentation. Gravity sedimentation often takes place in circular tanks, usually 1-7 m deep and 2-200 m in diameter. Gravity sedimentation therefore usually requires a considerable footprint area for the thickener section. The method is

relatively cheap and the energy input requirement is usually very low. As an example, a 60 m diameter thickener could be run using a 10 kW motor (Napier-Munn & Wills, 2005). The energy goes mainly to the raking mechanism that moves solids towards the central outlet in the bottom of the thickener from where the solids are taken out. The clarified solution will overflow at the top of the thickener.

A high solid to liquid density ratio favours sedimentation. Filtration might be needed instead where the density difference is small. Particle size also affects the settling rate and particles of micron size scale will correlate with very low sedimentation rates. In this case, it could be more favourable to apply centrifugal sedimentation instead (Napier-Munn & Wills, 2005). Coagulation or flocculation, two methods linked to sedimentation, could have been an option in order to increase the sedimentation rate for the tests presented in Section 4.2. Coagulation takes place when an additive causes smaller particles in the solution to stick together (coagulate). Several coagulates when combined and stuck together form in turn flocs when they flocculate. The use of additives like these, however, were not investigated in this thesis. It would require the addition of coagulants or flocculants, and the target for this thesis was to find ways to recover and streamline the process without the addition of new chemicals.

The main advantage of inclined settlers is to reduce the distance the particles have to travel before they concentrate at the bottom, which in turn will affect the settling time. The space requirements for the inclined tube settlers are also much smaller than the aforementioned thickeners, as indicated in Figure 5.
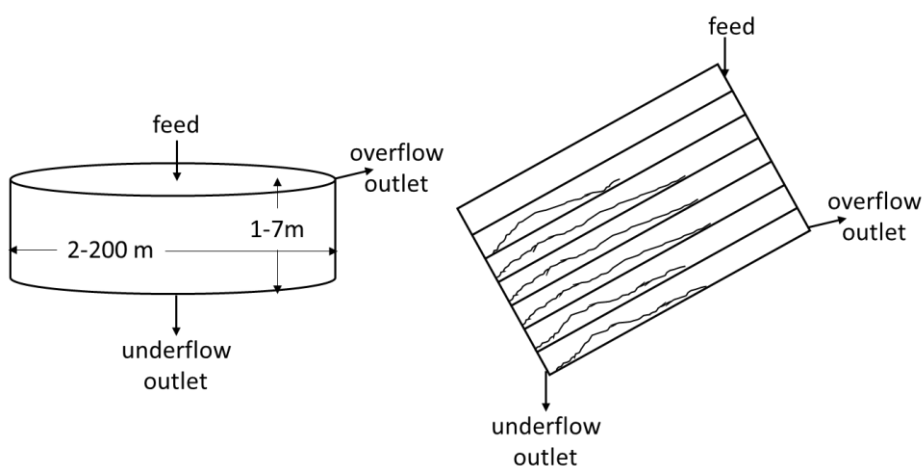

Figure 5. Simple principle schemes of a sedimentation tank (left) and an inclined plate settler (also called lamella thickener, right).

A drawback with inclined tube settlers is that hindered settling might be hindered at the bottom of the tube (Brock McEwen, 1997). Hindered settling is the mechanism that takes place when the settling particles are affected by nearby particles, which often is the case when the particles are brought together, e.g. in the lower parts of the settling tank. The opposite phenomenon is free settling where the particles settle with a rate mainly affected by particle size. The particle density becomes more important especially as hindered settling takes place. If the concentration of particles in a solution is too high, the settling will be affected by the collision of particles and the result might be that an increased share of the particles follow the clarified overflow (Quay Honaker & Richard, 2003). This phenomenon is referred to as hindered settling. The use of inclined plate settlers instead of inclined tube settlers can decrease the effect of hindered settling, but the significance of the shape of the settler was explicitly not studied here.

2.2.   Reverse Osmosis

The separation of particles was considered in the preceding section. Reverse osmosis, however, is a general mechanism for separating water from a solution, which means that this separation technique is more concerned with solutions containing dissolved salts or other ions, than with particles. The result after reverse osmosis is usually a very clean water stream (permeate), which is usually clean enough to meet the requirements for drinking water. Reverse osmosis is indeed commonly used for desalination of seawater for the production of drinking water but has many additional applications in several different purification and concentration areas, from the concentration of juices in the food industry to the crystallisation of Na_2CO_3 for CO_2 sequestration (Rastogi, 2018; Ye et al., 2015). Reverse osmosis is a pressure driven membrane separation process that can be used to separate a pure solvent (water) from its dissolved salt. The principle of the method is that the applied pressure on the membrane must exceed the osmotic pressure of the feed solution in order to achieve separation (Shukla et al., 2012). One of the most important parameters to take into account is thus the osmotic pressure of the actual solution. The osmotic pressure is dependent on the temperature and the amount of ions in the solution and can be calculated as

$$\prod = i \cdot M \cdot R \cdot T \tag{1}$$

where $\prod$ is the osmotic pressure in Pascal, i is the number of ions per dissociated molecule, M is the molarity, R is the gas constant and T is the temperature in

Kelvin (Chen & Lu, 2016; Zumdahl & Zumdahl, 2006). The osmotic coefficient can also be inserted to equation (1) for better accuracy, resulting in following equation

$$\Pi = \Phi \cdot i \cdot M \cdot R \cdot T \tag{2}$$

where Φ is the unitless osmotic coefficient describing the deviation from an ideal solution and is often <1 (Chen & Lu, 2016).

In order to achieve separation of water from a concentrated solution containing ions, the applied pressure over the membrane must be higher than the osmotic pressure difference of the solutions, i.e.

$$\Delta p > \Delta \Pi \tag{3}$$

This simple theory is the principle of reverse osmosis, illustrated in Figure 6. Pressure is applied on the retentate side of the membrane, resulting in solvent (often water) passing the membrane and ending up in a permeate stream.
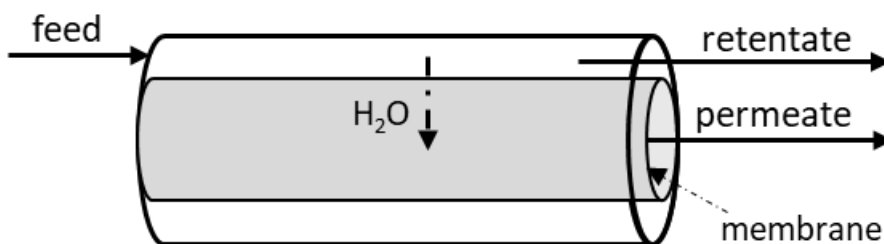
Figure 6. Principle scheme of a reverse osmosis membrane unit. The retentate is is the high concentrate solution and the permeate is in principle pure solvent.

Virtanen (2015) and Vahedi (2016) studied the separation of ammonium sulphate solutions by reverse osmosis at Åbo Akademi University. A concentration of 6 M ammonium sulphate is needed in order to reach sufficiently high concentrations for ammonium sulphate to crystallise. According to Virtanen (2015), a pressure of more than 200 bar is required to overcome the osmotic pressure of a process solution containing 4 M of ammonium sulphate. The aim with the reverse osmosis separation tests in Paper IV was mainly to follow up on initial studies by Virtanen (2015) and Vahedi (2016) to gain deeper knowledge and understanding of salt/water separation using a RO membrane.

2.3. Electrodialysis and Ion Selective Membranes

A substantial part of this thesis work was given to investigating the possibilities for applying electrodialysis (ED) to achieve separation and regeneration of flux salts used for CO_2 mineralisation. Special emphasis was also placed on the potential for using bipolar membranes (BPM). The principles of electrodialysis and the membranes used will therefore be presented in this section.

ED is a membrane process driven by electricity and has mainly been used to demineralise brackish water. The most important parameter is the ability for the solution to conduct electricity, such as a solution containing ions. Applying a DC voltage by inserting electrodes in pure water will not generate an electric current since no ions are available. The presence of ions plays hence a significant role in the performance of an ED system. By applying a DC voltage to a solution with a dissolved salt, the cations will start to move towards the negative cathode electrode and anions towards the positive anode electrode. By adding a sequence of alternating cationic and anionic membranes, it becomes possible to concentrate or dilute the solute, i.e. dissolved species, depending on how the membranes are arranged (Murray, 1995). The reactions taking place at the anode and the cathode, respectively, are

$$H_2O \rightarrow 2H^+ + 2e^- + \tfrac{1}{2} O_2 (g) \tag{R4}$$

$$H_2O + 2e^- \rightarrow H_2 (g) + 2OH^- \tag{R5}$$

The membranes used in papers IV-VI were Astom monovalent ion selective NEOSEPTA membranes as well as Astom bipolar membranes ordered via Eurodia (Eurodia, 2019). Table 1 shows some specifications for the membranes used.

Table 1. Membrane specifications (Astom Corporation, 2019a,b).

Membrane	CMS	AMS	BPM
Type	Strong acid (Na type)	Strong base (Cl type)	-
Characteristics	Monovalent cation permselectivity	Monovalent anion permselectivity	-
Electric resistance	$1.8\ \Omega \cdot cm^2$	$3.8\ \Omega \cdot cm^2$	no data
Burst strength	>0.15 MPa	>0.15 MPa	≥0.40 MPa
Thickness	0.15 mm	0.13 mm	0.22 mm
Temperature	<40 °C	<40 °C	no data
pH	0-10	0-8	no data

The monovalent ion selective membranes are not permeable for water, but they let anionic or cationic monovalent ions through. These were applied because of the fact that the HSO_4^- and SO_4^{2-} ions having different charges, could be separated from each other by this process, producing ammonium sulphate and ammonium bisulphate separately. The set-ups used are presented in Chapter 5, Key Findings.

Bipolar membranes are used with the aim of producing an acidic and an alkaline solution, respectively. The bipolar membranes split water into H^+ and OH^-, which will achieve this result together with separation of salt solutions using ion exchange membranes. Figure 7, also presented in paper VI, shows the principle of bipolar membranes and the products that are typically formed. Water splitting takes place in the space between the positively and negatively charged sides of the bipolar membrane. When a DC is applied, the ions will split and move towards the anode and cathode, respectively. Applying bipolar membrane electrodialysis (BPMED) could potentially form both acidic solutions and (dissolved) ammonia, which both are essential components in the ÅA route, or any alternative route. This has been studied in Paper VI.
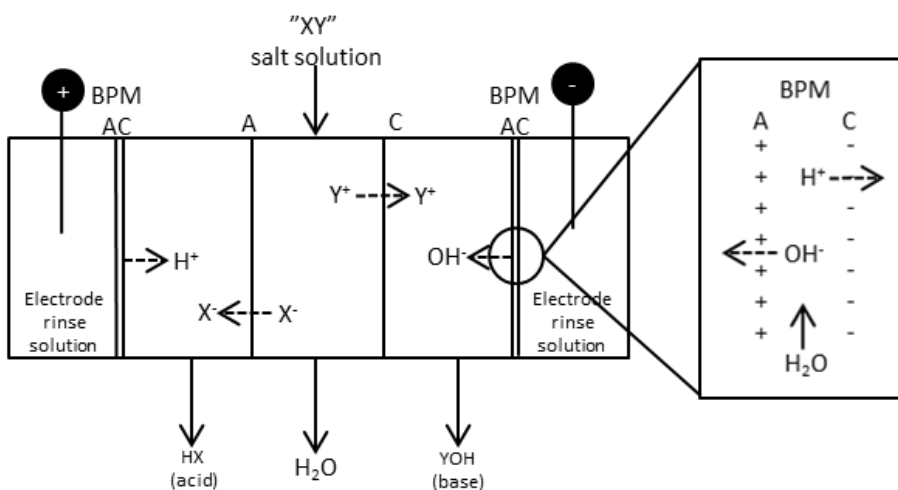
Figure 7. Principle of a bipolar membrane electrodialysis set-up. The sketch to the right shows in more detail the splitting taking place in the bipolar membrane itself. The figure was originally published in paper VI.

Very little literature has been found regarding electrodialysis in the treatment and separations in solutions with ammonium sulphate and ammonium bisulphate. A few studies were nevertheless available, indicating the importance of studying electrodialysis as a method for regenerating chemicals for the ÅA route. The

regeneration of sulphuric acid and ammonia from ammonium sulphate in waste waters from acid production was studied by Zhang et al. (2008). An electricity consumption of 0.207 kWh/mol sulphuric acid was found, which corresponded to a current density of 30 mA/cm^2 and average current efficiency (ACE) of 68.7%. The current efficiency was explained as the ratio (in %) between the amount of sulphuric acid multiplied by 100 and the theoretical concentration that may be obtained according to Faraday's law. The separation of monovalent ions from divalent ions was studied by van der Bruggen et al. (2004) and the separation of ammonium nitrate from sulphates by Koter et al. (2015), which resulted in a reduction in sulphate concentration from 0.8 M in the feed to 0.002 M in the final solution. The use of monovalent membranes and/or bipolar membranes in electrodialysis for the separation of sulphate or ammonium has been described by several authors (Campione et al., 2018; Galama et al., 2014, Gao et al., 2009; Xu et al., 2018, Yusuf et al., 2015).

