

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

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Doctor of Technology Thesis

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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).

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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^oC, 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^oC 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 350-450⁰C. 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 450⁰C in a laboratory scale rotary kiln and 70% Mg(OH)₂ carbonation in the PFB at 500⁰C, 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 400-440°C, 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 ~ 500°C 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

bestämna 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 tillräklig 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 2,48-5,09 GJ/t CO_2 sequestrado, enquanto que a decomposição térmica de AS em ABS resulta num processo que precisa de 2,48-4,47 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	Ehtylenediaminetetraacetic 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).

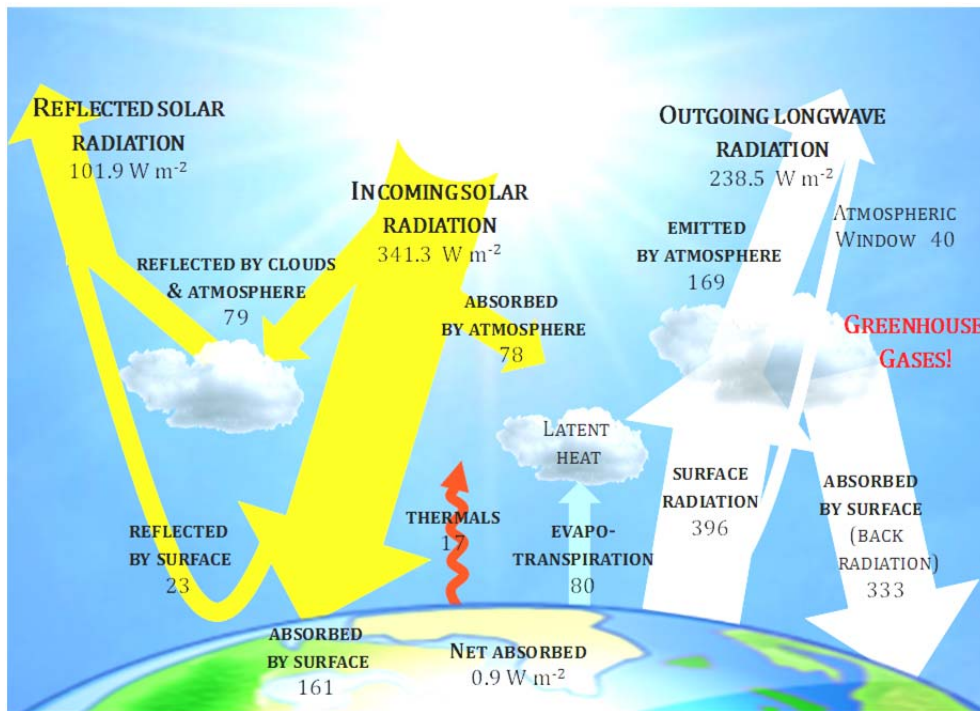


Figure 1 - Earth's energy budget. Adapted from Trenberth et al. (2009).

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).

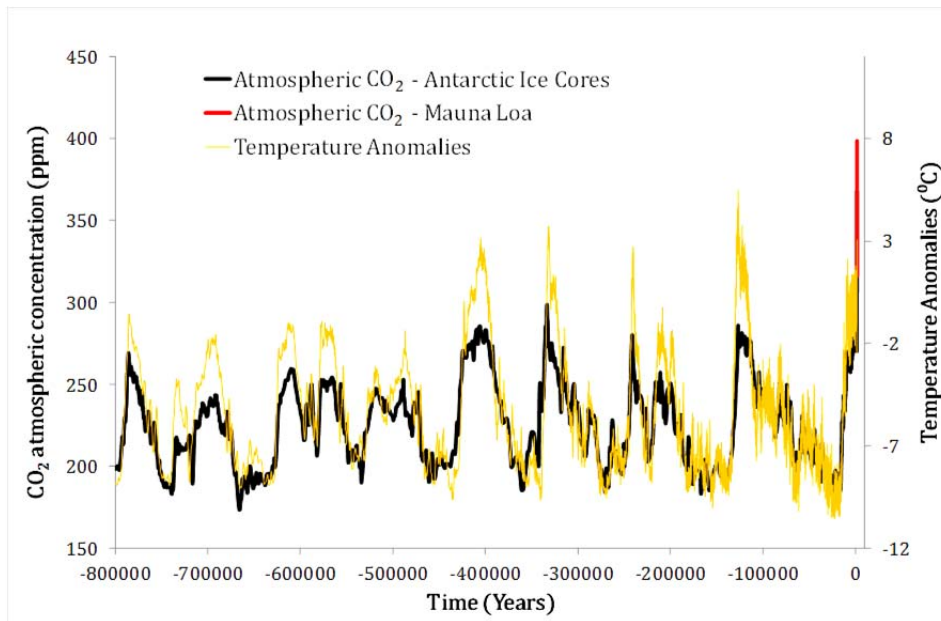


Figure 2 – Relation between CO₂ emissions and temperature anomalies over time. Data collected from Bereiter et al. (2015), Jouzel et al.(2007) and GMD, (2014).

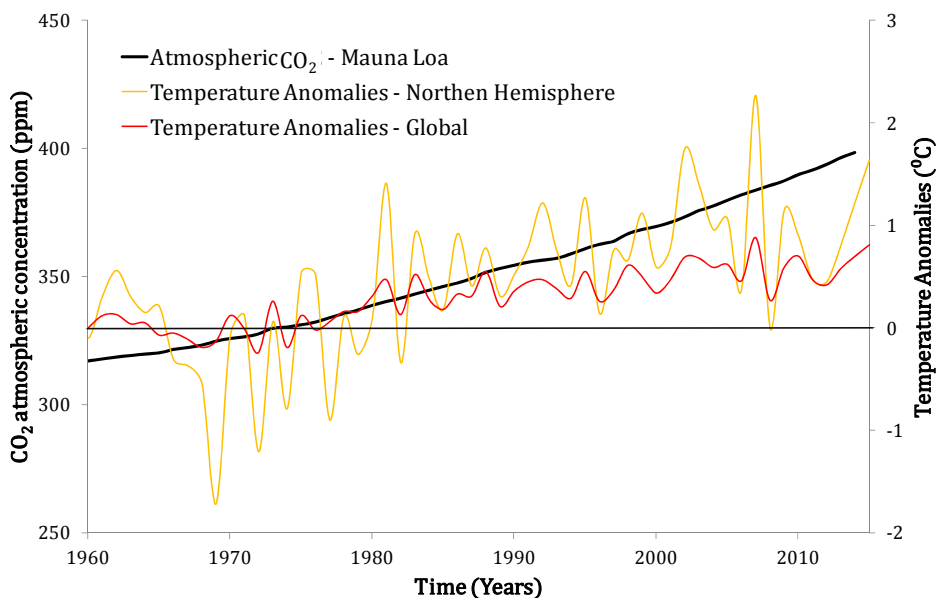


Figure 3 – Relation between CO₂ emissions and temperature anomalies from land and ocean since 1960. Data collected from (GMD, 2014) and (NOAA, 2015).

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).

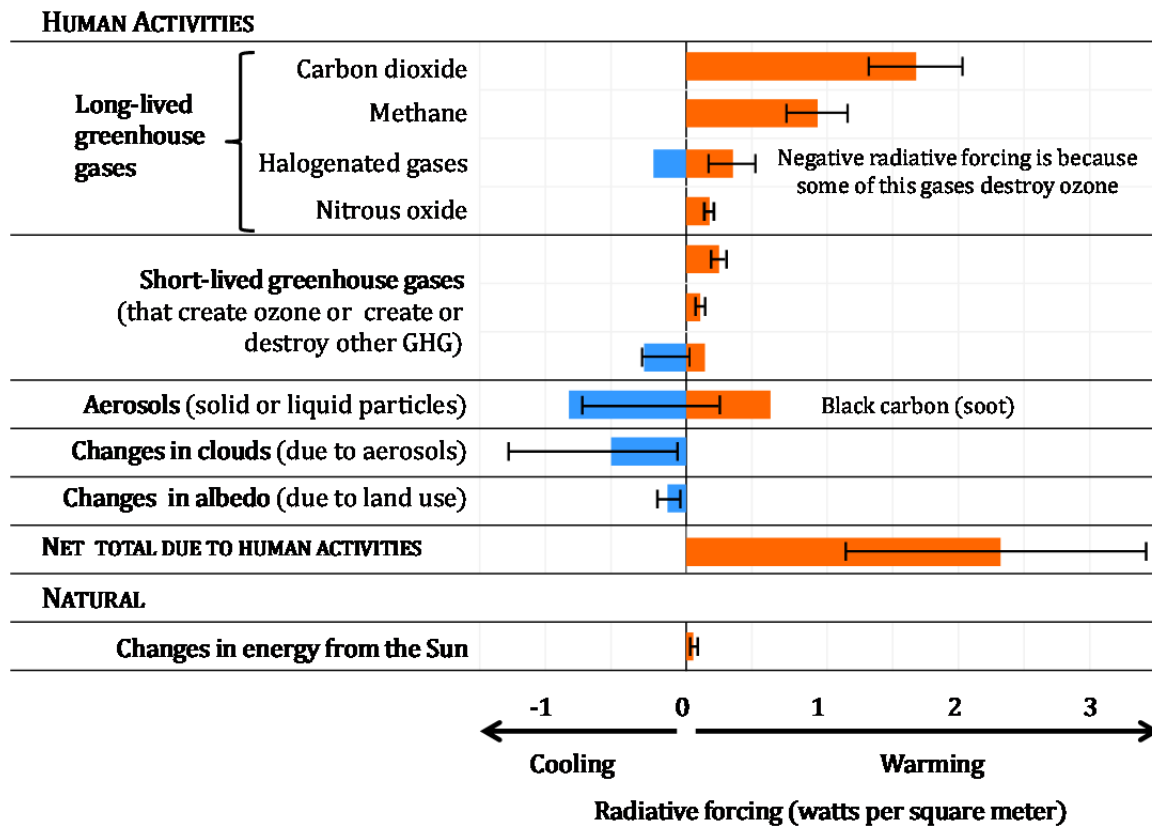


Figure 4 – Radiative forcing caused by human activities since 1750. Adapted from EPA (2014).

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):

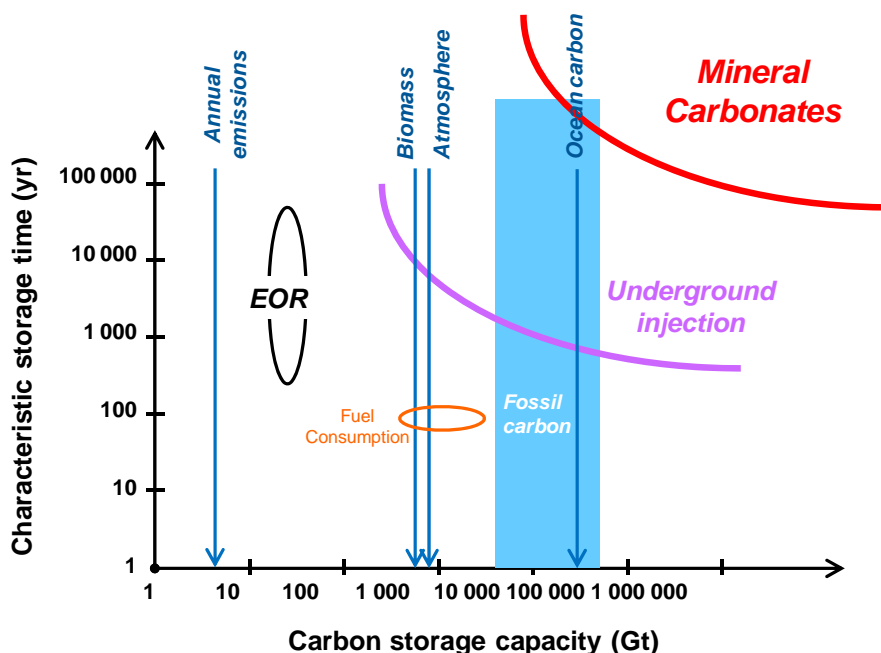
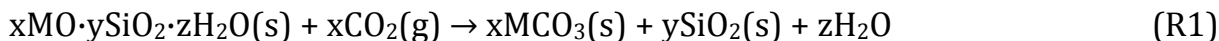
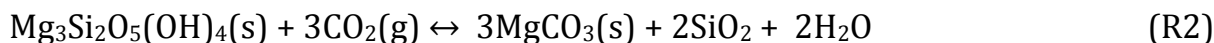


Figure 5 – Estimated times and storage capacities for the various options for CO₂ storage. Adapted from Zevenhoven et al. (2006).

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.

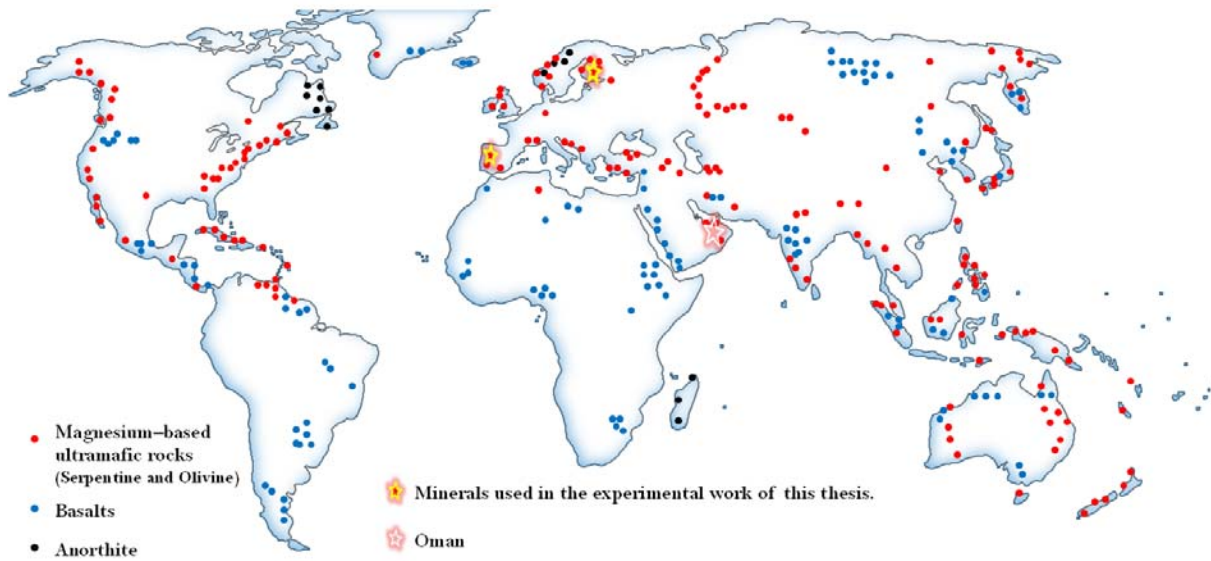


Figure 6 – Worldwide distribution of mineral feedstock suitable for mineral carbonation. Adapted from Sanna et al. (2014). In Oman is located a deposit of 30 000 km³ of magnesium silicates. It is estimated that this formation has the potential for storing all the CO₂ anthropogenic emissions resultant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

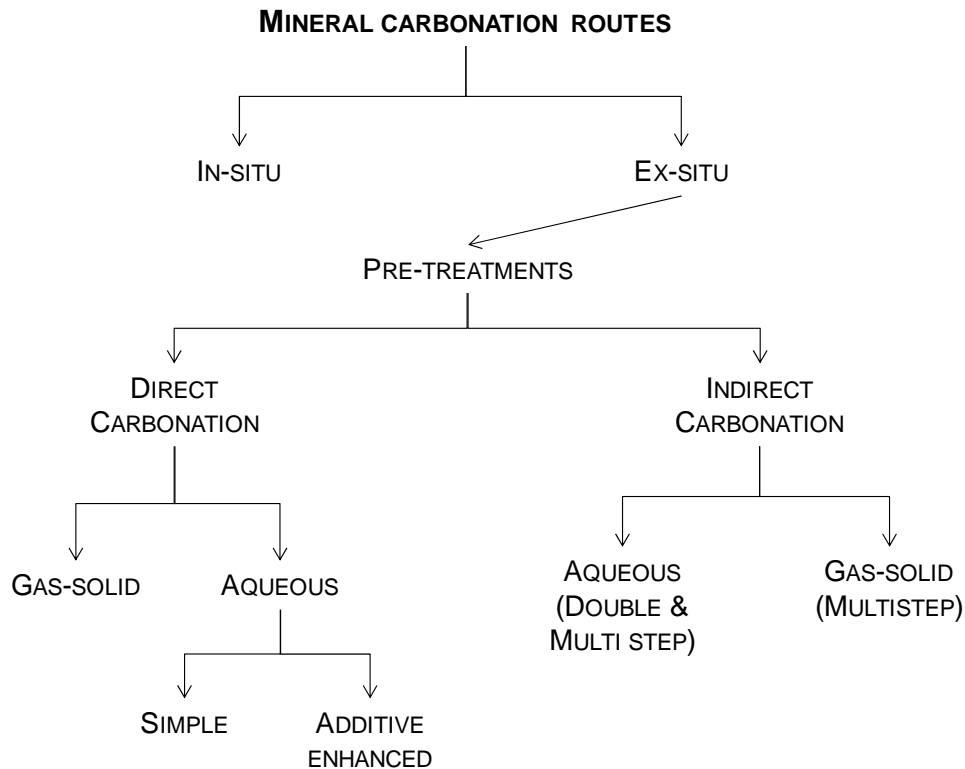


Figure 7 – Mineral carbonation pathways for naturally occurring minerals.

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 700⁰C for 20 min) present a prohibitive energy penalty.

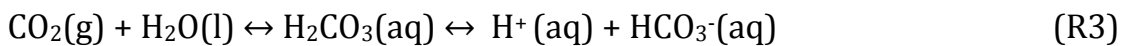
As it became clear that direct mineralisation of Mg/Ca natural silicates is an unviable process, research progressed to multistep (indirect) gas solid carbonation routes: these will be later addressed in detail.

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:

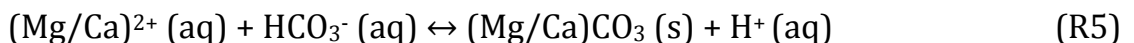
i) dissolution of CO₂ into water towards a mildly acidic solution



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. Bodénan 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 serpentinite 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 , $(NH_4)_2SO_4$, 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 $Mg(OH)_2$ slurries derived from silicate minerals and industrial wastes. Fricker and Park (2013) demonstrated the rapid and spontaneous nature of the $Mg(OH)_2$ 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 $Mg(OH)_2$ 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 serpentine, 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).

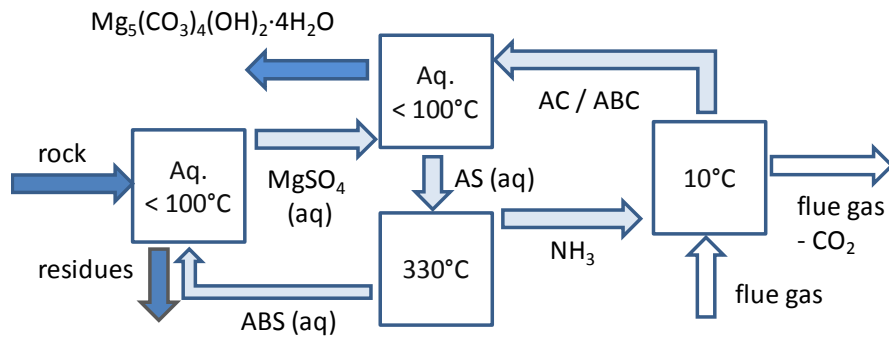


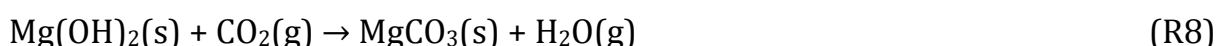
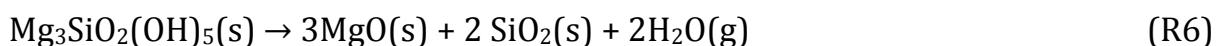
Figure 8 – pH swing process based on ammonium salts developed at the University of Nottingham, UK (taken from Geerlings and Zevenhoven (2013)).

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.

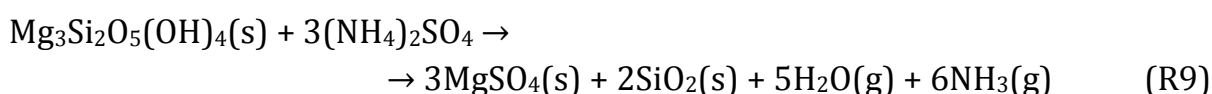
By and large, the mechanisms for aqueous CO₂ mineral sequestration are fairly well understood and it is established that the dissolution rate is speed up by: silicate ore pre-treatments/activation, application of additives and mechanic/chemical removal of the SiO₂ layer. Still, no aqueous process has 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:

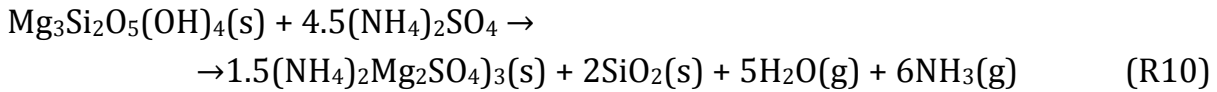


The initial Mg(OH)₂ carbonation studies showed that, at first, it proceeds quite fast, but rapidly becomes limited by the build-up of a carbonate layer on the surface of the reacting particles, thus prohibiting full carbonation of Mg(OH)₂ (Butt et al., 1996, Béarat et al., 2006, Zevenhoven et al., 2008). 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:



⁸In 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.

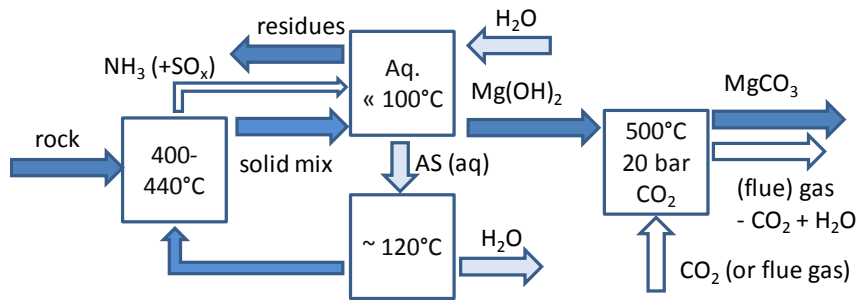


Figure 9 – Multi-staged gas/solid carbonation route developed at ÅA (taken from Geerlings and Zevenhoven (2013))

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

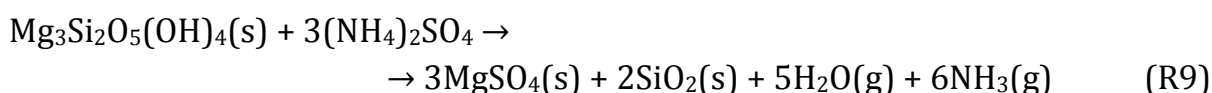
The “ÅA route” allure stands on some distinct and key benefit features:

- 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:



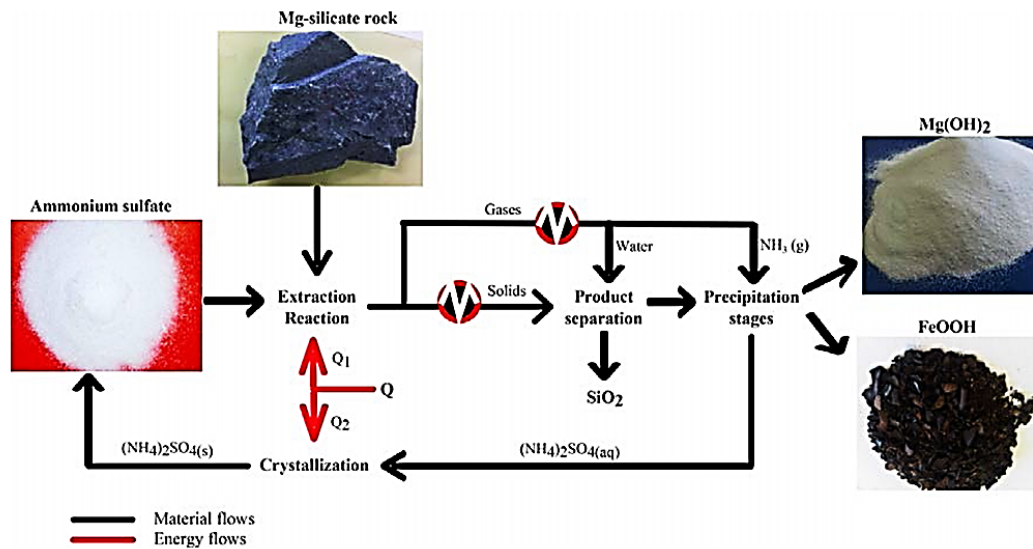


Figure 10 – Production of $\text{Mg}(\text{OH})_2$ from serpentinite – closed loop process (taken from Nduagu, 2012)

The optimal conditions for magnesium extraction from Finnish serpentinite (overburden rock from the Hitrua nickel mine) were found to be 400-440°C, 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 $Mg(OH)_2$

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 .

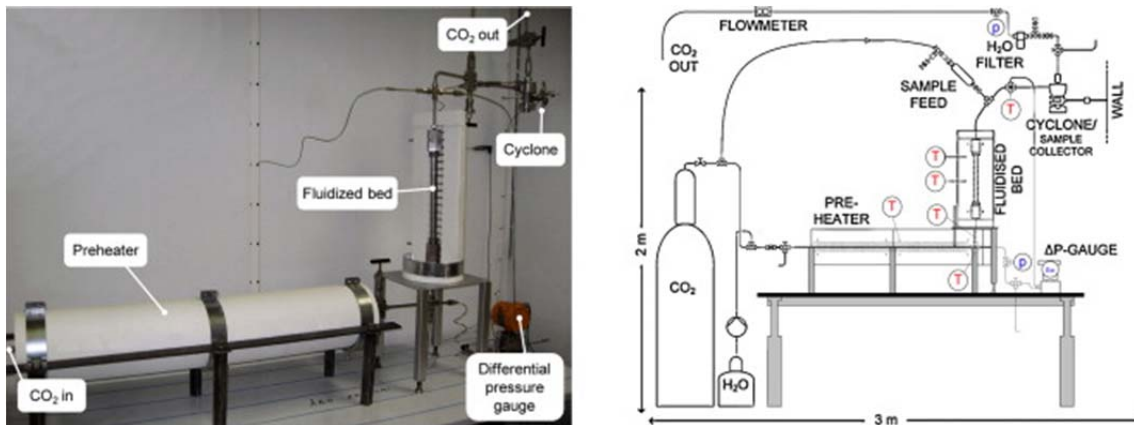
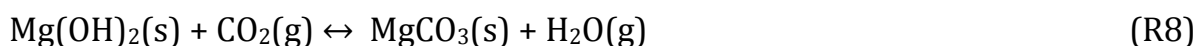
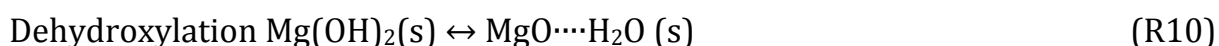


Figure 11 – A photograph and a schematic picture of the test PFB built for carbonation of $Mg(OH)_2$ at ÅA. The desired temperature of the gas is controlled by the pre-heater and the pressure by the simultaneous adjusting of the CO_2 bottle pressure (on the left) and the pressure release valve. The sample 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 $\sim 20 \text{ barCO}_2$. 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 Nduguagu (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.

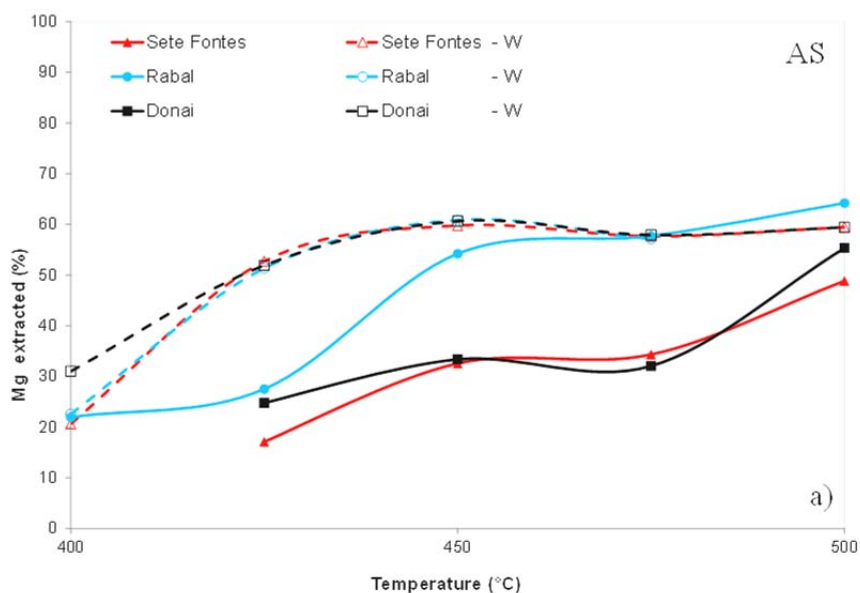
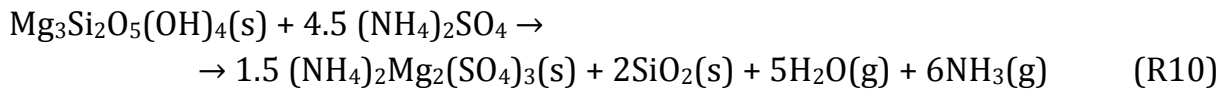


Figure 13 - Reactivity of the rock samples collected from Northeast Portugal: Sete Fontes, Donai and Rabal, with ammonium sulphate. Influence of moisture (W). Reaction time 30 minutes (Paper I).

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.

