

Production of magnesium carbonates from serpentinites for CO₂ mineral sequestration - optimisation towards industrial application

Inês Sofia Soares Romão



Doctor of Technology Thesis

Thermal and Flow Engineering Laboratory

Department of Chemical Engineering, Faculty of Science and Technology,
Åbo Akademi University, Turku, Finland

GERST - Environment, Reaction, Separation and Thermodynamics,
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Preface

The work presented in this thesis aims at contributing to the minimization of the thorny problem that is climate change. It was conducted under a double degree doctoral thesis at the Thermal and Flow Engineering Laboratory, Åbo Akademi University, Finland and the Chemical Engineering Department, University of Coimbra, Portugal. The research was partially funded by the Academy of Finland Sustainable Energy project "Carbonates in Energy Technology - CARETECH" (2008-2011), the Leonardo da Vinci project (2010-2011), the Ekokem environmental scholarship funding (2011), Tekes / A*Star Singapore, the "Novel low energy routes to activate minerals for useful products - NEACAP" (2010-2014) project and an Åbo Akademi University Rector's scholarship (2014).

I would like to emphasize that without Prof. Ron Zevenhoven this thesis would not have seen the light of day. It has been most gratifying to work with and learn from him. He is a remarkable supervisor and I am most indebted to him for his mentorship, support, continuous challenging, thoughtfulness and friendship. Thank you for making me feel at home 3500km away from me.

I was fortunate to have help and support from Prof. Licínio Ferreira as my supervisor since my master studies. I am most thankful to him for triggering my interest in and concern for the climate change crisis, for believing in my success and encouraging me to go to Finland.

I was given the chance of doing the work that I love, surrounded by intelligent, challenging and selfless people. I have to acknowledge and thank the personnel at the Thermal and Flow Engineering Laboratory that always showed desire to help and interest in my research work: Henrik, Frank and Mikko. A special appreciation goes to Affi and Vivéca for both friendship and infinite patience. I also would like to thank my co-workers (some co-authors) and friends: H-P, Martin F., Johan, XP, Martin S., Hamid, Hannu, Marketa, Evelina, Inga,

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Sten Lindholm from ÅAU Analytical Chemistry, even from a distance, was extremely helpful with procedures for digestion of rocks and hundreds of ICP analyses. I would like to thank Prof. Olav Eklund, Lauri and Sonja from the ÅAU Geology and Mineralogy and Prof. Manuela da Vinha from the UC Department of Earth Sciences for providing rock material and precious help with experimental work. Cooperation with James Highfield, ICES/A*Star, Singapore and with Matias Eriksson, Nordkalk Corporation, Pargas, Finland, was most valuable and played an important role in this thesis. I would also like to thank the laboratories of Analytical Chemistry and Process Design and Systems Engineering, ÅAU, Finland, for providing equipment support.

In addition to all the people that in some way contributed to my work, there are those who were essential for my joyful life both in Finland and Portugal. Leonor, Polytimi, Cátia, Maria Z. and Luís B., thank you for supporting, listening, caring and making me laugh until tears came out of my eyes.

To my parents I must say that I owe them a life of unconditional love. They are incredibly kind, supportive and strong people and I couldn't be more proud of being their daughter. Thank you!

Finally, it was João's endless love, wisdom, encouragement, patience, altruism and strength that kept my spirit alive and never allowed me to back down. Even from afar, no one ever believed more in me, gave me more confidence or had the power to pick-me-up with a simple smile. This thesis is as much yours as it is mine!

Abstract

Global warming is one of the most alarming problems of this century. Initial scepticism concerning its validity is currently dwarfed by the intensification of extreme weather events whilst the gradual arising level of anthropogenic CO₂ is pointed out as its main driver. Most of the greenhouse gas (GHG) emissions come from large point sources (heat and power production and industrial processes) and the continued use of fossil fuels requires quick and effective measures to meet the world's energy demand whilst (at least) stabilizing CO₂ atmospheric levels.

The framework known as Carbon Capture and Storage (CCS) – or Carbon Capture Utilization and Storage (CCUS) – comprises a portfolio of technologies applicable to large-scale GHG sources for preventing CO₂ from entering the atmosphere. Amongst them, CO₂ capture and mineralisation (CCM) presents the highest potential for CO₂ sequestration as the predicted carbon storage capacity (as mineral carbonates) far exceeds the estimated levels of the worldwide identified fossil fuel reserves.

The work presented in this thesis aims at taking a step forward to the deployment of an energy/cost effective process for simultaneous capture and storage of CO₂ in the form of thermodynamically stable and environmentally friendly solid carbonates. R&D work on the process considered here began in 2007 at Åbo Akademi University in Finland. It involves the processing of magnesium silicate minerals with recyclable ammonium salts for extraction of magnesium at ambient pressure and 400-440°C, followed by aqueous precipitation of magnesium in the form of hydroxide, Mg(OH)₂, and finally Mg(OH)₂ carbonation in a pressurised fluidized bed reactor at ~510°C and ~20 bar P_{CO2} to produce high purity MgCO₃.

Rock material taken from the Hitura nickel mine, Finland, and serpentinite collected from Bragança, Portugal, were tested for magnesium extraction with both ammonium sulphate and bisulphate (AS and ABS) for determination of

optimal operation parameters, primarily: reaction time, reactor type and presence of moisture. Typical efficiencies range from 50 to 80% of magnesium extraction at 350-450°C. In general ABS performs better than AS showing comparable efficiencies at lower temperature and reaction times. The best experimental results so far obtained include 80% magnesium extraction with ABS at 450°C in a laboratory scale rotary kiln and 70% Mg(OH)₂ carbonation in the PFB at 500°C, 20 bar CO₂ pressure for 15 minutes.

The extraction reaction with ammonium salts is not at all selective towards magnesium. Other elements like iron, nickel, chromium, copper, etc., are also co-extracted. Their separation, recovery and valorisation are addressed as well and found to be of great importance.

The assessment of the exergetic performance of the process was carried out using Aspen Plus® software and pinch analysis technology. The choice of fluxing agent and its recovery method have a decisive sway in the performance of the process: AS is recovered by crystallisation and in general the whole process requires more exergy (2.48–5.09 GJ/tCO₂sequestered) than ABS (2.48–4.47 GJ/tCO₂sequestered) when ABS is recovered by thermal decomposition. However, the corrosive nature of molten ABS and operational problems inherent to thermal regeneration of ABS prohibit this route. Regeneration of ABS through addition of H₂SO₄ to AS (followed by crystallisation) results in an overall negative exergy balance (mainly at the expense of low grade heat) but will flood the system with sulphates. Although the ÅA route is still energy intensive, its performance is comparable to conventional CO₂ capture methods using alkanolamine solvents. An energy-neutral process is dependent on the availability and quality of nearby waste heat and economic viability might be achieved with: magnesium extraction and carbonation levels ≥ 90%, the processing of CO₂-containing flue gases (eliminating the expensive capture step) and production of marketable products.

Svensk Sammanfattning

Global uppvärmning är ett av århundradets mest alarmerande problem. Den ursprungliga tvekan på dess verklighet överskuggas nu av ökningen av extrema väderhändelser med den stigande halten av antropogent CO₂ utpekad som den främsta orsaken. Största delen av utsläppen av växthusgas (GHG) är från stora punktkällor, så som värme- och elproduktion samt industriprocesser. Snabba och effektiva åtgärder krävs för att stabilisera CO₂ halten i atmosfären i samband med fortsatt användning av fossila bränslen för att möta världens energibehov.

Ramverket som kallas Carbon Capture and Storage (CCS) - eller Carbon Capture Utilization and Storage (CCUS) - består av en portfölj teknologier som kan utnyttjas i samband med storskaliga växthusgaskällor för att förhindra CO₂ utsläpp i atmosfären. Bland dem har CO₂-avskiljning och mineralisering (CCM) den största potentialen för CO₂ sekvestrering eftersom den förutsagda lagringskapaciteten av koldioxid (som mineralkarbonater) väl överstiger de beräknade mängderna av världens identifierade fossila bränslereserver.

Arbetet som presenteras i denna avhandling syftar till att göra ett steg framåt för utbyggnaden av en energi och kostnadseffektiv process för samtidig avskiljning och lagring av CO₂ i form av miljövänliga fasta karbonater. FoU-arbetet på den ansedda processen inleddes 2007 vid Åbo Akademi i Finland. Den involverar bearbetning av magnesiumsilikatmineraler med återvinningsbara ammoniumsalter för extraktion av magnesium vid atmosfäriskt tryck och 400-440⁰C, följt av utfällning av magnesium i form av hydroxid, Mg(OH)₂ ur vattenlösning, och slutligen karbonatisering av Mg(OH)₂ i en trycksatt fluidiserad bäddreaktor (PFB) vid ~ 500⁰C och ~ 20 bar PCO₂ för att producera MgCO₃ med hög renhet.

Stenmaterial från Hitura nickelgruva, i Finland, och serpentinit uppsamlat från Bragança, Portugal, testades för magnesium extraktion med både ammoniumsulfat och ammoniumbisulfat (AS och ABS). Detta gjordes för att

bestämma de optimala driftsparametrarna, främst: reaktionshastighet, reaktortyp och inverkan av fukt. Verkningsgraden för extraktion av magnesium vid 350-450°C varierar generellt mellan 50 och 80 %. I allmänhet presterar ABS bättre än AS och har en jämförbar verkningsgrad vid lägre temperaturer och kortare reaktionstider. De hittills bästa erhållna experimentella resultaten visar 80% magnesium extraktion med ABS vid 450°C i en laboratorieskalig roterande ugn och 70% Mg(OH)₂ karbonatisering i en PFB vid 510°C, 20 bar CO₂ tryck i 15 minuter.

Extraktionsreaktionen med ammoniumsalter är inte helt selektiva för magnesium. Andra element såsom järn, nickel, krom, koppar och så vidare är också extraherade. Deras återvinning och tillvaratagande behandlas också eftersom de är av stor betydelse.

Bedömningen av processens exergi prestanda genomfördes med hjälp av Aspen Plus® programvara och pinch analys. Valet av flussmedel och återvinningsmetod har en stor inverkan på. AS återvinns genom kristallisation och kräver i allmänhet mer exergi (2,48-5,09 GJ / t CO₂ sekvestrerat) än ABS (2,48-4,47 GJ / t CO₂ sekvestrerat) som återvins genom termisk nedbrytning. De korrosiva egenskaperna av smält ABS och de operativa problemen med termisk regenerering av ABS hindrar användningen av denna metod.

Regenerering av ABS genom tillsats av H₂SO₄ till AS, följt av kristallisation, resulterar i en totalt sett negativ exergi balans men huvudsakligen på bekostnad av låggradig värme. Detta kommer dock att översvämma systemet med sulfater. Fastän ÅA vägen fortfarande är energiintensiv, är dess prestanda jämförbar med konventionella CO₂ infångningsmetoder som använder alkanolaminlösningar. En energineutral process är möjlig ifall det finns tillgång till närliggande spillvärme av tillräcklig kvalitet. Processen är lönsam ifall en nivå på över 90 % kan uppnås för både magnesium utvinningen och karbonatisering och CO₂-innehållande rökgaser kan behandla direkt, vilket eliminerar dyra infångningssteget, och produkten kan säljas.

Resumo em Português

O aquecimento global é um dos problemas mais alarmantes deste século e o aumento gradual dos níveis atmosféricos de CO₂ é apontado como a sua principal causa. O ceticismo inicial acerca da sua validade é actualmente contrariado pela intensificação de eventos climáticos extremos. A emissão de gases de efeito estufa (GEE) é predominante em processos industriais e de produção de energia. No sentido de (pelo menos) estabilizar os níveis atmosféricos de CO₂, é necessário desenvolver um conjunto de medidas rápidas e eficazes que permitam o uso continuado de combustíveis fósseis e satisfazer a demanda mundial de energia.

A Captura e Armazenamento de Carbono (CCS) - ou Captura Utilização e Armazenamento de Carbono (CCUS) - dispõe de um portfólio de tecnologias aplicáveis às fontes de GEE em grande escala para prevenir a entrada de CO₂ na atmosfera. Entre eles, a captura de CO₂ através carbonatação mineral (CCM) apresenta o maior potencial de sequestro de CO₂ com uma capacidade prevista de armazenamento de carbono que (em muito) excede os níveis estimados das reservas mundiais de combustíveis fósseis.

O trabalho apresentado nesta tese tem como objetivo dar um passo em frente no desenvolvimento de um processo energética e economicamente viável para a captura e armazenamento simultâneos de CO₂, sob a forma de carbonatos sólidos, termodinamicamente estáveis e ambientalmente benignos. Os trabalhos de I&D sobre o processo considerado iniciaram-se em 2007 na Åbo Akademi University, Finlândia. Este envolve o processamento de silicatos de magnésio (serpentinitos) com sais de amónio (recicláveis) para extracção de magnésio (e outros metais como por exemplo o ferro) sob a forma de sulfatos (XSO₄) a 400-440⁰C e pressão atmosférica. Após dissolução dos produtos sólidos, magnésio e ferro são recuperados por precipitação selectiva na forma de hidróxidos. Finalmente, o Mg(OH)₂ produzido é convertido em MgCO₃ de

elevada pureza num reactor de leito fluidizado pressurizado (PFB) a $\sim 500^{\circ}\text{C}$ e ~ 20 bar PCO_2 .

Serpentinitos provenientes de Bragança, Portugal e de uma mina de níquel localizada em Hitura, Finlândia, foram testados para a extração de magnésio com sulfato e bissulfato de amónio (AS e ABS) para determinação das condições óptimas dos parâmetros ideais de operação, sobretudo tempo de reacção, design do reactor e presença de humidade. Eficiências típicas variam entre 50-80% de extracção de magnésio a $350\text{-}450^{\circ}\text{C}$. No geral, o ABS é mais eficaz do que o AS mostrando eficiências comparáveis com temperaturas e tempos de reacção mais baixas. Os melhores resultados experimentais obtidos incluem 80% de extracção de magnésio com ABS a 450°C num forno rotativo de escala laboratorial e 70% de carbonatação de $\text{Mg}(\text{OH})_2$ no PFB a 510°C , pressão parcial de CO_2 de 20 bar, em 15 minutos.

A reacção de extracção com sais de amónio não é, de forma alguma, selectiva em relação ao magnésio. Outros elementos, tais como ferro, níquel, crómio, cobre, etc, são também co-extraídos. A sua separação e recuperação são também discutidas nesta tese concluindo-se que a valorização destes produtos secundários é de grande importância para o sucesso económico do processo.

A avaliação do desempenho exergético do processo foi realizada utilizando o software de simulação Aspen Plus® e técnicas de análise pinch. A escolha do agente de extracção e seu método de recuperação tem uma influência decisiva no consumo energético: quando o AS é recuperado por cristalização, no seu total o processo requer $2,48\text{-}5,09$ GJ/t CO_2 sequestrado, enquanto que a decomposição térmica de AS em ABS resulta num processo que precisa de $2,48\text{-}4,47$ GJ/t CO_2 sequestrado. No entanto, a natureza corrosiva do ABS fundido e problemas operacionais inerentes à regeneração térmica de ABS, proíbem esta via. A regeneração de ABS por adição de H_2SO_4 (seguida por cristalização) resulta num balanço exergético negativo (essencialmente à custa de calor residual de baixa temperatura) mas satura o sistema com sulfatos.

Todavia, e apesar de o processo em estudo ainda ser energeticamente intensivo, o seu desempenho é comparável aos métodos convencionais de captura de CO₂, que utilizem solventes como alcanolaminas, por exemplo. A desejada neutralidade energética do processo depende da disponibilidade e qualidade de calor residual (proveniente de indústrias contíguas) e a viabilidade económica pode ser alcançada com níveis de extração e carbonatação de magnésio $\geq 90\%$, com o tratamento directo de gases de combustão contendo CO₂ (eliminando a dispendiosa etapa de captura) e com a produção de produtos comercializáveis.

Contribution of the author and list of publications

This thesis is based on the publications listed below. They can be found at the end of this thesis and will be referred to using the respective Roman numerals.

The author has planned and performed the experimental/theoretical work and is the main contributor in the publications I and III to VII. The contribution of the author to Paper II is not as significant as for the other listed papers. However, it is the first part of a two-part publication and was here included for clarification and contextualisation of Paper III.

Paper I **CO₂ sequestration with serpentinite and metaperidotite from North-East Portugal**

ROMÃO, I., GANDO-FERREIRA, L.M., ZEVENHOVEN, R.

Minerals Engineering, submitted

Paper II **CO₂ fixation using magnesium silicate minerals part 1: Process description and performance.**

FAGERLUND, J., NDUAGU, E., ROMÃO, I., ZEVENHOVEN, R.

Energy, 41(1), pp. 184-191 (2012)

Paper III **CO₂ fixation using magnesium silicate minerals. Part 2: Energy efficiency and integration with iron-and steelmaking.**

ROMÃO, I., NDUAGU, E., FAGERLUND, J., GANDO-FERREIRA, L.M., ZEVENHOVEN, R.

Energy, 41(1), pp. 203-211 (2012)

Paper IV **CO₂ sequestration with magnesium silicates—Exergetic performance assessment.**

ROMÃO, I., SLOTTE, M., GANDO-FERREIRA, L.M., ZEVENHOVEN, R.