The limiting current density together with current efficiency are parameters that often are used for measuring the separation efficiency. The limiting current density is the current density where concentration-polarisation will take place at the membrane surface and deplete the membrane surface in the feed compartment. This leads to very low concentrations locally, which means that there are no or at least very few ions being able to transport the currency through the compartment. Water splitting will also take place at the limiting current density, which also decreases the separation efficiency. Current efficiency (CE) can be defined as the amount of product actually produced compared to the amount of product that ideally should have been produced according to the electric input applied. Many ways of calculating this have been suggested (Heidekamp, 2013; Strathmann, 2004; Zhang et al., 2008).

2.4.   Exergy Calculations and Energy Efficiency

Exergy analysis is an appropriate tool for energy efficiency evaluation (Szargut et al., 1988) The efficiency of converting electrical energy into a separation effect was assessed experimentally and compared with exergy analysis, allowing for calculating efficiency based on the Second Law of Thermodynamics. The concept of exergy was used in paper V and VI for presenting the energy requirements of the electrodialysis separation options studied.

Here, the input energy, i.e., electric power, is equal to the input exergy in the case where electrodialysis was studied. This was then used to calculate the input exergy in Joules at any time according to

$$Ex_{in}(t) = P(t)_{in} = I \cdot U \cdot t \quad\quad\quad (4)$$

where the electric current, I (A=C/s), the voltage, U (V=J/C), and the time, t (s), must be known. The exergy input for a time interval was calculated taking an average value of two following measurements of the electric current and the voltage at times t_1 (s) and t_2 (s) according to

$$Ex_{in} = (U_1+U_2)/2 \cdot (I_1+I_2)/2 \cdot (t_2-t_1) \qu\quad (5)$$

The time between two measurements varied typically between 15 and 30 minutes, which meant that the calculations give an estimation of the exergy input. Finally, the cumulative exergy input was calculated summarising the calculated exergy input for the different intervals. Key findings of the cumulative exergy are shown as figures in the section Key Findings.

The input exergy as electrical energy was compared with the reversible exergy of (un-)mixing, Ex_{mix} , in paper V. The exergy of mixing takes mixing of ions from one compartment to another into account and can be calculated as

$$\Delta Ex_{mix} = R \cdot T_0 \cdot [(\sum_p n_{ip} \cdot \sum_i x_i \cdot \ln x_i) - (\sum_f n_{if} \cdot \sum_i x_i \cdot \ln x_i)] \qu\quad (6)$$

T_0 (K) being the surrounding temperature, n_{ip} and n_{if} the molar amounts of "i" in the product "p" and feed "f" streams, respectively. x_i is the molar fraction of "i" in the solution (Szargut et al., 1988). In order to be able to calculate the exergy of mixing both the feed composition as well as the final composition must be known. pH and the ammonium concentration were therefore measured. Knowing pH the ratio between HSO_4^- and SO_4^{2-} could be estimated. The sum of positively charged cations (NH_4^+, H^+) will equate with the negatively charged anions (HSO_4^-, SO_4^{2-}) and by this relation the presence of the different kind of ions were known, or at least could be estimated. The exergy of mixing was at this stage calculated for batch tests only.

The energy needs for separating 1 kg of NH_4^+ from the process stream were calculated in paper VI for four different types of tests. The NH_4^+ concentrations were needed for the calculations and the calculations were either based on the ammonium measurements using ISE electrodes in the feed, or based on the

external[2] ammonium analyses in the alkaline solutions obtained. External analyses were done on the alkaline solutions since the ammonium selective electrode used at the laboratory at ÅA has an optimum pH range of 0-8.5.

The equilibrium between ammonium, NH_4^+ (aq), and ammonia, NH_3 (aq), was also taken into account since the analysis methods used only measured ammonium ions, excluding dissolved ammonia from the calculations. At high pH, ammonia constitutes a large proportion of the total amount of ammonium and ammonia. Below pH 6.5, 100% is present as NH_4^+, while 95% is present as NH_3 at pH 10, increasing to 100% NH_3 at pH 11.5. Since pH in the alkaline solutions greatly exceeded pH 6.5, the presence of ammonium and ammonia were calculated using a combination of the following reactions and equations

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{R6}$$
$$K_b = [NH_4^+] \cdot [OH^-] / [NH_3] \tag{7}$$

where the equilibrium constant for ammonia, Kb, is equal to 1.8×10^{-5} at 25 °C (Zumdahl & Zumdahl, 2006). The exergy input was calculated in a similar manner in both paper V and VI, since the input exergy could be regarded as electric energy supplied to the electrodialysis stack. Pumping energy use was neglected.

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[2] External analyses were provided by Eurofins Environment Testing Finland Oy, Lahti, Finland.

3. Limitations

Methods being used in this thesis were limited to a few, which makes it appropriate to mention a few words about those methods not considered.

The initial study of inclined settlers for the separation of the precipitated intermediate product in the ÅA route involved an inclined tube. This could have been done using another kind of settling set-up, e.g. plate settlers or sedimentation tanks. The advantages with the tube settler were, however, the reason to why this set-up was chosen. At laboratory scale this was easy to handle and to wash and by inclining the settler the settling distance was shortened. The tube set-up made it possible to build a sealed set-up that still was convenient to handle and maintain. Solid/liquid separations of precipitated calcium carbonate (PCC) using inclined settlers were also studied at ÅA by Filppula (2012) and Mattila & Zevenhoven (2016). Mattila & Zevenhoven (2016) show that the separation using inclined settlers has usually been more efficient than using a similar capacity hydrocyclone, which was used for comparison in their study.

Micro, ultra and nanofiltration are methods often mentioned in the context of RO (Basile et al., 2015; Shukla et al., 2012). The main difference between these filtration methods and reverse osmosis is the larger pore size of the membranes, resulting in barrier filtration rather than permeating species dissolving in the membrane. Microfiltration membranes have a pore size of 100 nm and are often used for the separation of submicron size particles from solutions. Ultrafiltration membranes having a pore size of 3-30 nm are commonly used for fractionating solutes in a solution with respect to size or molecular weight. Nanofiltration membranes have even smaller pore sizes of 1-3 nm, which means that some molecules in addition to water molecules can be transported through the membrane. The driving force for these three separation methods are hydrostatic

pressure versus osmotic pressure differences across the membranes (Shukla et al., 2012). The comparison between inclined settlers and these different filter types for very fine precipitated particles were not studied here. Figure 8 (Murray, 1995) shows the most suitable membrane separation methods to use depending on particle or molecule size. The size range and the methods being considered here are marked in the figure.
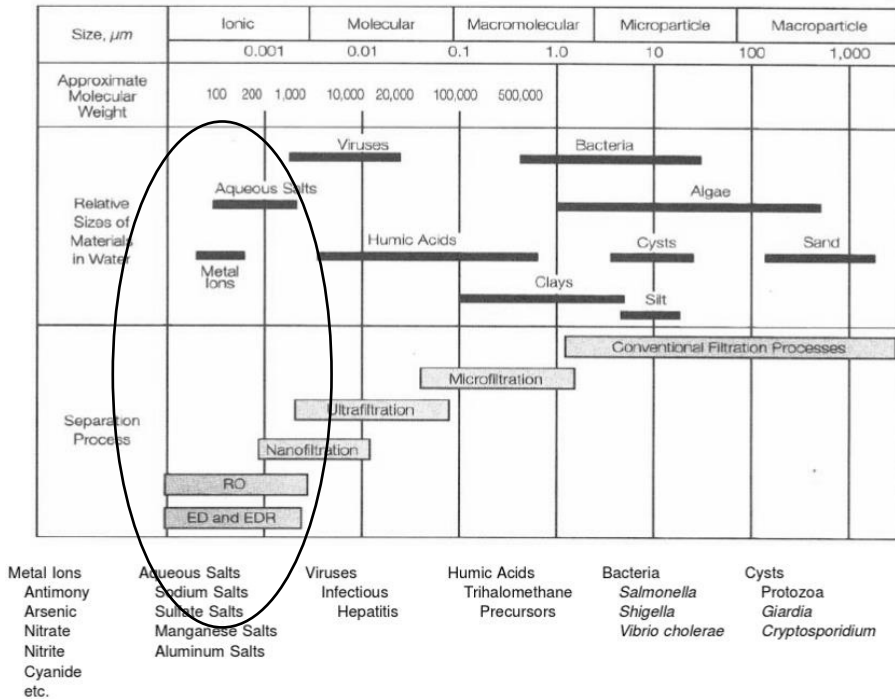
Figure 8. Overview of different membrane separation methods with respect to size (Murray, 1995).

Freeze crystallisation, evaporation and distillation were mentioned in the context of the ÅA route for CO_2 mineralisation by Vahedi (2016) and Virtanen (2015). These methods could possibly be used to separate any flux salt as a solid from the process stream in the case where the thermal solid/solid process step is chosen. However, if the aim is to have every ÅA route process step in aqueous solution throughout the process, it becomes more important to recover the individual flux salts and leave the aqueous solution as a solution. Evaporation and distillation would involve vaporisation of the solvent (here water) but if all process steps are held in aqueous solutions this would be an excess step that should preferably be avoided.

SEM/EDX was used for getting an indication of the composition and particle size of precipitated material. XRD could optionally have be used in order to confirm the mineralogy of the different precipitates. These analyses were not applied here, since the main interest was to study the particle size and correlate it to the difference in settling rates. Work by others (Nduagu, 2012; Romão, 2015; Lavikko, 2017) put focus on the more specific characterization of precipitated species occuring in the ÅA route.

Regarding the analysis methods used, the AS/ABS selectivity was in addition to pH measurements also based on the ISE measurements. Solution pH must be <7 in order to measure the total amount of ammonium ions present. Above this pH there will be both ammonia and ammonium present. Measuring pH was therefore used as main indicator to see in what direction the separation was going. ISE electrodes do not give reliable analyses at pH>10 and were not used for measuring NH_4^+ in such solutions.

The osmotic coefficient briefly introduced in Section 2.2 will not be taken into consideration in this work. The composition of the solutions were very complex, and significant work must still be done in order to find reliable osmotic coefficients. The test results would, however, probably not have been improved even if the osmotic pressures had been calculated with the osmotic coefficients and the discussions with these included has therefore been left out.

4. Aim of the Research - Research Questions

The aim of the research has been to further develop the work done by Nduagu (2012) and Fagerlund (2012), followed by Romão (2015), Slotte (2017) and Lavikko (2017), which have all been developing the concept called *the ÅA route*. Extensive research have already been done, but little effort has been allocated to the streamlining of the process steps nor the recovery of chemicals involved in the ÅA CO_2 mineralisation route. This thesis was therefore mainly focusing on finding ways to streamline and to regenerate the flux salt involved.

Two main questions were initially serving as a starting point for this work:

- What process units might be used to make the ÅA route more streamlined?
- How could input chemicals be (almost) completely regenerated?

together with following questions that were later added and developed:

- Are there more minerals than those known until today, preferably found as overburden rock from mining activities, that are suitable for use in the ÅA route?
- Can multiple extraction steps increase the extraction of magnesium from the rock?
- Are inclined settlers suitable for the separation of precipitated species from the process streams?
- Can electrodialysis serve for the separation and regeneration of flux salts involved in the ÅA route?

In practice, this means that the focus of this thesis has been on using different kind of processing methods, with special emphasis on membranes for separation of dissolved species from water to further optimize the ÅA route, or any alternative route based on it. Energy use and efficiency are of key importance.

Focus has also been on the separation of precipitated iron and magnesium from aqueous solution (Paper I) and on the regeneration of flux salts (Paper IV-VI), together with studies focusing on finding suitable raw materials for the magnesium extraction (Paper II-III). To the knowledge of the author, very few reports have been published especially regarding the (membrane) separation of the flux salts used in the ÅA route, which makes the subject of this thesis an important new area for research on mineral carbonation.

5. Key Findings

Several options for streamlining or making the CO_2 mineralisation process more efficient with respect to flux salt use and energy input requirements were studied (with focus on the conventional ÅA route or any alternative ÅA route) in several sub-projects;

1) Suitable raw materials were studied in order to find waste rock or processing sidestream materials from mining activities that could be utilised for mineral carbonation (Paper II-III).
2) Streamlining of the process by the application of inclined settlers in order to possibly achieve precipitation and separation of magnesium as magnesium hydroxide or nequehonite in the same process unit (Paper I).
3) Reverse osmosis was applied to achieve pre-separation of salt from the process stream (Paper IV).
4) Different options, e.g. extracting magnesium from the rock by a multiple step approach or separating AS from the process stream adding alcohol were presented (Paper IV).
5) Flux salt regeneration applying electrodialysis. Special attention was given to bipolar membrane electrodialysis in combination with monovalent membranes, resulting in acidic and alkaline solutions (Paper V-VI).