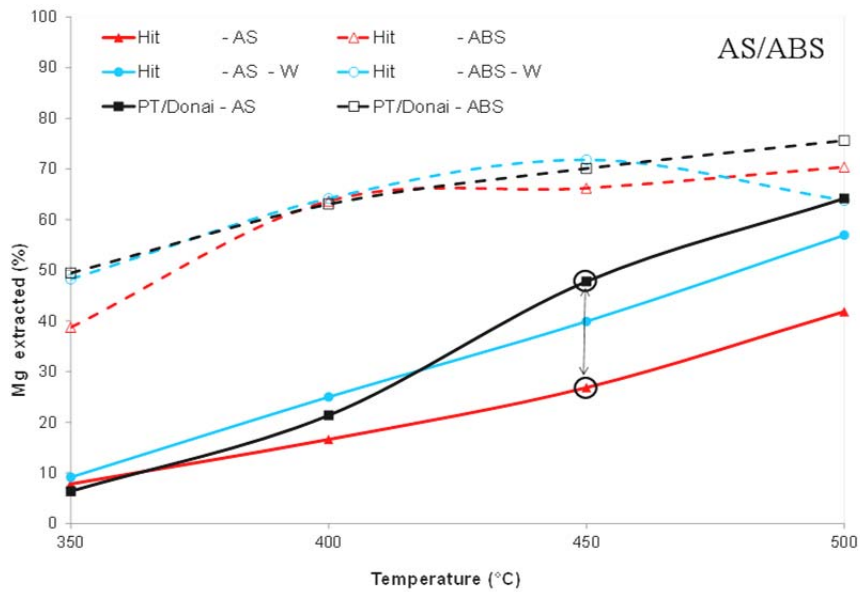


Figure 14 - Reactivity of the rock samples collected from Donai and Hitura nickel mine. Influence of moisture (W) and fluxing agent (AS – ammonium sulphate, ABS – ammonium bisulphate). Reaction time 30 minutes. (Paper I)

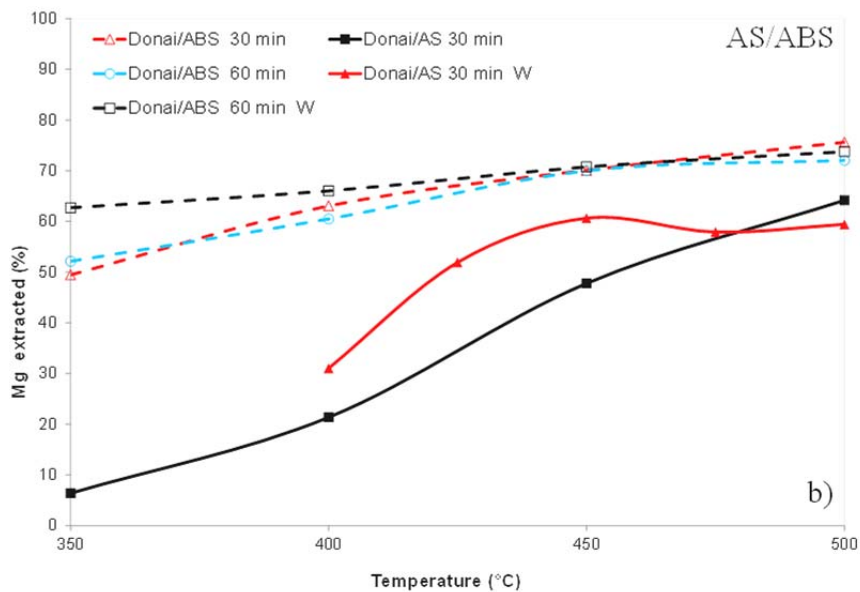


Figure 15 - Reactivity of the rock samples collected from Donai. Influence of moisture (W), fluxing agent (AS – ammonium sulphate, ABS – ammonium bisulphate) and reaction time. (Paper I).

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.

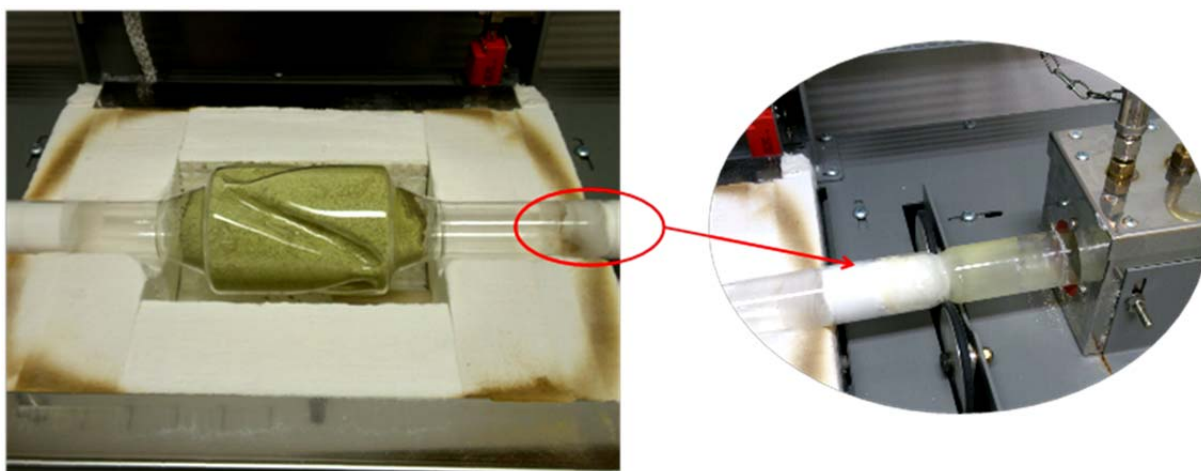


Figure 16 – Accumulation of ammonium salts in the side tubes of the glass rotary kiln reactor.

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.

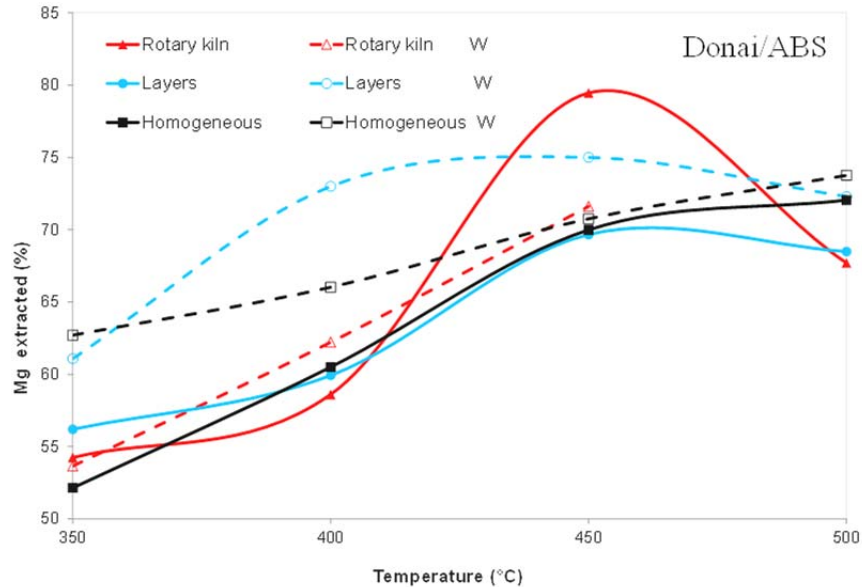


Figure 17 – Magnesium extraction results for reaction of rock material collected from Donai, with ABS, at 350°C-500°C, reaction time of 30 minutes. Influence of water (W) and reactor/mixing conditions. (Paper I).

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.

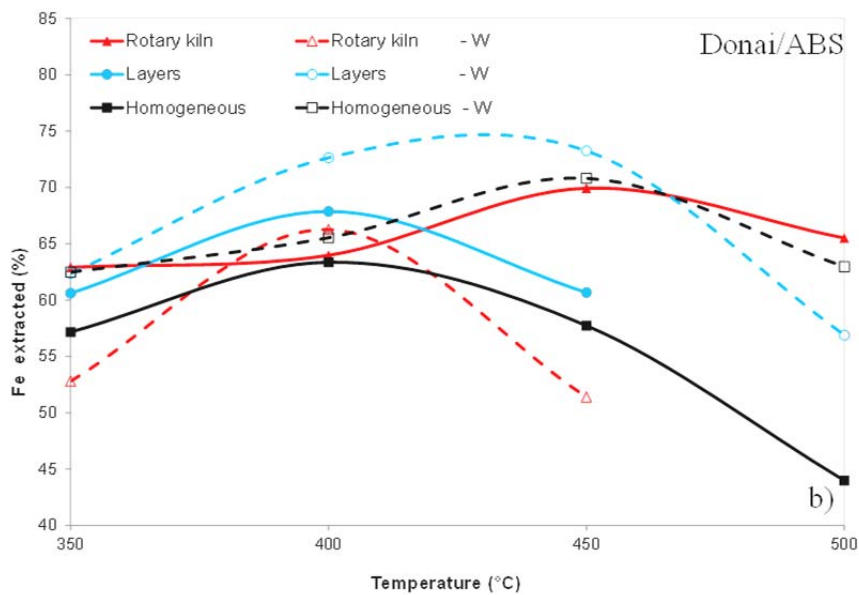


Figure 18 - Iron extraction results for reaction of rock material collected from Donai, with ABS, at 350°C-450°C, reaction time of 30 minutes. Influence of water (W) and reactor/mixing conditions. (Paper I)

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.

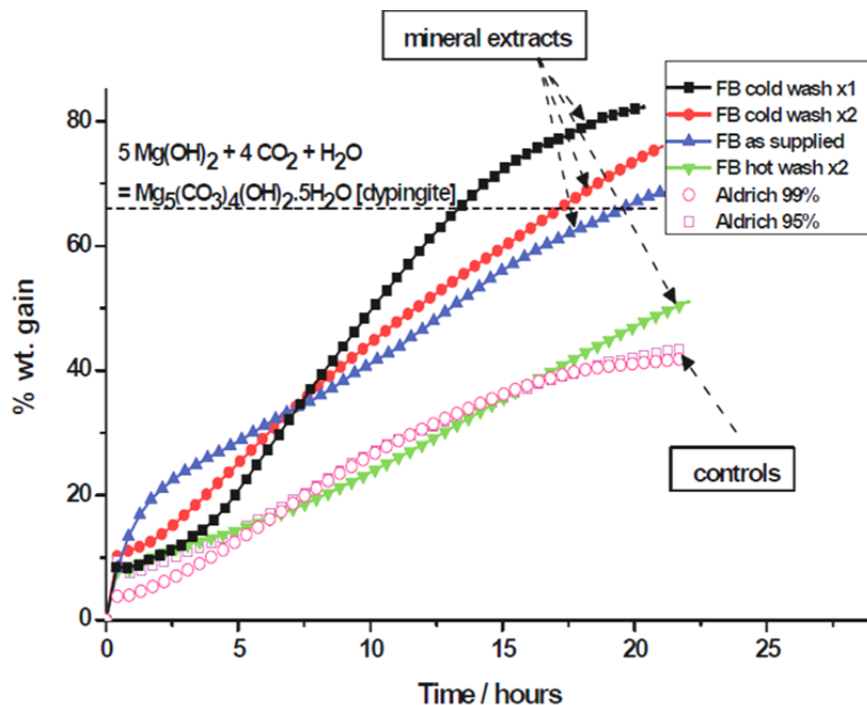


Figure 19 - Carbonation of brucite: Extracts vs. Controls at 45⁰C, 0.67 bar P_{CO2} and Relative Humidity > 90%. FB - brucite prepared at ÅA from Portuguese serpentinite. Aldrich - commercial controls. The theoretical weight gain is represented by the dashed limit at 66.6% and it is an indicator of probable 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)

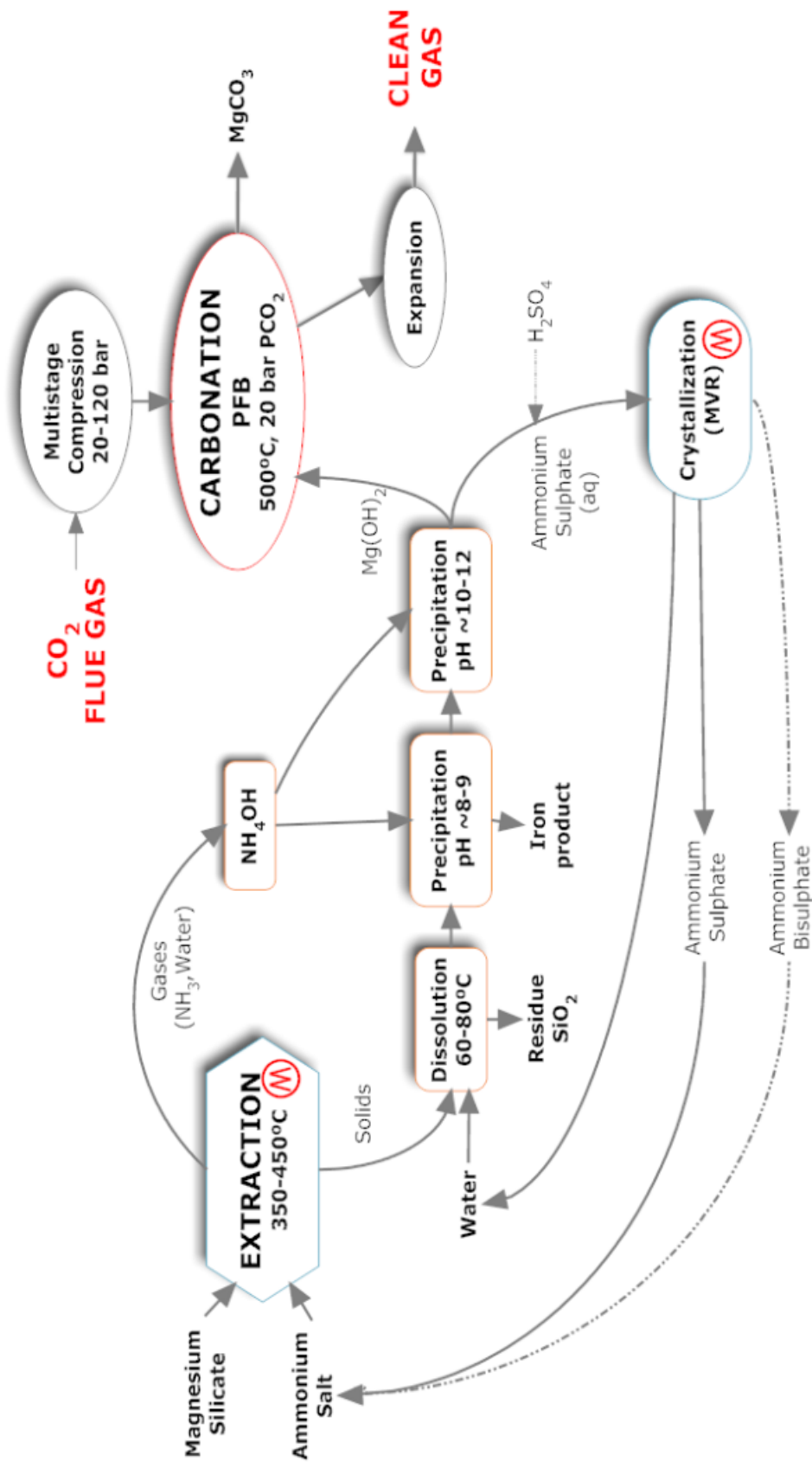


Figure 20 – General representation of the “AA route” modelled with Aspen Plus®.

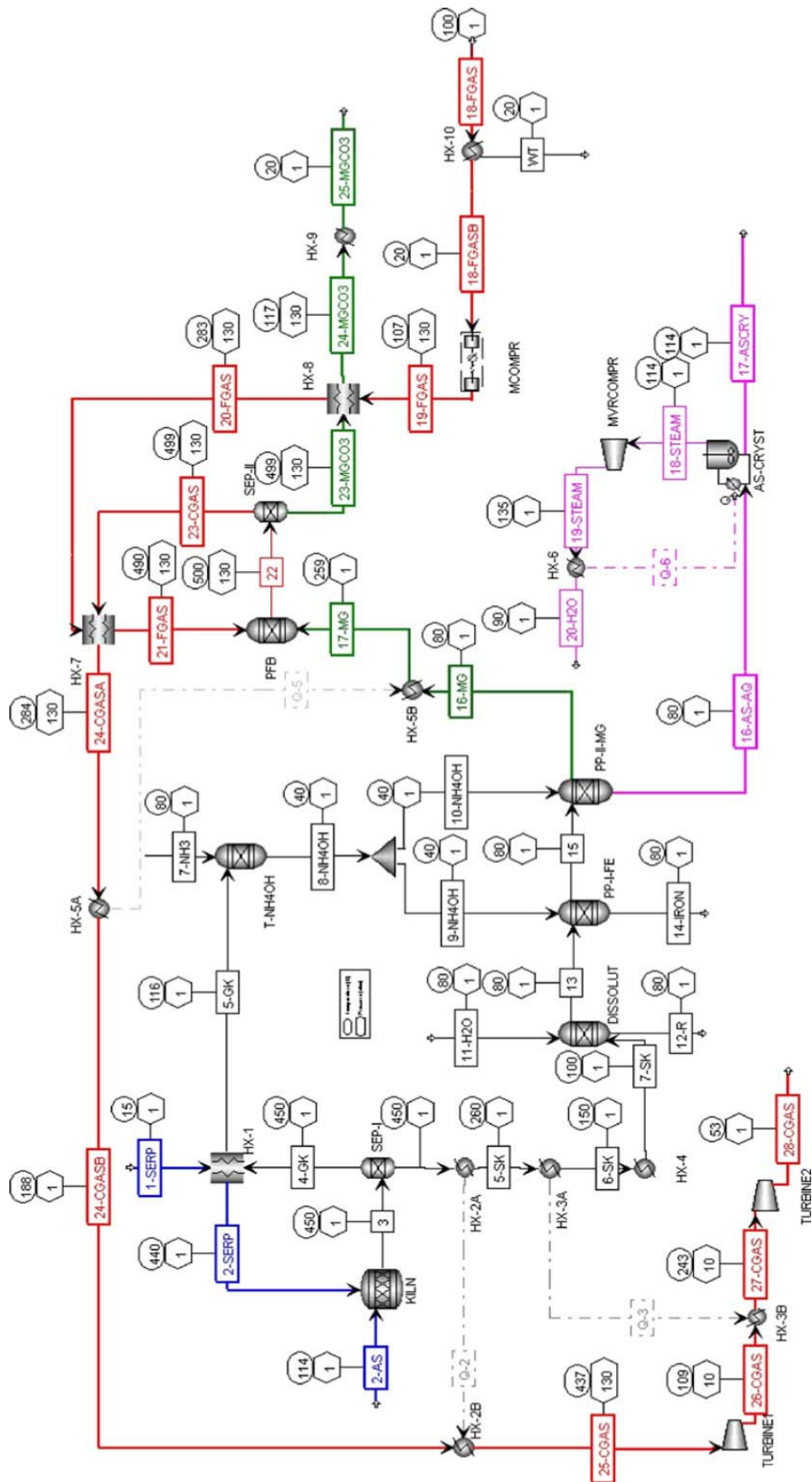


Figure 21 – Example of a model of the “ÅA route” developed in Aspen Plus®. Detailed description of the modelling procedure may be found in Papers III, IV and V.

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.

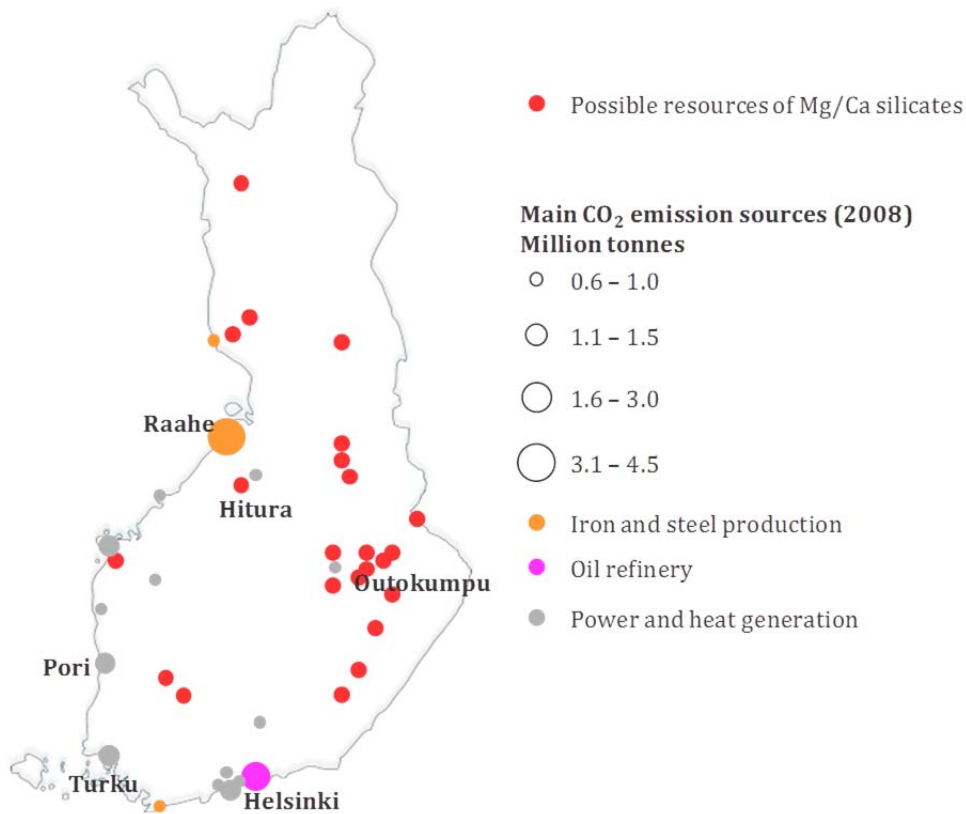


Figure 22 – Main resources of Mg/Ca Silicates in Finland and facilities emitting > 0.6 Mt CO₂/a. Distance Turku – Helsinki ~170 km. Adapted from Teir et al. (2006a, 2011).

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)

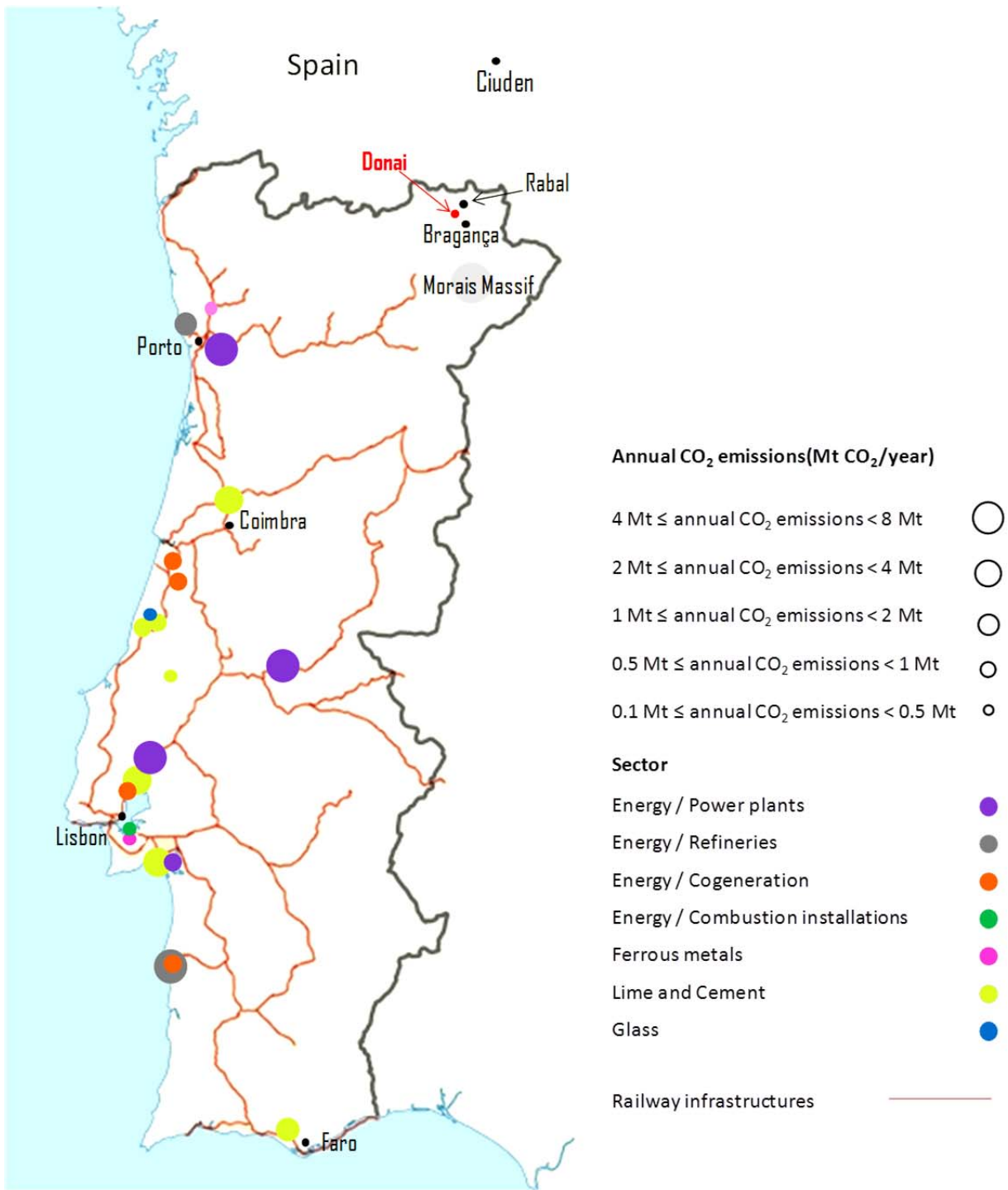


Figure 23- Map of Portugal with information on the main CO₂ sources, serpentinite reserves and railways infrastructures. Distance: Porto-Coimbra – 108 km; Porto-Bragança – 170 km.

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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PAPER I

Minerals Engineering

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CO₂ SEQUESTRATION WITH SERPENTINITE AND METAPERODOTITE FROM NORTH-EAST PORTUGAL

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Abstract The application of a staged process for CO₂ sequestration by mineralisation, studied at Åbo Akademi University (ÅÅ), to abundant minerals from North-East Portugal, is presented. Mg is extracted from magnesium silicates using recoverable ammonium salts (ammonium sulphate – AS and ammonium bisulphate – ABS), precipitated in the form of Mg(OH)₂ and subsequently carbonated at 20 bar CO₂ partial pressure. The concept of the process is promising since the Mg extraction requires heat at ~450°C while the Mg(OH)₂ carbonation produces heat at ~500°C. Samples of serpentinite and metaperidotite were collected from Bragança and their potential for CO₂ mineralisation in North-East Portugal was estimated to be 3.66 Gt of CO₂. All the samples were mineralogically and physically characterized using X-Ray diffraction and ICP-OES techniques and microscopic observation of thin sections. The samples' reactivity for Mg(OH)₂ production was tested at different temperatures (350-500°C) with AS and ABS, in different mixing conditions and both in the presence and absence of water. The produced Mg(OH)₂ was carbonated in a pressurized fluidized bed at ÅÅ. The maximum Mg extraction (using ABS) and Mg(OH)₂ carbonation levels reached were 80% and 70%, respectively.

Keywords: CO₂ Sequestration, Mineral Carbonation, Ammonium Salts, Portugal

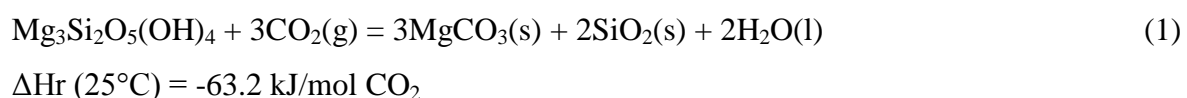
1. INTRODUCTION

Worldwide, fossil fuels provide the major source for both energy and CO₂ atmospheric emissions. Portugal is no exception. Despite the global efforts towards clean energy obtained from renewable sources, most of the energy used in Portugal comes from the burning of fossil fuels – natural gas (29%), coal (19%) and oil sources (6%) (Index Mundi, 2014) – releasing 47MtCO₂/a into the atmosphere (Eurostat, 2014). 21.5% of the energy used in Portugal comes from renewable sources; the National Energy Strategy for 2020 aims at increasing that value to 31% (Simões et al., 2011). Measures must be taken to decrease CO₂ emissions and CO₂ Capture, Utilisation and Storage (CCUS) (or CCS – CO₂ Capture and Storage) presents itself as a promising portfolio of options for lowering future

CO₂ emissions. Several technologies are being intensively studied and developed so that fossil fuels may be used also in the future, without increasing the concentration of CO₂ in the atmosphere. However, quite a few challenges remain, such as how to make the CCS/CCUS technologies more efficient and economically viable? and how to dispose of the captured CO₂ permanently or at least a thousand years?

The most widely advocated option for CO₂ storage is in geologic formations (saline formations, oil and gas reservoirs and un-mined coal areas), besides storage in the deep ocean, or as carbonated minerals. The deep ocean storage is quite risky because there is limited knowledge of how the CO₂ injection in the deep ocean would affect the ocean's acidity and ecosystems. Geologic formations would have to fulfil selection, safety and post-storage monitoring criteria. Besides this, there's always the risk of CO₂ leakage into the atmosphere making the effort invested on capturing the CO₂ wasted (IPCC, 2005). According to Carneiro et al., (2011), Portugal has no exploited hydrocarbon fields thus its geological storage options are limited to deep saline formations in sedimentary basins. In that study it was concluded that only the Porto basin might be suitable for CO₂ underground storage. In another recent study Machado et al., (2011) estimated a storage capacity of 42 Mt of CO₂ in the Setúbal Península. Nonetheless, both authors concluded that the necessary geological conditions for a safe CO₂ storage are hindered (amongst others) by the relatively high earthquake risk. Although Portugal is not a country with high seismic activity, indeed there is still some vulnerability, especially in centre and southern parts of the country. One cannot forget the earthquake that occurred in 1755 that caused a massive destruction of Lisbon, the 7.3 magnitude earthquake in 1969 with epicentre in Gorrige Ridge, SW Cabo de S. Vicente, or the recent, 2011, 5.3 magnitude earthquake that occurred in Lorca, South-Eastern Spain.

Mineral carbonation overcomes these setbacks as CO₂ is sequestered in the form of carbonates, benign and stable on geological timeframes (Teir et al., 2006). At Åbo Akademi University (ÅA) in Finland, a staged process for CO₂ sequestration by mineralisation, using magnesium silicates (mainly serpentinite), has been investigated since 2006. The process' concept, shown in Figure 1, is encouraging since the overall carbonation reaction is exothermic:



Unfortunately, the direct carbonation of Mg bearing silicate materials suffers from slow kinetics (with hours as the typical time scale) and low levels of conversion (Lackner et al., 1997), thus the need for a faster, stepwise approach such as the ÅA process. This involves three steps: 1) the extraction of Mg with recoverable ammonium salts which requires heat at 400 ~ 450°C (Nduagu, 2012), 2) removal of impurities and production of Mg(OH)₂ and 3) the carbonation of Mg(OH)₂. The carbonation step produces heat at ~500°C, corresponding to ~1/3 of the heat needed (at 400~450°C) for the extraction (Fagerlund et al., 2009, 2010, Fagerlund and Zevenhoven, 2011, Fagerlund, 2012)

The reaction of serpentinite (Finnish and Lithuanian) with ammonium sulphate was well studied by (Nduagu, 2012) who focussed on finding optimal reaction conditions: temperature (400°C - 450°C, time (30min - 60min), rock/AS ratio (2/3 kg/kg) and particle size (< 250µm). The present work aims at assessing the influence of the extracting agents ammonium sulphate (AS) versus ammonium bisulphate (ABS), temperature, water, crucible material (aluminium versus ceramic) and type of reactor/mixing on the reaction rate, using serpentinite rock collected from Bragança in North-East Portugal.

A detailed scheme of what is often referred to as the (conventional) “ÅA route” is presented in Figure 1. First the serpentinite rock material reacts with the ammonium salts at 350-500°C. Table 1 presents the process’ chemical reactions and thermodynamics for both ammonium sulphate (AS), (NH₄)₂SO₄, and ammonium bisulphate (ABS), NH₄HSO₄, salts used for Mg extraction.

Reactions involving the extraction of Mg and Fe, reactions (2),(3),(8) and (9), and concerning the ammonium salts decomposition, reactions (6) and (12), are the most important ones for this stage. The (solid) products, mainly MgSO₄ and FeSO₄ are readily soluble in water (step 2) while the unreacted material (residue) is insoluble, thus can be separated by filtration and discarded. In steps 3) and 4) the pH is raised using the ammonia released as vapour in step 1) to precipitate iron and magnesium in the form of hydroxides: Fe(OH)₂ or FeOOH is obtained at pH of 8~9, whereas Mg(OH)₂ is obtained at pH=11-13 and separated from the remaining ammonium sulphate solution, once more, by filtration. This is followed by the carbonation of the Mg(OH)₂ product (step 5) in a pressurized fluidized bed (PFB) at ~500°C and 20-30 bar CO₂ pressure. In step 6) the ammonium sulphate is recovered by crystallization.