Chemical Engineering Research and Design, 92, 2072-2082(2014)

Paper V **Carbon dioxide storage by mineralisation applied to an**

industrial-scale lime kiln

ROMÃO, I., ERIKSSON, M., NDUAGU, E., FAGERLUND, F., GANDO-FERREIRA, L. M., ZEVENHOVEN, R.

Proceedings of ECOS'2012, Perugia, Italy, June 26-29 2012 - paper 226, (13 pp.)

Paper VI **Combined extraction of metals and production of Mg(OH)₂ for CO₂ sequestration from nickel mine ore overburden.**

ROMÃO, I.S., GANDO-FERREIRA, L.M., ZEVENHOVEN, R.

Minerals Engineering, 53, pp. 167-170 (2013)

Paper VII **Separation and recovery of valuable metals extracted from serpentinite during the production of Mg(OH)₂ for CO₂ sequestration.**

ROMÃO, I., GANDO-FERREIRA, L.M., ZEVENHOVEN, R.

Minerals Engineering, 77, pp. 25-33 (2015)

List of related contributions

The author also contributed to (or wrote) publications and presentations at conferences and meetings with non-reviewed publications which are important to the work presented in this thesis.

Challenges in process scale-up of serpentinite carbonation to pilot scale

SLOTTE, M., ROMÃO, I., ZEVENHOVEN, R.

ENERGY - The International Journal, 62, 142-149 (2013)

Mineralisation of CO₂ using serpentinite rock - towards industrial application

ZEVENHOVEN, R., ROMÃO, I., SLOTTE, M.

Presented at the 2013 *World Resources Forum Conference*, Davos, Switzerland, October 6 – 9, 2013.

Stepwise serpentinite carbonation using the Åbo Akademi route - status and developments

ZEVENHOVEN, R. FAGERLUND, J. , NDUAGU, E., ROMÃO, I., SLOTTE, M. , HIGHFIELD J.

Proceedings of ACEME13, Leuven, Belgium, April 10-12, 2013, pp. 391-400

Carbon storage by mineralisation (CSM): serpentinite rock carbonation via Mg(OH)₂ reaction intermediate without CO₂ pre-separation

ZEVENHOVEN, R., FAGERLUND, J., NDUAGU, E., ROMÃO, I., BU, J.

Energy Procedia 37, 5945 – 5954 (2012)

(presented at GHGT-11, 11th Int. Conf. on Greenhouse Gas Control Technologies, Kyoto Japan, Nov. 18-22, 2012)

Production of Mg(OH)₂ for CO₂ Emissions Removal Applications: Parametric and Process Evaluation

NDUAGU, E., ROMÃO, I., ZEVENHOVEN, R.

Proceedings of ECOS'2012, Perugia, Italy, June 26-29 2012 - paper 245 (18 pp.)

CO₂ Sequestration with Portuguese Serpentinite and Peridotite

ROMÃO, I., GANDO-FERREIRA, L. M., MORAIS, I., SILVA M. M. V. G., FAGERLUND, J., ZEVENHOVEN, R.

Presented at *Clean Air 2011*, Lisbon, Portugal, July 5-8, 2011

Equilibrium and kinetic studies on removal of Cu²⁺ and Cr³⁺ from aqueous solutions using a chelating resin

GANDO-FERREIRA, L.M., ROMÃO I., QUINA, M. J.

Chemical Engineering Journal 172(1), 277–286 (2011)

Assessment and improvement of a stepwise magnesium silicate carbonation route via MgSO₄ and Mg(OH)₂

ZEVENHOVEN, R., BJÖRKLÖF, T., FAGERLUND, J., ROMÃO, I., HIGHFIELD, J., BU, J.

Proceedings of ACEME10, Turku Finland, Nov. 29 – Dec. 1, 2010, 41-49

A stepwise process for carbon dioxide sequestration using magnesium silicates

FAGERLUND, J., NDUAGU, E., ROMÃO, I., ZEVENHOVEN, R.

Front. Chem. Eng. China 4(2) (2010) 133-141

CO₂ sequestration with Portuguese serpentinite

ROMÃO, I., GANDO-FERREIRA, L.M., FAGERLUND, J., ZEVENHOVEN, R.

Proceedings of ACEME10, Turku Finland, Nov. 29 – Dec. 1, 2010, 77-87

Mineralisation of CO₂ and recovery of iron using serpentinite rock

ZEVENHOVEN, R., FAGERLUND, J., NDUAGU, E., ROMÃO, I.

Proceedings of R'09 (1 page poster), Davos, Switzerland, Sept. 14-16, 2009
(paper 149)

Nomenclature and Abbreviations

ÅA, ÅAU	Åbo Akademi University
ABS	Ammonium bisulphate
APA	Portuguese Environment Agency
ARC	Albany Research Center
AS	Ammonium sulphate
CCS	Carbon capture and storage
CCUS	Carbon capture utilization and storage
CLEEN Oy	Strategic research centre for the Energy and Environment Cluster
CCM	CO ₂ capture and mineralisation
EDTA	Ethylenediaminetetraacetic acid
ETH	Swiss Federal Institute of Technology in Zurich
GEE	Gases de efeito estufa
GHG	Greenhouse gas
GMD	Global Monitoring Division
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
IPCC	Intergovernmental Panel on Climate Change
LANL	Los Alamos National Laboratory
MC	Mineral carbonation
MVR	Mechanical vapour recompression
NETL	National Energy Technology Laboratory
NOAA	National Oceanic & Atmospheric Administration
PCC	Precipitated calcium carbonate
PFB	Pressurised fluidised bed
PLCR	Portuguese Low Carbon Roadmap
PTGA	Pressurised thermogravimetric analyser
S _{BET}	Specific surface area
TKK	Helsinki University of Technology
UC	University of Coimbra
XRD	X-ray diffraction

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1. Introduction

The Earth's climate is a complex system that relies on the balance between the incoming energy irradiated by the sun and the outgoing energy radiated out from the Earth's surface. When these two fluxes are equal, the Earth is in the so called "radiative state of equilibrium" (Ahrens, 1985) that allows for the maintenance of the life-supporting temperature of $\sim 15^{\circ}\text{C}$. A simplistic approach of the heat fluxes is presented in Figure 1. Once it reaches the atmosphere, sunlight follows two paths: it is either reflected back to space or adsorbed by the atmosphere and surface. In order to cool down, Earth emits thermal energy back to space, across the atmosphere, through latent and sensible heat fluxes. Gases like CO_2 and water, for example, are transparent to short wave radiation (sunlight) but quite opaque to long wave radiation (similar to window glass in a greenhouse) meaning that they absorb the thermal infrared energy which is later re-emitted in all directions (including the Earth's surface).

The global climate is affected by everything that changes this energy balance, as for example natural changes in the Earth's orbit, in the incoming solar energy (dependent on solar activity¹), or in the composition of our atmosphere². It is believed that man-made CO_2 emissions had a discernible continuous effect on the planet's temperature and ecosystems' delicate equilibrium during the 20th century (IPCC, 2007). This spawned a strong and concerted international effort to mitigate the climate change threat, leading to the Kyoto Protocol in 1997, which targeted the reduction of GHG emissions, by the industrialized countries to stabilise CO_2 atmospheric concentrations.

¹ Trends in the Sun over the past two decades, that could somehow influence the Earth's climate, do not follow what would be needed to explain the observed increase in globally averaged temperatures (Lockwood and Fröhlich, 2008).

² Composition of the Earth's atmosphere has changed with the Earth's formation and evolution and it is the part of the climate system more susceptible to human action (IPCC, 2005).

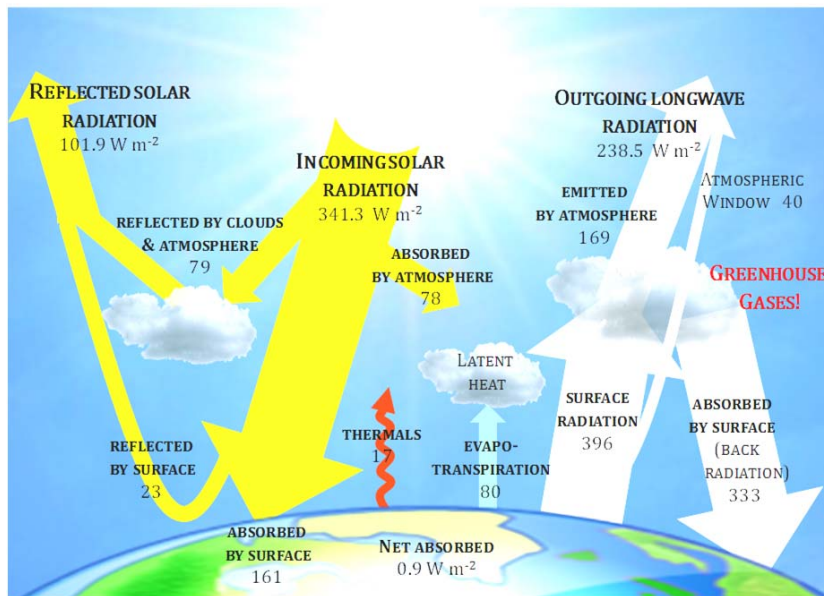


Figure 1 - Earth's energy budget. Adapted from Trenberth et al. (2009).

Meanwhile the scientific community continuously evaluates the validity of the climate change and post Kyoto negotiations are leaning for a new international climate change agreement, in Paris, 2015, to be implemented in 2020, and where EU will commit to a target of, at least, 40% CO₂ emissions reduction by 2030.

Even though our planet has natural mechanisms for reducing atmospheric CO₂ concentrations – transfers between plant life and oceans (Stephen A., 2010) – the reality is that CO₂ levels in the atmosphere have drastically increased since 1950. Human activity currently releases 34.5 billion tons of CO₂ into the atmosphere (Oliver et al., 2013) and the CO₂ levels measured at the Mauna Loa Observatory, of circa 400 ppm (GMD, 2014), exceed by far the natural CO₂ atmospheric concentrations ranging over the last 800,000 years (180 to 300 ppm), as determined from ice cores (IPCC, 2007) (see also Figure 2 and Figure 3).

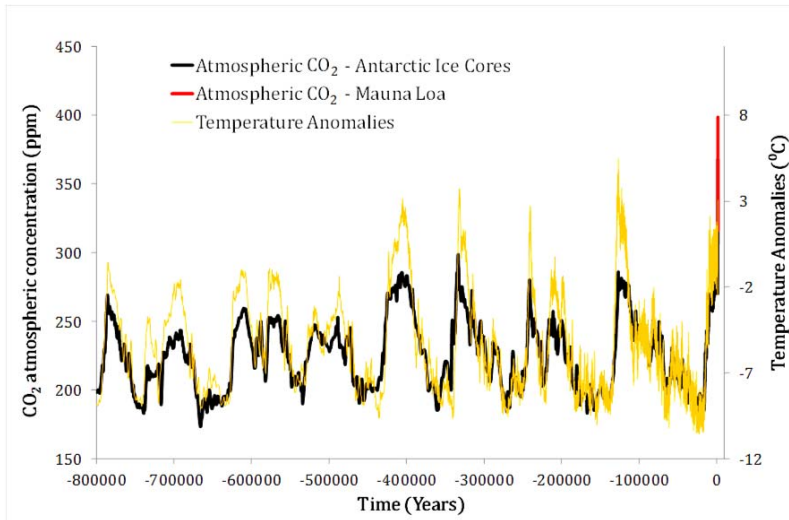


Figure 2 – Relation between CO₂ emissions and temperature anomalies over time. Data collected from Bereiter et al. (2015), Jouzel et al.(2007) and GMD, (2014).

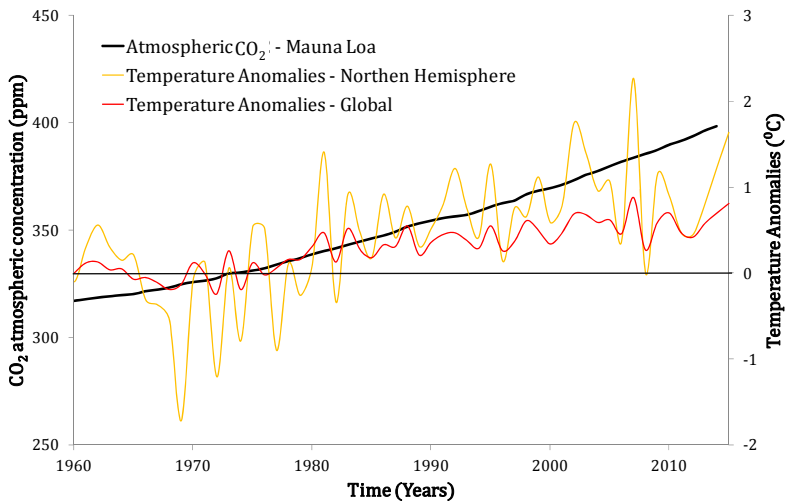


Figure 3 – Relation between CO₂ emissions and temperature anomalies from land and ocean since 1960. Data collected from (GMD, 2014) and (NOAA, 2015).

The radiative forcing³ caused by human activities (deforestation, changes in land use, burning of fossil fuels, etc...) is quantified in Figure 4 and it is alleged to be the cause of the global temperature changes occurring at an alarmingly fast rate

³ Radiative forcing is the net change in the energy balance of the Earth system due to some imposed perturbation. It is measured by the amount of warming or cooling that a change can produce (IPCC, 2013).

and with catastrophic consequences: surface temperature increase, ocean acidification, desertification, rise of sea levels, etc. (IPCC, 2014).

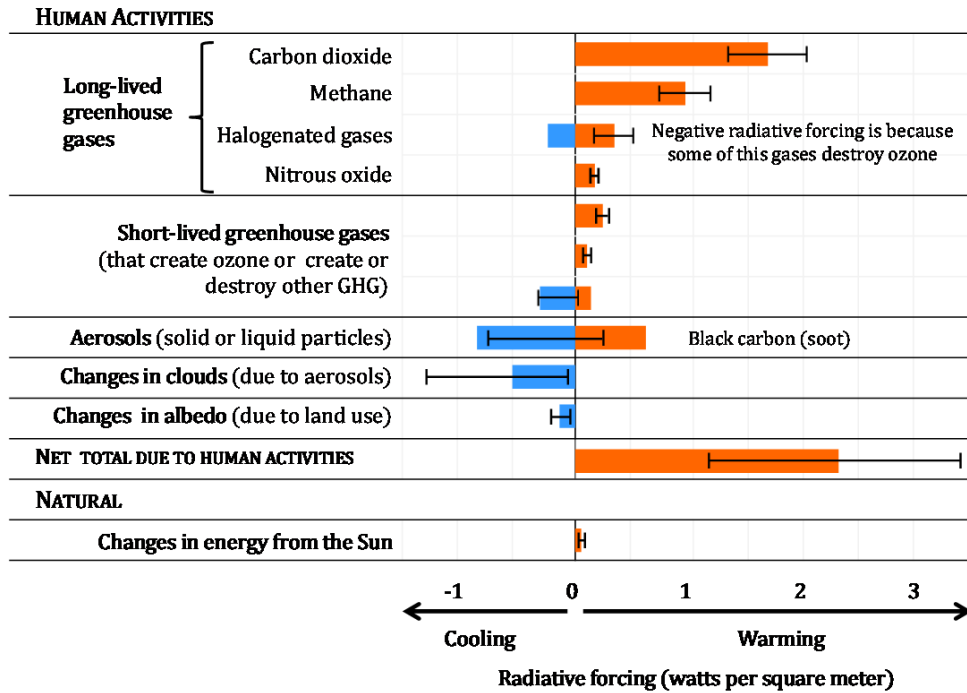


Figure 4 – Radiative forcing caused by human activities since 1750. Adapted from EPA (2014).

It is clear that strategies and solutions for CO₂ and climate change mitigation need to include complementary technologies: energy efficiency enhancement, the switch to less carbon-intensive fuels, nuclear power, renewable energy sources, enhancement of biological sinks, reduction of non-CO₂ greenhouse gas emissions and carbon dioxide capture and storage, CCS (IPCC, 2005).

CCS technologies, more specifically simultaneous capture and storage of CO₂ through mineral carbonation, eventually applicable at a large scale (i.e. 0.1 Mt CO₂/year or more) are the focus of the work presented in this thesis.

2. CO₂ capture and storage (CCS)

As the world is addicted to using energy, the massive use of fossil fuels, most likely, will not stop any time soon. Proven reserves⁴ of fossil fuels are currently estimated in 1 688 billion barrels of crude oil, 892 billion tonnes of coal and 186 trillion cubic meters of natural gas, with 53, 109 and 54 estimated years of extraction remaining, respectively (BP, 2015). Predictions point to an increased energy demand of 41% globally by 2035. Oil (32.6%) will remain the dominant fuel used, followed by coal (30%), natural gas (23.7%) and renewable sources (3%) (BP, 2015). Increasing energy efficiency will not be enough to reduce the anthropogenic emissions and stabilize atmospheric CO₂ concentrations. Hence the urgency for developing “end-of-pipe” technologies for CO₂ collection from industrial (cement, iron and steelmaking, refineries...) and energy related sources promoting its long-term isolation from the atmosphere.