Key findings from each of the sub-projects are presented below.

5.1.   Finding Suitable Raw Materials

Several studies have focused on finding suitable minerals for CO_2 sequestration by mineral carbonation according to the ÅA route both in Finland and abroad (Lavikko, 2017; Mäkelä, 2011; Nduagu et al., 2012a,b; Romão et al., 2016).

A potential suitable Finnish rock for magnesium extraction in the ÅA route is the serpentinite present as waste from the Hitura nickel mine, where a total volume of 2.1 Mm^3 of serpentinite has been extracted. The nickel mine was closed in 2013 as a result of the decreasing nickel prices, but the waste rock is still available at the site. A limekiln located in Raahe, at a distance of 140 km, at a steelmaking plant could possibly utilise this rock for CO_2 sequestration by mineral carbonation (Slotte et al., 2013). Slotte (2017) showed that transport of rock over significant distances (several 100 km) has a small environmental footprint and energy penalty using life cycle analysis (LCA). The amount of serpentinite waste rock at the Hitura nickel mine site is 5.6 Mt (corresponding to the density of serpentinite of 2.5-2.6 kg/m^3). This could be compared with the calculated abundance of serpentinite in the Outokumpu-Kainuu region (Western Finland) which is estimated to 10 600 Mt. This amount has theoretically the capacity to sequester all of Finland's CO_2 emissions for the next 200-300 years, if combined with other technologies that also aim to minimise the CO_2 emissions from industry. This would correspond to an annual CO_2 sequestration amount of 25 Mt (Teir et al., 2006). Actions taken by the forestry, transport and domestic heating sector were not mentioned by Teir et al. (2006), but will also affect the need for CO_2 sequestering.

However, in order to minimise the need for transport of either rock or CO_2 to other places in Finland, it would be desirable to find minerals at other locations in Finland as well. See also Slotte (2017) for LCAs addressing this. A CLEEN/CLIC CCSP project in cooperation with industry was focusing on the comparison between four different rocks, one on them being the serpentinite from Hitura serving as a reference rock. Part of this work was presented in Paper II-III of this thesis, of which paper II presents results from tests with thermal solid/solid extraction while paper III focused on the extraction through extraction in aqueous solutions. The locations and the compositions of the rocks are shown in Figure 9. The mineralogical compositions of the four rock types studied are given in Table 2. The Vammala rock also mainly consists of serpentine, while diopside, plagioclase and amphibole are the main minerals comprising the Diopside and Mg-hornblendite rock (the latter refered to as Mg-Horn in Figure 9 and Table 2), respectively.

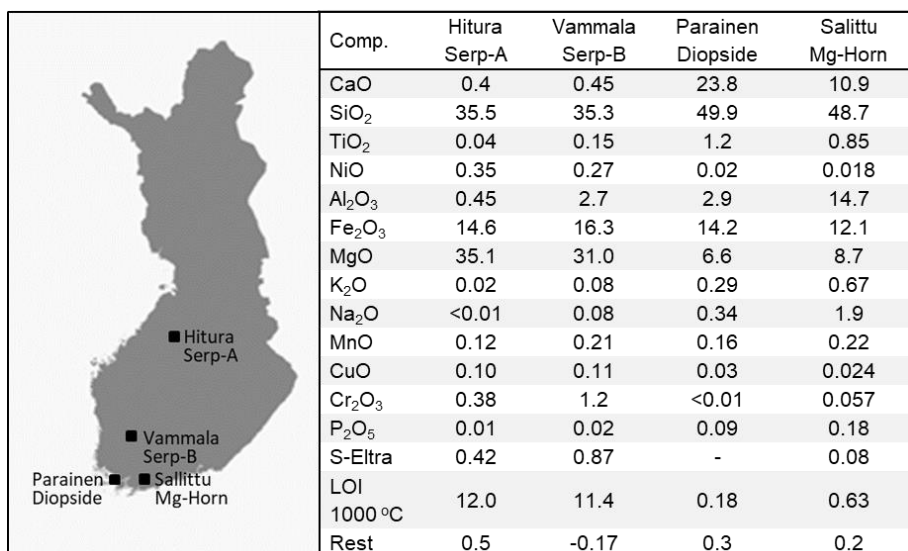| Comp.	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
CaO	0.4	0.45	23.8	10.9
SiO_2	35.5	35.3	49.9	48.7
TiO_2	0.04	0.15	1.2	0.85
NiO	0.35	0.27	0.02	0.018
Al_2O_3	0.45	2.7	2.9	14.7
Fe_2O_3	14.6	16.3	14.2	12.1
MgO	35.1	31.0	6.6	8.7
K_2O	0.02	0.08	0.29	0.67
Na_2O	<0.01	0.08	0.34	1.9
MnO	0.12	0.21	0.16	0.22
CuO	0.10	0.11	0.03	0.024
Cr_2O_3	0.38	1.2	<0.01	0.057
P_2O_5	0.01	0.02	0.09	0.18
S-Eltra	0.42	0.87	-	0.08
LOI 1000 $^{\circ}$C	12.0	11.4	0.18	0.63
Rest	0.5	-0.17	0.3	0.2

Figure 9. Presentation of the location (left) and the composition of the rock at the different locations (right) for the rocks studied in paper II and III.

Table 2. XRD analyses of samples with particle size 63-125 µm. The values are in %-wt.

Compound	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
Serpentines $(Mg, Fe)_3Si_2O_5(OH)_4$	70-80	60-70	-	<5
Magnetite Fe_3O_4	15-20	10-15	-	-
Diopside-Hedenbergite $CaMgSi_2O_6$- $CaFeSi_2O_6$	-	-	90-95	<5
Plagioclase $(Na, Ca)(Si, Al)_4O_8$	-	-	< 5	30-40
Amphibole (Magnesiohornblendite) $Ca_2[Mg_4(Al, Fe)]Si_7AlO_{22}(OH)_2$	-	< 5	-	30-40
Quartz SiO_2	-	-	-	15-20
Chlorite $(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2 \cdot (Mg, Fe)_3(OH)_6$	< 5	10-15	-	-
Calcite $CaCO_3$	< 5	-	-	-
Cordierite $Mg_2Al_4Si_5O_{18}$	-	-	< 5	-
Annite $KFe_3AlSi_3O_{10}(OH,F)_2$	-	< 5	-	-
Dolomite $CaMg(CO_3)_2$	-	< 5	-	-

According to (Lu et al., 2011), there is a possibility for diopside to react in an acidic environment and form serpentine according to

$$3\ CaMgSi_2O_6 + 6\ H^+ \rightarrow Mg_3Si_2O_5(OH)_4 + 3\ Ca^{2+} + H_2O + 4\ SiO_2 \qquad (R7)$$
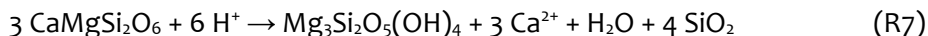
Since serpentine gave promising results when it came to the extractability of magnesium (Nduagu et al., 2012a,b; Romão et al., 2016; Sjöblom & Eklund, 2014) this study investigated if diopside through this reaction could serve as raw material for the mineral carbonation according to the wet ÅA route. After attempts to extract magnesium both by leaching and by thermal solid/solid extraction, however, it was concluded that the diopside rock (waste rock from industrial activities in the Parainen region at a limestone quarry) does not achieve sufficient extraction of magnesium for the purpose of providing raw material for CO_2 mineralisation. Mg-hornblendite (waste rock from Vammala mining operations) yielded, after aqueous extraction of magnesium, <10%-wt while close to 80 %-wt of the magnesium is extracted from both serpentinites. Figure 10 shows the significant, but not surprising, difference between the rocks for magnesium extraction in 1.4 M ABS solutions at 70°C. This again reaffirms the suitability of using serpentinite for mineral carbonation.
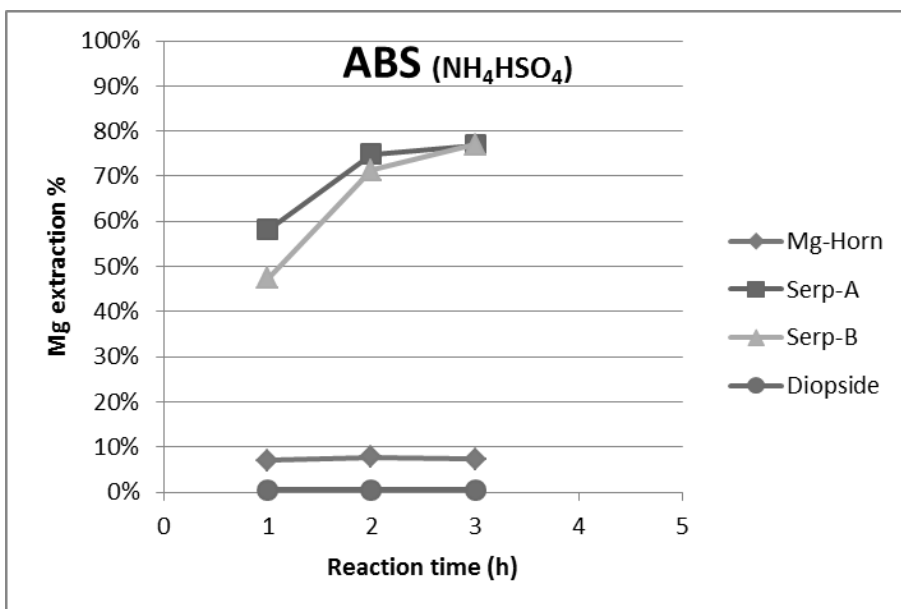

Figure 10. Mg extraction from four different rock types in 1.4 M ABS solutions at 70 °C. Figure adopted from Paper III.

Similar results were obtained in the tests applying thermal solid/solid conditions. 64 and 61.7 %-wt of the magnesium were extracted from Serp-A and Serp-B, respectively, in tests with ABS used as flux salt and a minor addition of water (2 ml) to the solids before the thermal treatment. The effect on metal extraction by the addition of water to the solid mixture of rock and flux salt was also studied and was found to enhance the extraction degree reported by Romão et al. (2013). Table 3 and Table 4 present the experimental parameters and the corresponding extraction results, respectively. The presence of ABS clearly enhances the extraction of magnesium.

Table 3. Experimental parameters for the tests where four different rock types were compared.

Test no.	Code	Reagent	Stoichiometric factor of reagent	Particle size (µm)	Mineral (g)	Furnace	T (°C)	t (min)	Dilution (ml)
1	ÅA-400/60	AS	1.15	125-250	40	Rotary	400	60	500
2	ÅA-440/60	AS	1.15	125-250	40	Rotary	440	60	500
3	ÅA-440/30	AS	1.15	63-125	40	Rotary	440	30	500
4	AS-440/30	AS	1.15	63-125	25	Chamber	440	30	315
5	WET-ABS	ABS	1.15	63-125	25	Chamber	440	60	315
6	DRY-ABS	ABS	1.15	63-125	25	Chamber	440	60	315
7	UK-90/3	ABS	1.15	125-250	40	Rotary	90	180	500
8	ÅA-440/60-1.5	AS	1.50	63-125	25	Chamber	440	60	315
9	WET-AS/ABS	AS+ABS 1:1	1.15	63-125	25	Chamber	440	60	315
10	DRY-AS/ABS	AS+ABS 1:1	1.15	63-125	25	Chamber	440	60	315

Table 4. Metal extraction from four different Finnish rocks.