Table 1 – Chemical reactions and thermodynamics. Estimated with HSC Chemistry for windows, version 5.11 (2002)

Reaction		ΔHr (25°C)	ΔHr (450°C)
		kJ/mol CO₂	
1	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2(\text{g}) = 3\text{MgCO}_3(\text{s}) + 2\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	-63.2	
		kJ/mol AS kJ/mol AS	
2	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3(\text{NH}_4)_2\text{SO}_4 = 3\text{MgSO}_4 + 2\text{SiO}_2 + 6\text{NH}_3(\text{g}) + 5\text{H}_2\text{O}(\text{g})$	244.3	216.9
3	$2\text{Fe}_3\text{O}_4 + 10(\text{NH}_4)_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + 20\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g})$	266.2	240.8
4	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3(\text{NH}_4)_2\text{SO}_4 = \text{Al}_2(\text{SO}_4)_3 + 2\text{SiO}_2 + 6\text{NH}_3(\text{g}) + 5\text{H}_2\text{O}(\text{g})$	298.8	274.9
5	$\text{CaSiO}_2(\text{s}) + (\text{NH}_4)_2\text{SO}_4(\text{s}) = \text{CaSO}_4(\text{s}) + \text{SiO}_2(\text{s}) + \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$		
6	$(\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_3(\text{g})$	451.4	424.5
7	$(\text{NH}_4)_2\text{SO}_4 = \text{NH}_4\text{HSO}_4 + \text{NH}_3(\text{g})$	110.5	114.9
		kJ/mol ABS kJ/mol ABS	
8	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{NH}_4\text{HSO}_4 = 3\text{MgSO}_4 + 2\text{SiO}_2 + 3\text{NH}_3(\text{g}) + 5\text{H}_2\text{O}(\text{g})$	188.3	159.9
9	$2\text{Fe}_3\text{O}_4 + 10\text{NH}_4\text{HSO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + 10\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g})$	155.7	125.8
10	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{NH}_4\text{HSO}_4(\text{s}) = \text{Al}_2(\text{SO}_4)_3 + 2\text{SiO}_2 + 3\text{NH}_3(\text{g}) + 5\text{H}_2\text{O}(\text{g})$	25.0	16.1
11	$\text{CaSiO}_2(\text{s}) + \text{NH}_4\text{HSO}_4(\text{s}) = \text{CaSO}_4(\text{s}) + \text{SiO}_2(\text{s}) + \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$		
12	$\text{NH}_4\text{HSO}_4 = \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_3(\text{g})$	340.8	309.5
		ΔHr (500°C)	
		kJ/mol	
13	$\text{Mg}(\text{OH})_2(\text{s}) + \text{CO}_2(\text{g}) = \text{MgCO}_3(\text{s}) + \text{H}_2\text{O}(\text{g})$		-59.3

Besides its potential for an energy neutral storage process (with suitable heat integration) another interesting feature of the ÅA process is the possibility of replacing the pure stream of CO₂ used in step 5) by a flue gas, or other CO₂ containing gas in general. This eliminates the need for the relatively expensive CO₂ capture step (Slotte et al., 2013), which is less attractive for oxygen-containing gases if nitrogen-based solvents are used. Also, the process gives substantial amounts of by-products like FeOOH or Fe(OH)₂, and the residue with a high content of Si makes the integration of mineral carbonation with other industries an opportunity for reducing the net CO₂ emissions and substituting raw materials input. This is in line with the current “shift” from CCS to CCUS, where costs must be covered by a product that is obtained, such as oil or gas from EOR/EGR (enhanced oil or gas recovery) using CO₂, or a carbonate material with market value.

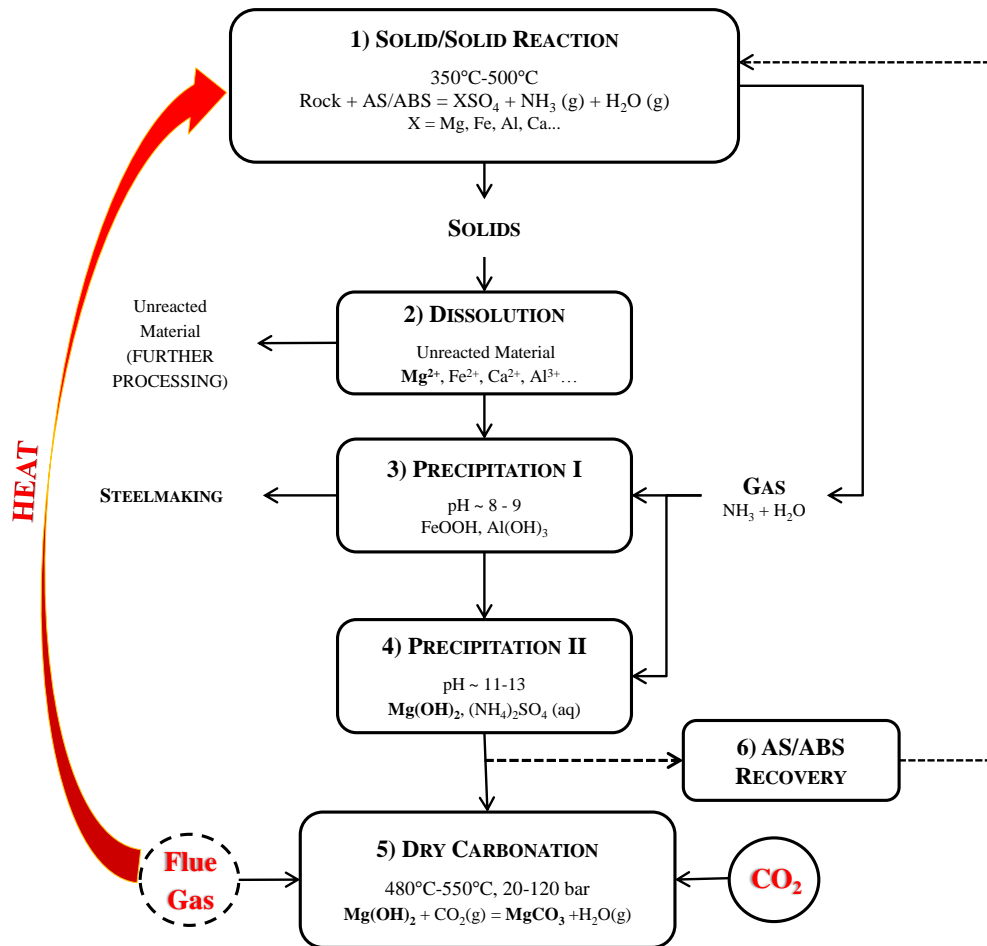


Figure 1- Scheme of the conventional “AA” carbonation process for serpentinite carbonation

2. MAGNESIUM SILICATE MINERALS IN NORTH-EAST PORTUGAL

2.1 Geology and Setting

Ultrabasic rocks, such as metaperidotites and serpentinites, are excellent candidates for mineral sequestration of CO₂ by magnesite formation (Goff and Lackner, 1998). In the North-East of Portugal, ultrabasic rocks suitable (i.e., rich in magnesium silicates and with appropriate volume) for mineral sequestration of CO₂ occur in the ophiolites of Bragança and Morais (Figure 2). They are mainly metaperidotites, with a high degree of serpentinization. Most of these rocks represent the base of the Bragança and Morais ophiolites (slivers of oceanic lithosphere that became incorporated into the continental crust during the Variscan/Hercynian collision).

For this study, samples were collected from three areas, Donai, Sete Fontes and Rabal, respectively, all near Bragança. Those from Donai and Sete Fontes are massive

serpentinites, but the metaperidotite from Rabal has an anisotropic fabric only observed with a polarizing microscope.

Apart from storage of CO₂ from Portuguese sources, storage of CO₂ separated at the CIUDEN Oxyfuel combustion plant near Ponferrada, North-West Spain, at 135 km from Bragança, currently a demonstration unit which produces ~1Mt CO₂/year, may be an interesting source-sink combination for large-scale CCUS/CCS (Lupion et al., 2013).

The reserves of the geological formations, from where the samples have been taken, were estimated using published geological maps, internal reports and assuming a specific weight of 2670 kg/m³. They are estimated at a total of 3.66 Gt of rock assuming a conservative (yet easily mineable) 50 m of thickness for the geological formation. Detailed results are presented in Table 2. (The table also gives capacity values for 80% Mg extraction from the rock followed by 70% carbonation of this Mg, as was achieved in the laboratory)

The ultrabasic rocks of Bragança ophiolite occur as an elongate WNW-ESE belt (Pereira and Ribeiro, 1999, Pereira, 2000), of circa 18 × 0.4 km, but dismembered in several lenses by shear zones and faults. The samples “Donai” and “Sete Fontes” are from this belt. In this region ultrabasic (metaperidotites, metapyroxenites) rocks, with variable degree of serpentinization, also occur associated with mafic granulites of presumably Proterozoic-Cambrian age. They occur as small WNW-ESE elongated lens (the biggest is ~0.6 km²) and also as one 20 km² intrusion cut by several faults (Pereira and Ribeiro, 1999, Pereira, 2000). The sample “Metaperidotite” is from one small lens.

Metaperidotites with variable degrees of serpentinization also occur in the Morais ophiolites (see Figure 2). They form two separated ellipsoidal masses with estimated areas of 26.3 km² and 10.2 km², respectively, besides several smaller lenses, the biggest being 0.73 km² (IGM, 1998, IGM, 2003). All the areas were estimated using the polygons method.

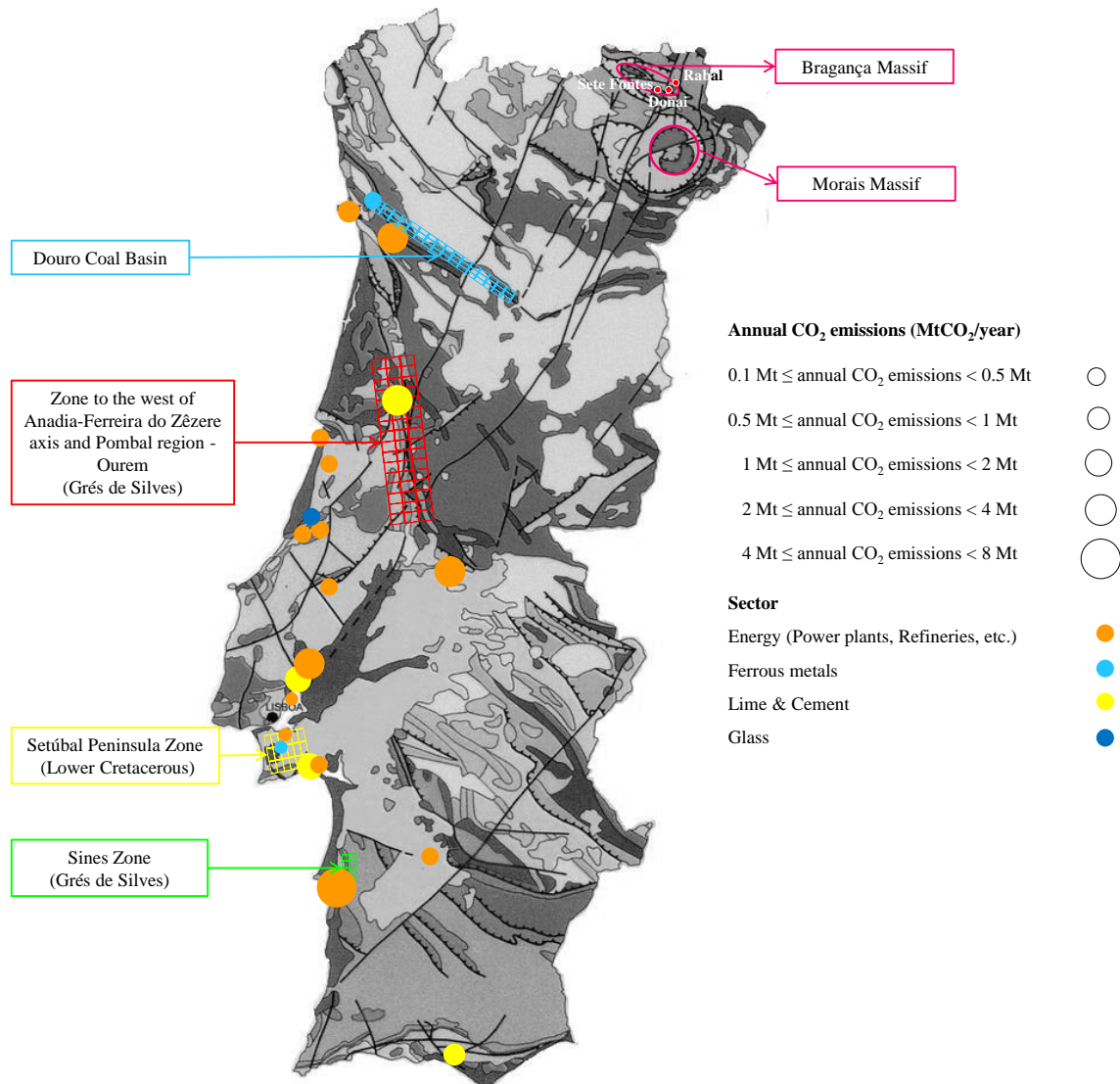


Figure 2 – Information of potential geological sinks in Portugal, main sources of CO₂ emissions and identification of silicate magnesium resources in Mainland Portugal adapted from (Gomes, 2008)

Table 2 – Geological reserves estimation and CO₂ capture potential.

	Mg (%)	Geological Reserves (Gt)	Mg Extraction (%)	Mg(OH) ₂ Carbonation (%)	CO ₂ capture potential (Mt)
Donai & Sete Fontes	22.69 ^c	0.96	100	100	395
			80	70	223
Rabal	23.08	2.67	100	100	1130
			80	70	632
Morais Massif	20.62 ^d	5.00	100	100	1890
			80	70	1050

^c Average of values presented in table 3.

^d Pacheco et al., 2002

3. MATERIALS AND METHODS

3.1 Mineralogical and physical characterization of the samples

All samples, weighing 2 kg each, were crushed with a jaw crusher, followed by grinding in a ball mill to obtain a size distribution of 75-125 μm . The rocks' composition and their structural analysis were determined using inductively coupled plasma - optical emission spectrometry (ICP-OES) and X-Ray diffraction (XRD) techniques, respectively. The mineralogical identifications carried out by XRD, were performed using a Philips PW 3710 X-ray diffractometer, with a Cu tube, at 40 kV and 20 nA and using the APD 3.6J software for mineralogical identification. For the ICP-OES analyses dried rock powder (~100 mg) was fused with a flux of lithium metaborate + tetraborate (500 mg), in a platinum crucible, at 950 °C, for one hour, using a muffle furnace. After cooling, the crucible with the fusion mixture was placed inside a beaker, added 4 ml of AnalaR nitric acid and 75 ml of warm Milli-Q water. The solution was stirred and kept warm in a magnetic stirrer until the solid was fully dissolved. The solution was transferred into a volumetric flask of 100 ml. A reagent blank was prepared the same way. The XRD results were complemented with the observation of thin sections using a Nikon polarizing microscope coupled with a Nikon digital camera.

3.2 Magnesium extraction – production of $\text{Mg}(\text{OH})_2$

The samples reactivity for magnesium extraction is dependent on several parameters: temperature, rock / (AS or ABS) mass ratio, reaction time, particle size, pressure, and presence of added water and aluminium, respectively (Nduagu, 2012, Romão et al., 2010). In a first set of experiments, the three rock samples collected from Portugal were studied towards their reactivity with AS both in the presence and absence of water. The samples were mixed with solid AS using a mass ratio of 2:3 of rock/AS (7g rock sample + 10.5g AS) in a reaction container (ceramic pot) and placed in an oven at different operating temperatures (400°C, 425°C, 450°C, 475°C, 500°C) for 25 minutes at atmospheric pressure. In half of the experiments, water was added using the mass ratio 1:2:3 of water/rock/AS (3.5 ml water + 7g sample + 10.5g AS) resulting in a slurry-like mixture of AS and rock powder. The sintered solid product was dissolved in 250 ml of distilled water at room temperature. The insoluble (unreacted) material was separated from the liquid solution by vacuum filtration. This liquid was then analysed by ICP-OES to determine the extent of elements (Mg, Fe, Al...) extracted.

The sample from Donai was further studied regarding the influence of the following parameters in the rocks' reactivity:

- 1) Type of reactor/mixture: two types of reactor were used, ceramic crucibles placed in a rectangular oven and a small scale rotary kiln (Carbolite HTR11 /75) shown in Figure 3. The solid reactants were either evenly mixed in the ceramic crucibles or distributed in layers (~ten) the first layer being ammonium salt and the last one (the top layer) the rock. In the rotary kiln the reactants were continuously mixed.
- 2) Temperature: the experiments were done at 350°C, 400°C, 450°C and 500°C. Both furnaces were pre-heated to the required temperature.
- 3) AS vs ABS as extracting agents: both mass ratios of rock/AS (2:3½) and rock/ABS (2:3) were kept constant. These ratio differences assure that the reaction occurs in the presence of an equal amount of sulphur.
- 4) Water presence: just before the reactors were placed inside the ovens, water was added to the solids to a mass ratio of ½:2:3 of water/rock/ABS.
- 5) Aluminium presence: the crucibles' inner surface was covered in aluminium foil. A similar amount of aluminium foil was added to the glass kiln reactor as small pieces.

After 1 hr of reaction time, the (sometimes sintered) solid products were dissolved in water at room temperature. The solid/unreacted fraction was separated by vacuum filtration. The solution's pH was raised to 8.5~9 by adding ammonia solution (NH₄OH, 28% v/v, Sigma-Aldrich) to precipitate a green product, mainly iron in the form of (oxy-) hydroxides. After filtration, a second precipitation at pH 12~13 allows for the recovery of the Mg in the form of Mg(OH)₂.

3.3 Mg(OH)₂ carbonation

The brucite produced was alternately dried and washed. The solid was sieved to obtain two particle size fractions: < 74µm and 74-250 µm.

The carbonation tests were performed with pure and dry CO₂ at ~20 bar and 485-515°C in the experimental pressurised fluidised bed (PFB) setup built and described by (Fagerlund and Zevenhoven, 2011) and that is presented in Figure 4. (Pressurisation is needed to be able to produce stable MgCO₃ at temperatures where the gas-solid conversion rate is high enough.)

The specific surface area (BET – Brunauer, Emmett and Teller analysis) of the produced brucite was measured by nitrogen adsorption. The carbonation degree was determined

using the experimental method improved by (Fagerlund et al., 2010) which is based on the reaction between a carbonated material and an aqueous solution of HCl, releasing CO₂.

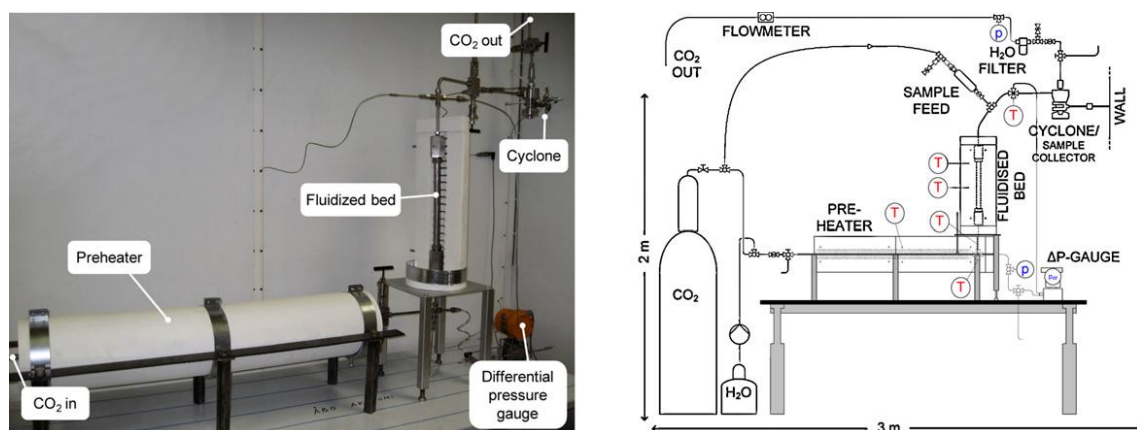


Figure 3 - A photograph and a schematic picture of the test set-up built for carbonation of Mg(OH)₂ at elevated temperatures and pressures. (Fagerlund and Zevenhoven, 2011).

4. RESULTS

4.1 Mineralogical and physical characterization of the samples

The chemical and structural compositions of the three samples considered in this work are presented in Tables 2 and 3. Figure 4 gives microphotographs of the studied samples.

Table 3 -Elemental analysis of the Portuguese rock samples (ICP-OES)

Elemental Analysis (%-wt)	Al	Ca	Cr	Fe	Mg	Si
Serpentinite (Donai)	0.84	0.18	0.27	5.10	22.15	19.94
Serpentinite (Sete Fontes)	1.02	0.09	0.23	5.71	23.22	19.51
Metaperidotite (Rabal)	0.74	0.18	0.27	6.26	23.08	17.31

Table 4 - Structural analysis (XRD + Polarizing Microscope) of the Portuguese rock samples

Serpentinite (Donai)	Antigorite, talc, lizardite, chrysotile, olivine, carbonates, iron oxides, bastites, tremolite
Serpentinite (Sete Fontes)	Antigorite, talc, lizardite, chlorite, iron oxides, chromite
Metaperidotite (Rabal)	Chlorite, lizardite, magnetite, talc, antigorite, iron oxides

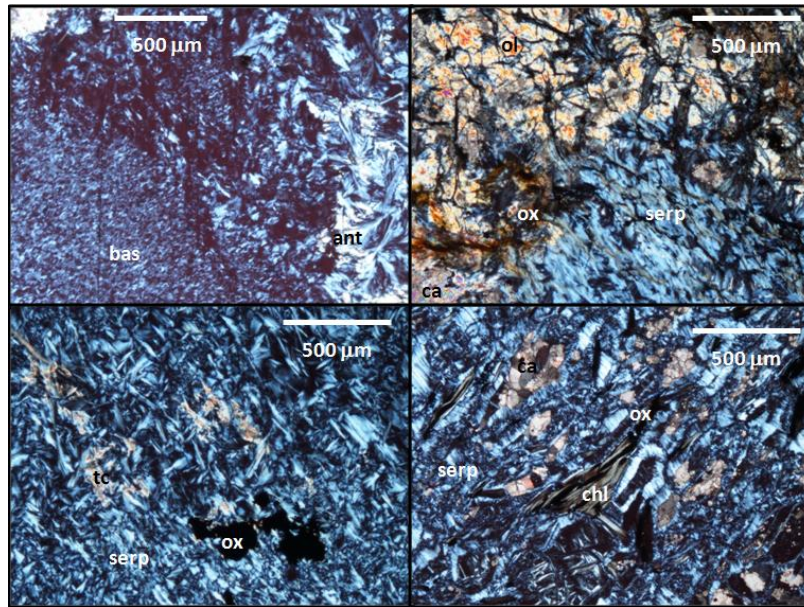


Figure 4 – Microphotographs of the studied samples: Donai (a,b); Sete Fontes (c); Metaperidotite (d). All microphotographs in XPL. Antigorite (ant); bastite (bas); olivine (ol); serpentine (serp); carbonate (ca); oxides (ox); talc (tc) and chlorite (chl).

4.2 Production of $Mg(OH)_2$

4.2.1 Magnesium extraction

The magnesium extraction results for the first set of experiments (a total of twenty-eight) with the three different rock samples collected from North-East Portugal are shown in Figure 5.

The magnesium extraction results for tests with Donai rock (a total of forty-eight) using either AS or ABS salt, some with added water, are given in Figure 6.

The magnesium extraction results for tests with Donai rock (a total of thirty six) using ABS salt, using a) a rotary tube, b) a pre-mixed sample or c) a layered sample, respectively, are given in Figure 7. Also the effect of added Al foil (Al) or water (W) is shown.

4.2.2 Magnesium and aluminium co-extraction

The magnesium and aluminium co-extraction results for tests with Donai rock (a total of thirty six) using ABS salt, using a) a rotary tube, b) a pre-mixed sample or c) a layered sample, respectively, are given in Figure 8. Also the effect of added Al foil (Al) or water (W) is shown.

4.2.3 Iron extraction

The iron extraction results for tests with Donai rock (a total of thirty six) using ABS salt, using a) a rotary tube, b) a pre-mixed sample or c) a layered sample, respectively, are given in Figure 9. Also the effect of added Al foil (Al) or water (W) is shown.

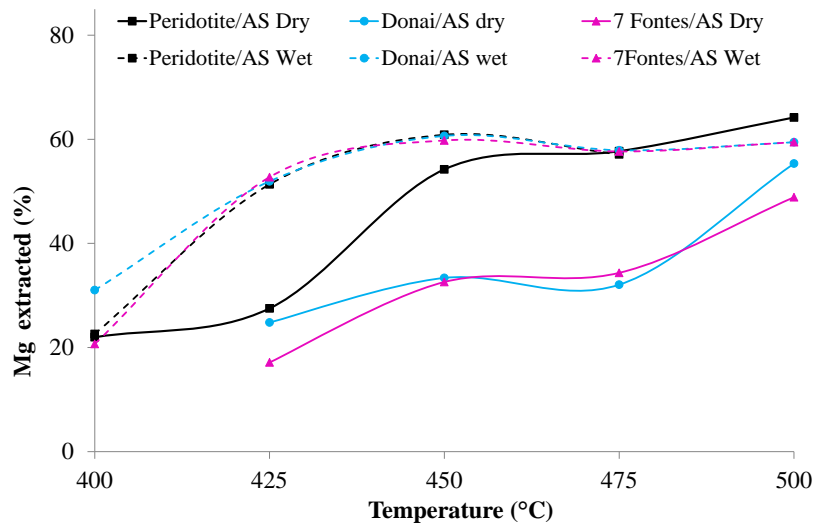


Figure 5 – Reactivity of the three rock samples collected from Portugal: Donai, Sete Fontes and Peridotite. Homogeneous mixture in porcelain crucibles placed in the rectangular oven.

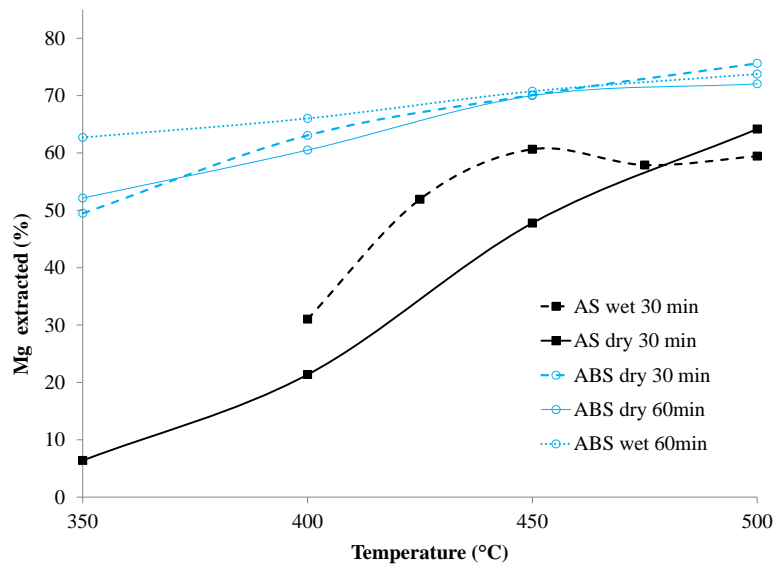


Figure 6 – Magnesium extraction for reaction of Donai sample with ammonium sulphate and bisulphate in dry and wet conditions. Homogeneous mixture in a ceramic pot placed in the rectangular oven.

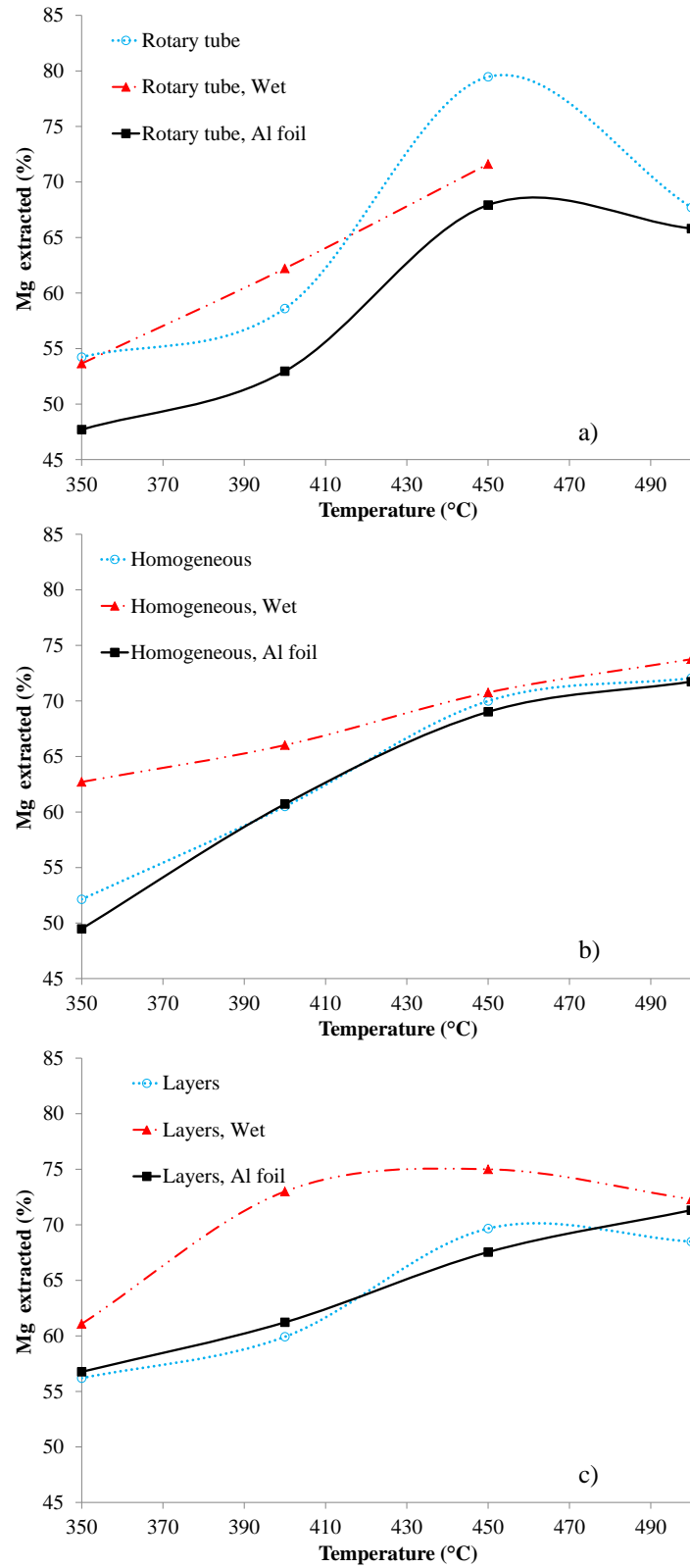


Figure 7 – Mg extraction results for the reaction of Donai's rock with ABS at 350-450°C. Influence of water and aluminium foil (Al foil) and reactors/mixing conditions: a) rotary tube reactor, b) homogeneous mixture, c) layers.