CCS (Carbon Capture and Storage) or, the nowadays more and more widely used CCUS (Carbon Capture Utilisation and Storage) includes a portfolio of technologies for collection of CO₂ from (large-scale) CO₂ producing processes. In most scenarios, the captured CO₂ is pressurised (>100-120 bar) and transported to a storage site. Some of the technologies for CO₂ separation/purification already exist and are widely applied in industrial processes (purification of natural gas, e.g.); transportation to a storage site and underground injection have already been demonstrated, yet presently, these stages do not seem to concatenate and the whole CO₂ capture process becomes energy intensive representing a penalty of ~10–40% for a power plant (IPCC, 2005).

Apart from this (capture) energy penalty, there is the problematic disposal of the large amounts of separated/purified CO₂. Geological/underground storage is suitable for large-scale applications and indeed it is the most advocated method

⁴ Reserves of fossil fuels correspond to the volumes which exploration is expected to be economically viable under current technology. Resources of fossil fuels, on the other hand, are much larger and include those volumes that are not fully characterised, or just that present technical, economical, and environmental extraction difficulties.

for CO₂ sequestration. Still, finding a suitable reservoir that fulfils all the safety criteria is problematic and often natural disasters (e.g earthquakes) pose CO₂ leakage as a likely risk (IPCC, 2005) leading to low public acceptance, especially for on-shore sites. Apart from the transportation of supercritical CO₂ (through pipelines, ships...) and engineering challenges of CO₂ underground injection, large-scale geological storage may, in fact, induce earthquakes, thus requiring careful and long-term monitoring (Mulargia and Bizzarri, 2014, Ellsworth, 2013).

Ocean storage, though it has a higher storage potential, has raised much discussion. The injection of liquid CO₂ into the deep ocean will change its chemistry and increase its acidity (as has already been observed). The narrow knowledge of the deep ocean ecosystems limits the predictions of further environmental impacts. Therefore, it seems unwise to pursue this alternative (IPCC, 2005).

Mineral carbonation (also known as CO₂ mineralisation) then arises as a safe and interesting technology for CO₂ storage, especially for countries lacking access to underground storage sites. Research is mainly driven by the benignity, thermodynamic stability and prospective revenue of mineral carbonation (by)products (Sanna et al., 2014). The direct mineralisation of CO₂ from flue gases is a quite attractive possibility, as the purification step of CO₂ typically accounts for 75% of the CCS chain costs (Feron and Hendriks, 2005). Mineral carbonation is the subject of this thesis and it will be addressed in more detail in chapter 3.

2.1 CCS in Finland

CCS inside Finland's borders is likely to be integrated with the power sector (combined heat and power plants, biomass, oil refineries) and other relevant industries in the country, such as pulp and paper and steel manufacturing, allowing for an 80% reduction of GHG emissions, provided that all CCS technologies are feasible in a near future (Koljonen et al., 2012).

Geology in Finland is not favourable to underground storage and since 2012 the implementation of the CCS Directive 2009/31/EC forbids CO₂ geological storage on Finnish territory (IEA, 2012). Thus, mineral carbonation is considered to be the only viable solution for CO₂ storage in Finland.

The FINCAP project, conducted by Fortum and TVO, was the first CCS venture in Finland, which aimed to retro-fit the Meri-Pori 565 MW IGCC-Post Combustion power plant with CCS tools. It was, however, suspended in 2010. Since then, several companies and universities have proceeded with R&D activities under the CCSP program (2011-2016) financed by the strategic research centre for the Energy and Environment Cluster (CLEEN Oy).

2.2 CCS in Portugal

Portugal has not been vigorously involved in CCS. In fact, not until 2012 did the Portuguese Environment Agency (APA) publish the first governmental report, the Portuguese Low Carbon Roadmap (PLCR), which adjudged CCS a necessary and cost-effective instrument to achieve the target of a 60–70% reduction of greenhouse gas (GHG) emissions reduction by 2050 (APA, 2012). Projections point out the power sector and cement production the most likely to adopt CCS technologies (Seixas et al., 2015).

So far, R&D focused on the identification and evaluation of geologic formations for CO₂ storage (Carneiro et al., 2011, Pereira et al., 2014). Although ~1/3 of the Portuguese on-shore territory is covered by sedimentary basins, with an estimated potential of 7.6 Gt of CO₂ storage, seismic hazard, especially in the south of Portugal, is often denoted as a constraint to the safety conditions required for long-term, viz. thousands of years, underground CO₂ storage (Pereira et al., 2014). Off-shore storage sites in the Porto and North Lusitanian basins were identified as the most promising formations, but exploration requires careful analysis of induced seismicity impact due to nearby active faults (Seixas et

al., 2015). In light of this seismic hazard, mineral carbonation is a compelling alternative to geological storage.

Under the EU FP7 COMET (2010-2012) project, Boavida et al. (2013) assessed the development and implementation of CO₂ transportation infrastructures in the West Mediterranean Region (WMR) – Portugal, Spain and Morocco – identifying possible CO₂ fluxes. However, inclusion of Morocco in this study is not currently practicable as since 2012 the CCS Directive 2009/31/EC (EC2009) was enacted into the Portuguese law (Decree-Law number 60/2012), establishing that CO₂ geological storage can only take place within the Portuguese territory, continental shelf and exclusive economic zone. Cross-border cooperation is possible merely within EU and EFTA states, as the CCS Directive does not allow storage of CO₂ in countries where it is not applicable (Rydberg and Langlet, 2014).

3. Mineral carbonation

The natural weathering of rocks is a very slow process in nature and has been responsible for the uptake of billions of tons of CO₂ from the atmosphere throughout times. Mineral carbonation, as a fast (and possibly cost-effective) industrial version of the natural weathering of rocks, was first brought up by Seifritz (1990).

The final goal of mineral carbonation is to trap CO₂ into benign carbonates that will sequester CO₂ for thousands of years. A major advantage comes from the fact that carbonates will remain in the solid form (long-time scales) as they have a lower energy state (Lackner et al., 1995). In fact, stability of carbonates even under strong acidic conditions was confirmed by Teir et al. (2006b) and later also by Allen and Brent (2010). Both authors concluded that, in all plausible conditions of pH and rainfall, leakage rates of stored CO₂ are insignificant.

To date, research has mainly focused on carbonation of alkaline materials such as natural minerals and industrial wastes. Therefore, CO₂ mineralisation is a more appropriate name that covers all processes that bind CO₂ into a solid inorganic carbonate (Power et al., 2013), while for this chapter mineral carbonation (MC) is appropriate, leaving industrial wastes largely outside the discussion.

The potential for CO₂ sequestration via mineral carbonation is enormous at 10 000–1 000 000 Gt CO₂ (see Figure 5), as the amounts of suitable and readily available mineral silicates far exceed the requirements for sequestering all anthropogenic CO₂ emissions from the known fossil fuel reserves (Lackner et al., 1995). This makes mineral carbonation particularly attractive for large point CO₂ sources: power generation, iron and steel making and cement manufacture, for example.

The chemistry behind CO₂ mineralisation is relatively simple: the minerals react with CO₂ (separated from flue gases or directly with the CO₂ containing flue gases) to form a carbonate, as shown in the general equation (R1), where *M* stands for the divalent metal (Mg, Ca or in some cases Fe):

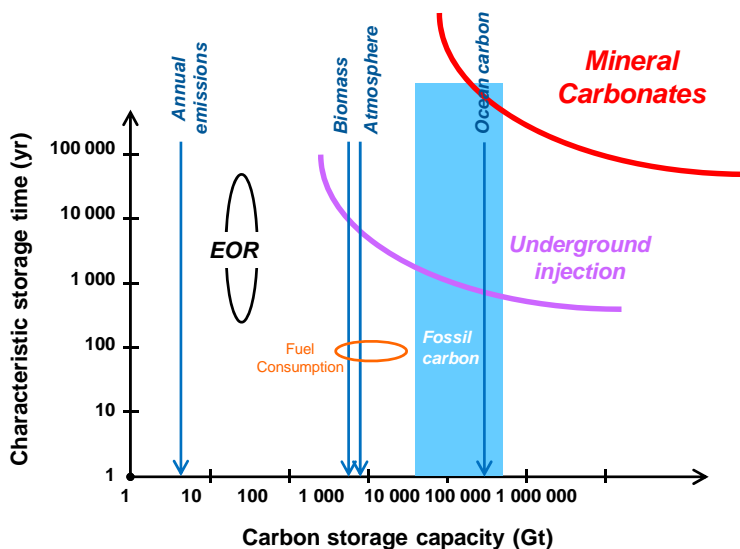
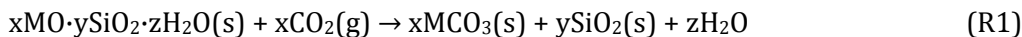
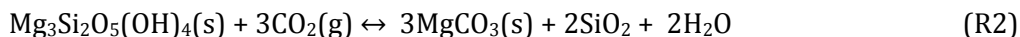


Figure 5 – Estimated times and storage capacities for the various options for CO₂ storage. Adapted from Zevenhoven et al. (2006).

Depending on the mineral in the reaction (given by values for x,y and z in the reaction), the overall heat output ranges from +50 to +100 kJ/mol of CO₂ converted. As an example, the carbonation of serpentine – reaction (R2) – releases ~ 64 kJ/mol CO₂ fixed.



The exothermic nature of the carbonation reaction hints towards a self-sustaining process. However, despite the simple chemistry, recreating the natural weathering at an industrial time scale is a challenge mainly due to slow kinetics and thermodynamic limitations (Huijgen and Comans, 2005, Zevenhoven et al., 2008, Torrónategui, 2010, Fagerlund, 2012, Nduagu, 2012, Olajire, 2013).

Natural Mg/Ca silicate minerals (olivines, serpentinites and basalts) are cheap and plentiful worldwide, as seen in

Figure 6, and highlighted as good candidates for mineral carbonation (e.g. (Seifritz, 1990, Lackner et al., 1995, Goff and Lackner, 1998, Huijgen and Comans, 2005, Sipilä et al., 2008). Typical contents of naturally occurring ultramafic rocks are presented in Table 1. Magnesium-based silicates (olivines, serpentinites) are preferable for large-scale CO₂ sequestration purposes, as their typical MgO content (35-50 %-wt) is much higher than the CaO content of the Ca-based minerals (~10%-wt) which would require the handling of impractical quantities of calcium-based material resources for carbonation.

Table 1 - Chemical composition of minerals suitable for mineral carbonation. Adapted from Penner et al. (2004).

Rock/Mineral group	Mineral	Formula	Chemical composition (w-%)		
			Ca ²⁺	Fe ²⁺	Mg ²⁺
Feldspar	Anorthite	CaAl ₂ Si ₂ O ₈	10.3	3.1	4.8
Serpentine	Antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄	< 0.1	2.4	24.6
Pyroxene	Augite	CaMgSi ₂ O ₆ (Fe,Al)	15.6	9.6	6.9
Olivine	Fosterite	Mg ₂ SiO ₄	0.1	6.1	27.9
Ultramafic	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	2.2	9.2	15.7
Ultramafic	Wollastonite	CaSiO ₃	31.6	0.5	0.3

Alkaline waste materials (steelmaking slags, fly ashes and cement, combustion, municipal and alkaline paper mill wastes) are also considered as an interesting feedstock for CO₂ emissions reduction. Besides being readily available and cheap, alkaline residues are highly reactive (compared to minerals) and their upgrading and stabilization, fulfilling environmental directives for landfilling whilst contributing (even in a small scale) to mitigation of CO₂ emissions, are of much interest. The carbonation of steel converter slags to produce PCC⁵ is one successful example of waste materials valorisation (Mattila and Zevenhoven, 2014). However, alkaline wastes resources are limited and the CO₂ fixed would not have a significant impact on the CO₂ sequestered globally. For this reason the carbonation of alkaline waste materials will not be discussed in detail.

⁵ Precipitated calcium carbonate – widely used filler material.

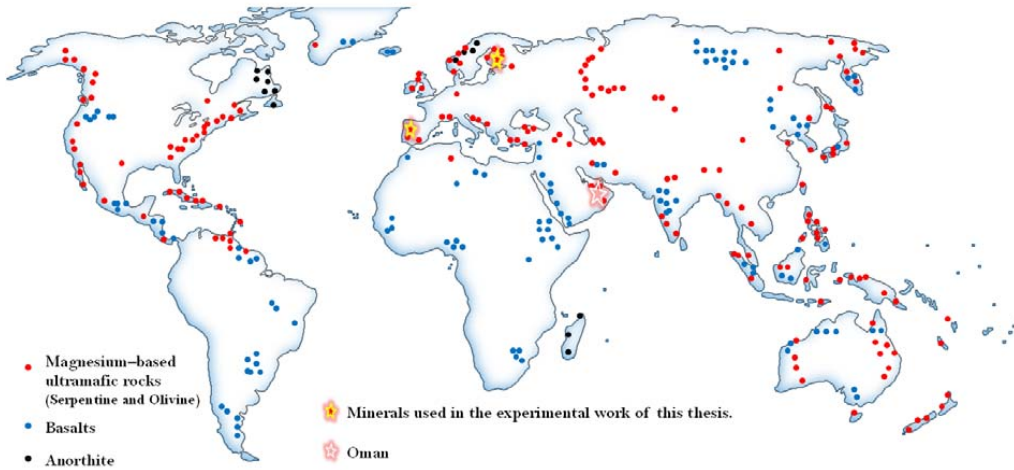


Figure 6 – Worldwide distribution of mineral feedstock suitable for mineral carbonation. Adapted from Sanna et al. (2014). In Oman is located a deposit of 30 000 km³ of magnesium silicates. It is estimated that this formation has the potential for storing all the CO₂ anthropogenic emissions resultant from the combustion of all known coal reserves (Lackner et al., 1995).

4. Mineral carbonation routes

For the last two decades, several reviews on mineral carbonation (e.g. Huijgen and Comans, 2005, Sipilä et al., 2008, Torrónategui, 2010, Khoo et al., 2011, Olajire, 2013, IEAGHG, 2013, Sanna et al., 2014, Azdarpour et al., 2015) have been reporting advances in mineral carbonation technology, mainly addressing the challenges imposed by the slow kinetics and thermodynamic limitations inherent to the carbonation process.

All the reviews come to the same conclusions: in general, mineral carbonation is too energy intensive, requires extreme operating conditions and the handling of large amounts of water, chemicals and minerals. Furthermore, the technology is not mature and pilot scale demonstration projects are indispensable.

Mineral carbonation is commonly seen as an inferior option towards CCS involving geological storage, mainly due to: 1) on the short run is it more energy intensive (although often estimations of energy inputs, and therefore costs, are distorted by wrong assumptions giving an unrealistic view of the economy of the process (Zevenhoven and Fagerlund, 2010)) and 2) it involves the mining of considerable amounts of minerals and the handling of high quantities of chemicals and water. It is, however, important to keep in mind that (under the right conditions) mineral carbonation may remove the conventional separation/purification step of CO₂ from the CCS chain (Verduyn et al., 2011). After all, most components of the flue gas will be inert during the carbonation process (requiring only a large gas flow compared to a purified CO₂ stream, which becomes less of a problem when pressurised), while co-binding of SO₂ is an interesting option (Zevenhoven et al, 2012). Still, at this point, it is clear that even if safer, mineral carbonation will only thrive through integration with large-scale CO₂ producers (Slotte et al., 2013) for reducing net CO₂ emissions and overall energy (primarily heat) input, and by producing marketable products.

4.1 In-situ accelerated mineral carbonation

The process routes for mineral carbonation (MC) are divided in two main groups: in-situ and ex-situ accelerated MC.

In-situ accelerated MC is a version of geological storage where the CO₂ is injected into a basalt (or Mg/Ca rich silicate mineral bed rock), under conditions that enhance the natural process. It overcomes some of the drawbacks associated with ex-situ version, primarily, the handling of considerable amounts of rocks and chemicals. If successful, it works as a semi-permanent storage option but does not avoid the expensive capture/purification of CO₂. Also, it is not easy to encounter basaltic and ultramafic formations sealed by an impermeable cap rock. There are ongoing projects in Iceland (Alfredsson et al., 2011, Alfredsson et al., 2013), Columbia River USA, and Oman (Paukert et al., 2012, Kelemen et al., 2011). This field has raised some interest in recent years and R&D focuses on a better understanding of the mechanisms of natural weathering (Boschi et al., 2009, Lafay et al., 2012, Kerisit et al., 2013, Miller et al., 2013, Schaef et al., 2013, Thom et al., 2013, Thompson et al., 2013, van Noort et al., 2013, Johnson et al., 2014, Lafay et al., 2014, Sissmann et al., 2014).

4.2 Ex-situ accelerated mineral carbonation

Ex-situ MC is the focus of this thesis, hence it will be addressed in more detail. Due to the increased complexity of the mineralisation processes, the categorisation of some studies is somewhat ambiguous. Commonly, the mineralisation routes are classified as direct (Mg/Ca extraction and carbonation take place in one step) and indirect processes (the Mg/Ca extraction and carbonation are sequential and take place in independent steps). Both direct and indirect methods can be further divided into dry and aqueous carbonation routes. A more detailed classification is presented in Figure 7 .