No	Code	Serp-A		Serp-B			Diopside			Mg-Hornblendite			
		Mg extr.	Fe extr.	Mg extr	Fe extr	Al extr	Mg extr.	Ca extr.	Fe extr.	Mg extr.	Ca extr.	Fe extr.	Al extr.
1	ÅA-400/60	28.9	20.2	16.4	21.1	-	-	-	-	4.4	2.7	5.8	2.7
2	ÅA-440/60	43.4	30.9	33.6	32.5	-	0.1	3.1	0.2	4.4	2.9	1.4	0.6
3	ÅA-440/30	37.6	24.5	22.7	27.2	20.0	-	-	-	-	-	-	-
4	AS-440/60	36.4	25.8	24.4	26.0	19.0	-	-	-	-	-	-	-
5	WET-ABS	64.0	40.3	61.7	25.3	23.3	1.2	4.5	1.8	8.4	6.8	3.2	3.1
6	DRY-ABS	55.8	38.4	54.2	24.2	-	1.7	4.6	2.1	7.3	6.4	3.5	3.0
7	UK-90/3	41.9	17.6	45.0	32.7	0.1	3.6	4.3	4.1	7.0	4.9	8.0	5.9
8	ÅA-440/60-1.5	-	-	26.6	25.4	16.9	-	-	-	-	-	-	-
9	WET-AS/ABS	-	-	52.3	47.5	24.8	-	-	-	-	-	-	-
10	DRY-AS/ABS	-	-	49.8	43.2	23.6	-	-	-	-	-	-	-

The equilibria for the extraction of magnesium from serpentine in either AS or ABS solutions were simulated as a preliminary study by Gibbs energy minimisation software, HSC Chemistry 8. This was done in order to get indications on how changing the flux salt would affect the presence of different species at different temperatures. According to Figure 11, 0.1 kmol of magnesium sulfate are already present at 25°C in ABS solutions, while a temperature of 40 °C is needed in AS solution to reach the same amount of $MgSO_4 \cdot H_2O$. ABS seems from this simulations to be a more efficient flux salt than AS, which was confirmed by experimental work later. Magnesium will be highly dissolved in aqueous solutions, but the formation of sulfates indicates that magnesium will extract from the rock. The simulations were based on the starting composition of 0.85 kmol serpentine, 0.15 kmol magnetite, 1.4 kmol ammonium salt and 5 kmol water, respectively. The presence of magnetite is common in serpentinite rock and is therefore included in the simulations.
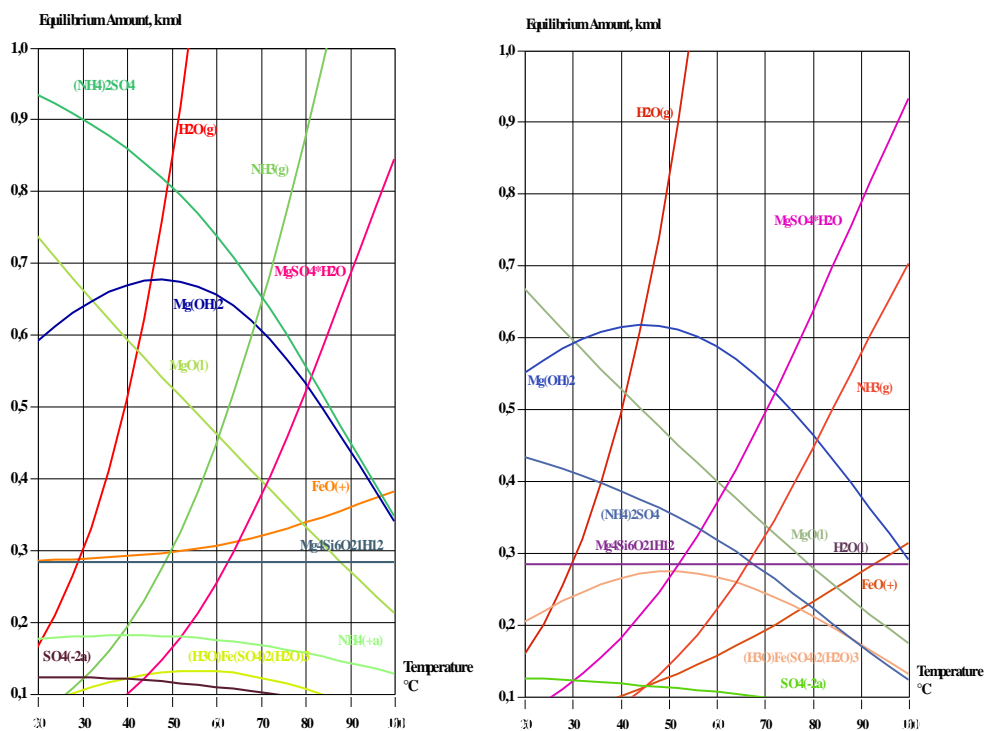

Figure 11. Simulation of the reaction with AS (left) or ABS (right) with serpentine and magnetite at a temperature range 20-100 °C. The software used was HSC Chemistry 8.

The tests did show, however, that the kinetics limited the extraction efficiency in an AS solution as these are characterised by a less acidic environment compared to extraction in an ABS solution.

Table 5 summarises the best results from the aqueous and thermal solid/solid extraction test in terms of binding capacity of kg CO_2/ ton of rock. The results indicate that the aqueous extraction route seems to give slightly better results as far as the binding capacities of CO_2 are compared.

Table 5. CO_2 binding capacity for two different Finnish serpentinites with either thermal solid/solid or aqueous extraction applied.

Rock type	Thermal solid/solid extraction Paper I	Aqueous extraction Paper II
Serp-A	240 kg CO_2/ton rock	292 kg CO_2/ton rock
Serp-B	207 kg CO_2/ton rock	260 kg CO_2/ton rock

5.2. Inclined Settlers

The ÅA route involves several separation steps, as described in Section 1.3. There is still a need for streamlining by means of 1) separating precipitated iron (hydr)oxides from the process solution before pH is increased further to precipitate magnesium as $Mg(OH)_2$ and 2) separating magnesium hydroxide from the solution before it can be carbonated in the PFBR. However, in the case where wet carbonation is applied, there will also be a need for 3) separating magnesium (hydro) carbonates from the process solution. Paper I focused on the potential for separating the precipitated matter using inclined settlers, as shown in Figure 12. One benefit of using the inclined settlers is that precipitation and separation could potentially take place in the same process unit.

The total length of the settler used in the study was 47 cm and the inner diameter 4.6 cm. The settler was equipped with an inlet at the lower end and two outlets (one at the lower end for the underflow and one at the upper end for overflow), together with an underflow control valve and openings in the top of the settler for enabling measurement of pH and temperature inside the settler.
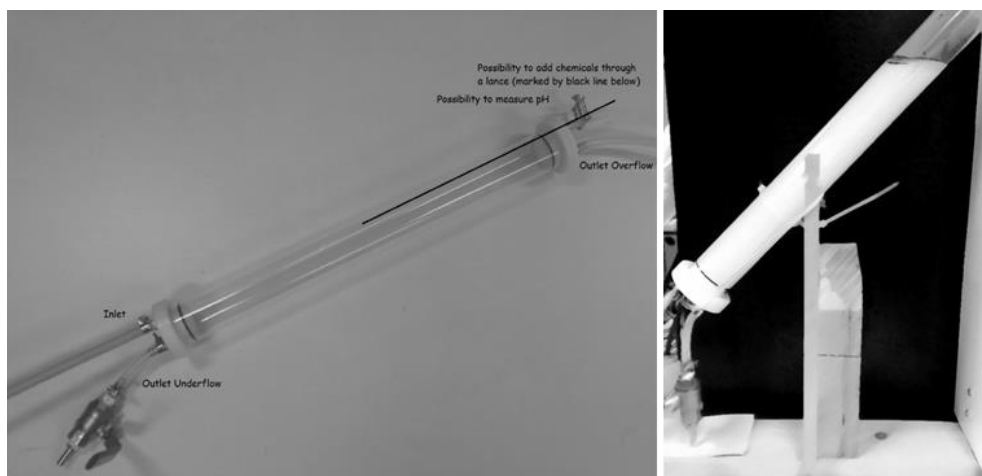
Figure 12. Images of the inclined settler used in the work presented in Paper I.

The solutions were prepared with both analytical grade magnesium sulphate and iron sulphates besides deriving a solution from Finnish serpentinite rock (see Figure 9 (Hitura) in the preceding Section 5.1. for composition). Different solutions were pumped into the settler with different flow rates. Some of the tests were done in batch mode (to see how long settling time the particles required without any turbulence caused by continuous or recirculating flow), while others were performed in continuous mode and some by recirculating the overflow back to the inlet. Ambient pressure and temperature was maintained in the tube for all tests. Temperature control was kept constant for some of the tests in the precipitation step. For these tests, the precipitation took place in a separate vessel.

Comparing the settling time in batch mode for magnesium hydroxide (Figure 13) with that for magnesium hydrocarbonate (Figure 14), it was found that the settling of magnesium hydrocarbonate was distinctly more rapid. The precipitation of solids was done in a separate vessel and the solution containing the particles was then pumped into the settler. A precipitation temperature of 80 °C was held for the test shown in Figure 13 to see if raising the temperature could result in larger particle size and thereby the settling rate. Increasing the temperature, however, does not seem to affect the settling rate substantially. Settling times were recorded from the moment the settler was filled.
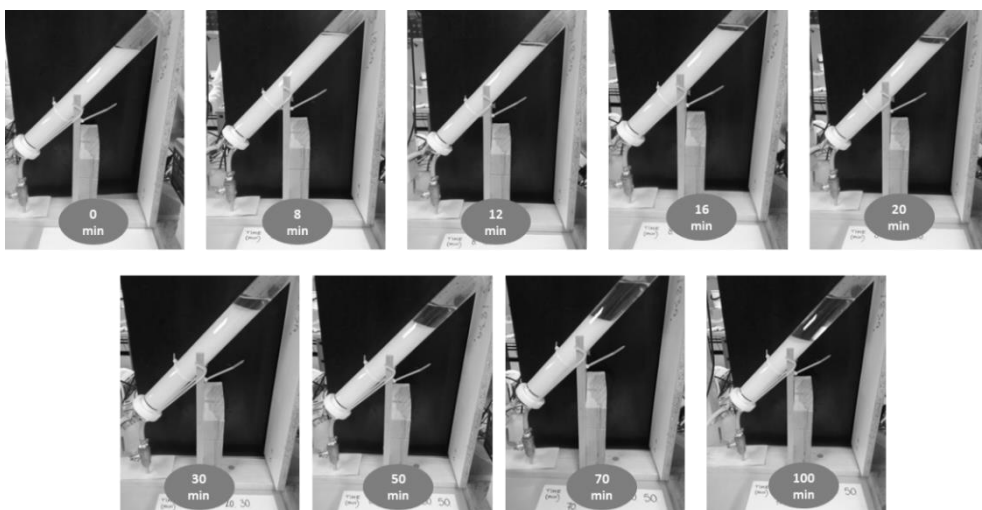
Figure 13. Sedimentation of Mg(OH)$_2$. Analytical grade anhydrous MgSO$_4$ was used as initial chemical. Precipitation was done with dropwise addition of NaOH (0.25 M and 1.0 M) at 80°C before the solution was pumped into the settler.
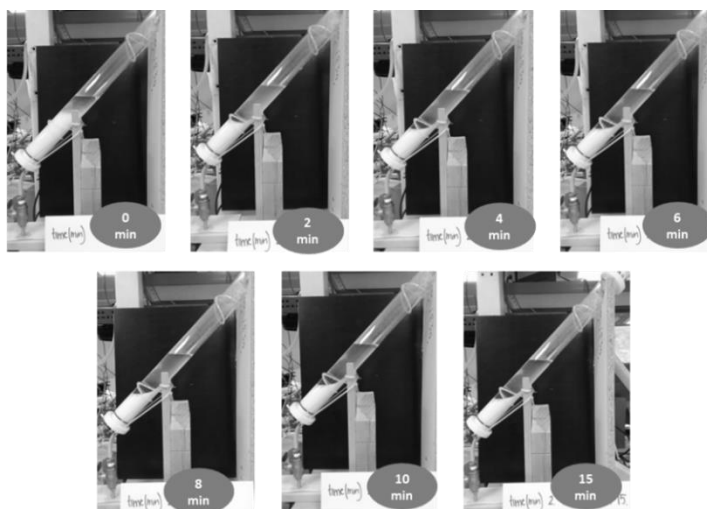

Figure 14. Carbonation and sedimentation of magnesium (hydro)carbonate. Precipitation with 10% NH$_4$OH followed by carbonation in water at ambient temperature. Only sedimentation took place in the settler.