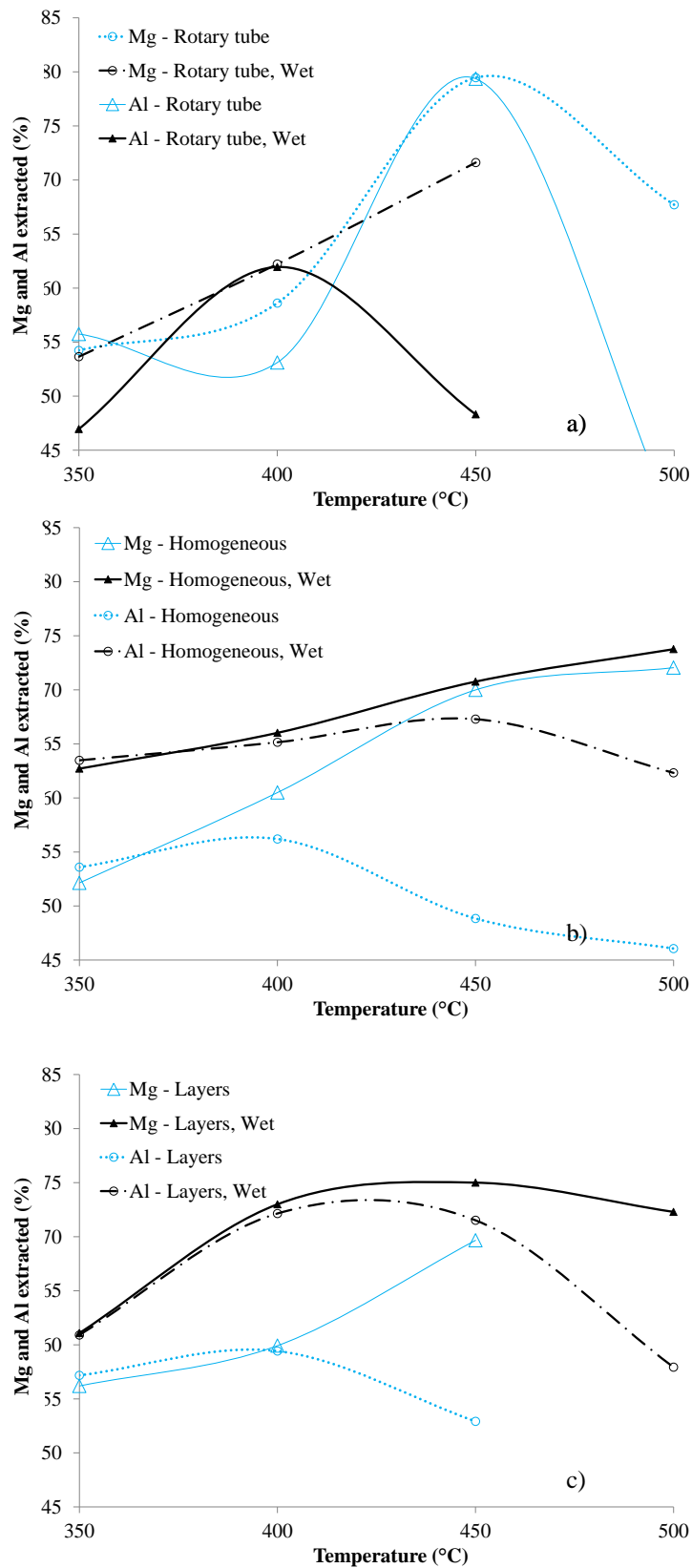


Figure 8 – Mg and Al extraction evolution with temperature for the reaction of Donai's rock with ABS at 350-450°C. Influence of water and aluminium foil (Al foil) and reactors/mixing conditions: a) rotary tube reactor, b) homogeneous mixture, c) layers.

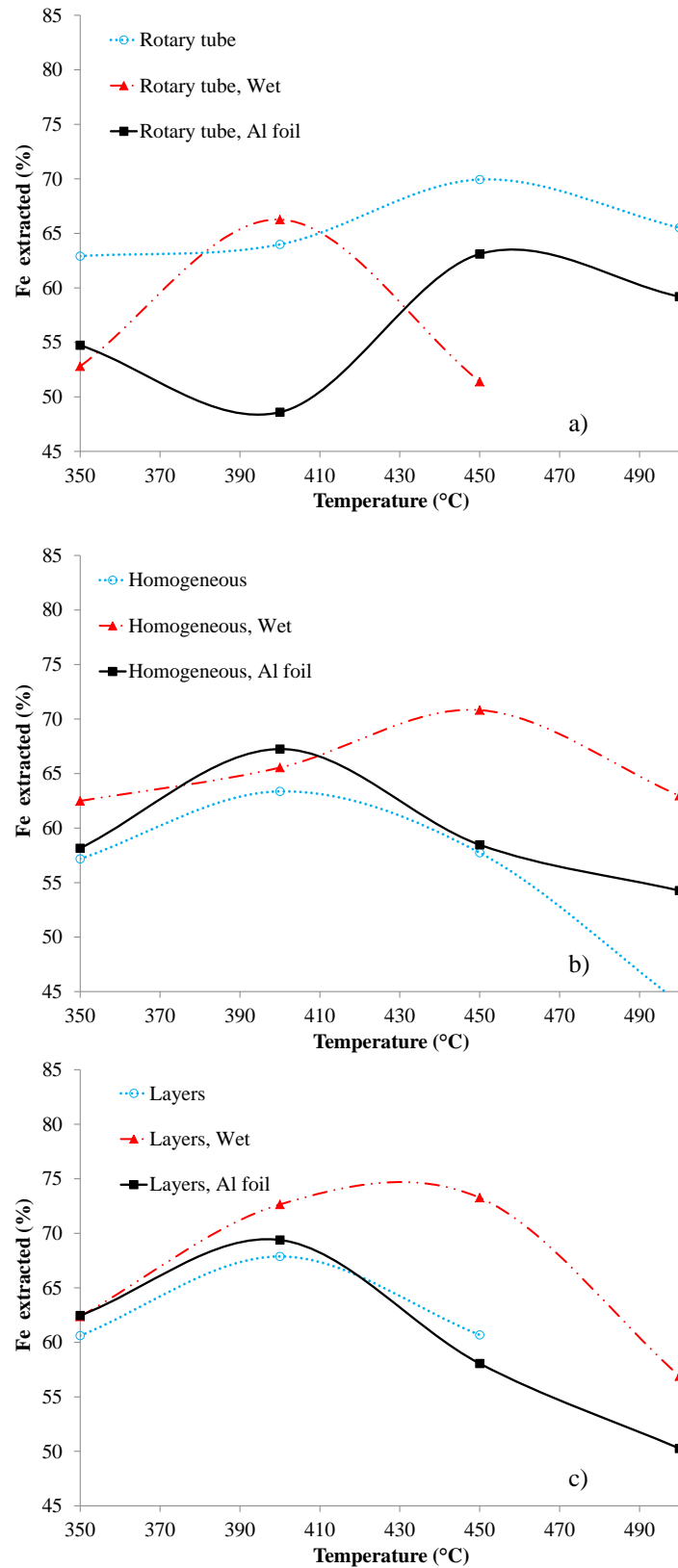


Figure 9 – Fe extraction results for the reaction of Donai's rock with ABS at 350-450°C. Influence of water and aluminium foil (Al foil) and reactors/mixing conditions: a) rotary tube reactor, b) homogeneous mixture, c) layers.

5. DISCUSSION

5.1 Mineralogical and physical characterization of the samples

The sample Donai is from a quarry which has been mined for ornamental stone. It is a very heterogeneous rock with dark green colour and contains light veins of carbonates and brownish spots of oxides. It is mostly constituted by serpentine (antigorite, chrysotile and lizardite), serpentinitised olivines, which are relicts from the precursor igneous rock, carbonates and iron oxides (Figure 4a, b). It also contains small amounts (< 10%) of talc and tremolite. Carbonates can be abundant, forming veins which cross the serpentinite. The sample Sete Fontes, taken in a road side-ramp, is a serpentinite with a massif fabric and a very dark green colour. The rock is formed by ~ 90% serpentine (antigorite and lizardite), but it also contains talc (5%), iron oxides, chromite and chlorite (Figure 4c). The sample Metaperidotite, taken in a new road side-ramp, is black, strongly serpentinitized and has an anisotropic fabric only expressed in thin section. It contains ~75% of serpentine (antigorite, lizardite), iron oxides, chlorite, magnetite, talc and carbonates (Figure 4d).

5.2 Production of $Mg(OH)_2$

5.2.1 Effect of extracting agent (AS vs ABS) and water presence

The rocks have similar chemical compositions yet, in the absence of water, metaperidotite from Rabal appears to be more reactive. Both temperature and water (“wet” reactions) affect the samples reactivity. In the presence of water all three samples present a similar behaviour and at 450°C the magnesium extraction for both Donai and Sete Fontes samples nearly doubles. These observations are probably due to: 1) Water dissolves part of the AS enhancing the contact between the rock material and AS thus improving the mass transfer; 2) The presence of water vapour appears to restrict the volatilization rate of the ammonium salts, thus the loss of reactants by sublimation/ degradation during extraction, granting thus a far longer contact time between flux and mineral (Nduagu et al., 2014). Furthermore, experiments via dry AS at higher temperatures resulted in a sintered solid product that is very compact, hard and it sticks onto the reactor’s walls. Thus, its removal from the crucible and its dissolution are rather challenging. In contrast, the solid product formed via wet AS is fluffy and very porous easily dissolved and taken from the ceramic crucible with small quantities of water. As a remark, an inefficient dissolution may compromise the

process as this step is essential for recovering the Mg extracted from the rock and it will directly influence the recovery and recycling of ammonium salts.

As shown in Figure 5, between 450°C and 475°C, temperature does not have a significant impact on the extraction efficiency. The maximum extraction for the dry reaction was observed at 500°C whereas for the wet reaction the maximum yield occurs at 450°C. Although the dry reaction at 500°C allows for better extraction, at this temperature the AS losses (due to its decomposition) are unfavourable for industrial application. According to Highfield et al. (2012) the high temperatures (>400°C) necessary for good kinetics of Mg extraction lead to irreversible decomposition and loss of AS (this can be identified by presence of SO_x in the product vapours from the reaction). Highfield et al. (2012) suggest the investigation of low temperature methods such as aqueous solutions of ammonium bisulphate. This has already been studied and reported by Wang et al. (2013) who achieved 80 % Mg extraction from serpentine (and 96% carbonation in a downstream aqueous reactor) but at the cost of a considerable energy penalty for ABS regeneration due to the use of much water.

The above constraints of AS's reaction with serpentinite motivated the study of the solid/solid reaction of ABS with serpentinites.

As shown in Figure 6, the second set of experiments (a total of forty-eight) with Donai's rock and both AS and ABS allowed for a better understanding on the optimal reaction conditions and fluxing agent. It is seen that ABS in all tests extracts more Mg than AS. In fact, at lower temperatures (350°C) the difference between AS and ABS is very significant: AS extracts less than 10% of the Mg whilst ABS completes 50% of Mg extraction, for a reaction time of 30 min. This finding is relevant from an energy consumption/integration perspective since lower extraction temperatures are favourable to the use of medium grade waste heat as the energy source for the ÅA process (Romão et al., 2012, Slotte et al., 2013). As mentioned above, also the addition of water to the rock/salt mixture allows for lowering the temperature.

Recently (Nduagu, 2012) concluded that 1 hr is the optimal reaction time for reacting the rocks with AS. In the case of dry ABS, reaction times of 30 min and 1 hr presented similar results. This outcome makes sense because, before reacting with the rocks, AS must decompose into ABS and NH₃(g) according to reaction 5 (section 1) thus requiring more time of reaction. It is interesting to see that, unlike what happens with AS, addition of water enhances Mg extraction only at 400°C. Afterwards its presence is not relevant.

Although ABS is a more powerful extracting agent, this does not ease the decision on whether to use ABS or AS as the fluxing salt. The success of the ÅA process is based (amongst other pluses) on the recycling of the ammonium salts. While AS is easily regenerated by crystallisation, the recovery of ABS is a more challenging and energy consuming procedure (Romão et al., 2014).

5.2.2 Effect of type of reactor/mixture

As shown in Figure 7, for the experiments with ABS, the rotary kiln presented the best Mg extraction result (~80%) at 450°C followed by the layers configuration in the presence of water, both at 450°C and 400°C (~72%). Clearly the continuous materials mixing provided by the rotary oven is beneficial as it provides better heat and mass transfer. On the other hand, the layers (resembling a downdraft gasifier) allow for the ABS decomposition products to be trapped between the rock powder layers (which are denser) instead of being removed with the gaseous products which gives higher extraction efficiencies.

As already observed in the first set of experiments, water enhances the extraction reactions at lower temperatures except for the rotary kiln where the free water addition is not always beneficial. Also temperatures higher than 450°C lead to excessive ABS decomposition and its loss as NH_3 and SO_2 thus lowering the extraction efficiency.

5.2.3 Effect of Al presence, magnesium and aluminium co-extraction

In previous tests (Romão et al., 2010) it was noted that rocks with higher Al content were less reactive and also reactions that took place in reaction vessels made of aluminium foil gave lower extraction efficiencies. Similarly the Metaperidotite (Rabal) sample which has the lowest Al content (Table 1) showed a higher reactivity.

Noting that having aluminium foil in contact with the samples is not the same as having a rock with greater content of aluminium oxide/silicate/etc., it is nonetheless interesting to infer on how Al presence in higher quantities will influence the reaction.

In fact, from Figure 7 it is visible, that for the rotary kiln the Al presence (added as small pieces of Al foil material) worsens the magnesium extraction. However this negative effect is not so significant for a both layered sample and homogenous mixing. In fact the difference between these results (< ~3%) may be due to the variation on the samples (a natural material) composition.

The extraction results plotted in Figure 8 for Mg and Al show a trend of higher Mg extraction against a lower Al extraction for temperatures higher than 400°C. The Al extraction results for the experiments in aluminium foil are not plotted since the results are erroneous due to the possibility of Al leaching from two very different sources.

5.3. Iron extraction

The iron by-product is of much interest since it might be supplied to the steelmaking industry (Romão et al., 2012, Koivisto, 2013) which, besides facilitating by-product disposal, can make the process economically more attractive. Although the Fe extraction behaviour is not consistent it is still inferable, as found by (Nduagu, 2012) and as shown in Figure 9, that the Fe extraction is mostly favoured at 350°C - 450°C. In fact, all experiments show that temperatures higher than 450°C do not give a benefit. The water effect on the reaction extent varies with the type of reactor, still for the layers configuration its enhancing impact is unquestionable. As for the Mg extraction results, in general the presence of Al appears to have a negative effect on Fe extraction. This may be the result of $\text{Al}^{3+}/\text{Fe}^{3+}$ chemical interferences that depend on iron's presence as Fe^{2+} or Fe^{3+} .

5.4 $\text{Mg}(\text{OH})_2$ Carbonation

The specific surface area (S_{BET}) of the $\text{Mg}(\text{OH})_2$ powder produced was measured by nitrogen adsorption and the calculations were done using the BET equation. The S_{BET} determined was 7 m^2/g while specific pore volume (SPV) was 0.146 cm^3/g . This S_{BET} is quite low when compared to the 46.85 m^2/g earlier measured by Fagerlund and Zevenhoven (2011) for serpentinite-derived $\text{Mg}(\text{OH})_2$ – see Table 4. In fact the S_{BET} is quite close to the commercial sample (Dead Sea Periclase) used in most of tests performed by Fagerlund (2012). Still it is interesting that despite the low S_{BET} the specific pore volume remains relatively high which may explain why the carbonation results presented in Table 5 are fairly good.

Table 5 – Summary of BET measurements on several Mg(OH)₂ samples.

	S_{BET} (m ² /g)	SPV (cm ³ /g)
Dead Sea Periclase ^a	5.4	0.024
Mg(OH) ₂ ^a	46.9	0.24
Mg(OH) ₂ ^b	42.18	--
Mg(OH) ₂ ^b (with iron impurities)	28.11	--
Mg(OH) ₂	7	0.146

^a Fagerlund et al., 2011b
^b Stasiulaitiene et al. 2011

Table 6 – 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

The best carbonation result of the Mg(OH)₂ product, 70%, was obtained at 510°C, 20 bar (pure CO₂) with the particle size fraction < 74 µm. As earlier found by Fagerlund and Zevenhoven (2011) the carbonation degree appears to be a function of temperature and particle size. There is some uncertainty if during the tests with the fine fraction the gas flow “channelled” through the bed instead of fluidising the particles. The fraction < 74 µm is very light and variations in the gas flow may either stop the fluidisation or blow out (entrains) the Mg(OH)₂ powder from the carbonation reactor. Also it was not easy to keep a steady pressure which gradually increased from ~19 bar to ~21 bar at the end of the tests.

6. CONCLUSIONS

The North-East of Portugal has significant resources of Mg rich silicate minerals (metaperidotites and serpentinites) with a conservatively estimated CO₂ fixation potential of 3.4 Gt. (The so far achieved Mg extraction and carbonation efficiencies of 80 and 70%, respectively, would exploit only 1.9 Gt of this.) All the tested samples showed a good reactivity for Mg extraction, especially in the presence of water. The optimum temperature for both Mg and Fe extraction lies in the range of 400 - 450°C. Still the best extraction result, 80%, was presented with the rotary tube reactor at 450°C. Ammonium bisulphate

allows for a faster and higher Mg extraction rates than ammonium sulphate especially for temperatures below 450°C but its recovery is more challenging.

7. ACKNOWLEDGEMENTS

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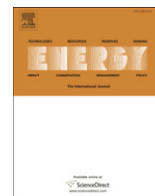
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PAPER II

Energy

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CO₂ fixation using magnesium silicate minerals part 1: Process description and performance

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ABSTRACT

This paper describes a staged carbonation process for magnesium silicate mineral carbonation. This carbon dioxide capture and storage (CCS) alternative involves the production of magnesium hydroxide, followed by its carbonation in a pressurised fluidised bed (PFB) reactor. The goal is to utilise the heat of the carbonation reaction to drive the Mg(OH)₂ production step. The results show that Mg(OH)₂ can be produced successfully (up to 78% Mg extraction extent achieved so far) and efficiently from different serpentinite minerals from locations worldwide (Finland, Lithuania, Australia, Portugal...). From the extraction step, ammonium sulphate is recovered while iron oxides (from the mineral) are obtained as by-products. The carbonation step, while still being developed, resulted in >50%-wt conversion in 10 min (500 °C, 20 bar) for > 300 μm serpentinite-derived Mg(OH)₂ particles. Thus the reaction rate achieved so far is much faster than what is currently being considered fast in the field of mineral carbonation.

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1. Introduction

Carbon dioxide capture and storage (CCS) is being considered as one of the options for CO₂ emissions mitigation in many countries, including Finland [1]. Although the storage of compressed CO₂ in geological formations currently receives most attention, the interest towards the alternative option of CO₂ mineralisation is increasing. In Finland, R&D work on this method has been ongoing for many years, motivated by a lack of other CCS options and the fact that the thermodynamics of a CO₂ mineralisation process, when properly optimised, could allow for energy-neutral operation [2–4].

The basic principle behind mineral carbonation can be found in nature, and it is called weathering. When rock, containing a material capable of forming carbonates, such as calcium or magnesium, erodes, small particles are separated and exposed to CO₂ which has been dissolved in rain water. This causes the rock particles to slowly break up, releasing metal ions into the mildly acidic water, which then become available to react with the dissolved CO₂. The result of this is the formation of mineral carbonates. Unfortunately, however, natural weathering is a very slow process that cannot keep up with the increasing atmospheric CO₂ level. Therefore the

goal of mineral carbonation has been [5] and still is to increase the reaction rate of mineral carbonation in an environmentally sound way.

There are several ways of increasing the carbonation rate artificially and most of the processes concentrate on precipitating carbonates from aqueous solutions [6]. While the aqueous route might seem more promising at first, with faster carbonation kinetics obtained so far, the energy economy of such an approach is less attractive. This is the main reason why we are studying a gas-solid carbonation process that aims at utilising the heat released from the exothermic carbonation reaction (R5) (see below) at elevated temperatures.

This paper describes a staged carbonation process for magnesium silicate mineral carbonation that involves the production of reactive magnesium in the form of magnesium hydroxide, followed by the carbonation of this in a pressurised fluidised bed (PFB) reactor that is operated at temperatures and pressures up to 600 °C, 75 bar. One specific goal was to operate the PFB at pressures above 74 bar (and 31 °C) where CO₂ is supercritical in order to assess if this has a beneficial effect on the carbonation reaction. However, the final process is likely to require far less severe conditions as will be shown below. A schematic illustration of the process described here can be found in Fig. 1.

Considering the final product, magnesium carbonate: this could find use in various applications, from simple landfill to fine chemicals (depending on purity). MgCO₃ is a stable and

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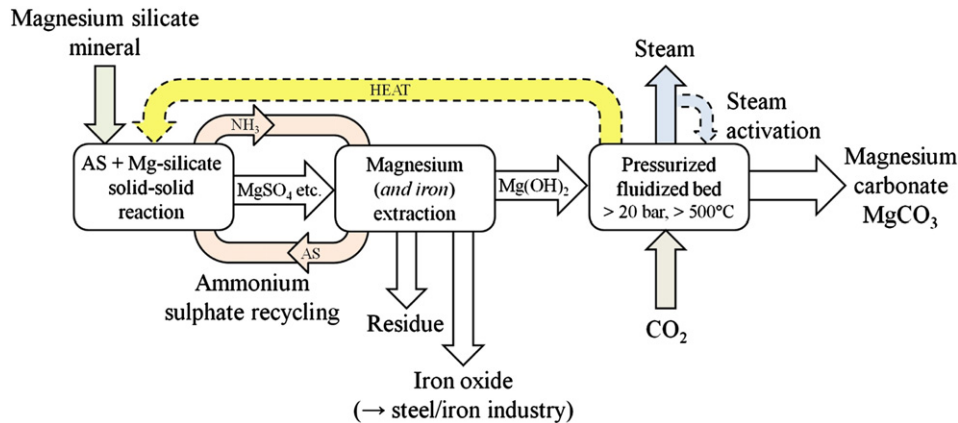


Fig. 1. A schematic illustration of the mineral carbonation process described in this paper.

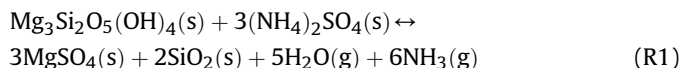
environmentally benign material [7], but large-scale operation could saturate current markets as a product or by-product (apart from landfill or land reclamation material) in the long run [8]. The focus of this paper (part 1) will be primarily on the process description and on test results. Details regarding the process energy and material streams for a modelled full-scale process are given in part 2 of this paper [9], together with a discussion around the possibility of integration with steel industry.

2. Stepwise carbonation of magnesium silicates

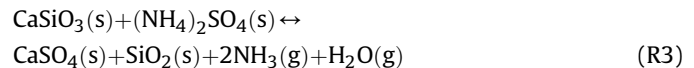
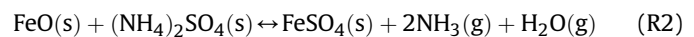
One of the features of CO₂ mineralisation using magnesium silicates is that the overall chemical reaction is exothermic, for example for serpentine 3MgO·2SiO₂·2H₂O, carbonation $\Delta H = -52$ (at 0 °C) to -49 (at 800 °C) kJ/mol CO₂ (~ 1.2 MJ/kg CO₂), with $\Delta G < 0$ for $T < 500$ °C. For forsterite 2MgO·SiO₂ the values found are $\Delta H = -106$ (0 °C) to -93 (800 °C) kJ/mol CO₂ (2.4–2.1 MJ/kg CO₂), with $\Delta G < 0$ for $T < 340$ °C. However, the direct carbonation of magnesium silicates is too slow, too energy demanding or otherwise economically unviable, although work on improving the rate of processes based on pressurised aqueous solutions is still ongoing [10]. Here, the process consists of three steps: magnesium extraction, Mg(OH)₂ production and Mg(OH)₂ carbonation. The following section presents each step in some detail.

2.1. Step 1: Extracting Mg from serpentinite

The method for extracting magnesium from serpentinite (and other magnesium silicate minerals), being developed at Åbo Akademi University (ÅAU), consists of heating the serpentinite to between 400 °C and 500 °C together with ammonium sulphate (AS) salt [11]. This causes the magnesium to form magnesium sulphate (R1), which can be further converted to Mg(OH)₂ (R4).



The reaction described by (R1) is endothermic and for this reason, the carbonation step has to be sufficiently effective to compensate for the heat input required. In reality we also have to consider the other minerals typically present in serpentinite, minerals containing significant amounts of iron and calcium. Assuming that iron is in the form of FeO and calcium in the form of CaSiO₃ two additional reactions take place when subjected to AS at elevated temperatures:



For the rock material composed of serpentine, calcium silicate and iron oxide the energy requirements for extraction of magnesium are of course somewhat higher than for pure serpentine, as a result of reactions (R2) and (R3) requiring energy as can be seen from Table 1. Reaction enthalpy data and the temperature range at which the reactions may occur ($\Delta G < 0$) are given in Table 1. The heat required for a typical serpentinite rock (Finnish rock with 84%-wt serpentine, 13%-wt FeO, and 3%-wt CaSiO₃) is given by R1+R2+R3 and was calculated by linear addition based on molar fractions.

A more detailed analysis of the reaction between serpentinite material and AS salt was made by Nduagu et al. [12], analysing the equilibrium product mix composition. The results, obtained with HSC Chemistry 5.11 software for the mixture reacting at an AS/Mg mole ratio 4:3 are shown in Fig. 2. It shows that MgSO₄ is the main solid product at temperatures above 200 °C, while above 450 °C the production of SO₃, basically from AS thermal decomposition, becomes significant.

Also, it was experimentally found that a longer reaction time (~ 1 h) at a somewhat higher temperature (~ 500 °C) increases extraction of iron relative to magnesium compared to shorter times (~ 20 min) and lower temperatures (400–450 °C). A detail that is not considered here is that the levels of extraction of Mg, Ca and Fe are different – see part 2 of this paper [9] for that.

2.2. Step 2: Mg(OH)₂ production

After the first process step, in which serpentinite rock is thermally treated with ammonium sulphate (AS) at 400–500 °C, atmospheric pressure, during 10–60 min (depending on the

Table 1
Reaction enthalpies and thermodynamics.

Reaction	$\Delta H_{373\text{K}}$ (kJ/mol)	$\Delta H_{873\text{K}}$ (kJ/mol)	$\Delta G < 0$ range (°C)
R1	243/mol Mg	174/mol Mg	>200
R2	183/mol Fe	149/mol Fe	>180
R3	131/mol Ca	91/mol Ca	>50
R1 + R2 + R3	264/mol Mg	220/mol Mg	>190
R4	-6/mol Mg	113/mol Mg	<136
R5	-56/mol Mg	-60/mol Mg	no limit ^a
R6	80/mol Mg	71/mol Mg	>265
R7	101/mol Mg	94/mol Mg	>304

^a Whole range 100–600 °C.

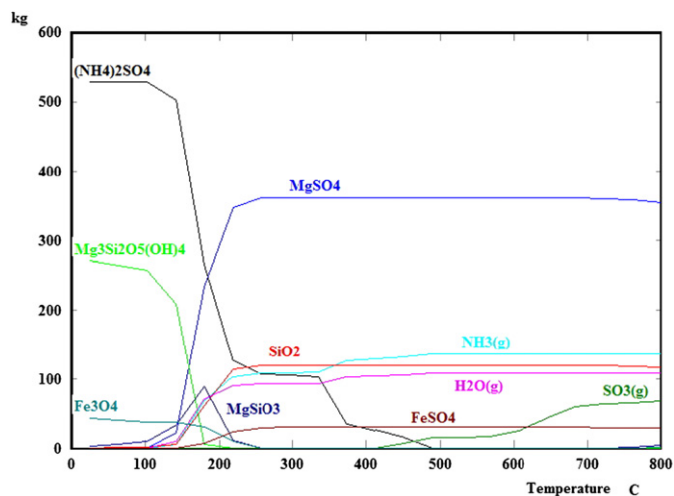
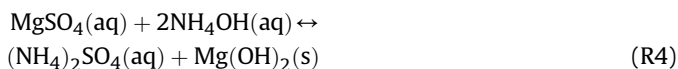


Fig. 2. Chemical equilibrium composition of reaction products of serpentinite heated up with ammonium sulphate (taken from [12]).

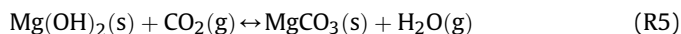
temperature that is selected). A significant amount of the serpentinite's magnesium, is converted to sulphate, MgSO_4 . Unfortunately however, MgSO_4 cannot be converted directly to carbonate, MgCO_3 , but in an aqueous solution it can be converted to $\text{Mg}(\text{OH})_2$. MgSO_4 is soluble in water at 260 g/l (at 0 °C) to 740 g/l (at 100 °C). After cooling, the solid product from the first step is put into water precipitating unreacted mineral and insoluble reaction products. The pH of the filtrate solution is raised stepwise to 8–9, precipitating iron and calcium extracted from the mineral as $\text{Fe}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$, respectively, while increasing the pH further to around 10–11 (depending on the mineral composition and the solid/solid reaction conditions) will produce the $\text{Mg}(\text{OH})_2$ according to the reaction:



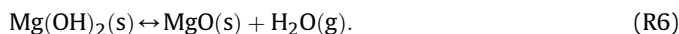
The amount of iron and calcium precipitated varies depending on the used rock material and the process conditions. Ammonia vapour, NH_3 , released during the thermal step (sum of R1, R2, R3) is collected and used to give the necessary pH increases. It thus stays in the process and is eventually recovered as AS salt downstream via crystallisation, using heat from another process step. More detail on the procedure and the extraction and recovery of species is given elsewhere [11,12].

2.3. Step 3: reacting CO_2 with $\text{Mg}(\text{OH})_2$

Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is relatively rare in nature, but magnesium in itself is not. The reactivity of the produced $\text{Mg}(\text{OH})_2$ is much better than that of serpentinite for instance or even MgO , allowing for faster carbonation and the utilisation of the reaction heat in accordance to the reaction below.



At ambient conditions, this reaction is slow, but by increasing the temperature the reaction rate can be increased significantly. Reaction enthalpies and ranges for $\Delta G < 0$ are given in Table 1 and compared to the reaction energy for magnesium silicate carbonation the reaction heat obtained from $\text{Mg}(\text{OH})_2$ carbonation is at the low end of the range. In addition to the carbonation reaction, dehydroxylation (R6) and calcination (R7) play a significant role in this process.



The balance between the equations above determines the success of the carbonation process and avoiding the forward reaction in (R7) is important. Preventing calcination (R7) from taking place can be assured as long as the CO_2 pressure is maintained above a certain level. Reaction (R6) on the other hand is governed by the water content of the gas and it should be noted that MgO is less reactive than $\text{Mg}(\text{OH})_2$ when it comes to carbonation [4].

In accordance to (R5) it should be possible to permanently trap CO_2 into magnesium carbonate in an exothermic reaction. As mentioned above, the proposed method consists of a fluidised bed maintained at a certain elevated temperature and pressure. The objective is to find the conditions that allow for continuous operation without the need for any heat input. In our lab, this can be reduced to the task of finding the conditions that give the highest carbonation degree in the shortest time. Another objective was to verify whether raising the pressure to levels where CO_2 becomes supercritical (>74 bar) gives any benefits.