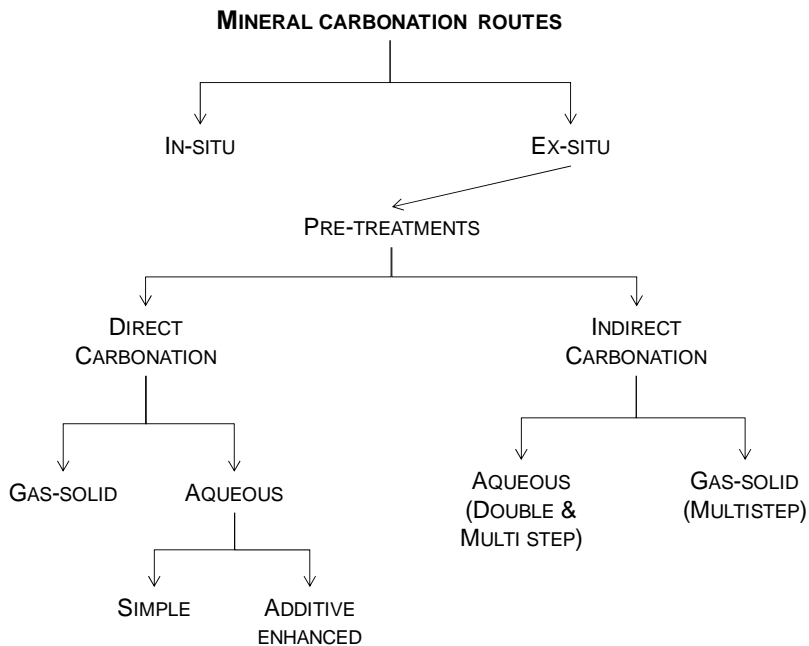


Figure 7 – Mineral carbonation pathways for naturally occurring minerals.

4.2.1 Mineral pre-treatment options

For ex-situ carbonation, conventional crushing and grinding are obligatory with typical particle sizes ranging from 50 to 250 μm . Activation of the mineral feedstock may be achieved by mechanical⁶ (Gerdemann et al., 2007, Baláž et al., 2008, Haug et al., 2010, Turianicová et al., 2013), thermal⁷ (McKelvy et al., 2004, Boerrigter, 2010, Balucan et al., 2013, Balucan and Dlugogorski, 2013, Dlugogorski and Balucan, 2014) and chemical means (Zhang et al., 1996, Maroto-Valer et al., 2005, Nduagu, 2008, Nduagu, 2012). The aim is to go beyond surface area increase and somehow disrupt the mineral lattice, decreasing the activation energy for any subsequent reactions (O'Connor et al., 2004, Haug et al., 2010). Although mechanically activated feedstock materials are more reactive, it is often argued that the high energy input requirements lead to unacceptable energy

⁶ Usually applied to olivines (Torróntegui, 2010)

⁷ Usually applied to serpentinites (Torróntegui, 2010)

penalties (Haug et al., 2010, Huijgen et al., 2007). Besides this, some work was reported on biological acceleration of magnesium silicate rock dissolution and/or carbonation. Indeed some activity is seen after time scales of weeks / months (Bundeleva et al., 2014). This new field may have future potential but it won't be considered here. For calcium silicates more promising results have been reported by Salek et al. (2013).

As for the heat treatment, at 500-700°C depending on the mineral, it was repeatedly reported to be too energy intensive and costly (Huijgen and Comans, 2005, IPCC, 2005, Gerdemann et al., 2007). However, Zevenhoven and Fagerlund (2010), Balucan et al. (2013) and Brent et al. (2015), argue that cost projections for serpentine carbonation in O'Connor et al. (2004) and Gerdemann et al. (2007), based on activation of mineral feedstock using electrical energy, are incorrect and negatively affect the economy of the process.

4.2.2 Direct dry (gas/solid) carbonation

Direct gas/solid carbonation is the simplest approach of mineral carbonation that, in theory, allows for recovery of the carbonation heat. The conversion of gaseous CO₂ into Mg/Ca solid material was first assessed at the Los Alamos National Laboratory (LANL) (Lackner et al., 1995, Lackner et al., 1997) and later in Finland at Helsinki University of Technology (TKK) (Kohlmann and Zevenhoven, 2001, Zevenhoven and Kohlmann, 2002). Both research groups concluded that the direct gaseous carbonation of minerals suffers from low conversion and slow reaction kinetics, thus requiring high temperature and pressure. At ~340 bar, Lackner et al. (1997) attained a maximum of 30% carbonation of serpentinised powder. Also, carbonation of pure serpentinite powder at 200°C-1000°C in a PTGA by Zevenhoven and Kohlmann (2002), showed only minor changes in the mineral's carbonate content, even after relatively long reaction time. Only almost a decade later, Kwon (2011) attempted the direct carbonation of olivine. Yet again, the author recognizes that the low

conversion (27% of olivine carbonation in 3.7µm size particles) due to thermodynamic limitations is the main drawback to overcome (Kwon et al., 2011). More recently, Larachi et al. (2012) attempted the carbonation of pre-treated chrysotile (serpentine) for 1 h between 100 °C and 220 °C at 3.2 MPa total pressure for CO₂/H₂O/H₂ mixtures. Despite uptakes as high as 0.7 CO₂ moles per mol of magnesium at 130 °C, the pre-treatment methods (eg. thermal activation of chrysotile at 700°C for 20 min) present a prohibitive energy penalty.

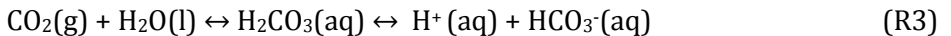
As it became clear that direct mineralisation of Mg/Ca natural silicates is an unviable process, research progressed to multistep (indirect) gas solid carbonation routes: these will be later addressed in detail.

On the other hand, dry carbonation of industrial alkaline wastes, which are more reactive than minerals, continues to stir interest. The trend is to use flue gases (avoiding the CO₂ separation step) to carbonate and stabilize waste materials – see Sanna et al. (2014).

4.2.3 Direct aqueous carbonation

Direct aqueous carbonation involves three co-existent mechanisms:

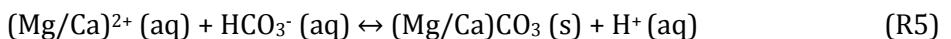
i) dissolution of CO₂ into water towards a mildly acidic solution



ii) to facilitate the dissolution of the Mg/Ca rich material



iii) and the subsequent the precipitation of the leached ions as carbonates:



The produced carbonates may be in the form of hydrates, for example hydromagnesite Mg₅(OH)₂(CO₃)₄·4H₂O. Difficulties arise from the fact that each reaction limits the others: steps i) and ii) require an acidic media while step iii) is

favoured at alkaline conditions. Thus, careful optimisation is required and direct carbonation must happen in narrow pH ranges. Temperature optimisation is also tricky, as a higher temperature enhances the leaching of magnesium from the mineral lattice but decreases the CO₂ solubility in water.

In general, it is agreed that the main constraint of the aqueous scheme for commercial application is the slow kinetics for the silicate dissolution (Huijgen and Comans, 2005, Sipilä et al., 2008, Fagerlund, 2012, Nduagu, 2012, Li et al., 2013, Olajire, 2013). Initially the reaction happens at a fast rate (Carey et al., 2003) but, as it progresses, the build-up of a passivating SiO₂ layer on the particle's surface prohibits the further magnesium release from the mineral's matrix (Teir et al., 2007a)

As experimental results showed that CO₂ did not produce enough acidity to accelerate mineral dissolution (O'Connor et al., 2002, 2004), addition of alternative chemicals (organic and inorganic) and feedstock pre-treatments (mechanical and heat activation) became imperative. As so, during the last two decades a wide range of acids and complexing agents were trialled: HCl was first studied at the LANL (Lackner et al., 1995, 1997) and by Park et al. (2003) at the Ohio State University. Studies by Fauth et al. (2000) and O'Connor et al. (2005) at NETL (former ARC) resulted in an optimised buffered saline solution of 0.64M NaHCO₃ and 1M NaCl (Gerdemann et al., 2007). The authors reported an 80% conversion of heat pre-treated (615 - 630⁰C) serpentine at 155⁰C and 115 bar. The thermal pre-treatment, fine grinding <70 µm and the difficulty in recovering the reactants, again, imply a process too expensive and impracticable for industrial implementation (Huijgen and Comans, 2005, Gerdemann et al., 2007). Nevertheless, this route was considered the state-of-the-art for many years (it was explicitly mentioned in the IPCC special report on CCS (IPCC, 2005)) and it is still a reference and comparison benchmark for many ongoing studies. In fact, recently, Eikeland et al. (2015) achieved full carbonation of olivine particles in less than 4 hours at 190⁰C in a solution of 0.5 M NaHCO₃ + 0.5 0.75 M NaCl, but at the cost of extra fine grinding (<10µm) and 100 bar CO₂ pressure. R&D went on

with mineral and organic acids: KHCO_3 (Mckelvy 2006), H_2SO_4 , HNO_3 , HCOOH , CH_3COOH (Teir et al., 2007a), oxalates (Olsen and Donald Rimstidt, 2008, Rimstidt et al., 2012), citrates and EDTA (Park et al., 2003, Krevor and Lackner, 2009, Krevor and Lackner, 2011, Rozalen and Huertas, 2013, Bobicki et al., 2014, Bobicki et al., 2015). Still, no significant breakthroughs were achieved, especially for the organic additives, thus discrediting a viable direct aqueous mineralisation process with organic additives.

Finding an additive to promote dissolution of the silicate mineral, under a pH favourable to carbonates formation, would be a significant step forward for direct aqueous carbonation routes (Krevor and Lackner, 2009). Seeking to overcome the limiting nature of the three coexistent carbonation mechanisms, Blencoe et al. (2004), proposed the dissolution of calcium silicates in an alkaline media. The long reaction times (~ 72 h) and large amounts of NaOH needed (50–80 wt%) were considered to be unaffordable for industrial application (Huijgen and Comans, 2005). Still, years later, the same authors patented an identical process for application to a wider range of metal silicates (Blencoe et al., 2012), yet, once more, without any report on the $\text{Mg}(\text{OH})_2$ production and carbonation efficiencies. In a recent study, Madeddu et al. (2014), obtained an 80 wt% conversion of dunite (ultramafic rock, mainly olivine) into $\text{Mg}(\text{OH})_2$, using a 40% NaOH solution at 180°C (pressure not mentioned) for 24hrs. The author emphasizes that producing the NaOH needed to process 1 kg of dunite would produce 13 kg of CO_2 , whilst the capture potential of the processed material is of $\sim 0.53\text{kg CO}_2$. Only after 26 recycling loops of NaOH, the process would become carbon neutral. These results utterly discourage the alkaline digestion route.

Researchers at the Swiss Federal Institute of Technology in Zurich (ETH) focused on the detailed understanding of the direct aqueous mineral carbonation chemistry and did an extensive work on olivine dissolution (Hänchen et al., 2008, Prigiobbe et al., 2009a, 2009b) at different temperatures, CO_2 pressure and salinity. The authors use a population balance approach to develop a model to describe the dissolution of olivine (Hänchen et al., 2007, 2008), also providing

insight on Mg-carbonate stability under the given conditions. Once more, the authors conclude that only high temperature (150°C) and pressure (100 bar) allow for rates convenient for industrial operation. In the attempt of skipping the costly step of CO₂ purification, R&D at the ETH progressed on routes that make direct use of flue gases. Werner et al. (2013) performed single step carbonation experiments in stirred reactors with gas-dip tubes with thermally pre-activated serpentine. The authors found that, once the experiments reached equilibrium conditions, the extent of the carbonation reaction did not exceed 20%. In such a way, Hariharan et al. (2013) and Werner et al. (2014) initiated dissolution studies far from equilibrium conditions. With a mandatory thermal pre-activation of rock material, in mildly acidic media, moderate partial pressure of CO₂ (2 bar of CO₂) and temperatures of 120°C, in flow-through operation conditions, 83% of the magnesium was dissolved within 100 minutes. Hariharan et al. (2014) developed a kinetic model, for the heat-treated lizardite, based on those experimental results.

Currently, in France, there is an ongoing effort to overcome the formation of the impervious carbonate layer using mechanical methods. Bodéan et al. (2014) and Julcour et al. (2015) propose an “attrition-leaching hybrid process” that couples the typical reactive carbonation with mechanical exfoliation (for physical abrasion and removal of the carbonate passivating layer). This approach allows for nearly 80% carbonation of mining residues, without heat activation, at 180°C and 20 bar CO₂ pressure, with a particle size fraction < 100µm, in less than 24 hours. Addition of the standard 1 M NaCl + 0.64 M NaHCO₃ inorganic solution proposed by Gerdemann et al. (2007), improved the carbonation reaction to 70% conversion in four hours and nearly 90% in less than 24 hours. The mechanisms for carbonation of mining waste are detailed discussed in this work, where is also highlighted that the extent of the carbonation reaction is greatly dependent on the serpentinisation degree of the feedstock. Pasquier et al. (2014a, 2014b) focused on the carbonation of thermally pre-treated serpentine at low temperature and pressure, under simulated flue gas conditions. Instead of increasing global pressure and temperature, the same solid material is

successively subjected to batches of gas and refreshed liquid phase. The author reports the interesting result of 64 wt.% Mg leaching and 62.5 wt.% CO₂ removal from the gas phase, after 18 hrs and under mild conditions: ~22°C and 10.5 bar.

At last, iron oxides that are commonly present in magnesium silicate ores are as well known to form a passive layer (of hematite) on the surface of the particles, also hindering carbonation mechanisms. Following Huijgen and Comans (2003) suggestion, Veetil et al. (2015) proposed the magnetic separation of the iron oxides - prior the carbonation step - and reports 71% efficiency in the removal of iron impurities from magnesium silicate ores (serpeninites). Results for carbonation of this iron-free material have not yet been reported.

Nowadays, the direct aqueous carbonation methods still present the main challenges pointed out by the IPCC (2005) report: it requires heat treatment, fine grinding, careful solution chemistry control for long reaction times (usually many hours!) and extreme operating conditions (high temperature and pressure), leading to high energy penalties and unfeasible industrial processes.

4.2.4 Indirect aqueous carbonation

Although the NETL (former ARC) direct aqueous carbonation was considered the most successful route for mineral carbonation, the high pressures needed (150-200 atm) and the fine grinding <20 µm of the feedstock, still stand as major energy inputs. Hence the interest in pursuing indirect routes that allow for an independent optimisation of the Mg/Ca extraction and carbonation, in two or more steps.

As carbonation proceeds much faster for magnesium hydroxides than for silicates, in most of the indirect routes, the first step focuses on the conversion of magnesium silicates to hydroxides. The use of HCl for magnesium extraction from the minerals matrix was early investigated by Lackner et al. (1995) and co-workers at the LANL (Butt et al., 1998). However, it was soon realised that the energy required for the recovery of HCl produces more CO₂ than the process

could possibly sequester (Huijgen and Comans, 2005). In order to reduce that energy penalty, Wendt et al. (1998) suggested a molten salt process that used MgCl_2 as the extraction agent. The process was shown to be unaffordable due to the corrosive nature of the reactants (Huijgen and Comans, 2003) and the unrealistic commercial supply of consumables (Newall et al., 1999). Kakizawa et al. (2001), proposed the carbonation of wollastonite in the presence of acetic acid, a non-corrosive acid. Yet, again, the problem stands in the additives recovery/recycling stages.

More recent R&D work on enhanced extraction with acetic acid focuses on the carbonation of industrial residues such as steelmaking slags (Teir et al., 2007b, Bobicki et al., 2012).

At the Ohio State University, Park et al. (2003) addressed the optimisation of a pH swing process where the magnesium is extracted from the mineral lattice, at low pH, and later converted to MgCO_3 , in an alkaline media. Complexing agents (EDTA, oxalic acid, orthophosphoric acid) and various other chemicals, as e.g. H_2SO_4 , HNO_3 , NaOH , KOH , NH_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , HCOOH and DL lactic acid, were tested as leaching enhancing additives (Park et al., 2003, Maroto-Valer et al., 2005, Teir et al., 2007a, Alexander et al., 2007, Ghoorah et al., 2014). Strong acids showed to be more effective at extracting magnesium than bases and complexing agents, making them good candidates for the pH swing process. Even so, the acid losses and the amounts of NaOH required for formation of MgCO_3 , besides arising environmental concerns, compel a process too expensive for industrial implementation (Sipilä et al., 2008).

Over the years, several authors (Botha and Strydom, 2001, Zhao et al., 2010) focused on R&D of mechanisms and methods for the carbonation of $\text{Mg}(\text{OH})_2$ slurries derived from silicate minerals and industrial wastes. Fricker and Park (2013) demonstrated the rapid and spontaneous nature of the $\text{Mg}(\text{OH})_2$ aqueous carbonation reaction. Following the same line of thought, Li et al. (2014) suggests the replacement of typical chemical sorbents (MEA amines, e.g.) by $\text{Mg}(\text{OH})_2$ readily available from magnesium-enhanced lime flue gas desulphurisation

processes. The authors present a detailed study on different operating parameters of a bubble column reactor and carbonation reaction kinetics, concluding that CO₂ removal efficiency is strongly influenced by the interaction between Mg(OH)₂ dissolution and MgCO₃ precipitation.