According to (Napier-Munn & Wills, 2005) it should be possible to remove 80% of the water from a process stream by sedimentation. The actual separation degree, however, depends for example on the particle size. Particles smaller than 50 μm will settle much slower than larger particles. Other parameters affecting the settling rate are the concentration and the shape of the particles. The settling rate may be enhanced by adding flocculants or agglomeration of the particles. The size

of the particles in the underflow from the test shown in Figure 13 were flakes were approximately 20-50 nm thick and 0.2-0.5 μm in diameter, while the particle size of magnesium (hydro)carbonate (Figure 14) was larger, either 50-100 μm or 2-20 μm, depending on the structure and the type of magnesium hydrocarbonate produced in the carbonation step. An elongated structure found in the SEM images indicated the presence of nesquehonite and a more plate-like shaped hydromagnesite. The structure of magnesiumhydroxide, nesquehonite/hydromagnesite and magnetite from the underflow are shown in the SEM images in Figure 15. The settling rate of iron (oxy)hydroxides was found to be very slow. A very low degree of sedimentation degree was still obtained even if the solution was left in the settler overnight. Attempts were made to precipitate magnetite (Fe_3O_4) with higher density, 5.15 ton/m^3, instead of iron (oxy)hydroxide, 3.8 ton/m^3, in order to obtain particles that thus may settle more rapidly (Webmineral, 2019). The particle size of these precipitated particles were found to be 40-50 nm, which is still well below the aforementioned 50 μm particle size that is needed to achieve a reasonable settling rate (Napier-Munn & Wills, 2005).
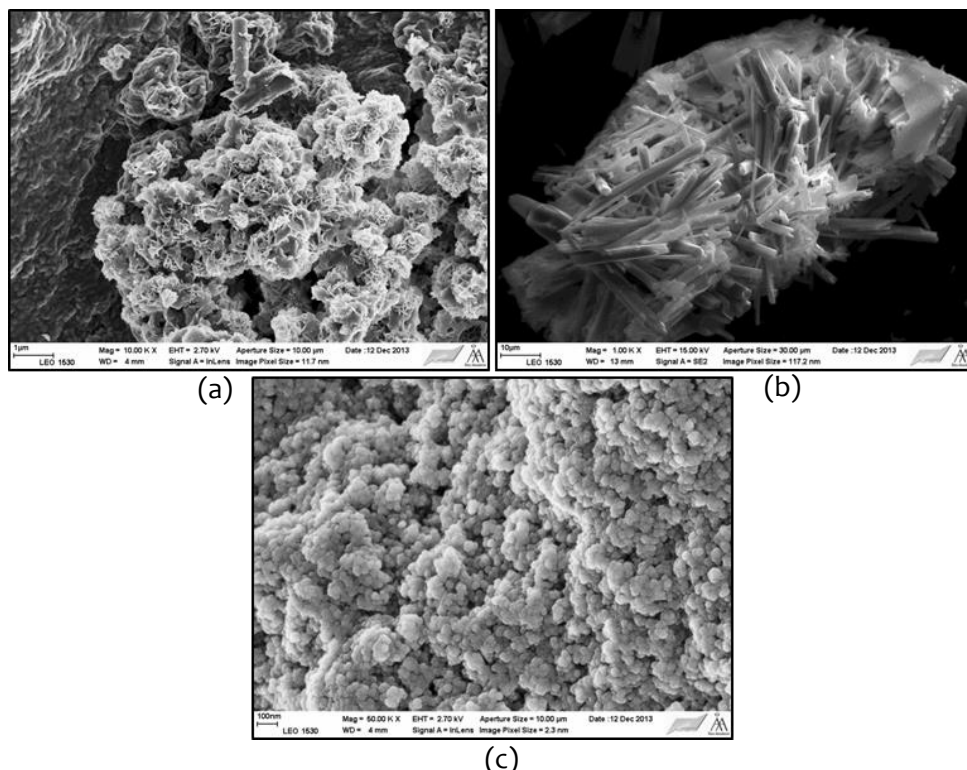

Figure 15. (a) Magnesium hydroxide; (b) Hydromagnesite (plate, right) and nesquehonite (elongated structure, left)); (c) iron (oxy)hydroxide particles. All images are of particles from the underflow.

Paper I describes more extensively how recirculation and carbonation was accomplished as well in a separate vessel as inside the inclined settler itself. Especially when it comes to magnesium, it was shown to be possible to both precipitate, carbonate and separate the solids directly in the settler. The retention time in each process unit should, however, be selected carefully since the carbonation reactions need some time to be completed. More details about this are found in Paper I.

5.3. Reverse Osmosis

A brief study of the possibility to apply reverse osmosis separation to the ÅA route is part of paper IV. Figure 16 shows the set-up of the RO membrane used. The RO membrane model is Filmtec XLE-2521 and provided by Dow Chemical Company. In the case where the aqueous process route is chosen, it was investigated if the water content could be controlled by reverse osmosis. An increased concentration of magnesium will also favour the carbonation process according to an earlier study by Åbacka (2014).
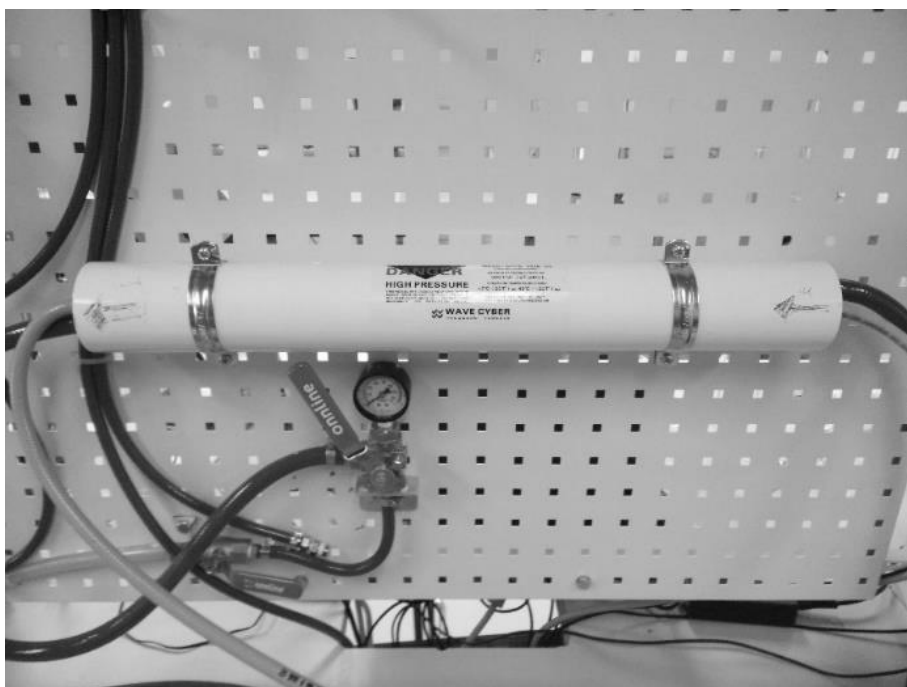

Figure 16. Filmtec XLE-2521 RO membrane unit, manufacturer Dow Chemical Company.

The osmotic pressure in a typical solution after extraction can be approximately 23 bar. This pressure must hence be overcome when pure water is run on the

permeate side of the membrane. One option that was studied was therefore the recirculation of a magnesium depleted solution, possessing higher osmotic pressure than water, on the permeate side. The difference in osmotic pressure becomes thus lower which in turn requires a lower applied pressure on the membrane according to the aforementioned equation

$$\Delta p > \Delta \Pi \qquad\qquad (8).$$

The results did show, however, that the osmotic pressure actually increased in the magnesium depleted solution (compared to the magnesium rich solution) and thus the idea of transporting water from the magnesium-rich solution to the magnesium-depleted solution did not work. Further optimising of the carbonation step might also result in a lower ion concentration in the solution after carbonation, but most likely the excess of ammonia together with magnesium still present in the solution keeps the osmotic pressure of the solution relatively high. The optimisation of the carbonation step has not been studied in this thesis. RO separation does not seem to be a viable option, at least with the specific reverse osmosis membrane and pumps (KNF liquiport pump, NF1.300 KT 18.S) used in this project, considering the very high pressure that would be needed, e.g. 200 bar pressure is needed for the separation of water from a 4 M ammonium sulphate solution (Virtanen, 2015). The water usage should already be primarily adjusted at the extraction step in order to keep it at a minimum level. The water volumes that are needed will also depend on whether the thermal solid/solid or the aqueous extraction step is applied. For the actual conditions, forward osmosis (FO) might have been a better option. Forward osmosis uses the natural driving force of osmosis, i.e. the transport of water from low concentration to high concentration solutions. This in turn require a draw solution, commonly some inorganic salt, that would require additional treatments to serve as part of the ÅA route. This was not studied any further at this stage (Kolliopoulos et al., 2015).

5.4. Precipitation of Ammonium Sulphate with Alcohol

A US patent (Greco, 1975) presents the option of precipitating ammonium sulphate by adding alcohol to a water solution with ammonium sulphate. Somewhat similar work was reported recently by Sanna et al., (2016), and this was around the same time also briefly tested and reported in Paper IV. The aim was to investigate if it was possible to separate ammonium sulphate from ammonium bisulphate, and to see how iron and magnesium sulphates present in the solution behaved. This could be an acceptable option when applying the thermal

solid/solid extraction route since AS will be separated in its solid state. The drawback is that the ethanol has to be separated from the process solution again after the separation of AS.

To test this, 10 ml samples with water and analytical grade chemicals were prepared as follows; 2 g $FeSO_4 \cdot 7H_2O$, 1 g $MgSO_4$, 1 g AS and 1 g ABS, respectively. 20 ml of ethanol was thereafter added to all samples. The solutions were stirred briefly. Ammonium sulphate, iron sulphate and magnesium sulphate were precipitating in their individual sample holders while ABS remained in solution even when ethanol was added. The precipitation efficiencies are shown in Table 6.

Table 6. Precipitation efficiency of three different 10 ml solutions when adding 20 ml of ethanol.

Species	Mass solid	Precipitation efficiency
$MgSO_4 \cdot 7H_2O$	1.03 g	50.3%
$FeSO_4 \cdot H_2O$	1.16 g	94.9%
AS	0.44 g	44%

5.5. Multiple Extraction Steps

Different magnesium extraction efficiency results have been reported in several studies (Lavikko, 2017; Nduagu et al., 2012a,b; Romão et al., 2016). The magnesium extraction has typically been around 30-80 %-wt for serpentinites, depending on the origin of the serpentinite, process parameters, flux salt used and presence of water. However, it is clear that some magnesium stays in the rock independent of conditions. Two options were studied in order to try to achieve increased extraction efficiency and and the results were reported in paper IV:

- The effect of extracting magnesium from unreacted rock using a solution that already had been used once for extraction by the thermal solid/solid extraction step was studied. pH of the solution after extraction and filtering if insoluble material is normally around 1.5-2, which indicates quite acidic conditions and the suitability of extracting metals from fresh rock was therefore also studied (extraction step 2 in Table 7).
- An attempt was also made to extract more magnesium from the already once-reacted rock, i.e. letting the rock undergo two sequential thermal solid/solid extraction steps with the aim of extracting as much magnesium as possible (extraction step 1 and 3 in Table 7). An extra extraction step

would, however, require additional energy input and would therefore require significant extraction of magnesium in order to be a feasible option.

Table 7. Process parameters, pH of the obtained solutions and insoluble mass (g) of the multiple extraction tests.

No.	Time (min)	Temp (°C)	Extr. step	Particle size (µm)	Initial mass (g)	H₂O (l)	pH AS	pH ABS	pH AS+ABS	Residue AS (g)	Residue ABS (g)	Residue AS+ABS (g)
1	60	440	1	125-250	30	0.25	1.53	2.87	1.9	25.53	24.57	24.88
2	30	22	2A	125-250	5	0.05	2.00	3.66	2.66	5.03	5.07	5.11
3	60	60	2B	125-250	5	0.05	2.43	4.17	2.50	4.99	5.05	5.12
4	120	60	2C	125-250	5	0.05	2.52	4.80	2.50	4.85	5.04	5.18
5	60	440	3	125-250	4.5	0.05	1.65	2.6	1.63	3.91	3.61	3.72
6	60	440	1	74-125	30	0.25	1.93	2.66	2.03	25.03	25.49	23.43
7	60	80	2	74-125	5	0.05	2.2	3.18	2.18	5.32	5.34	5.68
8	60	440	3	74-125	4.5	0.05	1.78	2.5	1.64	4.03	3.95	4.00

Each test (no. 1-8 in Table 7) was done three times with either AS, ABS or AS+ABS as flux salt, respectively. The ratios of the flux salts are given in Table 8 and the rock used was the aforementioned waste rock from Hitura nickel mine. Two different particle size fractions were also used; 74-125 µm and 125-250 µm, respectively. From Table 7 it should be noted that the longer extraction time of 120 min did not seem to enhance the extraction (no. 4) compared to a shorter extraction time of 60 min (no. 3). The extraction did not seem to become better even if the temperature was increased to 60 °C (no. 3) compared to room temperature (no. 2), either.

Table 8. Serpentinite (S):Flux salt ratio for the tests in Table 7.

Compounds	Ratio	Comment
S:AS	2:3	A commonly used ratio for the extraction tests
S:ABS	2:1.3	Same amount of ABS as in the S:AS+ABS case but no AS
S:AS+ABS	2:1.5+1.3	Half of the molar amount of AS in the S:AS case replaced with ABS

The results in Table 9 show that the best extraction efficiencies for both iron and magnesium are obtained when a combination of AS and ABS flux salts is present in the thermal solid/solid extraction tests at 440 °C. The concentrations of the

metal ions were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and verified by atomic absorption spectroscopy (AAS) in the solutions obtained after dissolution of solid material. Furthermore, comparing the tests with AS+ABS and ABS only, shows that AS plays a role in at least the thermal solid/solid extraction step.

Table 9. Magnesium and iron extraction efficiencies for multiple extraction step tests.