3. Experimental procedure

For the purpose of developing a method to store CO_2 as mineral carbonates two parallel tracks are being taken in the laboratory at ÅAU, one being the production of $\text{Mg}(\text{OH})_2$ from common minerals and the other being the production of MgCO_3 from $\text{Mg}(\text{OH})_2$.

3.1. Materials

For the purpose of producing $\text{Mg}(\text{OH})_2$ various rocks have been tested, most of them serpentinites from different regions. Serpentine is a magnesium silicate rock containing mostly serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). A typical serpentinite sample from Finland (Hitura, nickel mine tailing) also contains a significant amount (13 %–wt) of iron oxides. The iron from this iron-containing mineral is extracted and separated in the process described above and one goal is that it would be used by the iron and steel industry in the future.

Depending on the composition and structure of the rock sample being tested various amounts of magnesium are extracted; the more the better. While the magnesium hydroxide produced from serpentinite has been used in some of the experiments, most of the carbonation experiments have so far been performed using a commercially produced $\text{Mg}(\text{OH})_2$ (Dead Sea Periclase Ltd.). In addition, SiO_2 (i.e. sand) has been mixed with the hydroxide sample in some cases. The sand is inert and will not participate in the reaction, but it acts as a stabiliser during the fluidisation. Instead of being close to the limit of Geldart A particles (aeratable, or material having a small mean particle size and/or low particle density [14]), Geldart B behaviour (sandlike, these solids fluidize well with vigorous bubbling action [14]) is achieved for the mixture.

Regarding the particles size, typically between 125 μm and 212 μm , the correct particle size fraction is obtained by using a sieve shaker (Retsch AS 200 - time 15 min, amplitude 1.5 mm and interval 10 s). However, the $\text{Mg}(\text{OH})_2$ particles consist of agglomerates rather than separate particles.

3.2. Test methods

The work on this particular mineral carbonation route has been divided into two parallel sub-projects which in the end are highly

dependent. At this stage, more and more work is being directed towards integration of the two and possibilities to reduce cost and energy use as can be seen from part 2 [9] of this paper. Below, the two process steps are still separated and presented as they have been carried out in the laboratory.

3.2.1. $Mg(OH)_2$ production

For the production of $Mg(OH)_2$ according to the solid–solid reaction route presented above a temperature controlled tubular oven is used. A sample is prepared by mixing ammonium sulphate (AS) and serpentinite in typically a 3:2 mass ratio. The sample is allowed to react (without any mixing) in the oven for 0.3 h–1 h. Then the material is dissolved in water and, and the soluble compounds such as, $FeSO_4$, $MgSO_4$ (and some $CaSO_4$) are leached into solution. The filtrate is afterwards subjected to precipitation in an aqueous ammonia solution at different pH-levels as to stepwise precipitate hydroxides of iron, calcium and finally magnesium. For a more detailed description of this process see [11,12,15].

3.2.2. $Mg(OH)_2$ carbonation

Using a fluidised bed (FB) as a reactor for the carbonation reaction has been suggested by others [4,13] and the principal reason for this is the continuous motion of the bed. The particles inside the bed are constantly colliding with each other and the reactor walls, and the force of these impacts is the cause for particle attrition and/or abrasion. This is beneficial since it has been shown that the carbonation reaction can become limited by a layer of carbonates forming on the surface of the particles in a static environment [3,16]. Another benefit of the fluidised bed is the good heat distribution allowing for homogenous conditions inside the reactor. Note that only $Mg(OH)_2$ is used in the FB reactor and not the whole mineral; this gives a significant reduction in pressure drop losses. In addition, using $Mg(OH)_2$ in a pressurised reactor results in hot pressurised steam (with unreacted CO_2), that can be utilised in a steam turbine.

The main components of the test setup can be seen in Fig. 3 and they consist of a CO_2 bottle, a water pump (HPLC), a pre-heater (a spiralling tube inside heating elements), a fluidised bed (FB), a cyclone, a sample feeder for the $Mg(OH)_2$ (SiO_2 mixture) and measuring equipment for temperatures, pressure and mass flows. The inner diameter of the FB is only 14 mm and the height of the FB is almost 0.5 m.

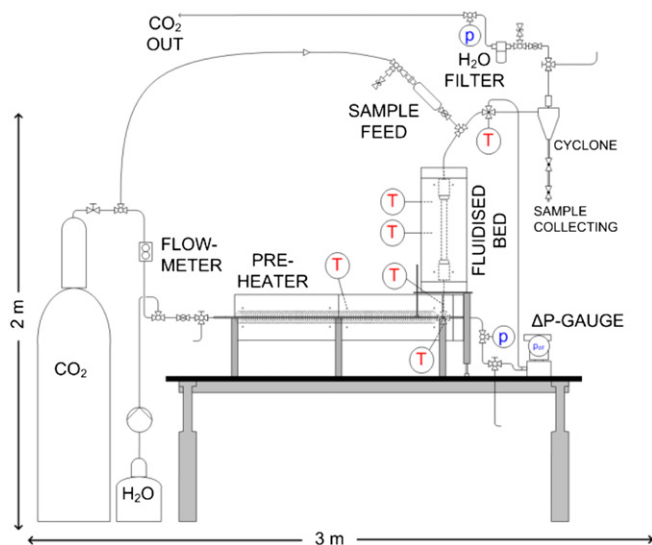


Fig. 3. Schematic illustration of the fluidised bed setup used for mineral carbonation.

4. Results and discussion

Although results from both $Mg(OH)_2$ production and its consequent carbonation are presented here, the latter will be presented in more detail. Recent results of $Mg(OH)_2$ production according to the method described earlier are described more thoroughly elsewhere [11,12,15].

4.1. $Mg(OH)_2$ production

Previous experimental data gave a maximum of 64–66% Mg-extraction with Finnish serpentinite at the following reaction conditions; reactants' AS/serpentinite mass ratio 3:2, reaction temperature, 400–440 °C and reaction time, 30–60 min [12]. Under the same conditions 0.33–0.34 g of valuable solid products (>70 wt-% $Mg(OH)_2$ and <30 wt-% $FeOOH$) were produced per gram of rock. The valuable solid products refer to the Fe containing (dark brown solid) compound and magnesium hydroxide (white solid), both precipitated after adding ammonia solution at pH 8–9 and 11–12, respectively. However, a more promising result was obtained recently with serpentinite from Bragança, northeast Portugal; 0.40 g $Mg(OH)_2$ per gram rock, representing a 78% extent of extraction, was obtained. Also a significant amount (0.08 g per g of rock) of Fe by-product was produced. In spite of the energy requirement of the process (see Part 2), it is important to note its significance. Mg-extraction shows promising results, and a high purity $Mg(OH)_2$ is produced while the Fe-rich compound ($FeOOH$) may be a useful raw material in the iron and steel industry. AS salt, used as reagent for extracting Mg from the minerals is relatively cheap, and is a product and by-product of several chemical processes, for example, flue gas scrubbing in coal-fired power plants. However, ammonia gas is a by-product of the reaction, which if collected in water can be used to act as or supplement the ammonia solution used for precipitation purposes. Interestingly, smaller volumetric amounts of ammonia solution are needed in the precipitation process compared to the amounts of base (alkaline) precipitants used previously in other reaction routes [11,17,18].

4.2. $Mg(OH)_2$ carbonation

So far, about a hundred $Mg(OH)_2$ carbonation tests were made, mapping the different experimental conditions contributing to the carbonation kinetics, and in general it can be stated that the carbonation of $Mg(OH)_2$ at elevated pressures and temperatures is relatively fast. This has also been noted by others [16] and our recent results suggest that most of the carbonation takes place only minutes into the experiment, after which reaction rates and final conversion degrees level off. Exactly how fast the initial reaction rate is has not yet been determined as the target has been to map the best carbonation conditions over a wide range of operational parameters. However, experiments have shown that a maximum carbonation level is generally reached within 15 min.

The benefits of using a PFB for the carbonation reaction were mentioned above, but it seems that there is another side to the particle–particle and particle–wall interactions. While the collisions of particles inside the PFB reactor is beneficial to carbonation because it exposes unreacted $Mg(OH)_2$ to CO_2 it also exposes the unreacted surfaces to dehydroxylation. Previously it has been noted that MgO is much less reactive than $Mg(OH)_2$ and its formation should be avoided.

In Fig. 4 the amount of $Mg(OH)_2$, MgO and $MgCO_3$ present in the particles after the tests is plotted as a function of temperature for a number of experiments. The scattered data shows an underlying trend of decreasing $Mg(OH)_2$ as a function of temperature caused by simultaneous carbonation and dehydroxylation. This suggest

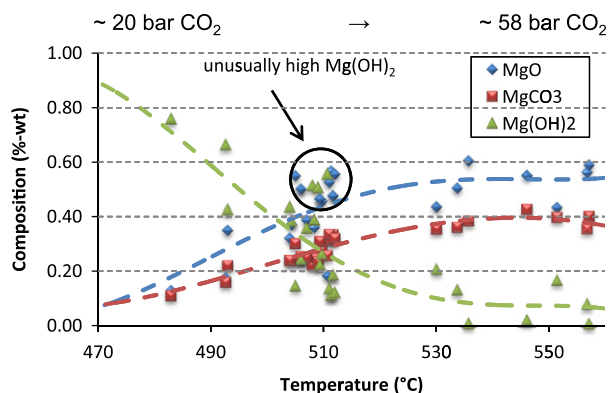


Fig. 4. Composition as Mg-species in the reaction products as a function of temperature for various experimental conditions using a PFB reactor. Note: different particle sizes, temperatures, pressures etc.

that the observed fast initial carbonation followed by a sudden drop in reactivity is the result of $\text{Mg}(\text{OH})_2$ depletion. Thus, preventing formation of MgO , which does not carbonate fast enough, is very important. There are three data points (indicated by the circle in Fig. 4) showing an unusually high $\text{Mg}(\text{OH})_2$ content compared to other experiments performed at the same temperature. Two of these experiments were performed with a mixture of CO_2 and H_2O , while one was performed using a very low CO_2 flow, basically reducing the PFB reactor to a static bed system. The differing conditions affected the dehydroxylation degree more than it affected the carbonation degree, which is why the MgCO_3 data appears less scattered.

It has been suggested that mixing small amounts of water with CO_2 could prevent dehydroxylation at pressures where MgCO_3 formation is thermodynamically favoured [4]. Others have also noted that H_2O plays a significant role in the carbonation kinetics of $\text{Mg}(\text{OH})_2$ carbonation [16,19], while Butt *et al.* (1998) [16] reported that small amounts of water vapour can act as catalyst and enhance the carbonation reaction rate. However this effect has not been demonstrated in our experiments. In contrary a small, but evident negative effect on the final carbonation degree with increased H_2O feed rate has been noticed [20]. Still, as shown by the unusually high $\text{Mg}(\text{OH})_2$ amounts for two of the experiments, the dehydroxylation degree can be reduced by the addition of steam to the system. This effect only becomes clear at higher H_2O contents than previously expected, at 4.6 and 15.1% H_2O in CO_2 respectively (Fig. 4).

In Fig. 5 the results obtained so far are collected in a triangular $\text{MgO} - \text{Mg}(\text{OH})_2 - \text{MgCO}_3$ composition diagram, showing that the presence of water is indeed a prerequisite for obtaining high conversion levels to MgCO_3 . This is one point of focus of current work, for which first results were recently presented [21]. A final goal is to produce a model expression for the conversion of $\text{Mg}(\text{OH})_2$ to MgCO_3 and MgO as function of temperature, time, pressures for H_2O and CO_2 , particle size and fluidization velocity.

Comparing the two different $\text{Mg}(\text{OH})_2$ types that have been tested so far shows that the (Finnish) serpentinite based hydroxide is much more reactive than the commercial one (Dead Sea Periclase). Under similar conditions (500 °C, 20 bar, 10 min) the former converted to 50% while the latter reached only a 29% conversion degree. This was later confirmed with tests with $\text{Mg}(\text{OH})_2$ produced from a Lithuanian serpentinite [22]. The particle size fraction was also comparatively large; 250 μm –425 μm for serpentinite-derived compared to 125 μm –212 μm for the commercial grade $\text{Mg}(\text{OH})_2$. The large difference in reactivity must be attributed to the much larger surface area (47 m^2/g vs. 5 m^2/g) and pore volume size

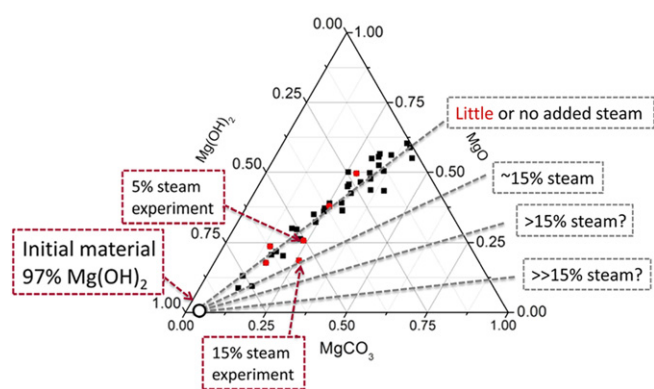


Fig. 5. Composition as Mg-species in the reaction products as a $\text{MgO} - \text{MgCO}_3 - \text{Mg}(\text{OH})_2$ diagram, indicating the apparent importance of water partial pressure. Note: different particle sizes, temperatures, pressures etc.

(0.24 cm^3/g vs. 0.024 cm^3/g) of the serpentinite-derived $\text{Mg}(\text{OH})_2$ [15,22].

That the serpentinite-derived $\text{Mg}(\text{OH})_2$ carbonates so well is promising, especially considering that the CO_2 pressure of these experiments was relatively low, at only 20 bar. Increasing the pressure up to, and beyond the supercritical point of CO_2 using this material is being planned while higher pressures with the commercial hydroxide have already been performed. With this material, the best results so far, 40–45% conversion, was achieved for several experiments ranging from 35 to 60 bar, 520–550 °C and reaction times less than 15 min. However, higher pressures and temperatures did not result in the expected increase in carbonation degree as discussed above. Furthermore, increasing the pressure above 60 bar, up to 75 bar (supercritical CO_2), actually reduced the overall reactivity of the samples. The reason for this could be in the reduced H_2O diffusion rate from the particles due to high external pressure as suggested by Béarat *et al.* [19]. In fact, there are strong indications (XRD-analysis results) that at a relatively high pressures so-called oxymagnesite, $\text{MgO} \cdot 2\text{MgCO}_3$ is formed [21].

Fig. 6 shows two graphs of the carbonation degree as a function of temperature and pressure. Graph (a) shows results from tests done in a fixed bed (pressurised thermogravimetric analyser) for 6 h [3,4]. The particles (75 μm –125 μm) used consisted of the same Dead Sea Periclase $\text{Mg}(\text{OH})_2$ that we have been using in the fluidised bed. The results obtained using the fluidised bed are depicted in graph (b). However, some of these results represent the average value of several experiments as other parameters, besides pressure and temperature, have been varied. These variables are reaction time (10 min–1 h), H_2O feed rate (0–2%-vol), fluid velocity (0.9–2.4 times minimum fluidisation velocity), particle size (typically 125 μm –212 μm , but also larger, up to 425 μm particles have been tested) and sample size (3 g–20 g). Note that the PTGA test results in Fig. 6, graph (a), represent the final conversion degree to MgCO_3 after 6 h in a gas mixture of 99 %-vol CO_2 and 1 %-vol H_2O .

For a fixed bed system one could expect the results to be fairly consistent, having a carbonation degree maximum at a certain temperature corresponding to some degrees below the equilibrium temperature of MgCO_3 . This also appears to be the case for the results in graph (a) in Fig. 6. Increasing the pressure increases the carbonation degree, but increasing the temperature too much will lower the final conversion degree.

Because of the fact that there are more variables in play using the fluidised bed, the results appear more scattered than in the fixed bed case. This only proves that it is not only temperature and pressure that influence the system although evidently these play a major role. All results are from experiments with much shorter

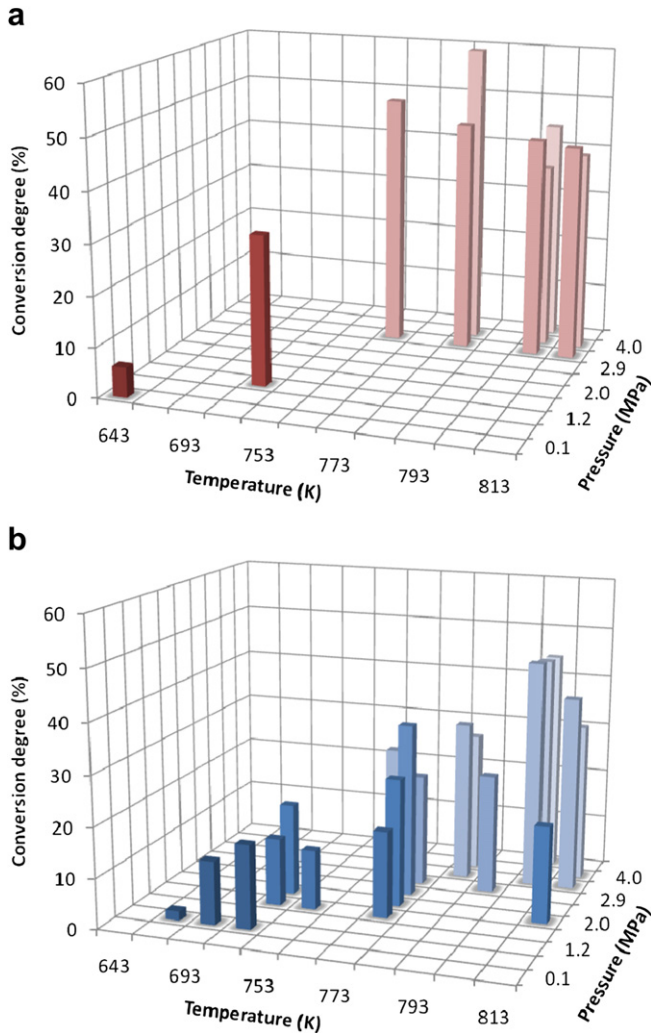


Fig. 6. Carbonation results as a function of pressure and temperature: a) PTGA, b) fluidised bed (other operational variables varied).

reaction time than the 6 h used for the static case, typically only 15 min.

4.2.1. Sample analysis

To determine the extent of carbonation after each experiment a fraction of the sample is subjected to HCl and the pressure increase due to CO₂ evolution is measured. This analysis method is simple yet accurate and more information can be found elsewhere [23]. However, this method cannot distinguish between Mg(OH)₂ and MgO. It is even difficult to tell the mass loss due to dehydroxylation apart from that of carbonate decomposition using thermogravimetric analysis (TGA) [24]. Fig. 7 displays a TGA result using a lightly carbonated (3.8%-wt) Mg(OH)₂ and clearly there is only one slope for both H₂O and CO₂ evolution around 400 °C. However, in order to determine the Mg(OH)₂ content of the sample at hand, it is possible to simply heat up the sample to such an extent that only MgO remains. The mass that is lost due to heating is the combined amount of H₂O and CO₂ in the sample, and by knowing the amount of CO₂, the Mg(OH)₂ content can be determined.

Besides indirect measurements on the sample composition, we have looked at the samples using scanning electron microscopy (SEM). The difference between the serpentinite-derived Mg(OH)₂ and the commercial one is clear, but it is much more difficult to

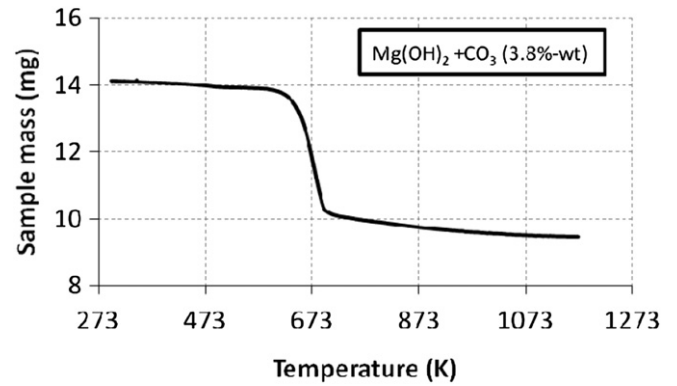


Fig. 7. TGA result of Mg(OH)₂ containing 3.8 %-wt CO₃. Heating rate 10 K/min.

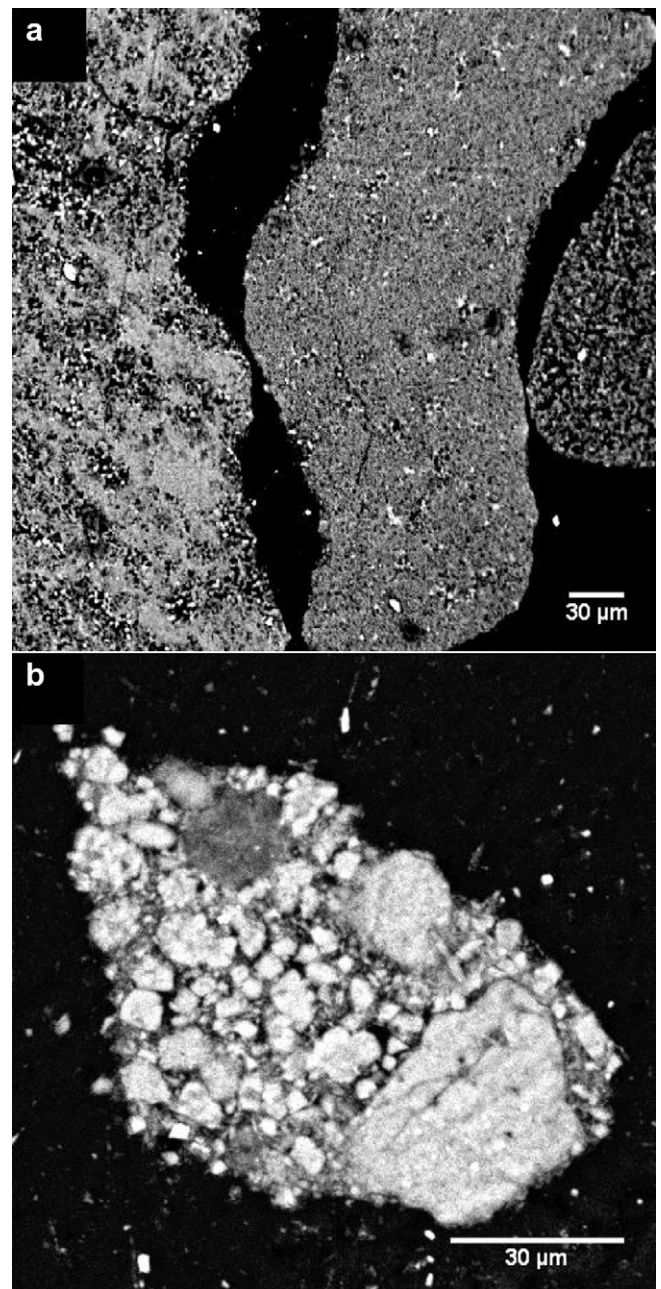


Fig. 8. Cross-sectional SEM images: a) (250×) carbonated (51%-wt) serpentinite-derived Mg(OH)₂ sample, b) (500×) an unreacted commercial Mg(OH)₂ sample.

distinguish between a reacted (*i.e.* partially carbonated) sample and an unreacted one. This gives no evidence of carbonates or of a carbonate rich layer forming around the particles as a result of carbonation.

In Fig. 8 two cross-sectional SEM images are shown. Image a) shows a carbonated serpentinite-derived $\text{Mg}(\text{OH})_2$ sample and image b) shows an unreacted commercial $\text{Mg}(\text{OH})_2$ sample. Image a) shows the cross-section of three magnesium-rich particles, while image b) only displays one.

Analysing for elemental composition, particularly evidence of CO_3 , isn't helpful as a carbon-based resin was used to produce the cross-sectional samples. Nonetheless, the difference between the two samples is evident and it is clear that the serpentinite-derived sample is much more porous than the commercial one, explaining the obtained higher carbonation degree.

5. Conclusions

Producing magnesium hydroxide for carbonation from serpentinite, an abundant magnesium containing rock for the purpose of mineral sequestration of CO_2 , is possible using the method presented here. However, the process requires energy in the form of heat and that energy has to be largely covered by the consequent $\text{Mg}(\text{OH})_2$ carbonation. As such the process described here can be divided into three steps, magnesium extraction, $\text{Mg}(\text{OH})_2$ production and $\text{Mg}(\text{OH})_2$ carbonation. How these processes can be integrated, the energy requirements and the possibilities of large-scale mineral carbonation are presented in part 2 of this paper.

Here, the concept and methods of mineral carbonation using a fluidised bed have been presented and the best results show that about 97% production extent of the magnesium hydroxide from serpentinite can be achieved. More so 50% carbonation can be achieved in less than 10 min at relatively mild conditions (20 bar, 500 °C) with serpentinite-derived $\text{Mg}(\text{OH})_2$ particles of 250 μm –425 μm , which is much faster than other currently considered mineral carbonation routes are offering. So far most of the experiments have been performed using commercially produced $\text{Mg}(\text{OH})_2$ however, which appears less reactive than the serpentinite-derived. The results indicate that while carbonate layer build-up might be the inhibiting mechanism at low temperatures and slow flow conditions, higher temperatures and flow-rates result in a highly dehydroxylated product with considerably reduced carbonation reactivity. In order to balance these effects, the option of adding considerable amounts of steam to the system should be studied in more detail. Previously we have shown that small amounts of water (0–3% H_2O in CO_2) mixed with the CO_2 does not result in any significant changes to the product. However, we have recently been able to increase the steam amount up to 15% H_2O in CO_2 and found that the dehydroxylation rate was considerably reduced while carbonation was maintained at the same levels as for experiments performed under similar conditions with dry CO_2 . Thus achieving high carbonation levels and rates could be possible by recycling the steam produced by $\text{Mg}(\text{OH})_2$ carbonation.

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Nomenclature

ÅAU	Åbo Akademi University
AS	ammonium sulphate
CCS	carbon capture and storage
G	gibbs energy, J/mol
H	enthalpy, J/mol
PFB	pressurised fluidised bed
PTGA	pressurised thermogravimetric apparatus
S	serpentine
SEM	scanning electron microscope

Greek symbols

Δ	difference
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PAPER III

Energy

(2012)



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

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ABSTRACT

Mineral carbonation presents itself as the most promising method to sequester CO₂ in Finland. A staged process for CO₂ mineralisation, using magnesium silicates, is being intensively developed at Åbo Akademi. A process energy analysis is made based on the most energy intensive steps, i.e. the heat treatment of the magnesium silicate rock and the carbonation reaction. Aspen Plus[®] software was used to model the process and pinch and exergy analyses were performed to acquire information on process layout for optimal heat recovery and integration. The simulations allow for concluding that the fixation of 1 kg of CO₂ requires 3.04 MJ and 3.1 kg of serpentinite mineral rock. Additionally, the process gives considerable amounts of FeOOH and Ca(OH)₂ as by-products making the integration of mineral carbonation with the steelmaking industry a very attractive opportunity to reduce CO₂ emissions and raw materials inputs.

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1. Introduction

Carbon dioxide is the major greenhouse gas responsible for our planet's global warming and for that, its capture and storage is imperative. Unfortunately Finland (and presumably also Portugal) lacks options for underground storage and CO₂ mineralization presents itself as a way to fix CO₂. A staged process for CO₂ mineralisation using magnesium silicates is being intensively studied at Åbo Akademi. It gives a significant amount of iron by-product from the mineral in the form of FeOOH. This may be used as an input stream for iron- and steelmaking industry, providing for a secondary raw material [1]. Moreover, as the serpentinite minerals used in this study contain around 5–20% wt iron oxides the size of the iron oxides by-product stream is quite significant. In Finland the iron and steel sector is the largest point-source CO₂ producer, therefore, integrating steel industry's CO₂ emissions with mineralisation is crucial and would result in emissions reduction, valuable carbonates, and iron oxide by-products useful as a raw material for iron and steel industry. In this second part of two papers, the energy and chemicals integration of a magnesium silicate mineral carbonation process, as described in [2], with a steelmaking plant is reported. It expands on a process where Mg

extraction from silicate mineral is combined with Mg(OH)₂ carbonation in a stand-alone process as it will be explained in this paper. Aspen Plus[®] (version 7.0) is used for most of the calculations/simulations. The results give valuable information on process layout for optimal heat recovery and integration. The integrated system calculations show how CO₂ emissions from iron and steelmaking and input requirements for iron ore and lime could be reduced. A feature that is briefly addressed as well is that calcium-rich slag from steelmaking (more specifically steel converter slag) can be carbonated too, producing synthetic calcium carbonate that is of great interest to pulp and paper industry.

2. Serpentinite carbonation

This section provides a description of the serpentinite carbonation process, and of the assumptions made in order to obtain a feasible process simulation using Aspen Plus[®] software.

2.1. Process description

The process system studied here is divided into six main steps, as shown in Fig. 1:

1. Solid–solid extraction for reactive magnesium production from magnesium silicate mineral, using ammonium sulphate (AS)

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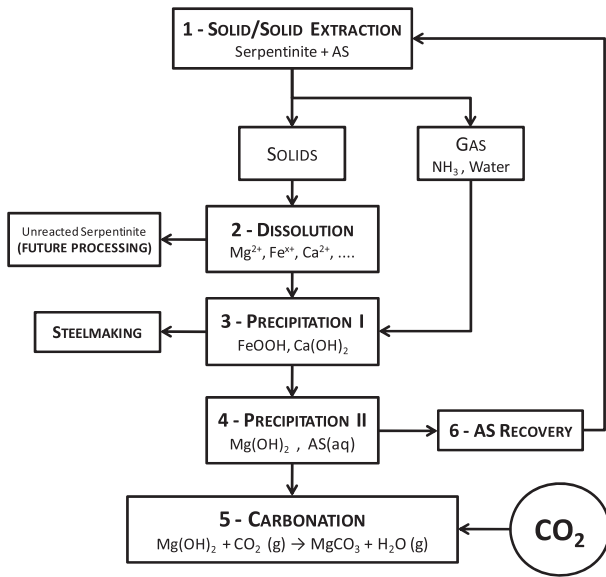


Fig. 1. Scheme of the serpentine carbonation process.

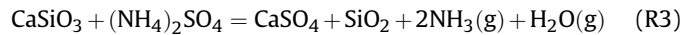
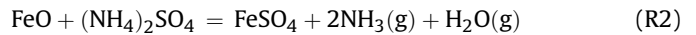
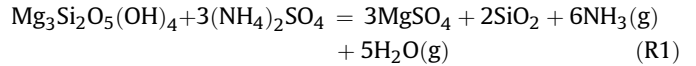
2. Dissolution of reaction products
3. Precipitation of calcium and iron in the form of hydroxides
4. Precipitation of magnesium as Mg(OH)₂
5. Carbonation of Mg(OH)₂
6. Ammonium sulphate recovery

Operating conditions and modeling of Steps 1 to 4 were based on experimental results obtained by Nduagu [3,4] whereas data for step 5 was based on Fagerlund's [2] experiments.

It is worth mentioning several problems which occurred along the simulation due to the lack of some components' properties in the Aspen's database. Therefore, in the simulation studies, data from HSC's database [5] was often used, particularly for stages 1–4.

2.1.1. Solid–solid (SS) extraction

In the Aspen model (represented in Fig. 2) this step is simulated by a stoichiometric reactor (presumably a kiln). It operates at 480 °C and atmospheric pressure. After being grinded, the serpentine is mixed with AS and the following reactions occur:



As shown by the above reactions, large amounts of NH₃ and water are released and further used in the precipitation stages.