In recent years, no noteworthy breakthroughs on the recovery of additives were accomplished and two steps aqueous carbonation routes evolved to multi-step configurations. At the University of Nottingham, United Kingdom, Wang and Maroto-Valer (2011b) proposed a pH swing process based on ammonium salts. The process is presented in Figure 8. It involves five steps: 1) CO₂ from flue gases is scrubbed with chilled ammonia to form ammonium (bi)-carbonate (NH₄HCO₃ or (NH₄)₂CO₃ AC/ABC); 2) extraction of magnesium from the silicate rock using an aqueous solution of ammonium bisulphate (ABS) at up to 100°C to produce mainly MgSO₄; 3) ammonia is used to increase the pH and remove impurities (Fe, Al, Cr, Cu, etc.) in the form of hydroxides; 4) the remaining aqueous solution of MgSO₄ is treated with NH₄HCO₃ to precipitate hydromagnesite and, finally, 5) the ABS is recovered (presumably) by evaporation and thermal decomposition of (NH₄)₂SO₄ at 330°C. The extraction experiments showed that NH₄HSO₄ extracts 100% magnesium from serpentine at 100 °C after 3 hours, followed by 96% magnesium carbonation. This multistage pH swing method was also tested for antigorite (Sanna et al., 2013) and olivine (Sanna et al., 2014), as well with promising results. The total cost to sequestering 1 t CO₂, using serpentinite, was estimated in 100 US\$ when using a solid/liquid ratio of 50g/L in extraction step. Regrettably, the recovery of reactants was not fully addressed, as the recovery of ABS through thermal decomposition of AS is complicated due to its corrosive nature and shown to be energetically and economically unattractive (Wilhamson and Puschaver, 1997, Romão et al., 2014). Also the process requires the handling of large streams: 4.9 t of serpentine, 0.6 t of NH₄HSO₄, 4.7 t of (NH₄)₂CO₃ and 16 t of water are required to sequester 1 tonne of CO₂ (Wang and Maroto-Valer, 2013).

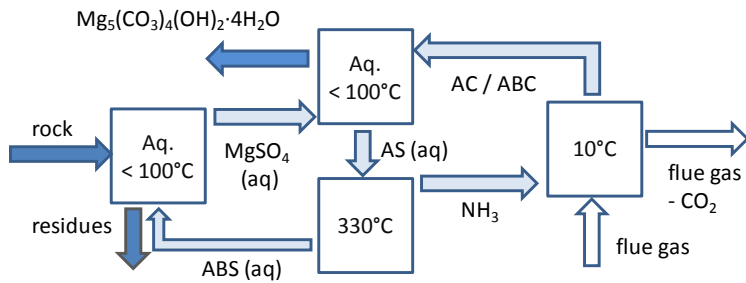


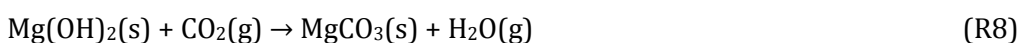
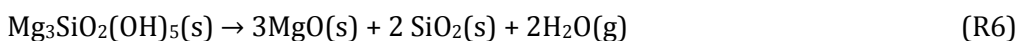
Figure 8 – pH swing process based on ammonium salts developed at the University of Nottingham, UK (taken from Geerlings and Zevenhoven (2013)).

In order to minimise the energetic penalty linked to ammonium bisulphate regeneration, Sanna and Maroto-Valer (2014), of Heriot Watt University, United Kingdom, propose the replacement of ammonium bisulphate by a sodium bisulphate solution, for extraction of magnesium. NaOH is used to capture CO₂ into Na₂CO₃ which is subsequently reacted with a MgSO₄ solution, to produce MgCO₃ and Na₂SO₄. After carbonation, the recovery of the sodium sulphate benefits from its low solubility at low temperatures (7 g/100 mL) avoiding an evaporation step. The reported efficiency for this approach, 50% magnesium extraction at 70°C and 90% carbonation, falls to the same range of the results reported by Wang and Maroto-Valer (2011a). The regeneration of Na₂SO₄ to NaOH and NaHSO₄ appears to be somewhat complex: it is mentioned to be achievable in three stages employing CO₂, an inorganic waste as source of CaO and an acidic environment but no further details are specified.

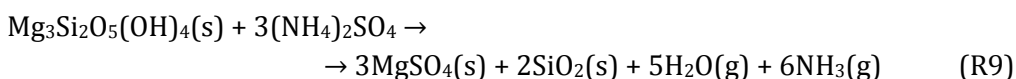
By and large, the mechanisms for aqueous CO₂ mineral sequestration are fairly well understood and it is established that the dissolution rate is speed up by: silicate ore pre-treatments/activation, application of additives and mechanic/chemical removal of the SiO₂ layer. Still, no aqueous process has yet shown to be attractive enough for developing towards pilot and/or industrial scale (Giannoulakis et al., 2014).

4.2.5 Indirect multi-stage solid/gas (dry) carbonation

As earlier discussed, the direct carbonation of silicate minerals is not viable due to low conversions and slow reaction rates. On the other hand, the carbonation of MgO, and especially Mg(OH)₂, was shown to occur much faster (Butt et al., 1996, 1998, Béarat et al., 2006). Magnesium is an element abundant in nature but mainly combined with minerals in silicate rocks. MgO and Mg(OH)₂ forms are scarce in Nature, therefore the necessity of developing a method for their production. Ergo, Zevenhoven et al. (2006), recommended a stepwise approach of the gas-solid mineral carbonation: first the MgO is produced from serpentinite in an atmospheric reactor which is then followed by its hydration and carbonation, at high pressure, according to:

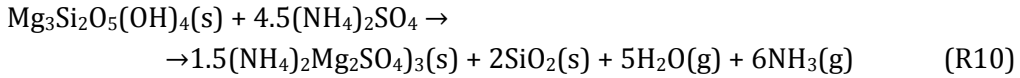


The initial Mg(OH)₂ carbonation studies showed that, at first, it proceeds quite fast, but rapidly becomes limited by the build-up of a carbonate layer on the surface of the reacting particles, thus prohibiting full carbonation of Mg(OH)₂ (Butt et al., 1996, Béarat et al., 2006, Zevenhoven et al., 2008). These findings were the leadoff for the construction of a test facility for carbonation studies at ÅAU⁸. Fagerlund et al. (2010) designed and built a lab-scale pressurised fluidised bed (PFB) reactor and initiated tests on the carbonation of MgO and Mg(OH)₂. At the same time, Nduagu (2008) worked on a method for production of Mg(OH)₂ using ammonium sulphate (AS) to extract magnesium from serpentinites, at a rock:AS mass ratio of 2:3, at 400-440°C, 30–60 minutes (optimized according to the rock's iron content and particle size) following:



⁸ In 2005, R Zevenhoven moved from Helsinki University of Technology to Åbo Akademi University.

while more detailed studies revealed that the actual conversion reaction is most likely:



and, in water, the solid product decomposes into (dissolved) AS and MgSO_4 (Nduagu et al., 2014, Highfield et al., 2015).

The merging of the $\text{Mg}(\text{OH})_2$ production and its subsequent carbonation processes (separately optimised), results in the multi-staged gas/solid (or three-stage dry/wet/dry) carbonation route developed at ÅA (frequently addressed in the literature as the “ÅA route”), as shown in Figure 9 and which is the focus of this thesis.

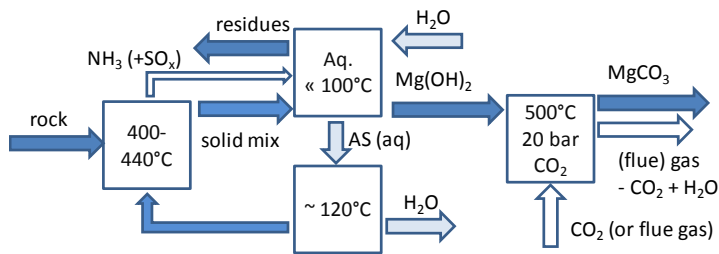


Figure 9 – Multi-staged gas/solid carbonation route developed at ÅA (taken from Geerlings and Zevenhoven (2013))

Since 2012, most work at ÅA focuses on direct carbonation with CO_2 containing gas (Slotte and Zevenhoven, 2013, Slotte et al., 2013b, Zevenhoven et al., 2012, 2013). An alternative “ÅA route” is being developed, as well, that involves carbonation of MgSO_4 in an aqueous solution – see Zevenhoven et al. (2015).

5. ÅA mineral carbonation route – detailed description

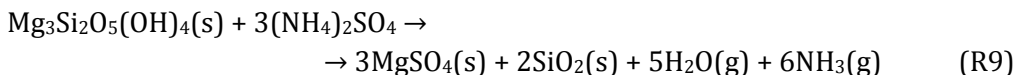
The “ÅA route” allure stands on some distinct and key benefit features:

- It provides simultaneous capture and storage directly from flue gases (thus removing the expensive CO₂ capture step from the CCS process chain);
- The heat from the dry carbonation (exothermic reaction) is available for recovery (unlike the aqueous routes where the heat is diluted in water at low temperatures) and can be fed back into the (endothermic) Mg extraction stage;
- The process is a closed loop as the used chemicals (and also water) are recycled;
- And, finally, the high purity MgCO₃ and iron (hydr)oxides produced make the integration of mineral carbonation with other industries an opportunity for a net reduction of CO₂ emissions and replacement of raw materials.

5.1 Production of Mg(OH)₂

The production of Mg(OH)₂ from serpentinite, a method developed by Nduagu (2012), aims at overcoming the drawbacks (low conversion, slow kinetics, chemicals consumption and energy penalties) inherent to ancillary aqueous routes (Huijgen and Comans, 2005, Sipilä et al., 2008, Olajire, 2013). The process consists of a closed loop involving three stages (represented in Figure 10):

1) Solid/solid reaction: extraction of magnesium from the silicate material with ammonium sulphate as the fluxing salt according to the overall reaction:



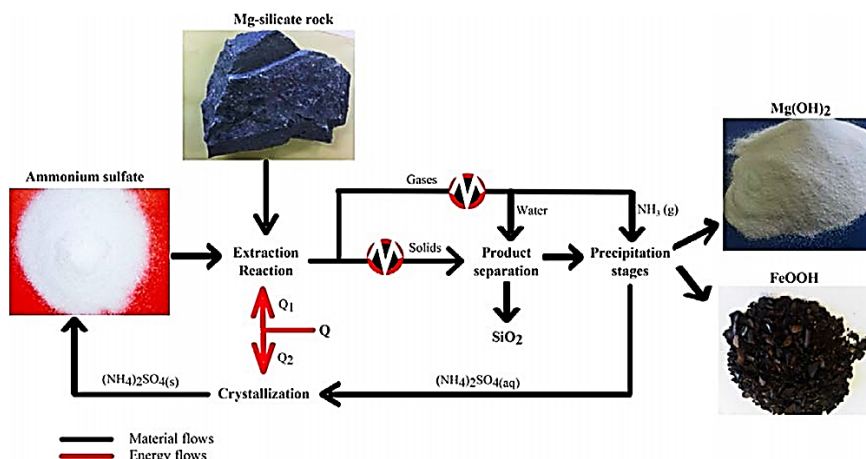


Figure 10 – Production of $\text{Mg}(\text{OH})_2$ from serpentinite – closed loop process (taken from Nduagu, 2012)

The optimal conditions for magnesium extraction from Finnish serpentinite (overburden rock from the Hitruva nickel mine) were found to be 400-440⁰C, mass ratio (serpentinite/AS) of 2/3 and a reaction time of 30-60 minutes (Nduagu et al., 2012c). After testing other magnesium silicate rocks from Lithuania, Australia and Norway, serpentinites were identified as being more reactive than olivines, mainly due to the synergetic effects of high Mg/Fe content, surface area and porosity (Nduagu et al., 2012b). The silicate structure appears, as well, to play a crucial role, not only in the conversion extent, but also in the energetic performance of this step: the processing of a rock with ~10 wt.% Fe as Fe_3O_4 instead of FeO leads to an increase of 60% in the energy input requirements, simply due to reactions involving iron oxides (Nduagu et al., 2012a).

2) Conversion of MgSO_4 to $\text{Mg}(\text{OH})_2$. The solid products are dissolved in water and the insoluble/unreacted fraction is separated by filtration and discarded. The unreacted fraction is rich in silica – up to 80%. Further processing of this residue may prove to be economically advantageous. The ammonia gas by-product of the solid/solid reaction is collected in water and used for recovery of iron (as goethite, FeOOH) at pH 8-9 and $\text{Mg}(\text{OH})_2$ at pH 10-12, through chemical precipitation.

3) Finally, in order to attain a closed loop process, AS is recovered through crystallisation. Although AS is a relatively cheap salt, its recovery/recycling is vital for the economy of the process. A mechanical vapour recompression (MVR) system appears to be the most effective way of reducing the energy penalty for this stage (Björklöf, 2010, Nduagu et al., 2012a).

5.2 Carbonation of $\text{Mg}(\text{OH})_2$

A pressurised fluidised bed (PFB) reactor provides good mixing of the solid phase, uniform heat distribution and should prevent the formation of a carbonate layer due to the frequent collisions/attrition between particles. The experimental PFB setup designed and built at Åbo Akademi by Fagerlund (2012) is presented in Figure 11 .

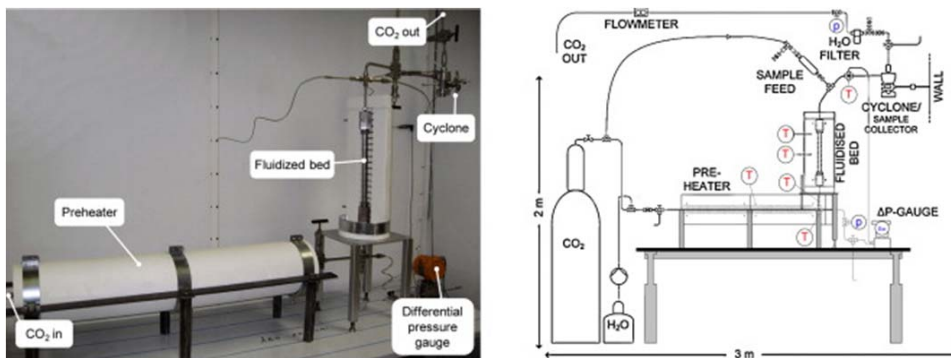
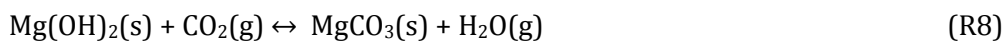
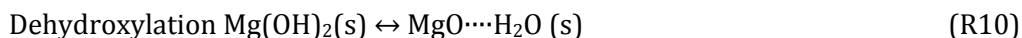


Figure 11 – A photograph and a schematic picture of the test PFB built for carbonation of $\text{Mg}(\text{OH})_2$ at ÅA. The desired temperature of the gas is controlled by the pre-heater and the pressure by the simultaneous adjusting of the CO_2 bottle pressure (on the left) and the pressure release valve. The sample is inserted through the sample feeder. After the test is complete the CO_2 flow is quickly increased above the terminal velocity and collected in the cyclone. Taken from Fagerlund et al. (2012b).

The overall reaction taking place in the PFB reactor is:



In reality, the exact carbonation of Mg(OH)_2 mechanism is still unclear and many intermediaries have been suggested. While it is more or less certain that MgO formation should be avoided, some $\text{MgO}\cdots\text{H}_2\text{O}$ intermediate is a precursor for MgCO_3 formation according to Fagerlund et al. (2012a):



The operating temperature and pressure are linked by the thermodynamic stability of MgCO_3 and the highest conversion degree is given near the dissociation temperature of MgCO_3 , dictated by the CO_2 pressure. In practice, this means that, for a given pressure, the experimental temperature must be kept a few degrees below the equilibrium temperature in order to avoid calcination. Still, above 40 bar, the carbonation rates do not increase and supercritical CO_2 even reduces the reactivity (Fagerlund, 2012).

Water/steam seems to play a key role in the final conversion degree. In his experiments, Fagerlund et al. (2010, 2012a), found that addition of small amounts of water (0-15%-wt) enhances reactivity of MgO . However, Mg(OH)_2 carbonation tells a different story. In fact, addition of higher amounts of steam hinders the carbonation reaction. It appears that, as long as water is present in the mineral form (e.g. Mg(OH)_2), there is no need for an external source of moisture. The reactivity of Mg(OH)_2 is, by default, enhanced by the presence of intrinsic water, thus adding steam shifts the equilibrium towards dehydroxylation and (consequently) to partial carbonation. At some extent, presence of steam may be beneficial to reactivate MgO that is inevitably formed, but it is still unclear what quantities of steam that would be optimal.

A fluidisation velocity just above the minimum fluidisation velocity is enough to significantly increase the number of collisions between particles and notably

increase the reactivity. Although higher velocities cause more contact between particles, this effect is nullified by an increase in the dehydroxylation of $\text{Mg}(\text{OH})_2$ (a higher flow rate enhances evaporation leading to an inert MgO). This may help to explain why the reaction levels off at 50-60% carbonation of serpentinite-derived $\text{Mg}(\text{OH})_2$, after 15 minutes, at 500°C and 20 bar CO_2 with particles of 250-425 μm , and why longer reaction times do not lead to the formation of more MgCO_3 .