No.	Extr. step	Thermal sol/sol or aqueous	Mg ext % AS	Mg ext % ABS	Mg ext % AS+ABS	Fe ext % AS	Fe ext % ABS	Fe ext % AS+ABS
1	1	Thermal	35.0	25.8	46.0	15.6	12.2	16.5
2	2A	Aqueous	-3.13	-13.99	-35.21	-0.09	-9.78	-5.08
3	2B	Aqueous	2.60	-5.69	-12.11	2.12	-7.66	6.00
4	2C	Aqueous	7.91	-4.49	2.89	-1.38	-9.42	1.66
5	3	Thermal	28.28	26.06	43.59	15.72	15.81	21.17
6	1	Thermal	29.97	25.88	37.65	22.44	23.35	31.19
7	2	Aqueous	5.69	2.43	5.00	-6.24	-13.86	-5.05
8	3	Thermal	42.85	25.28	45.60	25.16	14.69	25.87

Negative extraction results in Table 9 indicate that some complex formation or precipitation takes place instead of extraction of more metals from the rock. This makes it difficult to draw any conclusion as to whether the presence of AS and/or ABS are favourable for the aqueous extraction step. The reasons for the negative extraction efficiency number were also studied by analysing the solid samples by SEM/EDX. Only a few analysed points indicated significant sulphur contents, which in turn could imply the presence of insoluble sulphates. The solid/liquid ratio was also set sufficiently high in order to avoid reaching the dissolution saturation amounts of magnesium and iron sulphates. Magnesium and iron were clearly detectable in the solid residues, which also could indicate that amorphous material was formed in the solid fraction. The issue with negative extraction numbers seems also to be more prominent for the larger particle size fraction. Minor magnesium extraction was reported for the smaller particle size fraction for the aqueous extraction step, which indicates that more magnesium could possibly be extracted from the rock after a first thermal solid/solid extraction step. The application of multiple step extraction must be considered carefully with respect to the benefits from the additional magnesium extracted compared to the energy demands.

The particle size after the first thermal solid/solid extraction step was analysed in SEM, Figure 17. The particles are finer in the case where AS + ABS were used as flux salt, which confirms the results from the remaining residue in Table 7 and the metal extraction numbers in Table 9. More rock was dissolved with both AS and ABS present, which makes it natural to expect that the solid particles also become finer.
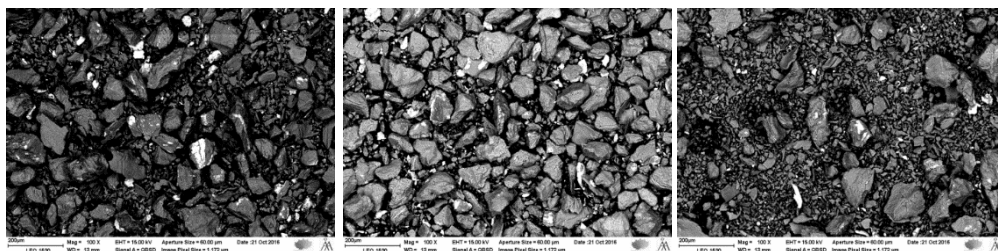

Figure 17. SEM images of the insoluble residue after the first thermal solid/solid extraction step using particle size fraction 74-125 μm. Flux salt used was AS (left), ABS (middle) and AS+ABS (right).

5.6. Electrodialysis

The last two papers of this thesis (V-VI) focused on the possibilities to apply bipolar membrane and monovalent ion selective membrane electrodialysis to the ÅA route, or some of the modified ÅA routes. Different concepts and set-ups have been studied;

- Paper V focused on the possibilities of applying separate ammonium bisulphate from ammonium sulphate using monovalent ion selective membrane electrodialysis. The idea was to separate the monovalent NH_4^+ and HSO_4^- ions from the process stream in order to recover ABS before the carbonation step (where the high pH needed implies that bisulphate ions will transform to sulphate ions). Suitable anode materials were tested and three or five compartments were used in the stack (of which two containing the electrodes).
- The work in paper VI applied bipolar membrane electrodialysis in order to obtain acid and bases that could be used for extracting more rock (acid) or increase pH in the carbonation step (base). Platinised titanium electrodes were used both for the anode and for the cathode.[3]

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[3] Note that since no funding was available for purchase of a professional set-up, a compartment made of 3-7 compartments was built in-house using Astom membranes ordered via Eurodia. Compartment widths were relatively large for the set-up used.

Figure 18 shows a set-up for the second case where the feed solution is continuously entering the middle compartment and collected afterwards in a separate vessel (right). The acidic and alkaline solution are recirculated in vessels (middle). pH and electric current are continuously measured (left) and the voltage adjusted with the power supply (right). The pumps placed in the background are used for recirculation of electrode solution. Figure 18 shows a set-up with five compartments, of which two used for electrodes. The number of compartments have varied between 3-7 depending on set-up used.
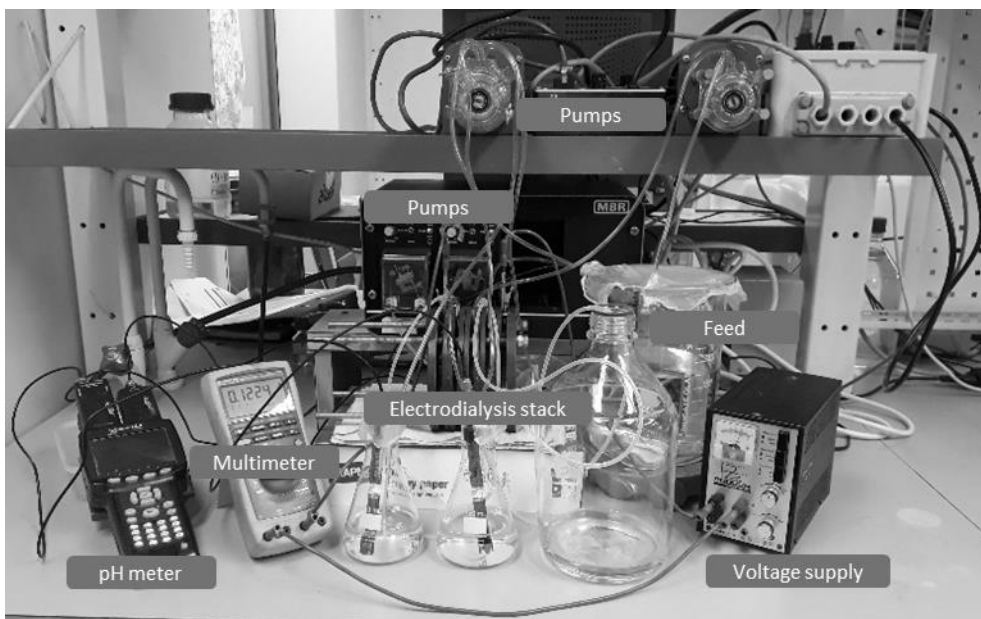

Figure 18. Bipolar membrane electrodialysis set-up with five compartments used in part of the tests.

5.6.1. Monovalent Membrane Electrodialysis - the Effect of Compartment Width, Number of Compartments and Performance

Several parameters might affect the performance of the membranes. Some tests were done to investigate the effect of;

- Number of compartments
- Compartment width
- Performance after several tests

These results have not been published previously in any of the papers I-VI and will therefore be presented in this section. The starting solution containing 0.05 M AS and 0.05 M ABS was added to every second compartment in the stack and set-ups of three, five or seven compartments were used in all tests in this section. Figure 19 shows the principle of a seven and a three-compartment set-up, respectively. The five-compartment set-up followed the same structure, with the difference that the middle compartment contained concentrate solution right from the start instead of distilled water, which was the case with the three- and seven-compartment set-up. The exergy need (i.e. electricity consumption) of the increasing number of compartments in the membrane stack was estimated calculating the exergy input for three, five and seven compartments, as shown in Figure 20. The figures show duplicate tests (referred to as A and B in the legends) and these do not deviate from each other significantly. For clarification it should be mentioned that the number of compartments also include the two electrode compartments at the ends. Figure 19 shows the principle scheme of the set-up used for these tests.
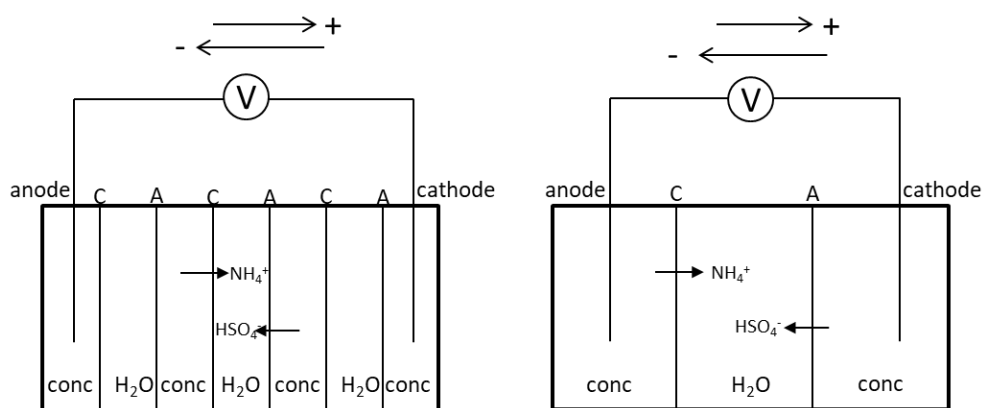

Figure 19. Principle scheme of seven (left) and three (right) compartment set-ups used in the tests. Different compartment widths were also used, either 40 mm or 18 mm.

Figure 20 and Figure 21 show that the exergy input is increasing with time, but decreases with an increasing number of compartments. This could be verified by the fact that common practice for electrodialysis is to place up to hundreds of repeating units (Drioli & Giorno, 2010). The more repeating units the less exergy goes to the water electrolysis at the electrodes. The exergy consumption would therefore become much lower as more repeating units (and narrowed compartment width) are present in the electrodialysis stack (Nir, O., 2019, personal communication).

Figure 21 shows the total exergy input after a test time of 135 minutes. A trend line corresponding to equation $y=196.57x^{-0.586}$ was defined where y is the exergy input and x total number of compartments. The equation is, however, only based on three points which makes it questionable for use as an estimation for a large number of compartments.
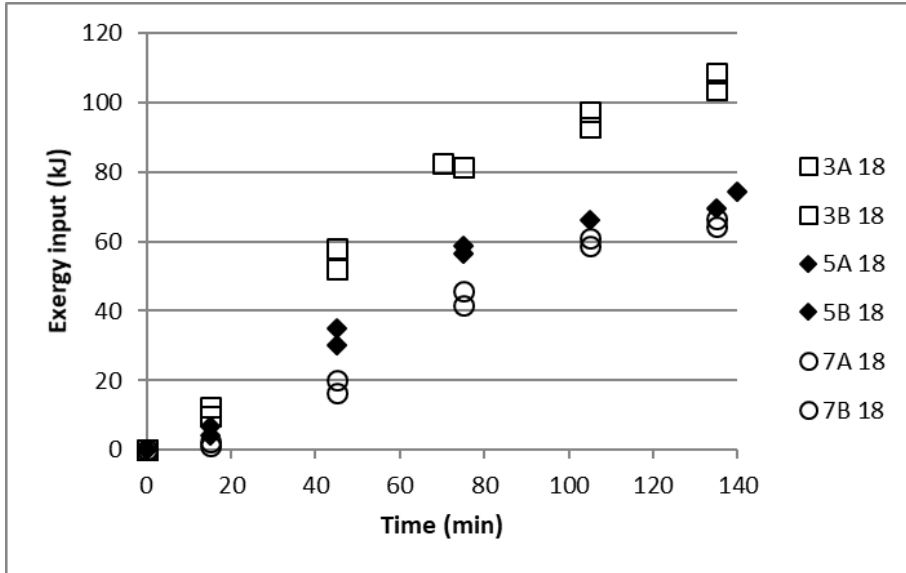

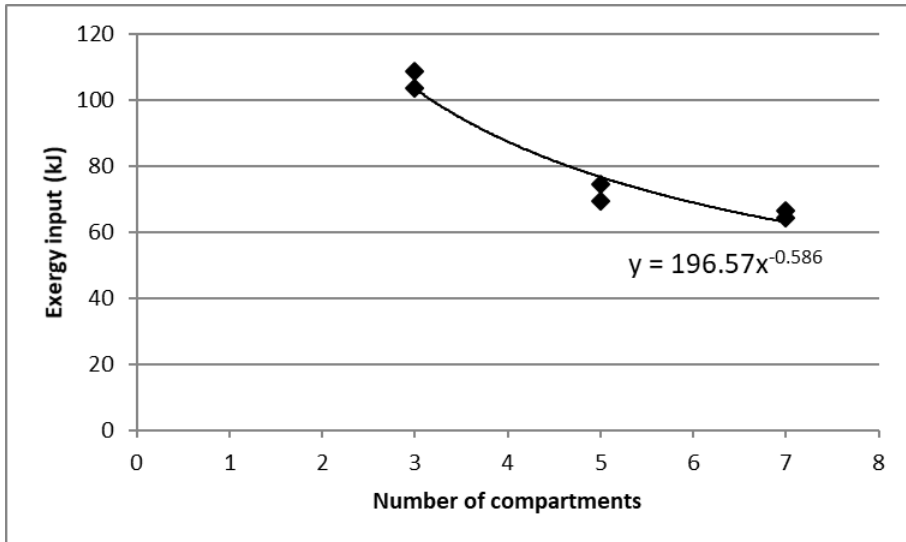*Figure 20. Exergy input as function of time for 3,5 or 7 compartments at 20 V.*

Figure 21. Exergy input as function of number of compartments after 135 min. The compartment width was 18 mm and the tests were performed at 20 V.