2.1.2. Solids dissolution

Unfortunately MgSO₄ cannot be directly converted to carbonate, MgCO₃, due to thermodynamic limitations, but in an aqueous solution it can be converted to Mg²⁺ (MgSO₄ is soluble in water at 260 g/l (at 0 °C) to 740 g/l (at 100 °C)). After cooling, the hot solid from the reaction with AS is put in water precipitating unreacted

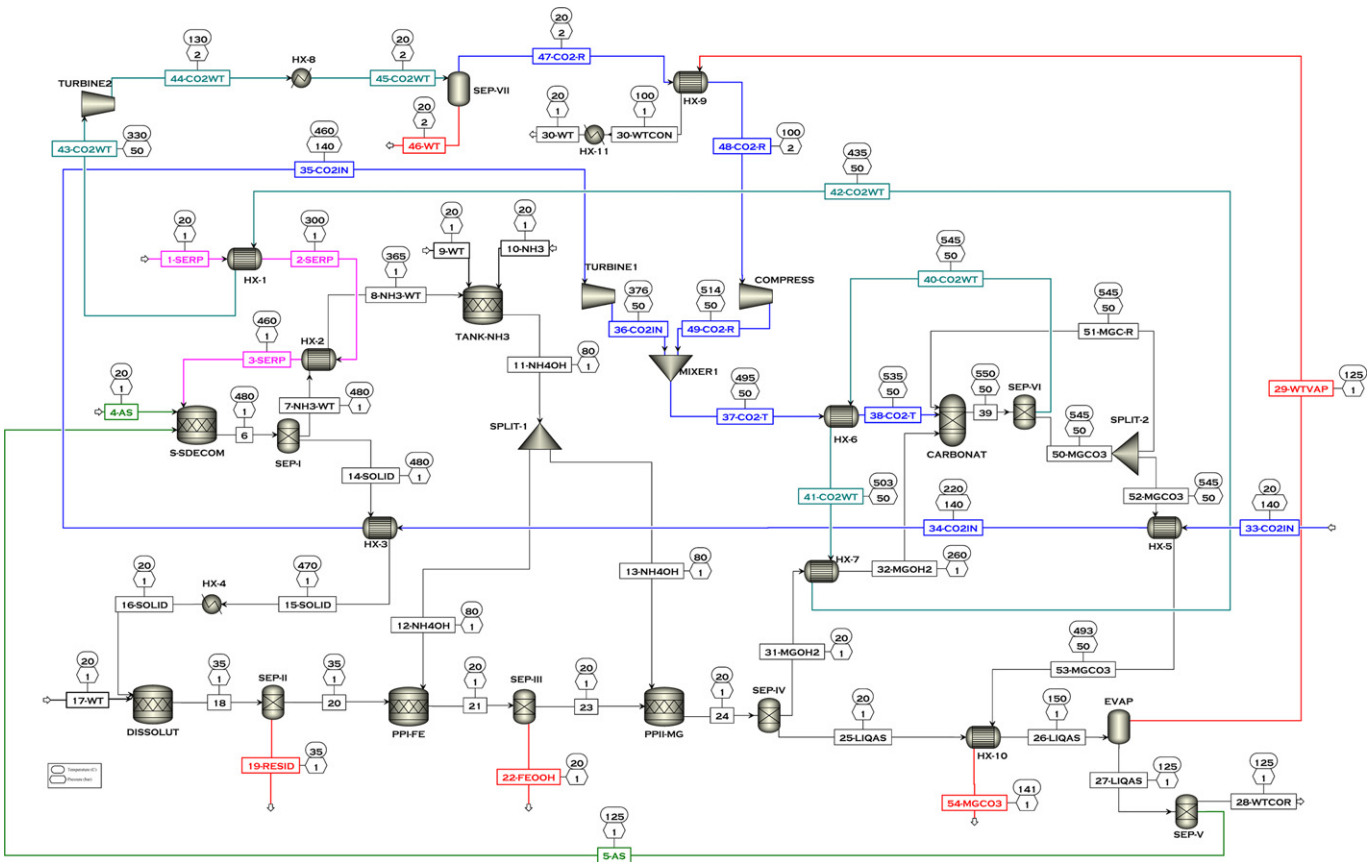


Fig. 2. Aspen Plus® model: magnesium silicate carbonation after Mg(OH)₂ production.

serpentine, iron oxide, wollastonite, insoluble reaction products (silica, e.g.) and finally $\text{Mg}(\text{OH})_2$.

The unreacted $(\text{NH}_4)_2\text{SO}_4$ will also dissolve releasing a considerable amount of heat. A rigorous control of this step is very important. Larger amounts of dissolved products result in larger amounts of recovered products in the two precipitation stages ahead. It is important to keep this dissolution tank at a temperature higher than 35 °C, since the solubility of MgSO_4 increases with temperature. Water must be carefully added as it on one hand increases the dissolution rate but later, during the AS recovery, its evaporation will require a considerable amount of energy.

This dissolution was difficult to simulate in Aspen and, once again, a stoichiometric reactor was used and HSC data, for the heat of dissolution of the salts formed in stage 1, was introduced in the simulation.

2.1.3. Iron, calcium and magnesium precipitation

For the sequential precipitation, pH is the most important operation parameter. The solution must be rigorously kept at $\text{pH} = 8\text{--}8.5$ so that, in this first precipitation step, only iron and calcium are precipitated and, consequentially, magnesium recovery is maximised in the second precipitation stage at a pH of 9.0–11.0, and this could vary slightly depending on the mineral and reaction conditions. The iron is precipitated in the form of goethite (FeOOH), calcium as $\text{Ca}(\text{OH})_2$ and magnesium as $\text{Mg}(\text{OH})_2$.

It is still not fully clear in which form the iron is present in the serpentinite ore. Probably it is a mixture of Fe_2O_3 and FeO partially combined as Fe_3O_4 . However it is only possible to separate by precipitation the Fe^{2+} because Fe^{3+} has a much lower pH for precipitation and will thus remain in the solid residue. Therefore, for simulation purposes, it was considered that all the iron is FeO but it is not possible to extract more than 60% of it, as was found experimentally [3,4].

2.1.4. $\text{Mg}(\text{OH})_2$ carbonation

$\text{Mg}(\text{OH})_2$ reacts with gaseous CO_2 to form MgCO_3 and water vapor in a pressurized fluidized bed reactor, taken here to operate at 50 bar and 550 °C. (These conditions are not excessive for fluidized bed reactors – see for example to the High Temperature Winkler process [6] developed during the 1920s). This stage was simulated in Aspen with a Gibbs reactor.

The CO_2 flow going into this reactor was calculated assuming particles with a diameter $d_p = 100 \mu\text{m}$ and a porosity $\epsilon = 0.6$. The minimum fluidizing velocity (u_{mf}) was calculated using Equation (1) [7]:

$$\frac{d_p u_{mf} \rho_g}{\mu} = \left[(28.7)^2 + 0.0494 \left(\frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \right) \right]^{1/2} - 28.7 \quad (1)$$

and the fluidizing velocity (u_f) was estimated to be preferably $5 \times u_{mf}$ to assure a strongly mixed bubbling bed reactor.

Finally a 2000 $\text{m}^3\text{CO}_2/\text{h}$ (STP) flow was estimated and used in the simulations. It was decided to keep the fluidizing velocity (u_f), porosity, and CO_2 flow constant. The purpose of that is to maintain, for each simulation, the carbonation conditions unchanged. The $\text{MgCO}_3/\text{Mg}(\text{OH})_2$ solid product mix will be recirculated until the $\text{Mg}(\text{OH})_2$ content becomes sufficiently low (a few %).

2.1.5. Use of the ammonia produced in the solid/solid extraction reaction

The ammonia gas produced during the extraction step is cooled and dissolved in water to form NH_4OH . A make-up of NH_4OH is necessary to achieve the desirable pH of the precipitation stages. Since Aspen's database lacks data for NH_4OH , a make-up stream of

ammonia (175 kg/h) is used instead. The appropriate temperature for this process unit was difficult to estimate. While modeling, and looking for conditions where the vapor fraction inside the reactor is negligible, the temperature calculated for this reactor was 146 °C. (Maybe it is possible to lower this temperature.) It was decided to keep this absorber reactor at a temperature of 40 °C which is roughly the boiling temperature of an aqueous solution with 40% NH_3 . The NH_4OH produced in this vessel is used to raise the pH in both precipitation steps.

2.1.6. Ammonium sulphate recovery

It is very important to recover the AS present in the remaining solution after the $\text{Mg}(\text{OH})_2$ precipitation not only for environmental reasons but also to make the process economically viable, although AS is a cheap chemical (cheaper than ammonia or sulphuric acid). The only way to achieve an AS recovery of 99% was to model two separators in series. This recovered AS is fed back to the S/S extraction reactor. In order to keep a mass ratio of serpentinite/AS equal to 2/3, a make-up stream of 400 kg/h of AS per 45 t/h of AS processed was added to the first reactor.

2.1.7. Unreacted CO_2 recovery

The streams leaving the carbonation reactor contain MgCO_3 , H_2O (g) and unreacted $\text{Mg}(\text{OH})_2$ and CO_2 (g). The solid must be separated from the gas, most likely by a cyclone. The gaseous stream leaving the separation unit contains 5–10% of water vapour, generated in the carbonation reaction. Decompressing and cooling this stream allows the removal of water so that the unreacted CO_2 can be recovered, recompressed to 50 bar and then feed back to the carbonator.

2.2. Process thermodynamics

The largest heat producing and consuming process steps are those that involve chemical conversion at elevated temperatures. Therefore the reaction heats for extracting magnesium from serpentinite (R1), from Finnish serpentinite rock (R1+R2+R3) and the carbonation of $\text{Mg}(\text{OH})_2$, respectively, are given as function of temperature in Fig. 3, indicating that producing $\text{Mg}(\text{OH})_2$, at 400–500 °C will require 4 × more heat than what is obtained, at 500–600 °C, from carbonating it.

With this, focusing on $\text{Mg}(\text{OH})_2$ production and its carbonation, the heat requirements for CO_2 mineral sequestration can be estimated, as MJ/ton CO_2 . What should be taken into consideration as well is that the degrees of extraction and conversion of the magnesium will not be 100% as a result of mixing limitations, limited reaction times and other rate-limiting processes. A low degree of conversion of $\text{Mg}(\text{OH})_2$ will lower the amount of heat produced, while a low degree of Mg extraction during the thermal treatment with AS salt will result in heat losses and large amounts of rock material to be processed. The conditions assumed are Mg extraction

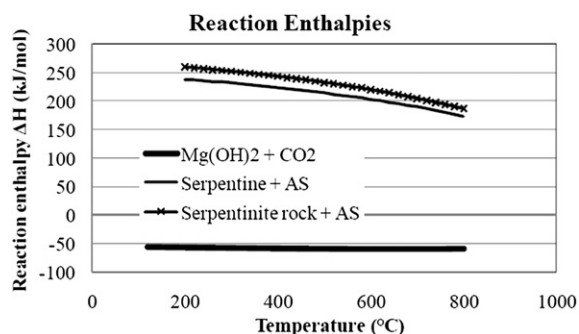


Fig. 3. Reaction enthalpies vs. temperature for extraction of 1 mol of Mg from pure serpentinite or from Finnish serpentinite, and for the carbonation.

at 480 °C ($\Delta H_E = 234.6$ kJ/mol Mg) and $Mg(OH)_2$ carbonation at 550 °C ($\Delta H_C = -59.5$ kJ/mol Mg), under pressurized conditions as described in [8]. The results are given in Tables 1 and 2, for varying $Mg(OH)_2$ carbonation degrees, X_C , and varying Mg extraction degrees X_E . Two different cases are considered with respect to the energetic efficiency of the $Mg(OH)_2$ production:

- Incomplete Mg extraction implies that less heat is consumed or needed for this
- Incomplete Mg extraction does have a heat penalty

With this, the energy requirements of the two processes combined can be calculated as

$$E(\text{MJ}/\text{kgCO}_2) = \Delta H_E - X_C \cdot \Delta H_C \quad (2)$$

or, with an energy penalty for inefficient Mg extraction:

$$E(\text{MJ}/\text{kgCO}_2) = \frac{\Delta H_E}{X_E} - X_C \cdot \Delta H_C \quad (3)$$

recalculated from kJ/mol Mg to MJ/kg CO_2 . The amount of rock material needed for these cases, as kg rock/kg CO_2 is given in Table 3.

It was found that the overall heat input requirements will be 4–5 MJ/kg CO_2 for accomplishing the $Mg(OH)_2$ production, assuming that Mg extraction and carbonation can both be accomplished at a level of 90% or more.

3. Process energy integration, pinch and exergy analysis

The assessment based on only chemical conversions as described above gives a good first impression of energy requirements, simply because most of the irreversibilities that are difficult to avoid occur there [9]. These results are very similar to those reported below, where a more detailed analysis is made using pinch analysis and process simulation tool Aspen Plus®.

The process presents the following heating and cooling needs:

- Heat-up of incoming serpentinite (AS cannot be preheated as it would decompose)
- Heat-up of incoming CO_2 .
- Heat-up of $Mg(OH)_2$ before carbonation, limited by a risk of decomposition to MgO.
- Cooling of solid reaction product from serpentinite/AS reaction to ambient temperature. (This could be used to produce steam: the rate for that would be $\sim 1.7 \times$ the amount (as kg steam) produced in the carbonator.)

Table 1
Process energy input requirements (MJ/kg CO_2) according to Equation (2).

Mg extraction efficiency	$Mg(OH)_2$ carbonation efficiency				
	50%	75%	90%	95%	100%
Any	4.66	4.32	4.12	4.05	3.98

Table 2
Process energy input requirements (MJ/kg CO_2) according to Equation (3).

Mg extraction efficiency	$Mg(OH)_2$ carbonation efficiency				
	50%	75%	90%	95%	100%
50%	9.99	9.65	9.45	9.38	9.31
75%	6.43	6.10	5.89	5.83	5.76
90%	5.25	4.91	4.71	4.64	4.57
95%	4.94	4.60	4.40	4.33	4.26
100%	4.66	4.32	4.12	4.05	3.98

Table 3
Serpentinite rock material requirements (kg serpentinite/kg CO_2).

Mg extraction efficiency	$Mg(OH)_2$ carbonation efficiency				
	50%	75%	90%	95%	100%
50%	10.00	6.66	5.55	5.26	5.00
75%	6.66	4.44	3.70	3.51	3.33
90%	5.55	3.70	3.09	2.92	2.78
95%	5.26	3.51	2.92	2.77	2.63
100%	5.00	3.33	2.78	2.63	2.50

- Cooling of $MgCO_3$ (plus unreacted $Mg(OH)_2$) product from carbonation reaction
- Cooling (and expanding) the steam/unreacted CO_2 gas product from the carbonation reaction
- Cooling (and absorbing in cold water) of NH_3 and SO_3 vapours produced in the serpentinite/AS reactor

Besides this, a significant amount of heat is needed to regenerate the AS salt, i.e. to produce solid AS from the aqueous solution that remains after the $Mg(OH)_2$ is precipitated. It was reported [10] that this can be accomplished at ~ 90 °C against a moderate heat input of ~ 120 kW/m³.

The transfer of heat from the carbonator to the serpentinite/AS reactor would involve solid/solid heat exchange with the solids from the carbonator reactor, not an optimal solution, or with the steam/unreacted CO_2 mixture from the reactor.

On the other hand, for a possible energy input to the process it is expected that CO_2 is delivered to the process site by pipeline, at pressures well above what's needed in the process: expanding the CO_2 from 100 to 140 bar transport pressure will yield a significant amount of energy, as power.

All this will require a more detailed assessment as will be shown below.

3.1. Pinch and exergy analysis

In this section a pinch analysis [11] was performed to obtain optimal heat recovery and integration of the process/model. Simulations were made for different levels of Mg, Ca and Fe (by-) product extraction and $Mg(OH)_2$ carbonation.

Although the S/S extraction, AS recovery, and recovered CO_2 recompressing are energy intensive stages of the process, it is possible to decrease the total energy demand by designing an efficient heat exchanger network, and recovering heat from the tank where the solids are dissolved and the reactor where NH_4OH is produced. Also it is assumed that the CO_2 feed to the process is

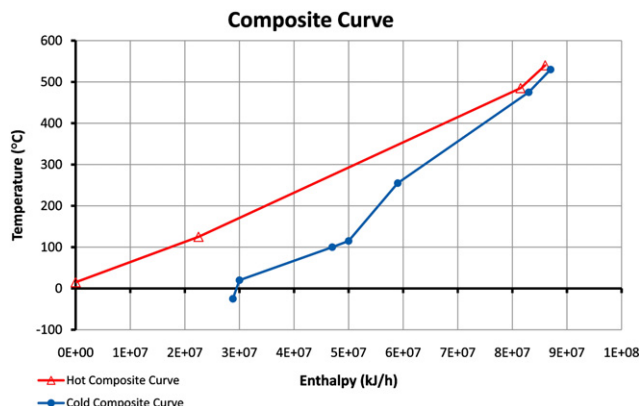


Fig. 4. Cold and hot composite curves.

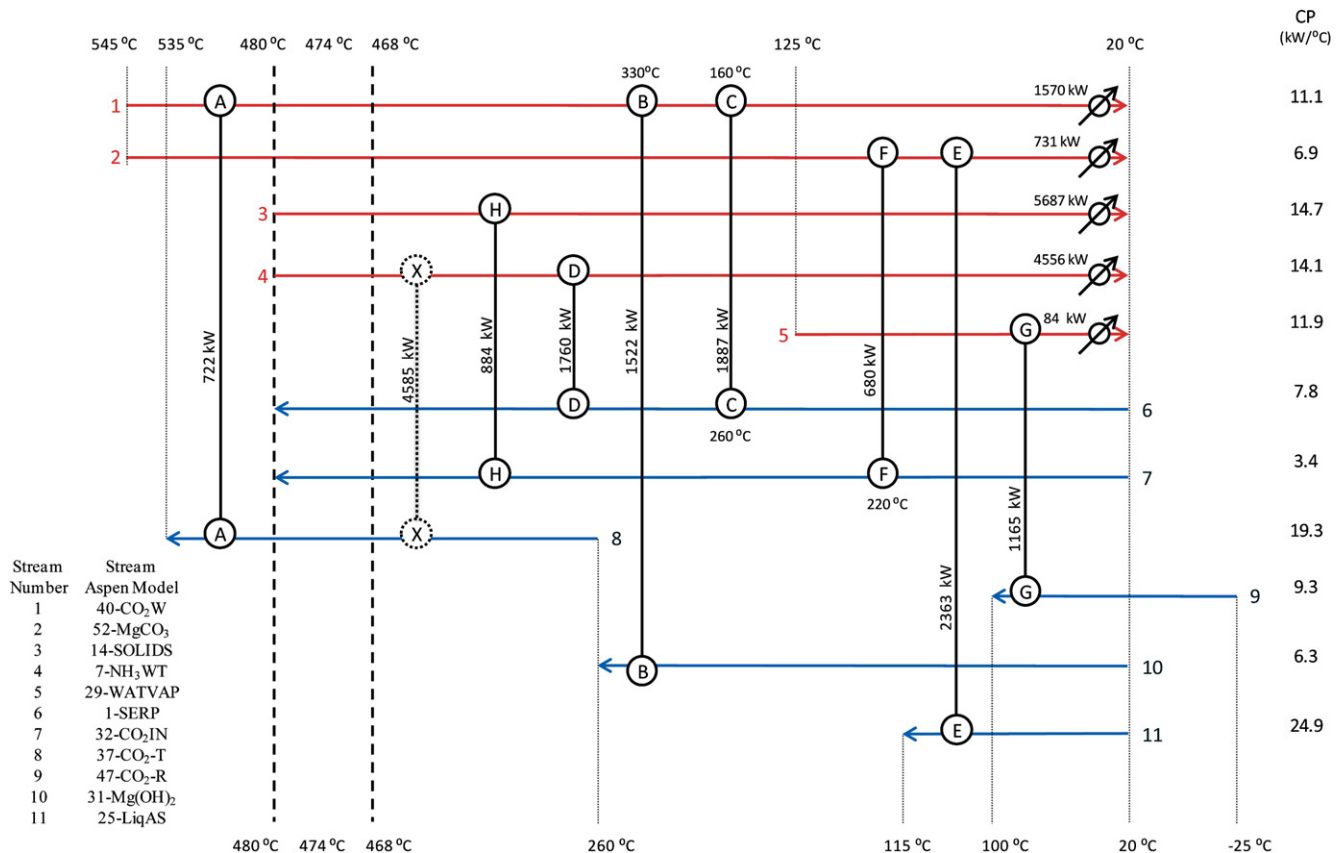


Fig. 5. Grid with the HX network proposed and applied.

delivered at 140 bar (transport pressure) and its decompression to 50 bar generates a considerable amount of energy.

The application of this methodology was not without difficulty. This design was optimized using data from the simulation relative to 90% of carbonation and an extraction of 80% of magnesium, 60% of iron and 100% of calcium, which is believed to be the real potential of this process. The numerical method given by Linnhoff and Flower was applied [11]. The composite curve of this problem was built using Aspen Energy Analyzer and it's shown in Fig. 4. The grid with the proposed (and applied) heat exchanger (HX) design is represented in Fig. 5.

The match between streams followed these main conditions:

- Above the pinch $CP_{hot} \leq CP_{cold}^1$
- Below the pinch $CP_{hot} \geq CP_{cold}$
- Solid streams must never be matched
- Temperature of stream 1 (mixture of unreacted CO₂ and water) must not go under the 120 °C to avoid condensation inside the turbine 2 (see Fig. 5).

All these criteria could be satisfied except for the HX E (see Fig. 5). Stream 11 should have been split in two and then matched with two hot streams. However, for reasons unclear to us, by following this theory the simulation does not converge to a result in Aspen®.

Moreover, an additional HX-X (see Fig. 5) would be necessary to take stream 8 to the pinch point, but this does not follow the condition $CP_{hot} \geq CP_{cold}$. Stream 8 is not more than the mixture of streams 7 and 9. And when these two streams are heated up by

heat exchangers F, G and H, stream 8 reaches a temperature higher than the pinch, making HX-X unnecessary.

Finally the cooler from stream 2 was not included because below 60% Mg extraction all the heat from this stream will go into stream 11.

3.2. Simulation results

Simulations were made for different levels of Mg, Ca and Fe (by-) product extraction, and Mg carbonation. Figs. 6 and 7 summarize the results. It is important to stress that the simulations do not include grinding of the minerals but do include energy recovery from decompression the CO₂, which is expected to be delivered at 140 bar.

Intensive study on aqueous mineral carbonation using olivine, serpentine and wollastonite minerals was carried out at the Albany Research Center (ARC), in the US [12]. According to their results 3.4–6.3 kg of serpentinite (heat treated, 75 μm) may sequester 1 kg of CO₂ requiring 3.7–7.6 MJ of energy (mainly heat at 630 °C) and including grinding, at ~ 150 kJ/kg CO₂ fixed, equal to approximately 3% of the energy needed.

The modeling approach used in this study gives similar values. Experimental results [3,4] show that currently² it is possible to extract 60% of magnesium while the level of carbonation aimed at is 90%, which requires 3.04 MJ (2.22 MJ as heat at 125 °C–550 °C + 0.82 MJ as power) and 3.1 kg of serpentinite to fix 1 kg of CO₂. However the energy requirements are still (too) high. Note that, as also for the ARC work, the CO₂ production associated with the energy requirements is not taken into account. The use of steam, at the right temperature, from a steam

¹ Stream heat capacity: $CP = \dot{m}c_p(W/K)$.

² Recently a magnesium extraction level of 78% was achieved at ÅA.

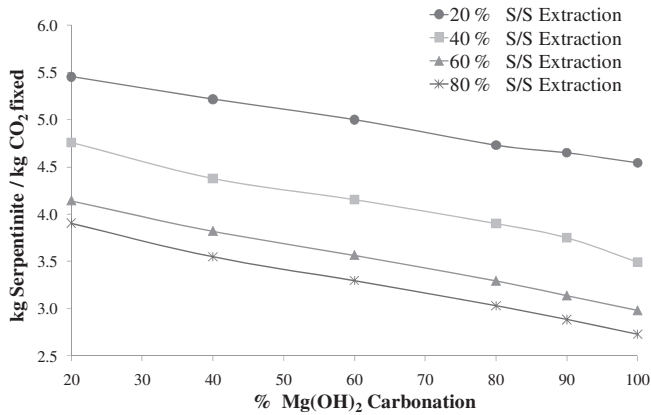


Fig. 6. Serpentine consumption per kg of CO₂ fixed.

cycle of a power plant or other process comes across as a good alternative to supply most of the energy needed for this process.

As shown in Fig. 8, the AS recovery presents a significant penalty to the process's total energy demand and it is imperative to modify and improve this step in order to avoid this energy penalty. Crystallization methods such as mechanical vapour recompression, use of anti-solvents such as alcohol, and membranes may be better alternatives to complete evaporative crystallization used in this simulation.

Considering the carbonation reactor, although the energy values given by the software implies an exothermic reaction, it was a goal that the released heat in this reactor would be enough to cover the energy input needed for the Mg(OH)₂ production [13], which is not yet achieved at this point. (In the current model the reaction heat released is used to bring reactants to the reaction temperature.) On the other hand, the values calculated by Aspen® for the enthalpy of carbonation reaction must be checked and compared to experimental results. These results may, in the future, be implemented into the simulation in order to obtain better results.

The HX network design appears to be quite efficient since the recovered exergy covers 78% of that of the total heat that is transferred (exergy destruction 1.36 MJ/t CO₂ for 6.48 MJ/t CO₂ exergy into the HX network).

4. Process by-products

In this section some potential applications of the by-products as well their contribution to minimize CO₂ emissions will be

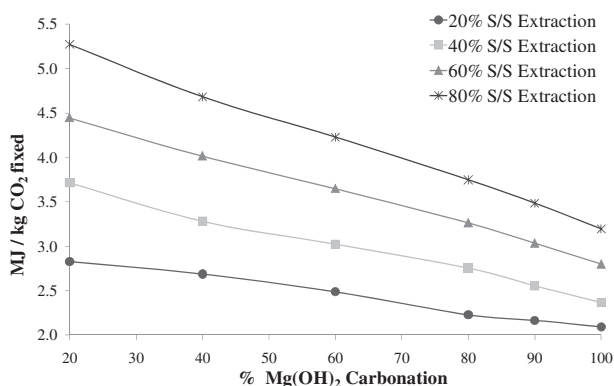


Fig. 7. Energy input requirements per kg of CO₂ fixed.

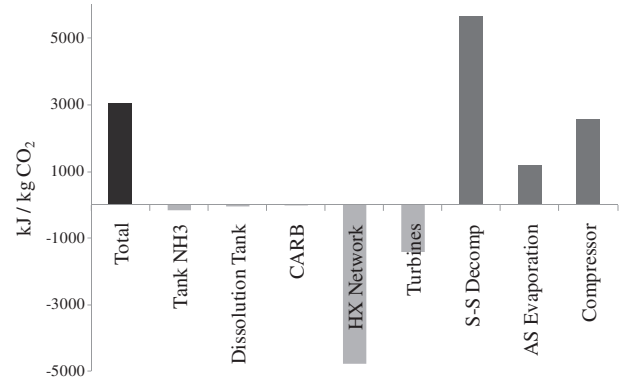


Fig. 8. Comparison of the energy input/output values in the different steps of the process.

discussed. The results presented in this next section are based on data provided by Raahe Works Ruukki (the biggest steelmaking company in Finland) for year 2006.

4.1. Goethite and calcium hydroxide

The iron and calcium based products can be supplied to the steelmaking industry, most likely to a sintering plant which is often integrated in a steel mill.

The sintering process is a pre-treatment stage of the raw materials to produce pig iron in a blast furnace (BF). The iron ore, limestone, small quantities of coke, and other fines are heated up to 1300–1400 °C to form a porous material suitable to be fed to the BF (see Fig. 9).

The main reactions of the process are:



By supplying pure goethite and calcium hydroxide it is possible to decrease the CO₂ emissions of the sintering process because no CO₂ is released when they are oxidized

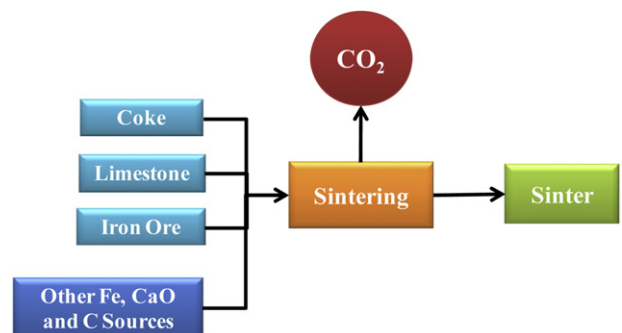


Fig. 9. Main inputs and outputs of a sinter plant.

Table 4
CO₂ emissions avoided by feeding iron and calcium by-products to a sinter plant.

	FeOOH kt/year	Iron ore replaced	Ca(OH) ₂ kt/year	Limestone replaced	Total CO ₂ avoided kt/year
A	331	17%	33	37%	28.4
B	365	18%	36	41%	31.2



A sintering plant producing 2.9 Mt of sinter per year requires 1800 kt iron ore, 165 kt of limestone, 118 kt of coke, 1080 kt of other products and emits 550 kt of CO₂. The calculation of how much CO₂ might be avoided by feeding the pure goethite and calcium hydroxide is then of very much interest.

Two case scenarios will be considered.

- A. 60% Mg Extraction, 45% Fe Extraction, 75% extraction of Ca, 80% Carbonation
- B. 80% Mg Extraction, 60% Fe Extraction, 100% extraction of Ca, 100% Carbonation

The Finnish steelmaking industry produces around 6.7 Mt of CO₂ per year from which 4.8 Mt are emitted by Ruukki (year 2006). The calculation of the quantities of goethite and Ca(OH)₂ produced is based on the assumption that all Ruukki's CO₂ emissions are fixed by this carbonation process.

The new sinter compositions were determined by mass balances as were also the iron ore and limestone amounts that may be replaced. Finally, the quantity of CO₂ avoided was calculated by summing up the CO₂ emissions prevented from iron ore and limestone³ mining and from the sintering process itself. The results are presented in Table 4.

The results might seem modest but is important to stress that this raw material replacement represents a reduction of ~5% emissions in a pre-treatment stage of the steelmaking process.

4.2. Different sinter plant input

In addition to the above, the extra energy required to calcine/dehydrate these new materials was (roughly) estimated. The reactions (R5), (R7) and (R8) were taken into account to perform the energy balances. Although the three reactions are endothermic⁴, the replacement of CaCO₃ by Ca(OH)₂ allows saving ~100 kJ per mol of Ca(OH)₂. Hence, the energy penalty becomes minor varying between 1.4 and 1.6% of the annual energy input into the sinter plant, which translates into an extra demand of 1.7–1.9 kt coke/year. This energy penalty is negligible and it may be easily overcome by providing gas from coke oven to the sintering.

The influence of these new sinter compositions in the blast furnace performance was as well evaluated. A first principles' thermodynamic model [17,18] was applied. Although the first aim of integrating mineral carbonation with the steelmaking industry was to check how much iron ore and limestone could possibly be replaced by goethite and calcium hydroxide, it became clear that it also has a slight positive effect in other parameters: reducing the coke, sinter and pellets consumption, while decreasing the blast furnace slag and carbon dioxide production.