Finally, Fagerlund (2012) also found that $\text{Mg}(\text{OH})_2$ derived from serpentinites from Finland and Lithuania is much more reactive than synthetic $\text{Mg}(\text{OH})_2$ from the Dead Sea Periclase Lda, used in his first studies. This is attributed to the increased pore volume of the serpentinite derived material (0.24 cm^3/g vs 0.024 cm^3/g) and surface area (47 m^2/g vs 5 m^2/g).

6. Experimental work

The experimental work focused primarily on the optimisation of the extraction of magnesium, mainly from Portuguese and Finnish rock material and on the carbonation of the produced $\text{Mg}(\text{OH})_2$ (Paper I). The valorisation of by-products such as iron oxides and valuable metals (nickel, chromium and copper) is studied in Papers VI and VII.

The Finnish rock material was collected from the Hitura Nickel mine (both nickel ore and mine overburden were tested) and the Portuguese minerals were mainly collected from Donai, Bragança. The rocks were crushed with jaw crushers and grinded with ball mills. Typical size fractions were in the range from 75 to 250 μm . The chemical composition of the minerals was determined by XRF and chemical digestion coupled with ICP-OES techniques. The structural composition was determined by XRD and polarizing microscopy. The Portuguese resources of suitable magnesium silicate minerals were estimated by using published geological maps and internal reports.

6.1 Extraction of magnesium and carbonation of $\text{Mg}(\text{OH})_2$

Regarding the magnesium extraction optimisation, aspects investigated were the influence of temperature, time of reaction, presence of water and aluminium, type of reactor/mixing (the extraction reactions took place in three different reactors presented in Figure 12), and the fluxing agent (ammonium sulphate vs. ammonium bisulphate). A typical test consists of:

- 1) Mixing of the powdered rock with the ammonium salts. The solids are placed in the oven (or rotary kiln) and allowed to react during 30 to 60 minutes.

- 2) After cooling down, the XSO_4 products (mainly MgSO_4 and FeSO_4) are dissolved in water and the insoluble fraction is separated by vacuum filtration and discarded. The ICP-OES technique is used for determining the elemental

composition of the aqueous product solution. The extraction efficiencies for the different elements are then determined through mass balances.

3) Ammonia solution (NH_4OH , as 25%-wt NH_3 in water) is added to increase the pH to 8~9 and recover the iron in the form of (hydr)oxides. This product is separated by vacuum filtration, thus giving a solution with Mg^{2+} and aqueous ammonium sulphate. The ICP-OES technique is again used for determining the accurate elemental composition of this solution.

4) The pH is further increased to 10-12 by addition of NH_4OH to convert Mg^{2+} to $\text{Mg}(\text{OH})_2$, which is separated by vacuum filtration. ICP-OES technique is used for determining the elemental composition of remaining aqueous.

5) $\text{Mg}(\text{OH})_2$ is carbonated in the PFB reactor at $\sim 500^\circ\text{C}$ and $\sim 20 \text{ bar CO}_2$. The extent of the carbonation reaction was determined by analysing the solid product using the procedure developed by Fagerlund et al. (2010).

Paper I compiles most of the experimental results that allow for drawing clear conclusions on the optimal conditions for the solid/solid extraction operation.



Figure 12 – Reactors used for the solid/solid reaction of magnesium silicates with ammonium salts, at ÅA (taken from Ndguagu (2012)).

6.2 Extraction, separation and precipitation of other metals

The co-extraction of valuable/marketable metals (Fe, Ni, Cr, Cu), typically present in serpentinites, was also studied and their potential for raw materials (inputs) replacement and net CO₂ emissions reduction assessed. The recovery of metals was optimised through a combination of selective precipitation and ion exchange techniques.

Amberlite IR-120 was the resin chosen for this study. It is a gel-type, strongly acidic cation exchange resin of the sulphonated polystyrene type. A typical test consists of contacting increasing amounts of resin with an aqueous solution containing the metals to be recovered, in a batch operation, at constant temperature for approximately seven hours to reach equilibrium. The resin uptake calculations are based on the initial and equilibrium compositions of the aqueous solutions (determined by ICP-OES technique).

7. Key findings and discussion

7.1 Mg(OH)₂ production

By 2012, quite a few tests with Finnish rock material had been performed by Nduagu et al. (2013) and soon it was clear that the preeminent challenge posed by the “ÅA route” was the high temperature (~450-500°C) required for achieving more than 50% extraction of magnesium. Whilst these temperatures favour the kinetics for magnesium extraction, they also lead to the degradation and volatilisation of the fluxing salt as sublimated ammonium sulphate (AS), besides NH₃ and SO_x (Nduagu et al., 2013, 2014, Highfield et al., 2015). This results in a cycle of high reactant losses and lower magnesium extraction efficiencies. The main objective of the experimental work presented in this section is to increase the magnesium extraction at temperatures near or below 400°C to accomplish a process more encouraging from an energy standpoint.

7.1.1 Extraction of magnesium - influence of water, fluxing agent and reaction time

The first experimental results with Portuguese rock samples, presented in Figure 13, showed that all three materials, although collected from different places, present a reactivity similar to the Hitura nickel mine overburden material. Further experimental work was carried out with samples collected from Donai⁹. It is known that the natural weathering of rocks occurs under specific conditions and that it is enhanced by temperature, surface area and availability of a natural acidic solution. Moisture is also known to augment thermal expansion of the rocks (Schaetzl and Thompson, 2015) reducing the rock's strength and favouring the cracking of crystalline bonds. Hence the interest in reacting the rocks in the presence of small amounts of water. As expected, moisture has a dramatic effect

⁹ Peridotite from Rabal seems to be more reactive but its resources are limited for large-scale applications. On the other hand, the resources of serpentinite material in Donai are much larger making it more attractive for industrial scale exploration

in the extraction¹⁰ of magnesium for both Hitura nickel mine and Donai materials, especially at temperatures below 450°C, as shown in Figure 13 and further in Figure 14.

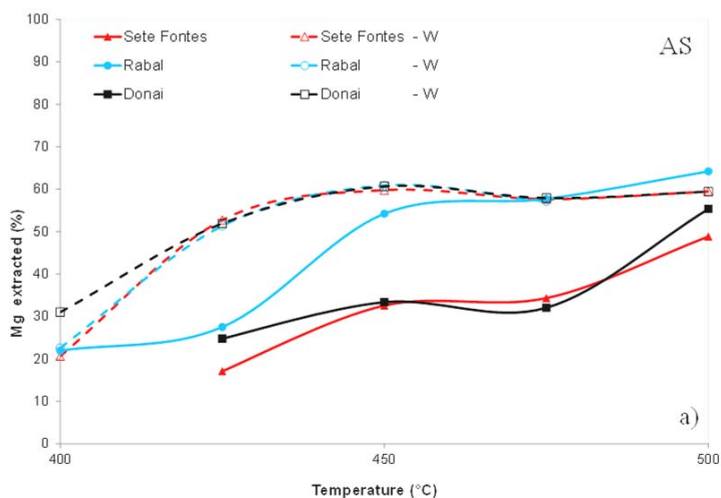
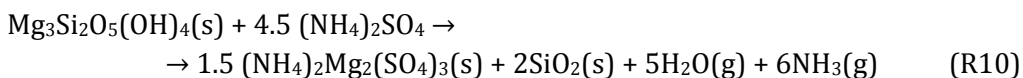


Figure 13 - Reactivity of the rock samples collected from Northeast Portugal: Sete Fontes, Donai and Rabal, with ammonium sulphate. Influence of moisture (W). Reaction time 30 minutes (Paper I).

The data existing in the literature concerning the temperature and reaction products of AS thermal decomposition are to some extent inconsistent. It is, however, generally accepted that before converting to NH_3 and SO_x , AS undergoes a transformation process into several intermediate products: triammonium hydrogen sulphate, ammonium bisulfate, ammonium pyrosulfate and sulfamic acid (Halstead, 1970, Kiyoura and Urano, 1970, Nduagu et al., 2014, Highfield et al., 2012, 2015). At a typical reaction temperature (400-500°C), magnesium extraction is thus limited by the volatilisation of the fluxing agent. Nduagu et al.

¹⁰ In the presence of moisture the final product is a “fluffy” solid, much easier to dissolve in water than the (quite often) sintered solid formed at higher temperatures.

(2014) and Highfield et al. (2015) investigated in detail the serpentinite/AS reaction chemistry, by means of thermogravimetry, differential scanning calorimetry, mass spectrometry and Fourier-transform infrared Spectrometry and determined that the reaction between AS and serpeninites goes according to:



It appears that moisture inhibits the volatilisation of ammonium sulphate, stabilises the intermediate products (favouring pyrosulphate formation) and, furthermore, restrains mineral transformation to the less reactive (towards AS) forsterite (Mg_2SiO_4).

In a different study, in the UK, Wang et al. (2013) presented interesting results on the extraction of magnesium from serpentinite in an aqueous solution of ABS but with an infeasible energy penalty for ABS recovery, mainly due to the high amount of water used in the process. On that account, it made sense also here to study the solid dry reaction between the magnesium silicate rocks and ABS. Indeed, the choice of fluxing agent has a dramatic sway in the extraction results (Figure 13-15) that are promising, as 60% of the magnesium present in the rock is extracted already at 350°C. The experimental results also show that the reaction time can be cut by half: 30 minutes with ABS instead of 1hr with AS, earlier determined by Nduagu et al. (2012), to be the optimal reaction time with AS). Oddly, although the Portuguese rock appears to be more reactive in a dry reaction than the Hitura Nickel mine material, as pointed out in Figure 14, in the presence of water, and independently of the fluxing agent, both rocks present similar behaviour.

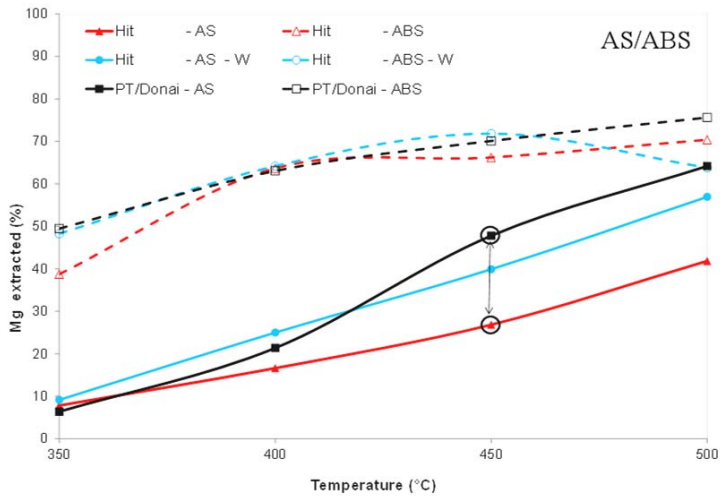


Figure 14 - Reactivity of the rock samples collected from Donai and Hitura nickel mine. Influence of moisture (W) and fluxing agent (AS - ammonium sulphate, ABS - ammonium bisulphate). Reaction time 30 minutes. (Paper I)

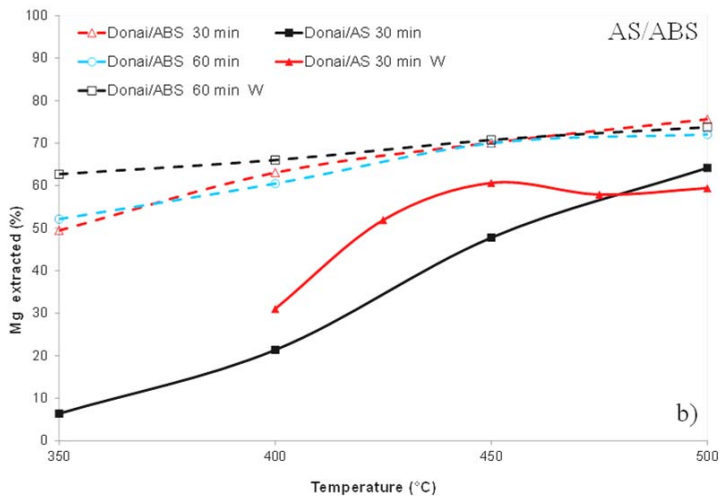


Figure 15 - Reactivity of the rock samples collected from Donai. Influence of moisture (W), fluxing agent (AS - ammonium sulphate, ABS - ammonium bisulphate) and reaction time. (Paper I).

This work does not include a detailed study of the influence of particle size in the extraction reaction. As it is inferable - and concluded by Nduagu (2012) - a lower particle size distribution is favourable to the extraction reaction. For controllability reasons, after crushing and grinding, the solids were washed and the fines (size fraction < 75 μm) were rejected. Still, in a real scenario this rejection is pointless and the addition of the smaller fraction is welcome to the process. To fathom how the inclusion of fines would reflect on the extraction, a few tests were conducted with a size fraction <125 μm and ABS as the fluxing salt - see Paper VI. The results are rather encouraging as $\sim 65\%$ magnesium was extracted at 250°C and 70% at 300°C. Yet again the plateau of $\sim 75\text{-}80\%$ extraction is achieved at 400-450°C. Conducting the reaction at lower temperatures will surely have a significant impact on the energetic performance of the process but at the cost of higher amounts of rock material to be processed. Overall, the decision of what fluxing agent and extraction conditions to use, must include not only material but also energetic and operating issues which are further discussed in section 7.3.

7.1.2 Reactor configuration

The extent of the solid/solid reaction is also lowered by mass and heat transfer limitations and the right reactor design certainly enhances the solid/solid extraction. For the first years, experimental studies at ÅAU were performed in reactor 1, presented in Figure 12 (section 6.1), with some disadvantages: difficulty in maintaining a steady temperature, use of small amounts of material (2g of rock) and only allowing for a grossly "homogeneous" mixture of AS and powdered rock. Reactor 2 permitted a better temperature control and higher amounts of reactants (up to 20 g of rock). Also, it was possible to disperse the reactants in several layers (with a thickness of circa 0.5 cm) starting with the ammonium salt at the bottom and ending with a top layer of serpentinite. This configuration works surprisingly well giving a 75% extraction of magnesium at 400°C. In 2011, the Thermal and Flow Laboratory at ÅAU acquired a small rotary

kiln (reactor 3) which can take up to 120 g of solid material. The constant rotating is undeniably beneficial giving the best experimental result: 80% magnesium extraction at 450°C, showing also that the scale up of the process is feasible. One downside is again the accumulation of ammonium salts precipitating / sublimating on the side (gas outlet) tubes (shown in Figure 16). Although the rotary kiln allows for high extraction yields and prevents sintering of products, the deposition of volatilised ammonium salts downstream, due to temperature drop, is a source of fouling and severe corrosion and imposes the use of advanced materials.

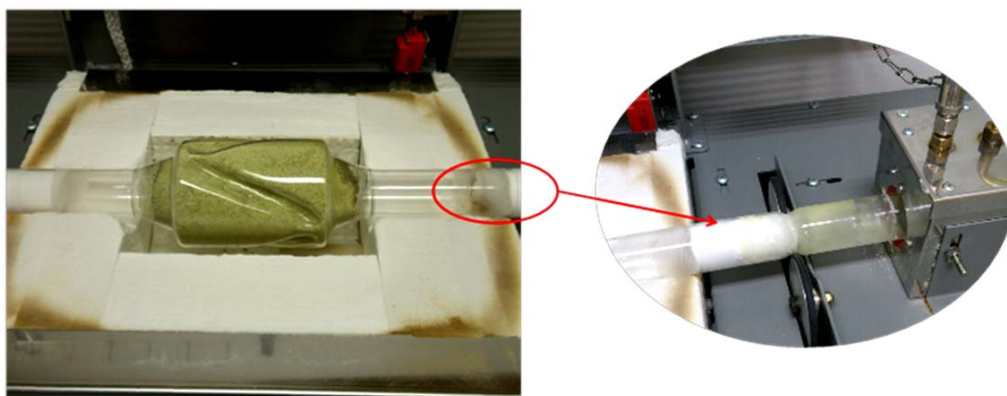


Figure 16 – Accumulation of ammonium salts in the side tubes of the glass rotary kiln reactor.

A (moving) downdraft reactor (mimicked by the layered configuration) should also work well – especially for temperatures below 450°C. Such a reactor would have three main advantages: 1) better trapping of the gaseous products increasing contact time between reactants; 2) efficient direct pre-heating of materials and, finally, 3) minimisation of the downstream corrosion problems as the volatilised material condenses in the colder upper section of the reactor. Even so, the sintering of the solid products may prove challenging and must be avoided at all costs.

The main experimental results for the extraction of magnesium in the presence of ABS/water, for the different reactors, are presented in Figure 17.