45

The influences of compartment width and distance between the electrodes were also tested. Two different compartment widths of 18 and 40 mm, respectively, were used. The set-up contained either seven 18 mm compartments with a total width of 126 mm, or three 40 mm compartments with a total width of 120 mm. Sampling was done from the middle compartment of the stack, initially containing distilled water. Every other compartment were filled with 0.05 M AS and 0.05 M ABS solution, respectively, and the tests were done in batch mode during 135 min. The remaining compartments were filled with distilled water. Figure 22 shows the NH_4^+ separation degree, pH, electric current and cumulative exergy (electricity) input against time for the duplicate test with either three or seven compartments. The NH_4^+ separation degree was calculated based on the quantity of ammonium ions that were permeating the membrane to the middle compartment versus the starting ammonium concentration in the compartment next to it. As expected, the separation degree increased when seven compartments were used instead of three. Common practice is to keep the compartment width as small as possible. The electric resistance will otherwise become very high in the electrolyte (Scott, 1995). For convenience of sampling, analysing and possible recirculation or continuous flow, the set-up was designed with a compartment width of 40 mm at first, but later it was reduced to 18 mm. At this stage the aim was to see whether it is possible to achieve separation at all. Scaling up the process will require that laboratory scale electrodialysis set-ups with narrower compartment width and more repeating units are used.

The electric current through the stack decreases after 40 and 75 minutes, respectively, for the seven and three compartment set-up, as shown in Figure 22. If the compartments initially containing concentrate become depleted with ions, the current will not be able to pass through the stack as easily. The fact that the electric current decreased can, at least partly, be referred to as concentration-polarisation described in Section 2.3). Keeping in mind that the seven compartment set-up has more depleted compartments and that the NH_4^+ separation degree reaches almost 100%, this could explain why the current becomes much lower for the seven compartment set-up than the three compartment set-up. The exergy input for the three compartment set-up becomes also higher, which is in line with the findings where the effect of compartment numbers are studied. pH levels in the two set-ups do not differ significantly.
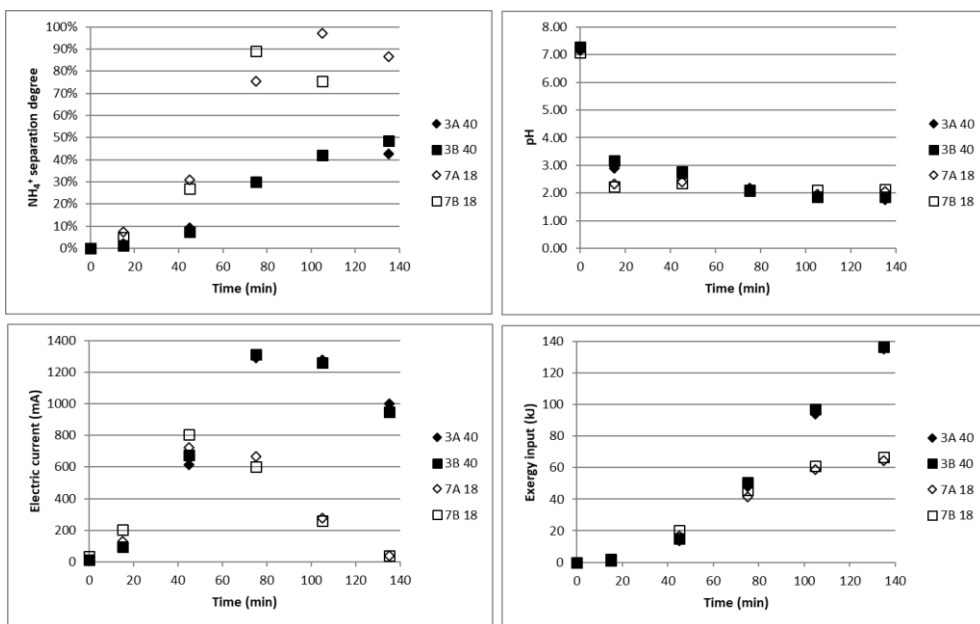
Figure 22. NH₄⁺ separation degree, pH, electric current and exergy input as function of time for a stack with 3 · 40 mm compartments or 7 · 18 mm compartments.

Figure 23 shows the result from five identical tests done in order to study if and how the performance of the membranes would change when used several times. The stack consisted of five compartments with fresh membranes inserted before the first test. The membranes were washed with water between the tests. No significant changes after repeating the test at 20 V and 135 min for five times were noticed. The monovalent membranes have not been used for further tests after this.
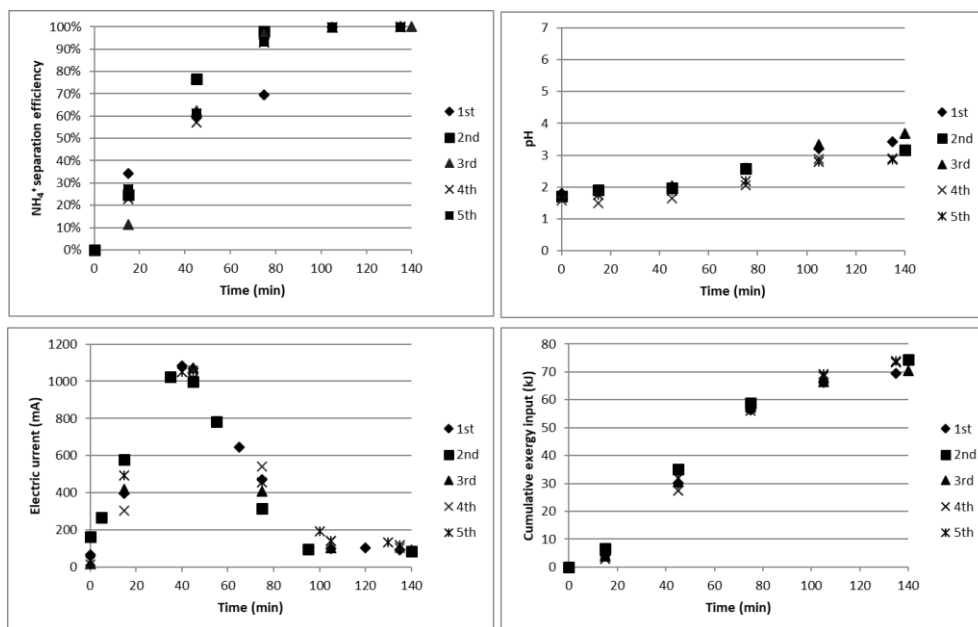
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Figure 23. Results from five identical tests with five compartments and 20 V. The analyses were done on the middle compartment with starting solution of 0.05 M AS + 0.05 M ABS.

5.6.2. Monovalent Membrane Electrodialysis - Exergy Input Compared with Exergy of Mixing

Paper V focused on finding a suitable electrodialysis set-up and input exergy was compared with exergy of mixing for set-ups with 40 mm width compartments. Common to all tests were that the input exergy, i.e. the electrical power input, was many times higher than the exergy of mixing. As an example, a test with 0.1 M AS + 0.1 M ABS reached an ABS separation degree number of 88.1 %. The total exergy (electricity) input for the separation was 85 kJ while the exergy of mixing using a three compartment set-up (Figure 19, right), was calculated to 0.0009 kJ and -0.0024 kJ in compartment 1 and 2, respectively. This significant and remarkable difference would certainly decrease if more repeating units and narrower compartment widths had been used. Paper V also focused on finding suitable electrodes. Platina wire as anode electrode material and stainless steel as cathode material was found to be suitable. As a result of this study, platinised titanium electrodes were therefore later used both as anode and cathode material in the experiments presented in Paper VI. Some results from these tests, with bipolar membranes combined with monovalent membranes, are presented in next section.

5.6.3. Bipolar Membrane Electrodialysis

Four different set-ups were tested in Paper VI. One set-up was arranged in such a way that it should be possible to produce H_2SO_4 and NH_4OH, which in turn could be used in the extraction or precipitation/carbonation steps, respectively, Figure 24.
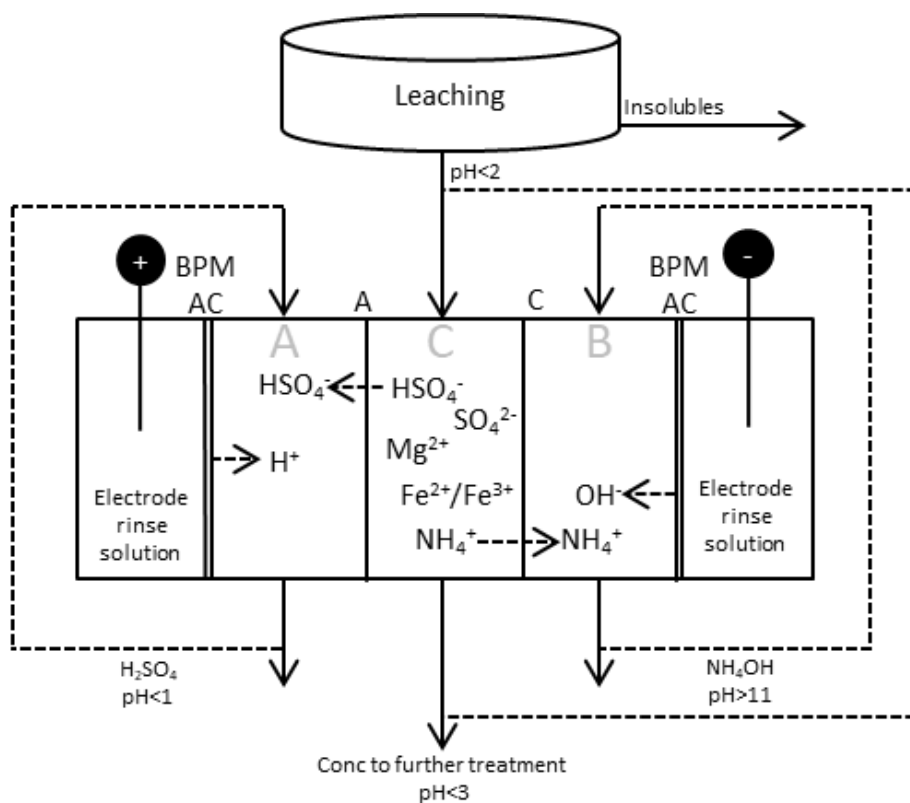

Figure 24. Bipolar membrane electrodialysis set-up for separation after the extraction step.

Both synthetic and rock-derived solutions were tested and voltages of 20 or 30 V were used in the tests. As shown in Figure 24 (dotted lines) different options were tested with designated batch, recirculating or continuous flow, respectively. The possibilities for producing acids and bases after the carbonation step was studied using three different set-ups, see Figure 25. It was verified by ICP-MS analyses provided by Eurofins that nickel present in the rock-derived solutions does not pass through to any other compartment and will in that context not disturb the electrodialysis separation process.
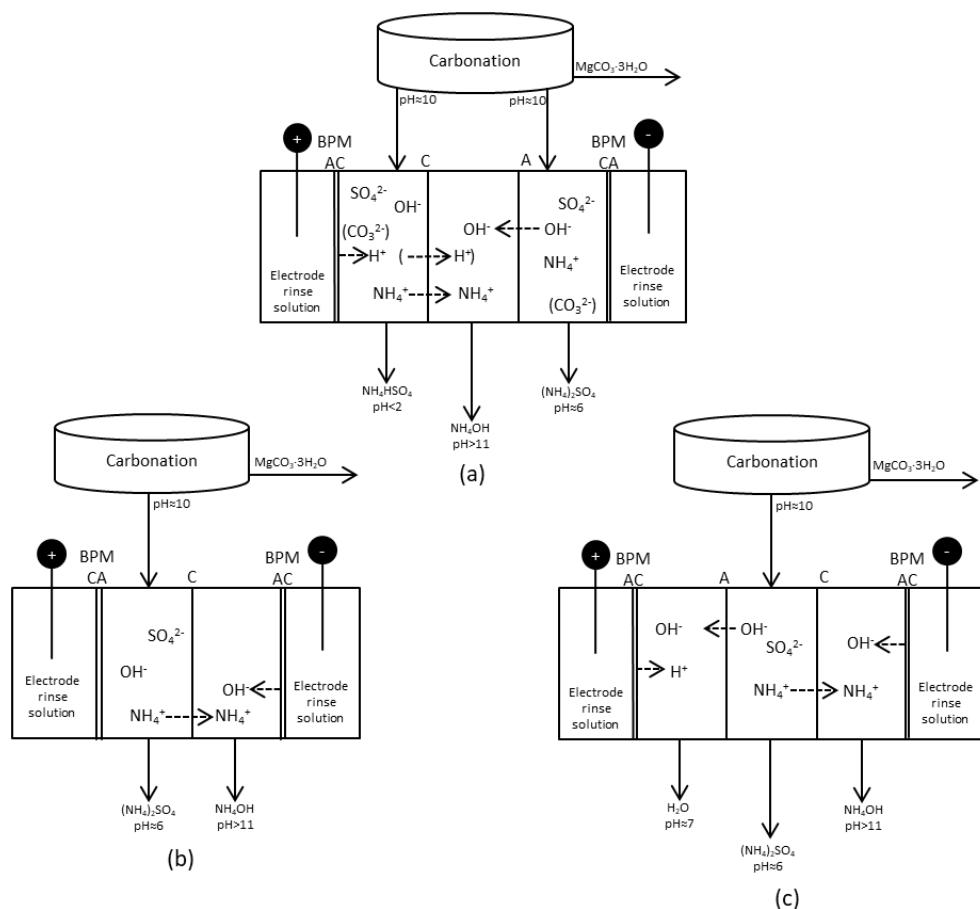
Figure 25. Bipolar membrane electrodialysis set-up for separation after the carbonation step.