³ Emissions from, iron ore mining: 7.1 kg CO₂/t ore [14], limestone mining: 2.3 kg CO₂/t limestone [15], Serpentinite mining: 1.5 kg CO₂/t serpentinite [16].

⁴ $Q_{(R8)(T=400^\circ\text{C})} = 57.4 \text{ kJ/mol FeOOH}$ [5], $Q_{(R9)(T=1100^\circ\text{C})} = 212 \text{ kJ/mol Ca(OH)}_2$ [5], $Q_{(R6)(T=1400^\circ\text{C})} = 310 \text{ kJ/mol CaCO}_3$ [5].

Further study on the chemical properties of this new sinter is needed to assure that this new feedstock is a real opportunity for the steelmaking industry.

4.3. Residue from mineral

The mineral residue after magnesium, iron and calcium extraction also has to be considered. Although it is logical that it should contain high amounts of valuable Si or SiO₂ more study and analyses are required to know its accurate composition and from there trace a plan for further processing and recovery of its constituents.

It's also important to note that the residue contains about 40% (depending on the reaction conditions and mineral) of the iron existent in the serpentinite rock. Therefore its future processing is perhaps also worth considering.

4.4. Contaminated water from AS recovery

In the second evaporation stage for the AS recovery, water with 5% of NH⁴⁺ is produced which implies a 0.7% loss (i.e. ~30 kg/ton CO₂ fixed) of the incoming AS stream. This contaminated water might be corrosive and therefore its use for utility purposes should be avoided. One option would be its use for removal of SO₂ from gaseous streams, to form (NH₄)₂SO₄ (Walther process) [19]. This can be used in the serpentinite carbonation process described in this paper.

4.5. Magnesium carbonate

Significant amounts of this product will be produced and the question of what to do with such big amounts of it still remains. But it must be stressed that, depending on its purity, it finds applications in a wide range of industries such as chemical, pharmaceutical, cosmetic, food and construction (flooring and fireproofing). However, large-scale operation would naturally saturate any market as a product or by-product in the long run [20].

5. Steelmaking slags carbonation

Another interesting issue, briefly addressed, in this paper is the carbonation of slags produced by the steelmaking (SM) industry. In 2006 Raahe Works produced 0.2 Mt of steel converter slags. Said [21] describes a method to carbonate these slags and also models it using Aspen Plus[®] Software. According to his results, with solvent recycling, 5.26 kg of steel slags sequester 1 kg of CO₂, producing 2.18 kg of CaCO₃ (PCC). PCC is a valuable product mainly consumed by the paper industry as filler and coating pigment for paper.

6. CO₂ NET emissions reduction and energy demand

Equation (4) predicts the net reduction of CO₂ emissions when mineral carbonation is integrated with the SM industry. Table 5 presents the values obtained when 4.8 Mt of CO₂ are mineralised

Table 5
Net CO₂ emissions, mineral and energy demand for case scenarios A and B.

Case	Mineral Carbonation (model)		
	CO ₂ kt/year	Serpentinite Mt/year	Energy GJ/year
A	4881	16.1	15.9
B	4881	13.3	15.6

Case	Sintering kt CO ₂ /year	Steel Slags kt CO ₂ /year	Net Reduction kt CO ₂ /year
A	28.4	38	4923
B	31.2		4930

and the subsequent products supplied to an SM plant for the two scenarios as in Section 4.1.

$$\text{CO}_2 \text{ net reduction} = \text{CO}_2 \text{ sequestered} - \text{CO}_2 \text{ serpentine mining} \\ + \text{CO}_2 \text{ avoided sintering} + \text{CO}_2 \text{ avoided steel slags} \quad (4)$$

In both cases A and B, the net reduction of CO₂ is higher than the CO₂ fixed by the mineralization process modeled, due to the emissions avoided when the goethite, and calcium hydroxide by-product are fed to the SM industry. Improvement of the S/AS extraction and of the carbonation percentages appears to have a greater impact on the amount of serpentinite consumed than on the final CO₂ emissions.

7. Conclusions and future work

The CO₂ mineralization process studied and simulated requires 3.04 MJ and 3.1 kg of serpentinite mineral rock to fix 1 kg of CO₂. This includes making use of the heat released by the carbonation reactor (~31 kJ/kg CO₂).

Clear benefits are that oxides of iron and calcium are obtained as separate by-product streams and that only Mg(OH)₂ is fed to the carbonation reactor. A cheap and recoverable salt, ammonium sulphate, is used for Mg extraction.

The heat input is needed at a moderately high temperature of 450–500 °C⁵, which may be available as waste heat from other processes and should not be confused with (electric) power needs. Finally, it may be possible to operate the carbonation process with CO₂-containing flue gas or process gases instead of with almost-pure CO₂: this would remove the need for expensive CO₂ separation methods. More information and detail is given in part 1 this paper.

The mineralization of all the CO₂ emissions of a single steel company operating in Finland (Ruukki) is enough to reduce the Finnish CO₂ emissions by 10%.

The integration of mineral carbonation with the steel industry is of great interest since it permits a considerable reduction of raw materials inputs and a net CO₂ reduction superior to the initial CO₂ fixed, despite the faster rate of the carbonation reactor.

Nevertheless, this process is still very energy intensive and has to be optimized in order to make it energy-neutral. A less energy consuming alternative for the AS recovery must be found and the S/AS extraction must be improved, not only for energetic reasons, but also to recover more by-products thereby reducing the amount of solid residue. In addition, the level of carbonation achieved in the fluidised bed so far is still too low (50–55%, within several minutes and leveling of after that, compared to at least 90% aimed at).

Acknowledgments

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Nomenclature

AS	Ammonium sulphate
BF	Blast Furnace
CCS	Carbon Capture and Storage

CP	heat capacity, J/K
C _p	specific heat, J/(kg K)
ARC	Albany Research Center
d	diameter, m
G	Gibbs energy, J/mol
H	enthalpy, J/mol
HX	heat exchanger
\dot{m}	mass flow, kg/s
PCC	precipitated calcium carbonate
SM	steelmaking
S	Serpentine
STP	Standard Temperature and Pressure
u	velocity
X	degree of conversion, –

Greek symbols

Δ	difference
ε	porosity
ρ	density

Subscripts and superscripts

C	Carbonation
E	Extraction (of Mg)
f	fluidizing
g	gas
mf	minimum fluidizing
p	particle
s	solid

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⁵ Although, based on recent experiments, this value can be dramatically decreased to an optimum of 400–440 °C.

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PAPER IV

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IChemE



CO₂ sequestration with magnesium silicates—Exergetic performance assessment

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ABSTRACT

A staged process for CO₂ sequestration by mineralisation, using magnesium silicates, studied at Åbo Akademi (ÅA) involves the production of magnesium hydroxide from suitable rock (requiring heat at ~350–450 °C) using recoverable ammonium salts and its subsequent carbonation (generating heat at ~500 °C). In addition, the process gives substantial amounts of solid by-products making the integration of mineral carbonation with other industries an opportunity to both reduce CO₂ emissions and substitute raw material inputs.

Aspen Plus[®] v7.2 software is used to optimize the ÅA process towards minimal energy use and to study the impact of the flue gases' CO₂ concentration (conventional coal firing (CCF) vs. oxyfuel combustion (OXY) flue gases) in the carbonation step instead of pre-separated and compressed CO₂ (providing an additional benefit compared to “conventional” CO₂ capture and storage (CCS) options). Also the influence of using either ammonium sulphate (AS) or bisulphate (ABS) as the fluxing salts on the process's exergetics is evaluated. It was concluded that ABS lowers the energy requirements in the Mg extraction by 40% but its regeneration (fundamental feature for the route's success) by: (i) thermal decomposition of AS appears to be unviable, (ii) addition of H₂SO₄ saturates the process with sulphur. The simulation results showed that the extraction with ABS and carbonation with OXY flue gases requires less energy input.

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Keywords: CO₂ mineral sequestration; Serpentinite; AS/ABS salt; Exergy; Energy efficiency

1. Introduction

During the last two decades the interest in carbon capture and storage technologies has increased and established itself as worthy part of the portfolio of methods for reducing anthropogenic emissions. Post-combustion, pre-combustion and oxyfuel combustion systems are the three main carbon capture (CC) paths under study to be combined with transport and storage of the CO₂. These all require upgrading and development of new technologies and equipment and, despite all the efforts invested in R&D, they remain largely unproven and energy intensive. Complications and worries also arise when deciding how to keep the captured CO₂ permanently away from the atmosphere. Long term storage options include

geological formations, the deep ocean or carbonated materials. Mineral carbonation, the fixation of CO₂ into benign and thermodynamically stable carbonates may be the answer for countries like Portugal (Carneiro et al., 2011), Finland (e.g. Fagerlund et al., 2012) and Lithuania (Stasiulaitiene et al., 2014) that lack geological and oceanic storage opportunities for CO₂. There have been and still are several processes under study for binding CO₂ into Mg and Ca rich materials. The description and evolution of the different carbonation routes being developed at different research institutions is well described in several literature reviews on the field of mineral carbonation: Huijgen and Comans (2003, 2005), Torrónategui (2010), Zevenhoven and Fagerlund (2010) and recently Olajire (2013), IEA-GHG (2013), Mattila and Zevenhoven (2014). Typical for

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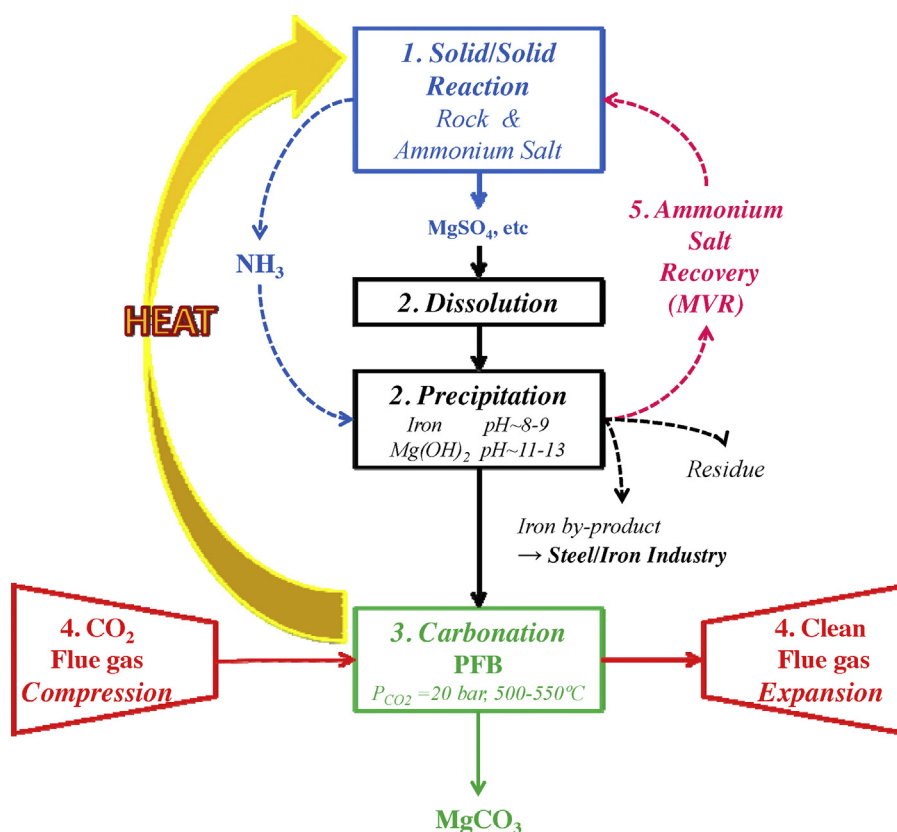
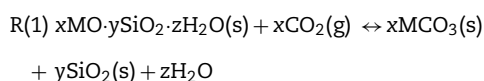


Fig. 1 – Magnesium silicates carbonation process.

current developments is the use of ammonium salts as a flux and the goal of producing an available solid product that yields revenue or reduces costs.

This work focuses on the staged process for CO₂ sequestration by mineralisation using magnesium silicates currently under investigation at Åbo Akademi (ÅA) that is being developed towards industrial application (Romão et al., 2012a; Slotte et al., 2013).

The ÅA process outlined in Fig. 1 was initially driven by the exothermicity of the carbonation reaction of (Ca, Mg) silicates:



where M = Mg, Ca.

In the case of serpentine (3MgO·2SiO₂·2H₂O) this reaction releases 55.8 kJ/mol CO₂ (Zevenhoven et al., 2008).

Unfortunately, direct carbonation of the Ca, Mg silicate rock with acceptable kinetics is not straightforward thus the process is divided into two main steps: (1) solid/solid reaction between Ca, Mg silicate rock and recoverable ammonium salts (which requires heat at ~350–450 °C) followed by dissolution in water and subsequent production of magnesium hydroxide, as described by Nduagu (2008, 2012) and (2) and the subsequent gas/solid (dry) carbonation of Mg(OH)₂ (which releases reaction heat at ~500–550 °C) as explained by Fagerlund (2012) and Fagerlund et al. (2012). In addition, the process gives substantial amounts of by-products making the integration of mineral carbonation with other industries an opportunity to reduce CO₂ emissions and substitute raw materials inputs (Romão et al., 2012b). Also the process can use flue gas in lieu of a CO₂ captured stream thus avoiding expensive (and still quite challenging) separation steps applied in pre and post

combustion systems. The fixation of CO₂ as stable carbonates avoids time and money spent on complex assessments of geological, geophysical and engineering feasibility for storage sites selection. Future costs associated with monitoring, in order to minimize the risk of leakage, are likewise avoided. Moreover the ÅA route cancels out part of the electricity demand for the CO₂ compression stage that typically precedes the geological/oceanic storage.

So far the main setbacks of this process are a combination of slow kinetics, low conversion and high energy requirements (Zevenhoven et al., 2008). This paper focuses on the exergetic performance of the ÅA route whilst the kinetics and conversion issues are addressed in detail elsewhere (Nduagu, 2012; Fagerlund, 2012). Aspen Plus[®] v7.2 software is used to improve previous simulation models (Romão et al., 2010, 2012a,b) in order to find a process with (1) minimal energy input requirements (2) study the impact of the flue gases CO₂ concentration in the carbonation step and (3) the influence of two different salts for Mg extraction from serpentine-type rock: ammonium sulphate (AS) and ammonium bisulphate (ABS).

2. Aspen Plus[®] V7.2 simulations

2.1. Model description

The simulations are based on the latest results obtained at ÅA with serpentine rock material collected in Donai, Bragança, Portugal since this rock has shown good reactivity towards both ammonium salts (Romão et al., submitted for publication). Not all the rock's elements (containing also Cr, Cu, Ni, e.g.) were considered relevant and its chemical composition was normalized to: Mg₃Si₂O₅(OH)₄ – 84.16 wt%, FeO – 6.5 wt%, Al₂Si₂O₅(OH)₄ – 4.00 wt%, SiO₂ – 5.00 wt% and CaSiO₃ – 0.34 wt%.

Table 1 – Reactions that take place in a stoichiometric (solid/solid) reactor (kiln) and thermodynamic data calculated with HSC for use in Aspen Plus® v7.2.

R #	Solid/solid extraction	ΔH_r (350 °C) kJ/mol	ΔH_r (450 °C) kJ/mol
R(2)	$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) = 3MgSO_4(s) + 2SiO_2(s) + 6NH_3(g) + 5H_2O(g)$	683.4	657.0
R(3)	$FeO(s) + (NH_4)_2SO_4(s) = FeSO_4(s) + 2NH_3(g) + H_2O(g)$	167.2	163.3
R(4)	$Al_2Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) = Al_2(SO_4)_3(s) + 2SiO_2(s) + 6NH_3(g) + 5H_2O(g)$	841.1	828.3
R(5)	$CaSiO_3(s) + (NH_4)_2SO_4(s) = CaSO_4(s) + SiO_2(s) + 2NH_3(g) + H_2O(g)$	116.3	112.5
R(6)	$(NH_4)_2SO_4(s) = 2NH_3(g) + H_2O(g) + SO_3(g)$	167.2	163.3
R(7)	$Mg_3Si_2O_5(OH)_4(s) + 3NH_4HSO_4(s) = 3MgSO_4(s) + 2SiO_2(s) + 3NH_3(g) + 5H_2O(g)$	346.0	312.2
R(8)	$FeO(s) + NH_4HSO_4(s) = FeSO_4(s) + NH_3(g) + H_2O(g)$	58.2	48.4
R(9)	$Al_2Si_2O_5(OH)_4(s) + 3NH_4HSO_4(s) = Al_2(SO_4)_3(s) + 2SiO_2(s) + 3NH_3(g) + 5H_2O(g)$	515.0	483.4
R(10)	$CaSiO_3(s) + NH_4HSO_4(s) = CaSO_4(s) + SiO_2(s) + NH_3(g) + H_2O(g)$	7.2	-2.416
R(11)	$NH_4HSO_4(s) = NH_3(g) + H_2O(g) + SO_3(g)$	320.9	309.4
Regeneration of ABS		ΔH_r (80 °C ^a) kJ/mol	
R(12)	$(NH_4)_2SO_4(aq) + H_2SO_4(l) = 2NH_4HSO_4(aq)$	-70.6	

^a 80 °C is the temperature at which the AS (aq) is obtained from Mg(OH)₂ precipitation.

Two different flue gases were considered: purified (i.e. after SO_x, NO_x, ash, etc. removal) flue gas from a conventional coal-fired (CCF) power plant, (13 vol.% CO₂, 71 vol.% N₂, 6 vol.% O₂, 10 vol.% H₂O) and likewise purified flue gas from oxyfuel coal-fired (OXY) plant (82 vol.% CO₂, 3 vol.% N₂, 5 vol.% O₂, 10 vol.% H₂O) (Fan et al., 2012; Spero, 2013; White and Allam, 2006). For the oxyfuel gas the N₂ and O₂ help the bed fluidization thus avoiding the need of recycling unreacted CO₂ back into the carbonator as it was earlier simulated (Romão et al., 2010) and shown to be a penalty.

The simulation model comprises five main simulation areas (defined in Fig. 1):

- 1) The solid/solid extraction, which presumably will happen in a downdraft reactor or (similar to what was done in the lab at ÅA) in a kiln, is modelled with a stoichiometric reactor and property model SOLIDS. The chemical reactions change according to the ammonium salt used and are shown in Table 1. The operating conditions, 1 atm and 350–450 °C are in agreement with experimental results obtained at ÅA (Romão et al., submitted for publication; Nduagu, 2012) and at ICES, A*Star (Highfield et al., 2012). Due to the lack of some thermodynamic data and properties of components in Aspen Plus® v7.2's database, the heat of reaction and enthalpy of formation of some components were calculated using HSC chemistry (2002) and are listed in Tables 1 and 2. Magnesium extraction efficiency was set at 60 or 80%.
- 2) The dissolution and separation (by precipitation) of the metals extracted in step (1). This stage is modelled by a series of Gibbs reactors (Dissolut, PP-I-Fe and PP-II-Mg) using an ENRTL-RK model for predicting the amount of NH₃ to raise the pH for selective recovery of the extracted elements. The model was adjusted/checked according to experimental data obtained during the last five–six years (Nduagu et al., 2012, 2013; Romão et al., 2010, submitted

for publication) and the pH for iron and magnesium precipitation was set at 8.5 and 12 respectively. The residue (unreacted/insoluble fraction of the solid products) is discarded and (in theory) may be further processed as it is quite rich in SiO₂. Magnesium conversion into Mg(OH)₂ efficiency was set at 100% which has been achieved experimentally (Sjöblom and Eklund, 2014).

- 3) The gas/solid carbonation area, which aims to represent a pressurized fluidizing bed reactor (PFB) was also simulated with a Gibbs reactor (model PENG-ROB) at 500 °C. Depending on the CO₂ concentration in the flue gas each case runs at a different carbonation pressure in order to keep the CO₂ partial pressure constant at 20 bar. The magnesium hydroxide carbonation efficiency was set at 90%.
- 4) The compression/expansion of the flue gases to be stripped from CO₂. Due to the high pressures required to keep a 20 bar p_{CO₂}, the inlet flue gas stream is compressed in a multistage compressor (model PENG-ROB) with the number of stages varying with the stream's final pressure. Each compressor was set at 85% of polytropic efficiency while the turbines in which the post-carbonation gas is de-pressurized were set at 85% isentropic efficiency.
- 5) The recovery of the ammonium salts AS/ABS from aqueous solutions for re-use as (wet) solid in step (1). AS is recovered in a crystallizer (properties model ENRTL-RK) at ~115–125 °C with a mechanical vapour recompression (MVR) system where the steam leaving the AS-crystallizer is compressed to 1.15 bar.

The regeneration of ABS is more challenging and two options were considered: (A) conversion of the crystallizer's product (always AS) into ABS by thermal decomposition. According to some authors (Galway and Brown, 1999) X-ray diffraction shows that at 160 °C (NH₄)₂SO₄ decomposes into the intermediate double salt (NH₄)₃H(SO₄)₂ which forms NH₄HSO₄ at 180 °C. At higher temperatures (≥200 °C) the NH₄HSO₄ decomposition proceeds to form NH₂SO₃H and H₂O. On the other hand a pilot-plant study on ammonia absorption – ABS regeneration process for SO₂ removal from flue gases (Wilhamson and Puschaver, 1977) concluded that a minimum temperature of 375 °C would be necessary for the ABS to be regenerated. HSC calculations (presented in Fig. 2) show that ABS is regenerated at 325–375 °C. Hence the ABS regeneration temperature was kept at 375 °C. The ammonia absorption pilot-plant study moreover concluded that

Table 2 – Thermodynamic data extracted from HSC for use in Aspen Plus® v7.2.

Component	$\Delta_f H$ (25 °C) (kJ/mol)
Serpentine	-4365.598
Ammonium sulphate (AS)	-1180.850
Ammonium bisulphate (ABS)	-1024.369

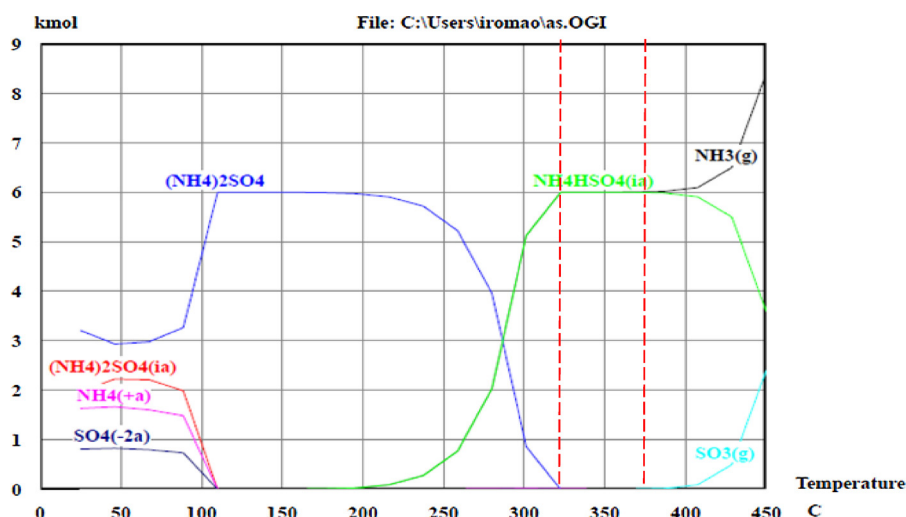


Fig. 2 – Thermal decomposition of ammonium sulphate. (Gibbs energy minimization software HSC).

thermal regeneration of ABS is not economically attractive. Besides this, at 280–300 °C, the AS forms a sticky grey melt that immediately hardens (solidifies) when it is taken out of the oven. It is then difficult to remove it from the reaction container and its dissolution in water is too slow.

Hence it was decided to pursue an alternate option (B), being addition of H_2SO_4 to the aqueous solution of AS to form ABS, according to reaction R(12) in Table 1. This step is modelled using a stoichiometric reactor. The ABS is then recovered in a crystallizer/evaporator at 180 °C (estimated with HSC – see Fig. 3, at 180 °C ~95% of the water is vaporized) also using a MVR system. This optimum temperature was experimentally confirmed by adding H_2SO_4 to an AS solution (with similar composition to the “final AS solution” in the process) at 80 °C. This was then placed in an oven for one hour at 160 °C, 180 °C and 200 °C. The results showed that 80%, 88% and 95% (respectively) of the water was evaporated. Still at 200 °C the material was difficult to remove from the crucible because ABS began to melt, hence the decision of crystallizing the ABS at 180 °C. The solid product was confirmed to be ABS due to its high hygroscopicity (see Figs. S1 and S2 in the supplementary material section).

A serious drawback of option (B) is that this introduces a sulphur stream that must be added to balance the

addition of ammonia in the precipitation stages (changing the initial ratio $\text{NH}_4^+/\text{SO}_4^{2-}$), and if this exceeds making up for ABS losses then the mineral carbonation process becomes a significant ABS producer at the same time (at up to 1 mol ABS produced per mol of CO_2 sequestered). A potential solution might be regeneration of the exact amount of ABS needed in the kiln while the remaining AS is recovered by crystallization (up to 1 mol AS is produced per mol of CO_2 sequestered). This AS product finds applications in agriculture, pharmaceutical and cosmetic industries.

The list of species included in the models may be found in Table S1 in the supplementary material section.

Mineral pre-processing stages like the crushing and grinding of the rocks were not included in the models. Nonetheless, the energy needed for this was included, as calculated via the Bond work Index using Bond’s equation (1) (Bond, 1952):

$$E_0 = W_i \left(\frac{\sqrt{F} - \sqrt{P}}{\sqrt{F}} \right) \sqrt{\frac{100}{P}} \quad (1)$$

where E_0 is an energy required for pulverization [kWh/t]; W_i is the work index [kWh/t], assumed to be 19 kWh/t (Tavares et al., 2009); F is the size of feed particles [μm], assumed to be

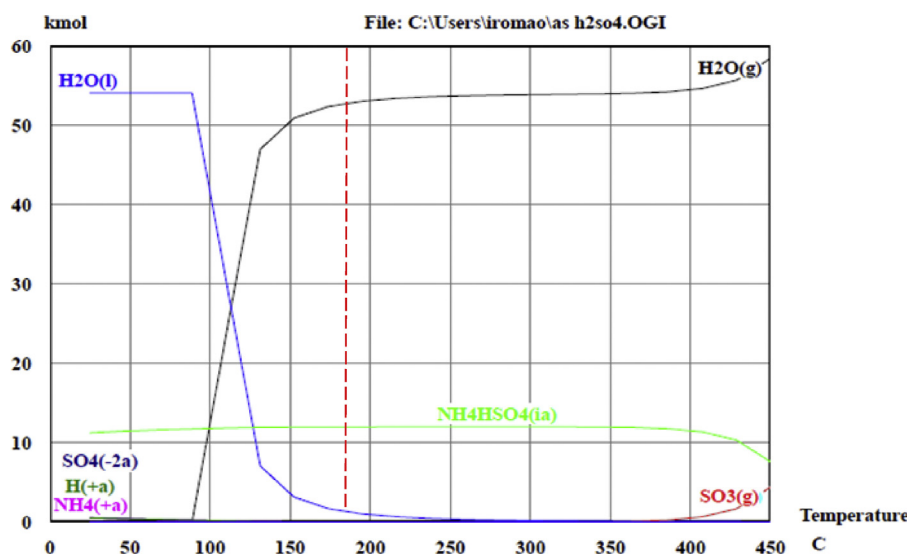


Fig. 3 – Regeneration of ABS by addition of H_2SO_4 . (Gibbs energy minimisation software HSC).

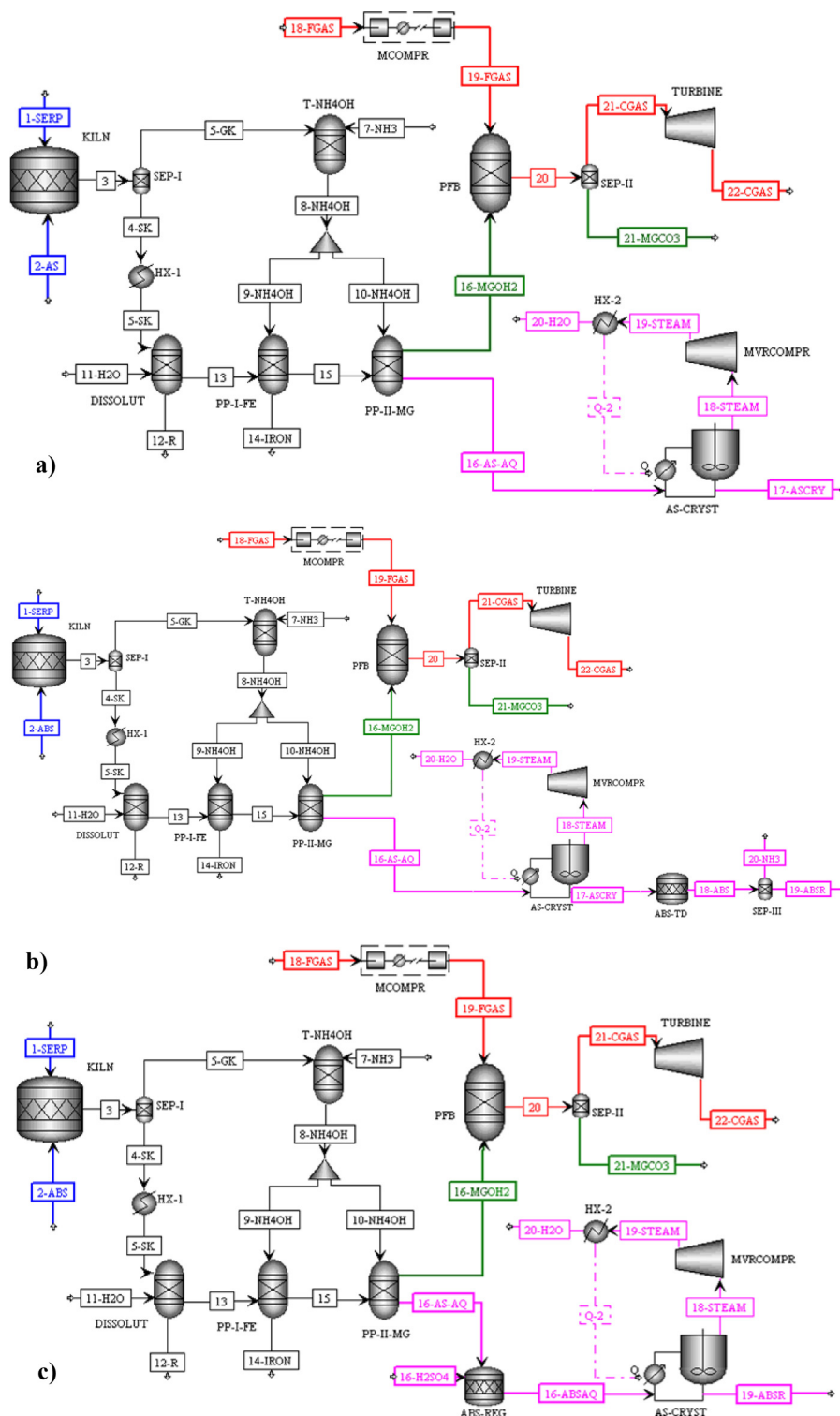


Fig. 4 – Representation of the overall model without heat integration. (a) Reaction with AS, (b) reaction with ABS and ABS recovery by thermal decomposition and (c) reaction with ABS and ABS recovery by addition of H₂SO₄.