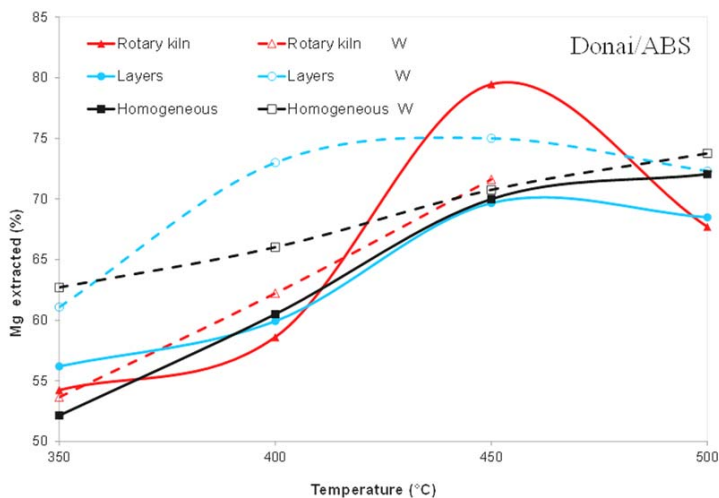


Figure 17 – Magnesium extraction results for reaction of rock material collected from Donai, with ABS, at 350°C-500°C, reaction time of 30 minutes. Influence of water (W) and reactor/mixing conditions. (Paper I).

7.1.3 Extraction, separation and precipitation of other metals

The ÅA process is by no means selective towards magnesium. In fact, all the metals (Al, Ni, Cr, Cu, etc.) in the rocks will be (to some extent) extracted along with magnesium. The co-extraction of metals – see Papers I, VI and VII – besides being unavoidable, is also quite energy consuming (Nduagu et al., 2012a). Their separation and recovery is thus crucial to improve the economics of the process.

Extraction of iron

As detailed earlier, the method under study here produces significant amounts of an iron by-product and its potential application for the steelmaking industry is appealing for reducing waste, replacing raw materials and increasing profitability. Calculations in Paper III show that the mineralisation of all the CO₂

emissions of a steelmaking plant, Ruukki (currently SSAB Europe) in Finland, would (by)produce enough iron to replace ~17% of their iron ore requirements. Similarly to magnesium, the iron extraction is favoured at 400-450°C and by longer times, especially in the presence of water as is shown in Figure 18. It is also interesting to see that iron extraction is clearly benefited by a layered distribution of materials (resembling a downdraft reactor).

A side note on the suitability of this iron by-product to the steelmaking industry: in a typical experiment the iron product is recovered as a mixture of goethite, hematite and magnetite. However, under controlled temperature, oxidation rate, stirring speed pH and addition of alkaline during precipitation, it is possible to favour the formation of magnetite (Koivisto, 2013). Also, as reported in Paper III, if this by-product is fed to a sintering plant, it is predicted that it will also further reduce the carbon dioxide production in the blast furnace.

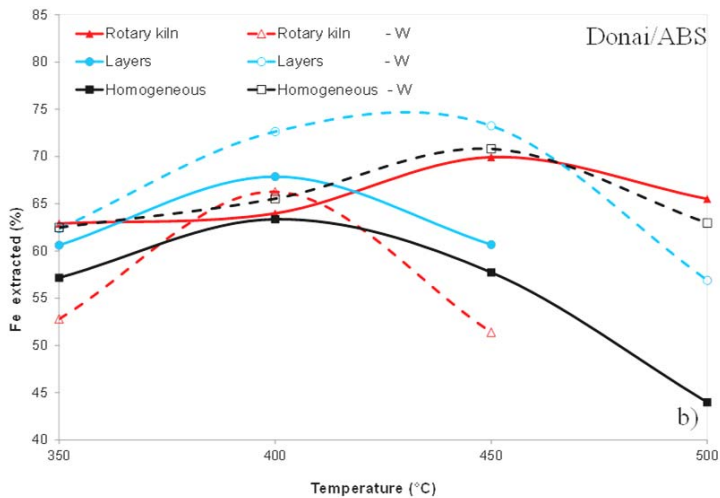


Figure 18 - Iron extraction results for reaction of rock material collected from Donai, with ABS, at 350°C-450°C, reaction time of 30 minutes. Influence of water (W) and reactor/mixing conditions. (Paper I)

Extraction of nickel

Papers VI discusses a scenario where the ÅA process is used for simultaneous extraction of nickel, copper and magnesium from the Hitura mine nickel ore.

Regarding the fluxing agent, nickel does not present a behaviour consistent with the other metals: ABS appears to be more efficient in a dry reaction (28% nickel extraction at 450°C) while, in the presence of water, AS showed the best result at 500°C with 27% nickel extraction. Also, and opposed to the other metals, nickel extraction is favoured at temperatures > 450°C.

As for copper, 70% extraction with ABS is attainable already at 250°C. On the other hand, AS performs much worse as only 40% of the copper is extracted at 450°C. Also, in both cases, moisture does not seem to be a key player.

The replacement of chemically intensive metallurgical methods by the simultaneous CO₂ capture and Ni/Cu extraction process could be environmentally beneficial but, unfortunately, the extraction of nickel from Hitura nickel mine ore material with ammonium salts falls far short of the traditional metallurgical extraction process, which in the case of Hitura is already typically low (~66.5%).

On the other hand, it might be interesting to use low grade ores simultaneously for CO₂ capture and storage and metals extraction through an environmentally friendlier process. In the case of Portuguese serpentinite, the extraction of nickel and chromium amounted to 63%-71% and 42%-52%, respectively, in a wet reaction of powdered material (<125 µm) with a mixture of ammonium salts (50/50-W% AS/ABS) at 450°C. Their recovery is thus appealing and is discussed in Paper VII and in the next section.

Separation and recovery of metals

The separation steps that follow the dissolution of the solid products are not yet fully optimised. Efficient mixing combined with slow addition of alkaline, tight control of pH, effective filtration (centrifugation) and the concentration of the

metals in solution¹¹ seem to be key factors affecting the efficiency of the by-products recovery process.

The high pH (8~9) required to precipitate iron (II) is the source of significant losses (up to 20%) of magnesium. The introduction of an oxidation step upstream allows for the recovery of all the iron as iron (III) at pH ~4 while minimising magnesium losses due to co-precipitation mechanisms. If present, chromium will precipitate along with the iron (III) making this product even more interesting for special alloys in the steelmaking industry.

At pH 5.35, aluminium is easily recovered in the form of a white gel leaving in solution (ideally) only nickel. Contrary to the other elements (Mg, Fe, Al, etc.), nickel concentration in solution is too low for a successful precipitation of Ni(OH)₂ through addition of alkaline. Its separation, however, is readily achieved with ion exchange techniques. The recovery of metals thus becomes a more complex method, as described in Paper VII.

Nevertheless, in the particular case of Portuguese rock, although the quantities of nickel extracted seem modest, they are worthwhile recovering as per ton of serpentinite processed, 1.6kg of Ni are recovered which is equivalent to 1/3 of the average Hitura nickel mine production: 4.8 kg of Ni/ton of ore.

7.2 Carbonation of Mg(OH)₂

7.2.1 Carbonation experiments at Åbo Akademi University, Finland

Only a few carbonation tests were conducted at ÅAU using the PFB reactor presented earlier in Figure 11, since earlier work showed insignificant differences between Mg(OH)₂ samples produced (by precipitation from solution) from rocks from different locations. The experimental results fall to the same line as those obtained by Fagerlund (2012). The carbonation is strongly influenced by

¹¹ The range of concentrations of the different metals in solution varies from 45 mg/l of nickel to 16280 mg/l of magnesium.

temperature and the best result, 70%, was obtained with pure CO₂ at 510°C and 20 bar and Mg(OH)₂ size fraction < 75 µm – see Table 2. Fagerlund (2012) concluded that both the specific surface area (S_{BET}) and the specific pore volume (SPV) of the Mg(OH)₂ product are key factors for the carbonation reaction. Oddly, the Mg(OH)₂ powder carbonated in this work had a much lower S_{BET}: 7 m²/g vs 46.85 m²/g as measured by Fagerlund and Zevenhoven (2011), but still maintaining a relatively high SPV (0.146 cm³/g) and suggesting that the SPV has a larger influence on the final carbonation extent.

Table 2 – Mg(OH)₂ carbonation tests: experimental conditions and results.

Test #	Temperature (°C)	Pressure (bar)	Time (min)	Size fraction (µm)	Carbonation degree (%)
1	485	19~21	15	< 74	14.0
2	485 - 495	19~21	20	< 74	30.7
3	510	19~21	30	< 74	70.3
4	515	19~21	30	74 - 250	38.8

7.2.2 Carbonation experiments at ICES/A*Star, Singapore

Most of the Mg(OH)₂ produced at ÅA was sent to ICES/A*Star, Singapore, for carbonation in a pressurised Thermogravimetric Analyzer (TGA).

The carbonation tests were conducted at pressure and temperature akin to flue gas conditions under high relative humidity to address the role of steam and specific surface area both in the rate and extent of the reaction. Commercial brucites carbonated under the same conditions were used as control tests. The results and discussion of these tests are reported in Highfield et al. (2013) and summarised in the next paragraphs.

Typically, the brucite produced according to the ÅA method is contaminated with sulphur (in this case up to 4%) of the fluxing agent (AS/ABS) which was removed by cold/hot aqueous washing, reducing the sulphur content below 1% and

progressively increasing surface BET area up to 30 m²/g. The carbonation results are summarised in Figure 19.

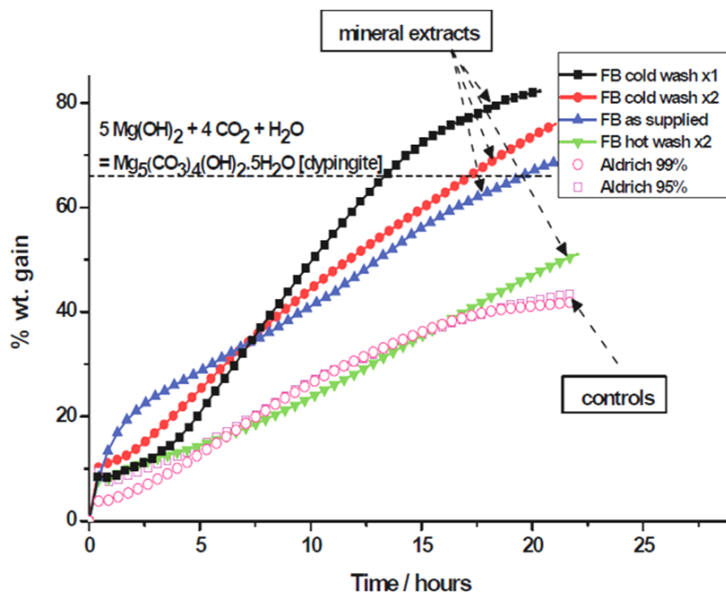


Figure 19 - Carbonation of brucite: Extracts vs. Controls at 45^oC, 0.67 bar P_{CO2} and Relative Humidity > 90%. FB - brucite prepared at ÅA from Portuguese serpentinite. Aldrich - commercial controls. The theoretical weight gain is represented by the dashed limit at 66.6% and it is an indicator of probable product identity – dypingite. The weight gain above this limit is possibly due to two factors: weakly-bound water that usually scales with porosity and the formation of surface bicarbonates that are typically desorbed after discharge and equilibration with ambient air. Elemental analysis of the FB Cold wash X1 sample revealed a 90% conversion. S_{BET}: FB as supplied – 12 m²/g, FB cold wash – 23 m²/g, FB hot wash – 30 m²/g, Aldrich – 10 m²/g. (taken from Highfield et al.(2013))

Contrary to the findings of Fagerlund et al. (2012a)¹², in the TGA, water remarkably enhances the carbonation of Mg(OH)₂ apparently acting both as a reactant and promoter to form dypingite¹³. Interestingly, it seems that initially

¹² Modest levels of steam are ineffective for increasing of Mg(OH)₂ carbonation rate in the PFB.

¹³ Control tests without steam at 45°C resulted in little or no conversion of brucite to carbonates.

sulphur influences the wetting properties resulting in the rapid initial weight gain of sample “FB as supplied”, but after a few hours it stops being a governing factor. Surface area again does not seem to be the determining factor of carbonation rate, as the hot washed solid (with higher $S_{\text{BET}} \sim 30\text{m}^2/\text{g}$) performed nearly as bad as commercial samples.

Albeit a comparison between experiments in the PFB and TGA is complicated by the dissimilar equipments and operating conditions, it is clear that brucite carbonation involves a complex chemistry governed by thermodynamic constraints, the physical properties of the solid particles and the composition (water %) of the CO_2 gas.

7.3. Modelling and process simulation

This section discusses the main results presented in Papers III, IV and V.

The ÅA route was modelled with Aspen Plus® software to acquire information on process layout for optimal heat recovery and minimum material inputs. The exergetic performance of the process was assessed with the combined use of Aspen Plus®, HSC Chemistry¹⁴ software and pinch technology. A simplified schematic of the modelled process is presented in Figure 20 and an illustrative example of the models developed in Aspen Plus® is presented in Figure 21 .

The simulation results allowed for inferring the determining factors in the performance of the process: the operating temperature and efficiency in the solid/solid extraction reactor, the fluxing salt, the composition of CO_2 containing gas and the recovery method for the ammonium salt.

¹⁴ Outotec's Chemical Reaction and Equilibrium Software HSC version 5.1 (2002)

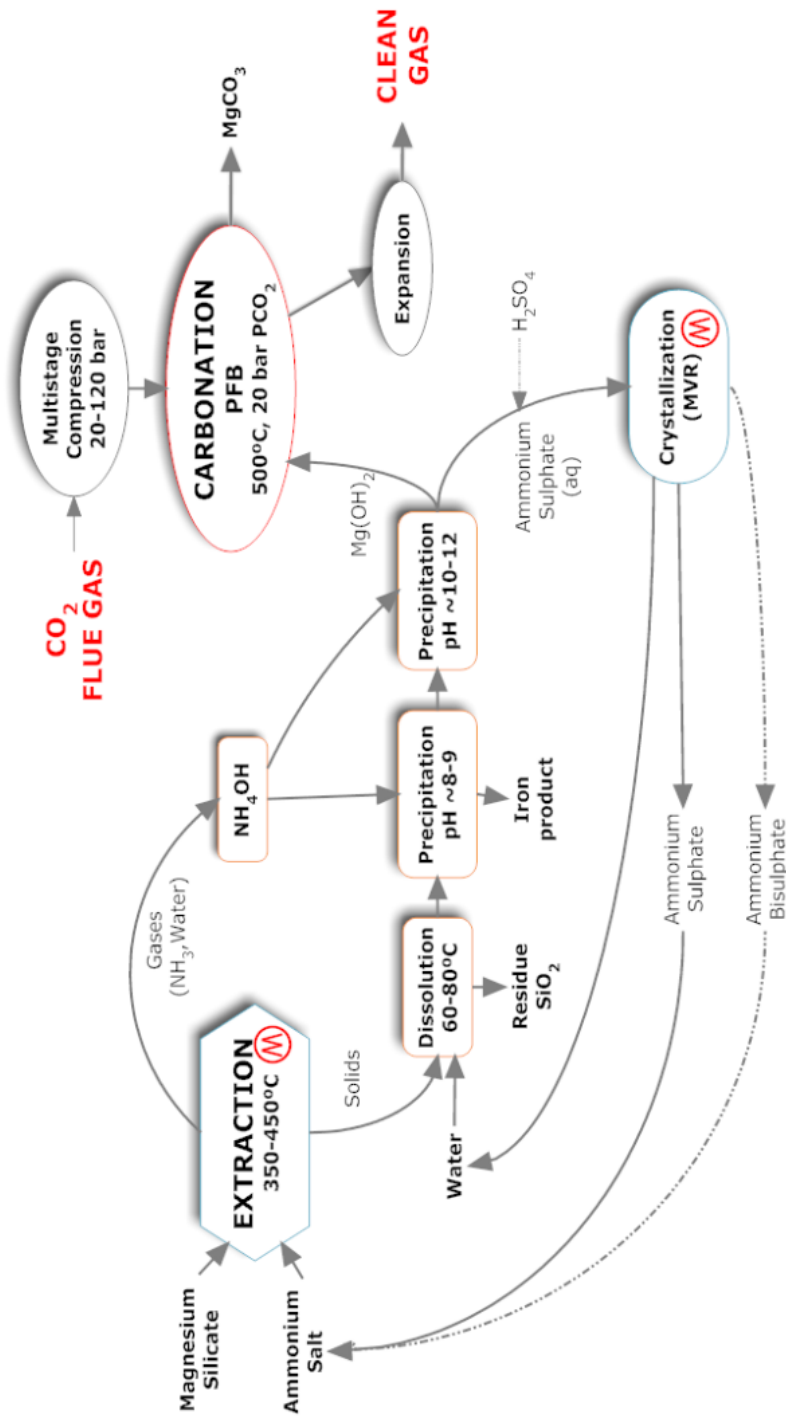


Figure 20 – General representation of the “ÅA route” modelled with Aspen Plus®.

The PFB reactor and the dissolution and precipitation tanks are heat producing units, while the solid/solid extraction and crystallisation of the fluxing salt are endothermic operations. Thermodynamic calculations in Paper III estimated that, due to its exothermic nature, the carbonation reaction could supply ~25% of the heat demand for production of $\text{Mg}(\text{OH})_2$. However, the co-extraction of metals¹⁵ and the incomplete extraction and carbonation reactions have a dramatic sway in the energetic demand of the process. The first simulation models immediately cleared out that the dry carbonation of $\text{Mg}(\text{OH})_2$ produces no more than ~2 to ~5% of the heat required in the extraction reactor.