Set-up (a) was found not to be a viable option as SO_4^{2-} and NH_4^+ were ending up in all compartments using this set-up. It had been expected that separation of NH_4^+ ions would occur from compartment 1 to 2 but hardly any ammonium ions were transported from compartment 1. The CMS membrane used also became discoloured in a way that was not noticed in any other set-up. Four different tests were compared to give an indication of how much energy for separation the set-ups need in comparison to each other, see Table 10. The tests selected from following tests types gave the highest exergy input and highest NH_4^+ separation degree in each type of test, respectively;

- Batch mode- after extraction
- Continuous flow at 30 V
- Using rock-derived solutions
- Batch mode- after carbonation

Table 10. Process parameters and energy demand for separating 1 kg of NH_4^+

No.	Set-up	Synthetic or Rock-derived	pH	Analysis method	Analysis solution	Voltage (V)	Flow rate	Type of test	MJ/kg NH_4^+
1	Figure 24	Synthetic	2.2	ISE	Conc. sol	20	-	After leaching-batch	350
2	Figure 24	Synthetic	10.4	External	Alkaline sol.	30	0.67 L/h (C) 0.33 L/h (A, B)	After leaching-continuous	302
3	Figure 24	Rock der.	10.9	External	Alkaline sol.	30	0.25 L/h (C) 0.084 L/h (A,B)	After leaching C continuous A, B recirculated	3.4
4	Figure 25 (c)	Synthetic	11.2	External	Alkaline sol.	30	-	After carbonation-batch	1.7

According to the energy calculation result presented in Table 10, there are two tests resulting in lower energy demand in set-ups both applied after the extraction, or after the carbonation step, respectively. These should be further tested, ideally in larger laboratory scale set-ups with more repeating units and narrower compartment width. It is at this point too early to draw any strong conclusions about the best set-up, but according to the initial test, it seems that the set-up used for the separation of rock-derived solutions after the leaching step should be further tested together with set-up (c) applied after the carbonation step. Sufficient separation/production of ammonia solution which could be used for the carbonation step must be achieved if BPMED will be seen as a viable option for streamlining the aqueous option of the ÅA route. The same applies to the production of acid and the extraction of magnesium from the rock. If upscaling with a larger number of repeating units and narrower compartment width gives promising results, then a good option for the recirculation and regeneration of chemicals would have been demonstrated.

5.7. Preliminary Design of ÅA *Route 3*

As a summary of the work with BPMED it should also be pointed out that applying BPMED to the solutions also implies preferential favouring of the wet alternative of the ÅA route, keeping all process steps in aqueous solution. Paper VI thus serves as a feasibility study for future work, where the most important effort will be to study the separations of ions at larger scale, with the aim of achieving better separation (mainly as a result of narrower compartment width) and lower exergy (electricity) input relative to the volumes (a result of more repeating units).

Based on the laboratory scale results in this thesis, it seems as if the application of electrodialysis could be part of the ÅA route. This will require scale-up and tests with commercial laboratory scale ED stacks. An inclined settler could be used at least for the separation of magnesium carbonates, based on the results from Paper I. Improvement of the settling rates by the addition of flocculates might enable the use of inclined settlers also for the separation of iron (oxy)hydroxides. Separation of ABS using ethanol, RO, and multiple step extraction are not seen as options at this stage, also based on the result presented in this thesis that were mainly negative. Figure 26 below serves as a summary of improvements to the wet ÅA route, leading to the new concept called ÅA route 3. The configuration of the BPMED/ED stacks as well as the separation of magnesium hydrocarbonates in an inclined settler needs still to be further tested, but tests this far has shown that separation can be achieved with BPM and ED as well as inclined settlers as shown in Figure 26.
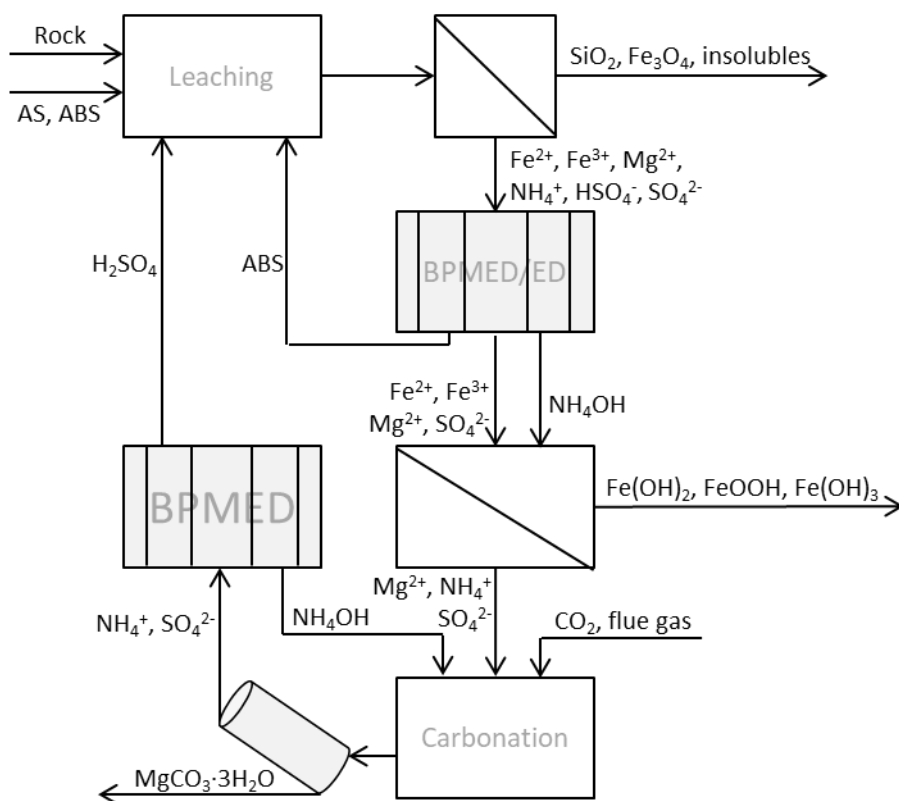

Figure 26. Process scheme over ÅA route 3, modified from earlier versions like the conventional ÅA route and the wet ÅA route. Possible additional process units (grey-marked) serve for the regeneration and separation of flux salts and end-products involved in the process.

6. Conclusions

Different methods for finding options for streamlining and regeneration of chemicals involved in the CO_2 mineralisation route referred to as ÅA route were studied in this thesis. The methods studied were divided into different sub-projects and presented in the Papers I-VI of this thesis. The sub-projects will be briefly summarised in this section and suggestions for future work will be given.

Four different rock types were compared in paper II and paper III, one of them being the already studied serpentinite from the waste stockpiles of Hitura nickel mine and the three other an amphibolite from the Sallittu region, a diopside from Pargas region and another serpentinite from the Vammala region. Only the serpentinites show potential for being used in the ÅA route, or any alternative route based on it. Binding capacities of 292 and 260 kg CO_2/ton rock in aqueous solution extraction were obtained. The capacities were somewhat lower when applying the thermal solid/solid extraction step; 240 and 207 kg CO_2/ton rock, for the Hitura serpentinite and the Vammala serpentinite, respectively. This work shows that the mining overburden rock types from Parainen and Sallittu do not fulfil the requirements for the use in mineral carbonation. This gives a negative answer to the research question about the suitability of these two overburden rocks tested as feed stock for mineral carbonation.

Attempts to separate magnesium and iron precipitates in an inclined tube settler were made in order to make the process more continuous. The sedimentation rate for magnesium hydrocarbonates was more rapid than that of magnesium and iron hydroxides, respectively. This was confirmed by SEM images showing that the magnesium hydrocarbonates had larger particle size, which will be beneficial for the settling rate. The settling rates were still low at this stage of research, and the separation of inclined settlers should therefore be studied further, especially with respect to continuous tests and in larger scale. The fact that magnesium

hydrocarbonates settle faster than iron and magnesium hydroxides makes the wet ÅA route a better option, with the possibility to separate at least the final product with the use of inclined settlers.

A reverse osmosis membrane was used in order to try to separate water from the process stream. The osmotic pressure of typically 23 bar in a solution after the magnesium extraction step must be overcome before any separation can take place. The membrane device and pumps used were designed for a maximum pressure of 10 bar. In order to solve this issue, the downstream magnesium depleted solution was allowed to enter the permeate side of the membrane to lower the osmotic pressure difference. This did not give any improved results, and the suggestion is that other membranes could be studied and that the use of water should already be kept to a minimum at the dissolution step of the ÅA route. The problem could be, however, that some excess water must be used in order get all reacted rock washed out from the kiln when the thermal solid/solid route is used.

Different methods for AS/ABS salt recovery and some test results were presented in paper IV. Ammonium bisulphate was separated from ammonium sulphate by the addition of ethanol. At the same time magnesium and iron sulphates also precipitated. The separation of ammonium sulphate from ammonium bisulphate is therefore possible, but the ethanol has to in turn be recycled and magnesium and iron sulphates will need to be separated from the precipitated ammonium sulphate. The patent method describing the separation by addition of alcohol was, however, still tested since it is the only method found in the literature for specifically separating ammonium sulphate from ammonium bisulphate. Effort was also given to the extraction of magnesium by multiple extraction steps using subsequent thermal solid/solid and aqueous solution steps. The resulting extraction efficiency became, however, negative which could indicate that amorphous material is formed or that some sulphates remain in the solids fraction. Hardly any sulphur was found in SEM/EDX analyses, however. Based on data from these tests, however, the multiple step extraction does not seem to give significant amounts of additional magnesium extracted compared to the initial extraction step. This answers the research question about the possibility to extract even more magnesium applying multiple extraction steps. The combination of extraction steps could still be further investigated in order to increase the degree of extraction of magnesium from the rock.

Paper V demonstrated the use of an initial set-up of monovalent ion selective membranes for electrodialysis to see if the separation of ammonium sulphate from ammonium bisulphate could be achieved. The compartment width was 40 mm. The degree of separation of ammonium ions was quantified by measuring the concentration obtained with ion selective membranes. By comparing the exergy of mixing with the input exergy, it was shown that an exergy input many times higher was needed compared to theory, i.e. to what extent the ions were separated. One improvement in paper VI was therefore to narrow the compartment distance to 18 mm to partly overcome the electrical resistance in the solutions.

Finally, in paper VI, the application of bipolar membrane electrodialysis to the ÅA route salt solutions was studied. Four different set-ups were used resulting in energy demands ranging from 1.7 to 350 MJ/kg NH_4^+ separated. The two best cases, which were two different types of set-ups placed after the extraction step or after the carbonation step, respectively, should be further studied. Focus should be placed on running experiments in a commercial lab-scale set-up with sufficiently narrow compartment width and more repeating units than was used here. This would then give better indications of the suitability of the individual set-ups and could also give more accurate numbers of the exergy (electricity) input needed for the electrodialysis step. The separation using more repeating units will still require two electrodes so the energy used for the water electrolysis will not increase. A significantly lower exergy input will most likely be the case where more repeating units are used. However, results obtained this far has shown that separation of ions from input chemicals by ED is possible which makes it beneficial to continue research in order to find the optimal solution for the application of BPMED to CO_2 mineralisation as described here.

The regeneration of the chemicals involved in the ÅA route or any alternative route was only briefly studied in the context of reverse osmosis separation of ammonium sulphate solutions before this work was started. This thesis serves as a preliminary feasibility study of several methods from which it is possible to continue to design and optimise regeneration options depending on whether a dry or wet process route is chosen. The research questions stated were, if not fully, at least partly answered through the different sub-projects presented in this work. Challenges and results were presented, indicating what efforts should be made next in order to streamline and regenerate chemicals involved in the CO_2 mineralisation process here called ÅA route 3.

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