The energetic integration of the process is, thus, crucial but not straightforward for three main reasons:

- 1) The extraction is a solid/solid reaction at ~400°C, the separation and precipitation of metals are carried out in aqueous phases at 60-80°C and the carbonation is a gas/solid process at 500°C and 20 bar of CO_2 partial pressure. This implies indirect heat transfer between solids and gases (restricting equipment options). Also the pressure differences limit the application of pinch methodology for optimisation of the heat exchanger network.
- 2) Greater difficulties arise from the fact that most of the heat (low and medium grade) available comes from solid streams. Besides the typical low thermal efficiency on recovery (and supply) of heat from solid streams¹⁶, industrial experience and solutions on this matter are rather limited as well.
- 3) Paper IV presents an exergetic analysis of several scenarios with different combinations of fluxing agent and its recovery process, extraction and carbonation efficiencies and CO_2 content of the gaseous stream to be

¹⁵ Calculations performed by Nduagu et al. (2012) showed that small changes in the composition of the rock, particularly the form in which Fe is present in the mineral, play a key role on the energy consumption in the solid/solid reaction.

¹⁶ Due to poor heat transfer coefficients between solids and low surface area in comparison with fluids.

treated. In some cases, the process presents a deceptively positive exergetic balance that is the result of the high availability of low grade heat. Unfortunately, this heat finds no use in the process but its recovery would make sense for external applications. Albeit, one strength of the exergy concept as demonstrated, is that the temperature of heat is directly translated into quality of energy.

Consequently, the energy for the extraction reaction at 350°C-450°C (depending on the fluxing agent) must come from an external source. In that sense, large CO₂ producers often include within their processes medium grade waste heat that can be channelled towards the mineral carbonation (MC) plant minimising heat inputs. Paper V assesses the (pilot) operation of the MC process on waste heat from a lime kiln (210 t/day) located in Parainen, southwest Finland. The heat content of the gas is supplied to the process in a cascading concept (followed by its mineralisation) and simulations estimate that it is possible to:

- 1) process 550 kg/hr of serpentinite (Hitura nickel mine overburden) with a 190 kg/hr CO₂ capture rate, reducing the CO₂ content of the flue gas from 23.5 w% to 1.0 w%.
- 2) achieve an auto-thermal process, with 0.71 MJ/kgCO₂ captured as the electrical input for crushing and gas compression units.

Apropos of the fluxing agent, experimental work – see Paper I – showed that ABS extracts more magnesium at a significantly lower temperature favouring 40% of energy saving in the extraction reactor. Unfortunately, this comes at the cost of a rather more complicated recovery/recycling method of the ammonium salt. The aqueous solution that remains after the precipitation stages is not of ABS but of AS (due to the addition of NH₃ upstream). The first approach was to crystallise the AS followed by its thermal decomposition into ABS and NH₃. As discussed in Paper IV, this route proved to be impracticable and presents an unacceptable energetic penalty as AS thermal decomposition requires 60-75% of the total heat consumption (corresponding to ~4.3-5.8 MJ/kg CO₂). The second option is the addition of H₂SO₄ to the AS solution to produce ABS, followed by its

crystallisation. This method proved to be energetically favourable, but it floods the system with sulphur as, per mole of AS, the addition of H_2SO_4 produces two moles of ABS. As a final note on this subject, although energetically intensive, the crystallisation of ammonium sulphate does not present a significant penalty for the process when using a mechanical vapour recompression (MVR) system (Björklöf, 2010).

Last but not least, the composition of the CO_2 containing gas is also quite important. Seeing that, at first, the process in study was envisioned as a storage option, the models presented in Paper III were based on the mineralisation of a pure CO_2 stream coming from a capture plant. Ideally, this stream reaches the mineral carbonation plant at 100-110 bar and its decompression to 20 bar grants the partial recovery of compression electricity. Yet, in order to keep optimal fluidisation conditions of the $\text{Mg}(\text{OH})_2$ in the PFB, it is necessary to introduce at least 25% more CO_2 than the stoichiometric amount needed. This implies the cooling and separation of the gaseous PFB products and recompression of unreacted CO_2 . On the other hand, flue gases have enough inert components to fluidize the bed without interfering with the carbonation mechanisms and eliminating the expensive CO_2 capture step from the CCS equation (Zevenhoven et al., 2012, 2013, Fagerlund et al., 2012a). Flue gases from oxyfuel combustion, due to its higher concentration of CO_2 (~80% vol), require less compression to reach the optimal 20 bar (of CO_2 partial pressure) in the PFB, thus being the most attractive towards an auto-thermal process. Although the carbonation in the PFB reactor requires high pressures, the expansion of the CO_2 free gas allows for recovering up to ~90% of the electricity requirements of the process.

8. CO₂ mineral sequestration – application to Finland and Portugal

A challenge often encountered in implementation of mineral carbonation is the source/sink (CO₂/Mg-Ca silicate) matching which ultimately implies the assessment of four scenarios:

- Build the MC plant near the Mg/Ca silicate source and deliver the compressed CO₂ gas through a transportation network (of pipelines and boats, e.g.).
- Build the MC plant close to the CO₂ source and convey the rock material by ship, train or trucks avoiding the penalty of a capture step and enabling energetic integration.
- If waste heat is available near the Mg/Ca silicate source: produce Mg(OH)₂ and then transport it to the CO₂ source for carbonation.
- The 4th scenario is the "carbon solution" by Brent et al. (2012): build the power and MC plants at the Mg/Ca silicate source site and transport the fuel (e.g. coal) there.

8.1 Finland

In the case of Finland, the good transportation infrastructures and the widespread mineral resources simplify the source/sink matching process, although unfortunately distances can be large – see Figure 22. A point of advantage is the fact that several suitable minerals are located in formations previously explored by the mineral and metallurgical industries, also resulting in plenty of overburden material fit for CO₂ sequestration. The potential for CO₂ sequestration is vast: as an example, Teir et al. (2006a) points out that, if combined with low-emission technologies, the Outokumpu-Kainuu ultramafic rock belt is (theoretically) sufficient for 200-300 years of CCS activities.

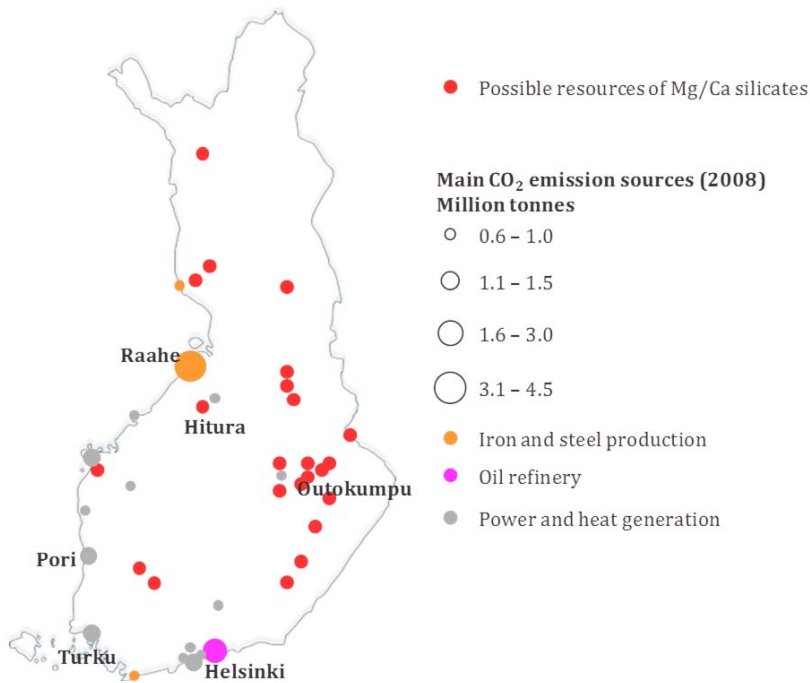


Figure 22 – Main resources of Mg/Ca Silicates in Finland and facilities emitting > 0.6 Mt CO₂/a. Distance Turku – Helsinki ~170 km. Adapted from Teir et al. (2006a, 2011).

8.2 Portugal

In the case of Portugal, the source/sink matching is challenging. Transportation of the rock material to the MC unit by train or truck might be the simplest option, as the railway and road infrastructures already exist nearby the mineral resources and are extended throughout the entire west coast, where the main sources of CO₂ are located, as is shown in Figure 23.

The resources of serpentinite in Northeast Portugal were estimated (using internal reports, geological published maps and assuming a conservative, yet easily mineable, thickness of 50 m for the geologic formation – see Paper I for more details) to a total ~8.3 Gt with a CO₂ (theoretical) capture potential of

~3.4Gt of CO₂, such being equivalent to more than 120 years of CO₂ emissions by the Portuguese power and industry sectors¹⁷ - see Table 3.

Table 3– Estimation of Portuguese serpentinite geological reserves and CO₂ capture potential.

Estimated geological reserves (Gt)		CO ₂ captured (MtCO ₂)		
		Theoretical	90% extraction & carbonation	Experimental data (80% extraction & 70% carbonation)
Donai	0,96	399	323	224
Rabal	2,67	1130	915	633
Morais Massif	5	1890	1531	1058
Total		3419	2770	1915
Years of Portuguese CCS activities*		122	99	68

* These values will greatly increase if CCS activities are combined with low emission technologies.

Portugal is a country smaller than Finland and, perhaps, it would be wiser to think of mineral carbonation as an Iberian goal. In fact, not so far away from Bragança, one can find the Ciudad de la Energia (Ciuden) Oxyfuel combustion plant (Perrin et al., 2015, Lupion et al., 2013). This would be a nearly perfect source/sink match as a gas transport tube can be drilled through mountainous rock.

¹⁷ In 2012, the energy and industry sectors accounted for ~28 Mt CO₂ emissions (Seixas et al., 2015)

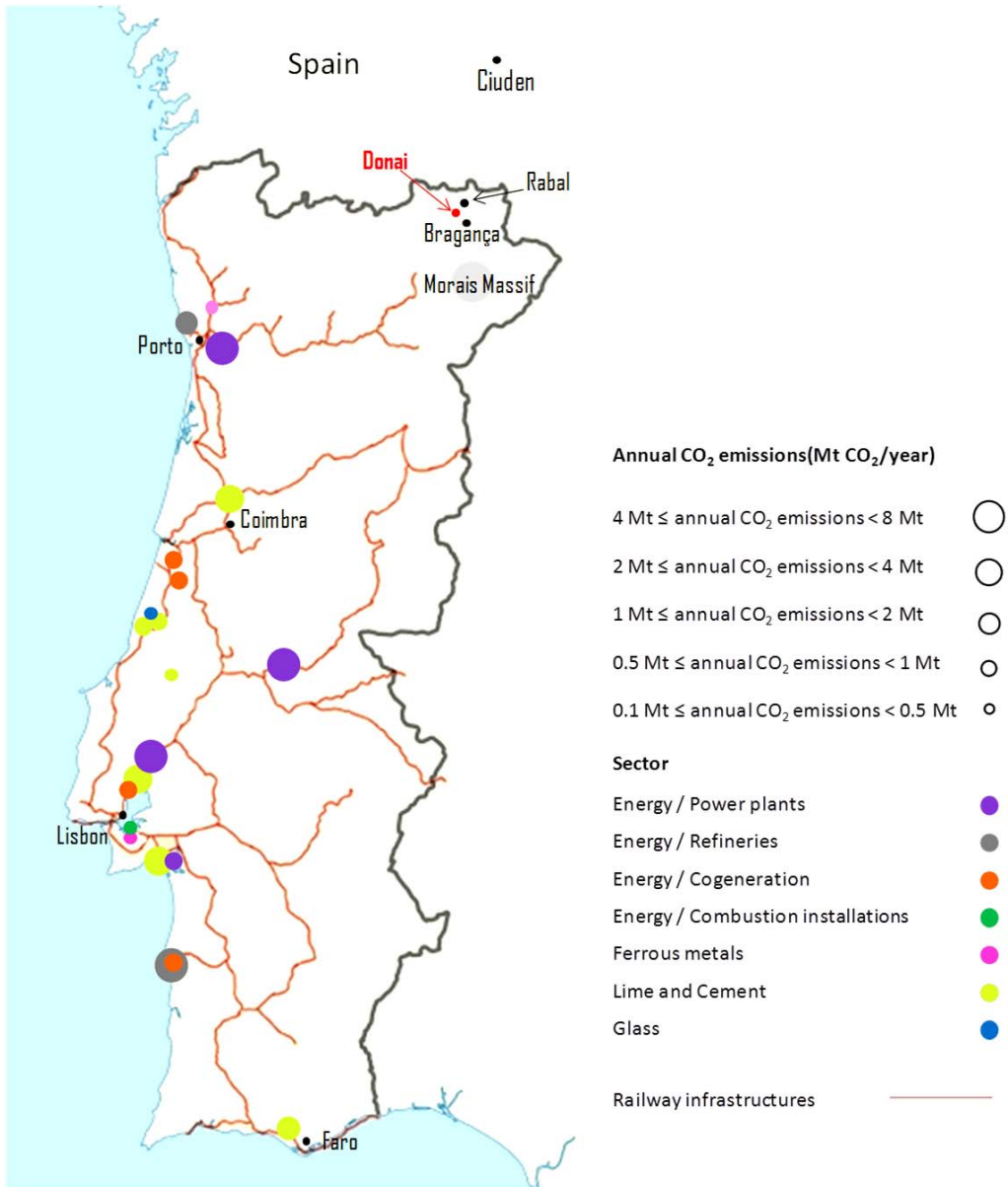


Figure 23- Map of Portugal with information on the main CO₂ sources, serpentinite reserves and railways infrastructures. Distance: Porto-Coimbra – 108 km; Porto-Bragança – 170 km.

9. Conclusions and remarks

Mineral carbonation (MC) technology was first envisioned as a safer and more permanent alternative to ocean and/or geological CO₂ storage, especially for countries that lack suitable geological formations for underground CO₂ injection. So far, its industrial application is mainly constrained by slow kinetics, extreme operation conditions and high energy requirements for activation of the mineral feedstock.

After more than 20 years of R&D activities, carbon dioxide mineralisation has yet much to progress and a factor that does not benefit the development and deployment in Europe is that the technology is excluded from CCS, as defined in the EC directive of 2009 (EC2009), limiting it to methods that involve underground storage of (pressurized) CO₂.

The MC process studied here, known as the “Åbo Akademi route”, uses ammonium salts to extract magnesium from Mg-bearing silicate rocks at 250-450°C. The solid products (mainly MgSO₄ and FeSO₄) are dissolved in water and a gradual increase of pH allows for recovering an iron hydroxide by-product and Mg(OH)₂, which is further converted into MgCO₃ in a pressurised fluidised bed reactor (PFB).

Fortunately, both Portugal and Finland have abundant resources of rather reactive magnesium silicates. Experiments showed that it is possible to extract >50% magnesium from serpentinite at relatively low temperatures (~250-350°C), with ammonium bisulphate (ABS) as the fluxing agent, whilst ammonium sulphate (AS) requires somewhat higher temperatures (350-450°C). Yet, the plateau of 80% Mg extraction with ABS at 450°C has not been surpassed.

The extraction reactor design will be dependent on the desired (or possible according to the quality of the (waste) heat source available) temperature for the reaction: a moving downdraft reactor appears to be more advantageous for lower temperatures ($\leq 400^{\circ}\text{C}$), while a rotary kiln seems to perform better at temperatures $\geq 400^{\circ}\text{C}$.

The fluxing agent regeneration is essential for a closed loop process. AS is easily recovered by crystallisation, while the regeneration of ABS (despite its extraction efficacy) is problematic: thermal decomposition of AS into ABS is energetic and industrially unattractive and regeneration with sulphuric acid results in an AS-ABS producer/ CO₂ sequestration process.

In accordance with other studies, the carbonation in the PFB reactor is quite fast (70% conversion to MgCO₃ in 15 minutes) and experimental results suggest that, amid others, the specific pore volume of Mg(OH)₂ particles is a key parameter on the carbonation reaction extent.

Even though the use of the carbonation heat to drive the extraction reaction (which represents the major energetic penalty) was a promising concept, simulations in Aspen Plus® predict that relying on that for offsetting energy requirements is unfeasible, as that heat is merely enough to keep an autothermal PFB. An effective heat-exchanger network in combination with the expansion of “CO₂-free” gas (for recovery of up to ~90% of the electricity requirements) is thus essential for attaining a reasonable in/output energy balance.

The temperature swings imposed by the ÅA process result in high exergy destruction rates lowering the efficiency of the process. This is the reason why currently R&D proceeds on an alternative method with the direct carbonation of magnesium (as MgSO₄) in an aqueous solution that would keep all the advantages of the ÅA process without the energetic penalty of gases compression and also avoiding the need of expensive/complex equipment: multistage compressors pressurised fluidised beds, for example.

In short, although the route studied here overcomes some typical drawbacks in ancillary processes (e.g. recovery of consumables and de-watering energy penalties) and reasonable kinetics and reaction times suitable for industrial application are within reach, the energy requirements (although fair for a simultaneous CO₂ capture and storage method) are still considered unattractive for a cost-effective CCS process. Economic feasibility hinges on running the

process on flue gas and production of marketable products (iron hydroxides, valuable metals and MgCO_3). Integration with suitable industries like mining, steelmaking, limestone and even fertilisers, will also be of great importance to minimise/replace raw materials and energy inputs with subsequent reduction of net CO_2 emissions.

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