2 cm; P is the size of the pulverized particles [μm], assumed to be 250 μm .

The overall Aspen Plus® v7.2 model (without heat integration) is simple and is shown in Fig. 4. It was necessary to build two different versions: one for the Mg extraction from rock reaction with AS and other for ABS. The main differences involve the chemical reactions between the rock and the ammonium salt (listed in Table 1) and the salt recovery method. Moreover, each model was optimized vis-à-vis the

inlet stream of flue gas (fired coal vs. oxyfuel combustion raw gas).

Twelve different scenarios were evaluated and are listed in Table 3. The Mg extraction efficiency is based on experimental data for Portuguese rock. The average extraction of Mg with AS is of the order of 60% (Romão et al., submitted for publication) thus the two cases (A2 and B2) aim merely to study the influence of Mg extraction on the exergy balance (Mg extraction values up to 80% have been obtained experimentally

Table 3 – Operating conditions for the twelve cases simulated in this paper.

Case #	A1	A2	B1	B2	C1	C2	C3	C4	D1	D2	D3	D4
Method	Operated on flue gas	Operated on flue gas	Operated on CO ₂	Operated on CO ₂	Operated on flue gas	Operated on flue gas	Operated on flue gas	Operated on flue gas	Operated on CO ₂	Operated on CO ₂	Operated on CO ₂	Operated on CO ₂
Flue gas	CCF	CCF	Oxyfuel	Oxyfuel	CCF	CCF	CCF	CCF	Oxyfuel	Oxyfuel	Oxyfuel	Oxyfuel
Serpentinite (kg)	550	550	550	550	550	550	550	550	550	550	550	550
Ammonium Salt (kg)	AS/825	AS/825	AS/825	AS/825	ABS/740	ABS/740	ABS/740	ABS/740	ABS/740	ABS/740	ABS/740	ABS/740
Mg extraction (%)	60	80	60	80	60	60	80	80	60	60	80	80
Kiln temperature (°C)	450	450	450	450	350	350	450	450	350	350	450	450
Water (t)	1.1	1.3	1.1	1.3	1.1	1.1	1.3	1.3	1.1	1.1	1.3	1.3
AS/ABS recovery			Crystallization		TD ^a	H ₂ SO ₄	TD	H ₂ SO ₄	TD	H ₂ SO ₄	TD	H ₂ SO ₄
Carbonation %	90	90	90	90	90	90	90	90	90	90	90	90
Pressure (bar)	130	130	25	25	130	130	130	130	25	25	25	25
Temperature (°C)	500	500	500	500	500	500	500	500	500	500	500	500

^a Thermal decomposition.

with AS with other rock (Aarnio, 2013; Sjöblom and Eklund, 2014)).

2.2. Pinch analysis and heat integration

A pinch analysis methodology (Coulson and Richardson, 1993) was used in combination with Aspen Energy Analyser[®] v7.2 to obtain optimal heat recovery and integration of the process/model. Unlike previous simulations (Romão et al., 2010, 2012b) the flue gas does not enter the CO₂ mineralisation plant in a compressed form nor is there an external heat source through integration with an industrial process (Romão et al., 2012a; Slotte et al., 2013). Finding the optimum heat exchanger network (HXN) for the process is somewhat challenging since the target is now to simultaneously minimize both electricity and heat loads. The composite curves, drawn with Aspen Energy Analyser[®] v7.2 are shown in Fig. 5a and b. The composite curve represented in Fig. 5a is based in the direct exportation of data from the model presented in Fig. 4a. At a first glance it looks like the process could be autothermal. However, when the match between solid streams is forbidden (avoiding solid/solid heat exchange) the opportunities for heat recovery and the demand of utilities change dramatically as seen in Fig. 5b.

Prior to designing of the HXN it was also noted that the 500 °C heat of the “CO₂ free” gas leaving the PFB should not be used for bringing other streams to their right temperature. In that case, the expansion of gases will result in a stream with unrealistic temperatures being calculated and a non-convergent turbine block in the simulations. Yet, in the case of the fired coal flue gas (see Fig. 6), due to its lower concentration of CO₂, the flow to be processed is quite high and the hot solid (23-MgCO₃) stream leaving the PFB is not enough to take the CCF flue gas to the desired temperature, hence the need to add an extra heat exchanger block (HX-7) to use part of the heat content of the stream leaving the PFB (23-CGAS), still at 125 bar.

The HXN found optimal for this process was thus obtained through an iterative process implementing the different designs recommendations provided by Aspen Energy Analyser[®] v7.2 in the Aspen Plus[®] v7.2 files. Two of the final simulation models (of a total of six) are presented in Figs. 6 and 7.

The direct expansion of the gases from the PFB does not allow for recovering all the energy input (as electricity) in the multistage compression. There is a “mass loss” (gas mass becomes solid mass) between the inlet and outlet gaseous streams in the PFB due to the carbonation reaction (Mg(OH)₂ + CO₂ → MgCO₃ + H₂O) since H₂O has a much lower molar mass than CO₂. This “mass loss” effect becomes higher as the CO₂ concentration in the flue gas stream increases. The clean (“CO₂ free”) flue gas expansion in two stages with a temperature boosting in between (provided by the hot solid products from kiln in HX-2 and HX-3 – see Figs. 4 and 5) proved to be the best design for recovery of the initial work input in the compression of gases.

3. Aspen Plus[®] V7.2 simulations results

The main results for each simulated case are presented in Table 4.

Electricity consumption (results presented in Fig. 8) does not seem to be a serious setback of the process especially

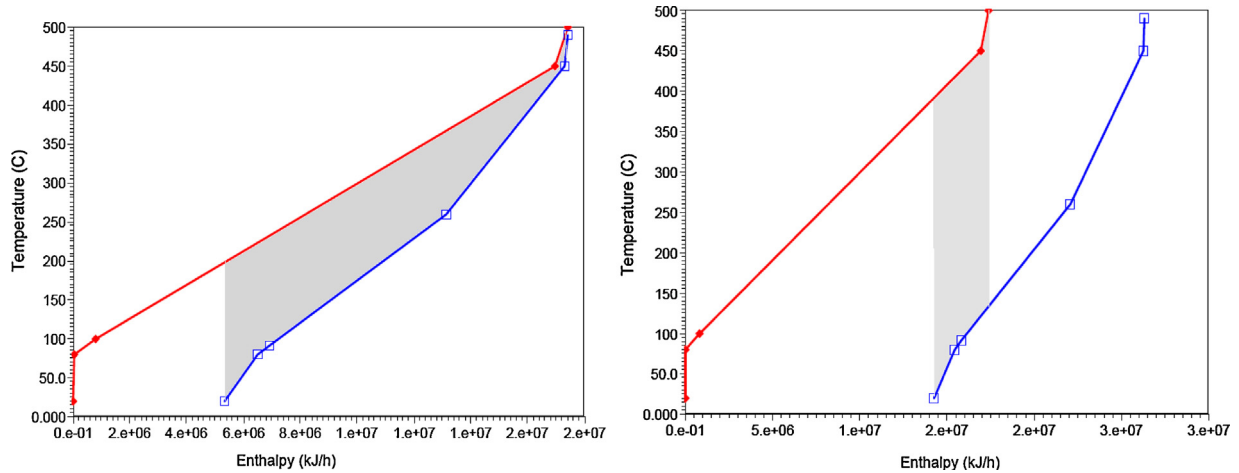


Fig. 5 – Cold and hot composite curves for (a) no restrictions in matching streams, (b) solid streams match forbidden.

when processing CCF flue gas. In these cases it is possible to recover up to ~90% of the electricity requirements of the process (multistage compression, MVR and crushing of the rock). The weaker performance of oxyfuel combustion flue gas is due to its high concentration of CO₂ leading to a greater “mass loss” between the inlet and outlet gas streams of the PFB carbonator. It should also be noted that in cases D1 and D2 the kiln (for Mg extraction from rock) runs at a lower temperature (350 °C) which reduces the gas temperature boost up between expansion stages, hence their lower percent of electricity recovery.

In general ABS gives better overall energy efficiency (see Fig. 9). Experimental results (Romão et al., submitted for publication) showed that ABS extracts more magnesium from the serpentinite rock material with the subsequent advantages of using less serpentinite rock producing less waste while binding more CO₂ per kg of rock processed. But looking closely to cases A2 versus C3 (where the only difference in the kiln is the fluxing salt), the main reason for the better energy efficiency when using ABS results from the fact that the reactions between ABS and rock are much less endothermic (as one can confirm in Table 1) and allow for a reduction of more than 40% in the kiln’s heat requirements (see Fig. 10).

As for the ABS recovery route, clearly its regeneration by thermal decomposition presents a considerable penalty requiring 60–75% of the total heat consumption compromising the process.

On the other hand, as one can see from Fig. 9, the regeneration with H₂SO₄, is energetically much more favourable. Nonetheless there is problem of over flooding the system with sulphur because according to R(12) each mol of AS will be converted in 2 mol of ABS. The simulations do not consider losses of sulphur and ammonia that will happen mainly in the filtration stages. An option to overcome this issue is to add H₂SO₄ enough to simply make up for losses. The process would then require two make-up streams of NH₃ and H₂SO₄ in lieu of ABS and in kiln, instead of only AS or ABS, a mixture of AS/ABS. This improves the extraction of Mg in the kiln with a lower energy penalty (but without over flooding the system with sulphur and ammonia)

The initial motivation for the AA process was the exothermicity of the reaction R(1)

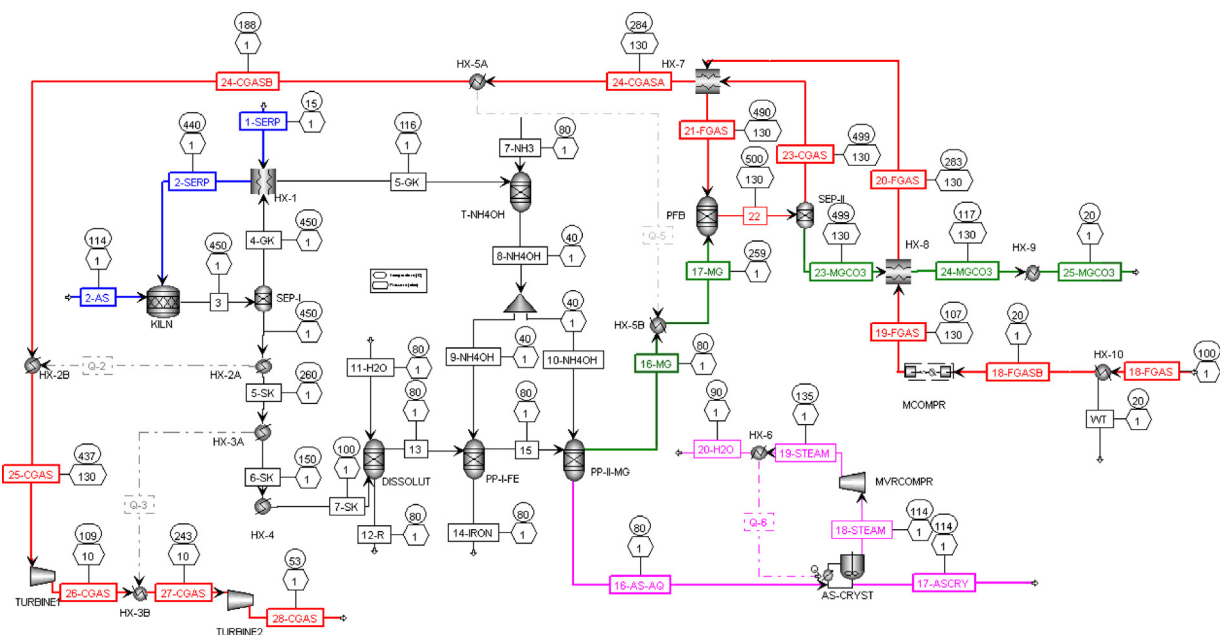
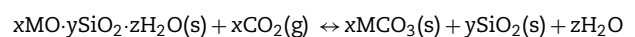


Fig. 6 – Model for case 1: combination of AS with FC flue gas. Cases (A1 and A2). ○ – temperature (°C), ◻ – pressure (bar).

Table 4 – Materials and exergy balance.

Case #	A1	A2	B1	B2	C1	C2	C3	C4	D1	D2	D3	D4
CO ₂ fixation (%)	93.9	95.8	95.9	95.1	93.9	93.9	95.8	95.8	95.9	95.9	95.1	95.1
CO ₂ captured (kg)	119	159	119	159	119	119	159	159	119	119	159	159
MgCO ₃ (kg)	246	328	246	328	246	246	328	328	246	246	328	328
t _{rock} /t _{CO₂}	4.62	3.46	4.62	3.46	4.62	4.62	3.46	3.46	4.62	4.62	3.46	3.46
<i>Reactants (kg/kgCO₂)</i>												
AS	6.93	5.20	6.93	5.20	–	–	–	–	–	–	–	–
ABS	–	–	–	–	6.00	6.00	4.50	4.50	6.00	6.00	4.50	4.50
ABS regeneration (NH ₃ /H ₂ SO ₄)	–	–	–	–	–	1.00/5.00 ^a	–	0.70/3.80 ^a	–	1.00/5.00 ^a	–	0.70/3.80 ^a
<i>Exergy balance (GJ/tCO₂ captured)</i>												
<i>IN</i>												
Kiln, heat (350–450 °C)	7.04	5.90	7.04	5.90	1.91	3.19	2.45	3.52	1.91	3.52	2.44	3.52
AS crystallization (115–125 °C)	0.07	0.09	0.07	0.09	0.07	–	0.09	–	0.07	–	0.09	–
ABS thermal decomposition (375 °C)	–	–	–	–	5.83	–	4.37	–	5.83	–	4.37	–
ABS crystallization (180 °C)	–	–	–	–	–	0.83	–	0.59	–	0.83	–	0.59
<i>Electricity</i>												
Multistage compressor	2.59	2.54	0.29	0.27	2.59	2.59	2.54	2.54	0.29	0.29	0.27	0.27
MVR	0.31	0.31	0.31	0.31	0.31	0.27	0.31	0.27	0.31	0.27	0.31	0.27
Crushing	0.32	0.24	0.32	0.24	0.32	0.32	0.24	0.24	0.32	0.32	0.24	0.24
Total	3.22	3.09	0.92	0.82	3.22	3.18	3.09	3.06	0.92	0.88	0.82	0.78
<i>OUT</i>												
HG heat (500 °C) - carbonator	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18	–0.18
MG heat (150–450 °C)	–	–0.39	–3.42	–2.53	–1.00	–0.49	–0.80	–0.36	–2.49	–2.41	–1.90	–1.55
LG heat (<150 °C)	–1.85	–1.71	–1.03	–1.01	–2.57	–3.52	–2.51	–3.27	–1.84	–2.53	–2.56	–3.33
<i>Electricity</i>												
Turbines	–2.76	–2.75	–0.39	–0.37	–2.52	–2.52	–2.70	–2.70	–0.39	–0.39	–0.37	–0.37
Total exergy	5.09	3.82	2.70	2.48	4.47	–0.16	3.42	0.29	3.31	–1.09	2.48	–0.96

^a This value drops to half if only the exact amount of ABS (needed for Mg extraction) is regenerated.

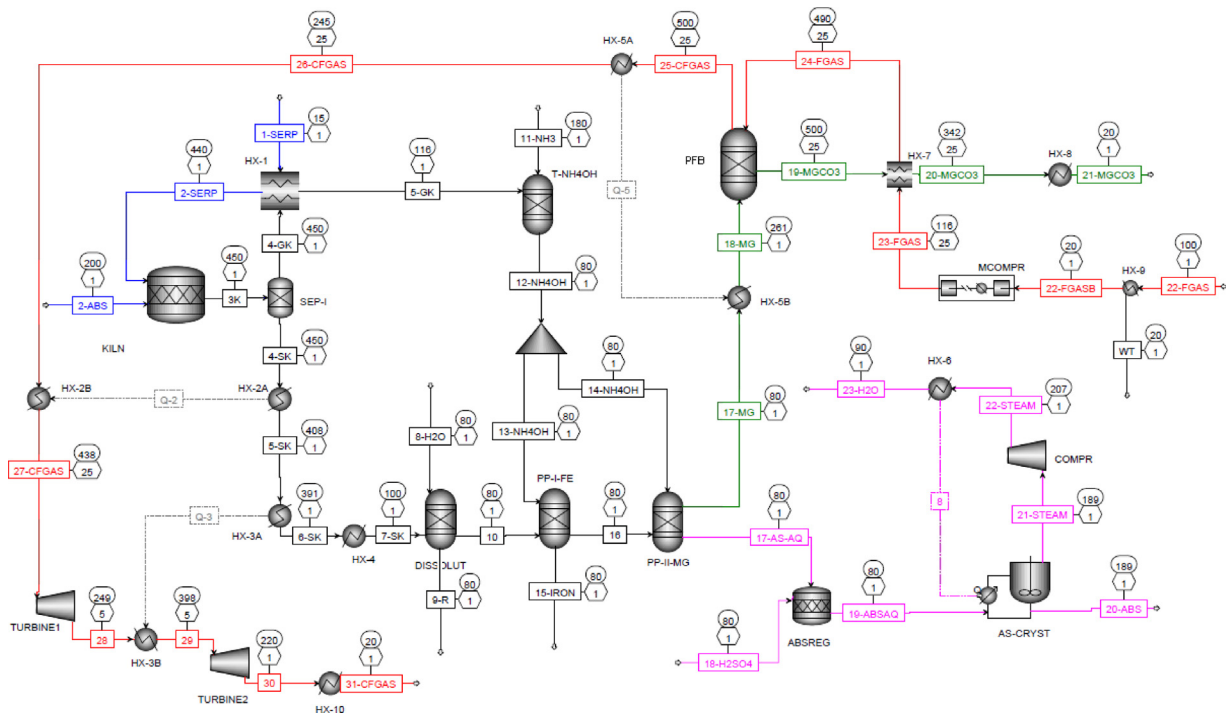


Fig. 7 – Combination of ABS with oxyfuel flue gas. Cases (D1 and D2). ○ – temperature (°C), □ – pressure (bar).

and after recognizing the fact that this carbonation could not be done in one step, it was expected that the 500–550 °C heat released in the PFB carbonator could cover as much as possible for the 400–450 °C heat needed to extract the Mg from the rock material. As one can see in Fig. 10, the exergy of the carbonator is insignificant (2.5–5.7%) when compared to that necessary in the kiln (and for ABS recovery by thermal decomposition).

The process has a considerable amount of exergy but unfortunately at the wrong (too low) temperature as predicted by the composite curve in Fig. 3b which is also why the exergy balance is sometimes negative (cases C2, D2 and D4 which do not have the energy penalty of the ABS thermal decomposition – see Fig. 10) and therefore unsuitable for the process. Hence, integration of MC with industries that typically generate HG waste heat (steel, ceramics, cement, etc.) is of much benefit (Romão et al., 2012a; Slotte et al., 2013). Note that ABS achieves good Mg extraction at 350 °C whereas the reaction of

serpentine with AS at $T < 400$ °C results in much lower extraction of Mg and this may be the tipping point for choosing the fluxing salt.

Looking closer to Portugal, storage of CO₂ separated at the CIUDEN Oxyfuel combustion plant near Ponferrada, north-west Spain, at 160 km from Donai, Bragança, may be an interesting source-sink combination for large-scale CCUS/CCS (Lupion et al., 2013).

In some cases, the energy penalty that results from CO₂ capture and storage can be reduced by running this only at night, or during low electricity demand hours. Instead of operating at partial load and lower efficiency, the same electricity output is produced day round, compensating for the energy penalty related to CCS when electricity demand is lower.

This MG and LG waste heat is well suited for district heating (especially for cold countries) but in the case of warmer countries it may be justifiable to use organic rankine cycle systems to recover it as work (Bundschuh and Hoinkis, 2012).

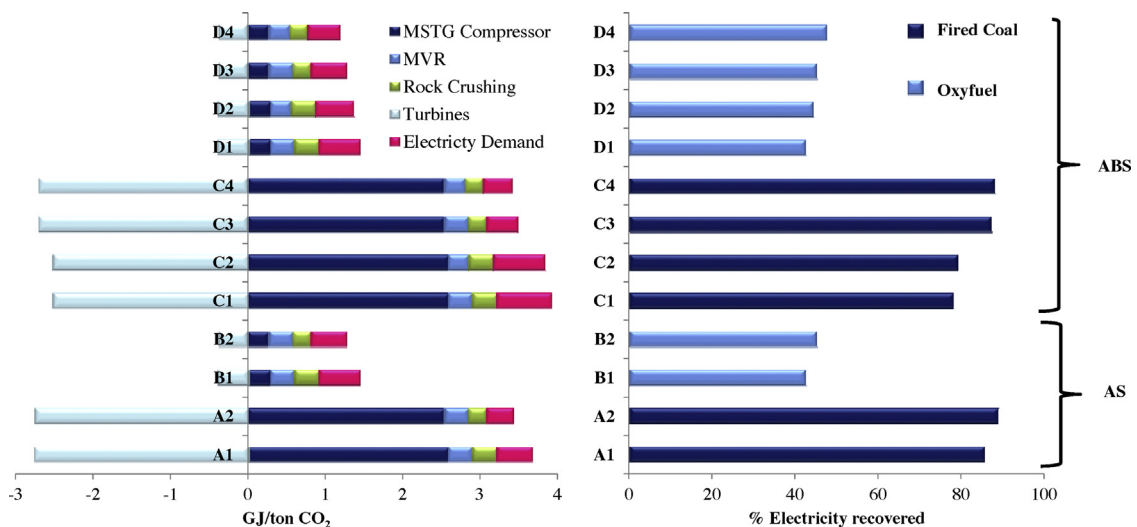


Fig. 8 – Electricity consumption/production for each simulated case.

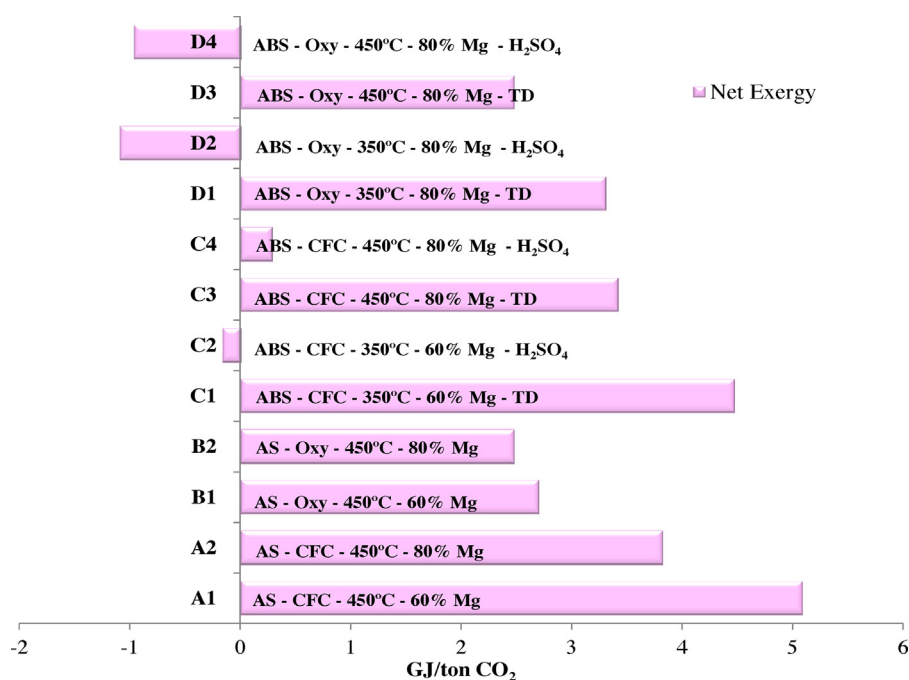


Fig. 9 – Net exergy input requirements for each simulation case. TD – thermal decomposition of AS into ABS at 375 °C.

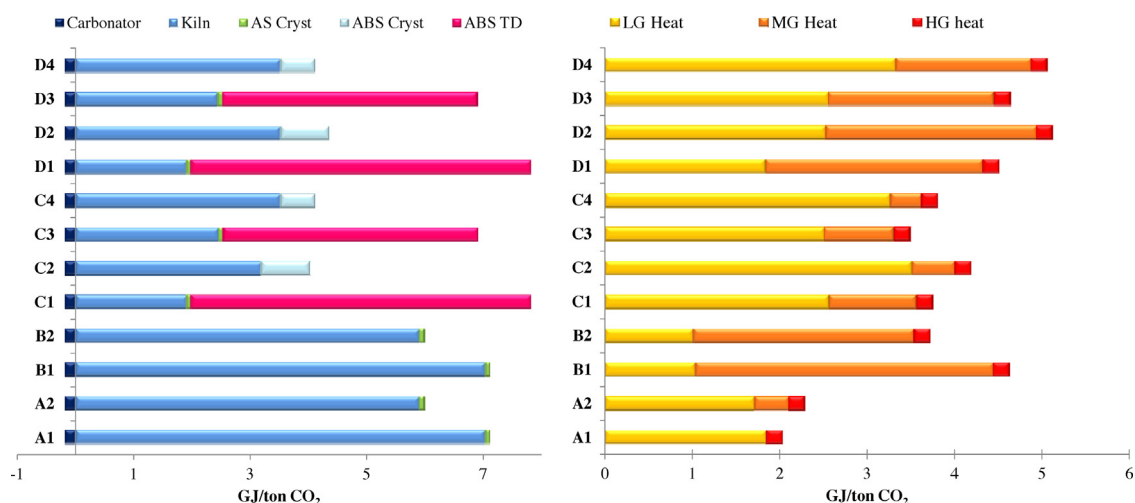


Fig. 10 – Heat consumption/production for each simulated case. TD – thermal decomposition of AS into ABS at 375 °C. LG: low grade heat, $T < 150$ °C; MG: medium grade heat, $150 < T < 450$ °C; HG: high grade heat, $T > 450$ °C.

4. Conclusions

Several process routes for binding CO₂ to Mg extracted from Portuguese serpentinite rock were analyzed for minimized energy and chemicals use per tonne CO₂ fixed. Aspen Plus®v7.2 combined with pinch analysis was used for the simulations that produced data for process route comparison using exergy analysis.

The AS route in general requires more exergy and more rock to fix the same amount of CO₂, 2.48–5.09 GJ/t CO₂ captured, while ABS route with ABS recovery by thermal decomposition of AS requires 2.48–4.47 GJ/t CO₂ captured. Still this regeneration scheme presents operational problems due to the energy penalty it presents and the corrosive nature of molten ABS. The regeneration of ABS by addition of H₂SO₄ results in a negative exergy balance (mainly at the expense of low grade heat). Also the mass balance for the ABS route shows that regeneration with H₂SO₄ will saturate the process with sulphur making the process a mineral carbonation plant and an

AS or ABS producer. A possible solution is to work with a mixture of AS/ABS in the kiln benefiting from a more efficient extraction of Mg with lower energy input needs.

Direct carbonation of flue gases removes the need for costly and also energy intensive CO₂ separation steps. In general, using ABS as the flux salt and oxyfuel combustion flue gas involves lower heat input needs.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at [doi:10.1016/j.chemd.2014.05.016](https://doi.org/10.1016/j.chemd.2014.05.016).

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PAPER V

Proceedings of ECOS 2012

(2012)

Carbon dioxide storage by mineralisation applied to a lime kiln

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Abstract:

This paper describes a design, for a pilot-scale application, of a two-staged process that is under study at Åbo Akademi University (ÅA), for Carbon dioxide Storage by Mineralisation (CSM). The ÅA route implies the production of brucite (besides Ca- and Fe- based by-products) from a magnesium/calcium silicate rock, using recoverable ammonium sulphate (AS), followed by carbonation of the Mg(OH)₂ in a pressurised fluidised bed at ~ 500°C, 20-30 bar CO₂ partial pressure. An assessment is reported for operating the CSM process on waste heat from a limekiln (lime production: 210 t/day) in Pargas, Southwest Finland, i.e. without external energy input apart from what is needed for crushing the rock to the required particle size (a few % of the overall CSM process energy requirement) and compressing the flue gas to be treated. Part of the off-gas from the limekiln (CO₂ content ~21%-vol) will be processed without a CO₂ separation step. The feature of operating without CO₂ separation makes CSM an attractive and cost-competitive option when compared to conventional CCS involving underground storage of CO₂. An exergy analysis is used to optimise process layout and energy efficiency, and at the same time maximise the amount of CO₂ that can be bound to MgCO₃ given the amount of waste heat available from the kiln. Also, experimental results are reported for producing Mg(OH)₂ (and Fe,Ca(OH)₂) from local rock material.

Keywords:

CO₂ mineral sequestration, Scale-up, Lime kiln.

1. Introduction

1.1 CO₂ mineralisation

For Finland, carbon dioxide storage by mineralisation (CSM) was identified as the only option for CCS (carbon dioxide capture and storage) application. It is a permanent storage option and has an estimated storage potential that is much larger than underground storage as pressurized CO₂ [1-2], the currently most intensively studied option for CO₂ disposal. The purpose of CSM is to promote CO₂ fixation by metal oxides into thermodynamically stable carbonates while benefiting of the exothermicity of the carbonation reaction:



Magnesium in particular is abundant in the earth's crust, as silicates such as serpentinite and olivine. These reactions occur in nature over geological timescales (hundreds of thousands of years). Research has focused on improving the reaction rates by treating the mineral rock by thermal, mechanical or chemical means [1-4]. Due to the exceptionally large scale of CCS processes, all additives must be recovered, and the energy input minimised.

A process under development at ÅA uses recoverable ammonium sulphate (AS) salt to extract Mg from grinded serpentinite rock, at elevated temperatures. The extraction has shown conversions of up to 70 % of Mg into either reactive $\text{Mg}(\text{OH})_2$ or MgSO_4 , depending on the desired intermediate. $\text{Mg}(\text{OH})_2$ reacts directly with CO_2 under elevated temperature in a pressurised fluidised bed. The ÅA process may also be used as a scheme to capture the CO_2 directly from a flue gas stream. The direct mineralisation of flue gas instead of separated and compressed CO_2 , eliminates the need of expensive and energy intensive processes to isolate and compress CO_2 , thus significantly lowering the materials and energy requirements for the overall CCS process chain. Besides, the simultaneous CO_2 separation and capture avoids the main risks associated with geological storage (potential leakage of CO_2 into the atmosphere) and the costs associated with monitoring [5]. Hence, CSM is a promising, safe and permanent CO_2 fixation route and for that reason has been studied at ÅA since 2006.

In addition, metal and mineral processing and papermaking sectors (but not the power sector) have shown much interest in using CSM for CO_2 emissions mitigation. The prospect of simultaneously making use of and (in some cases) upgrading/stabilising process' by-products and waste materials (ashes e.g) is another interesting benefit [6,7].

This paper explores the possibility of running the ÅA CSM process on waste heat provided by a limekiln (lime production: 210 t/day) in Pargas, Southwest Finland (Nordkalk Corporation) and assess the performance of a pilot plant, with direct mineralisation of flue gases. Nordkalk is one of the European leading producers of lime emitting a total of 0.79 MtCO_2/a [8]. Along with the limestone mining comes significant amounts of diopside. The use/upgrading of this by-product by CSM is discussed at the end of this paper.

The serpentinite rock material, used in this particular simulation, comes from a nickel mine located in Hitura, Central Finland, 500 km from Pargas. This mine has significant resources of magnesium silicate rocks (<1000 Mt) and experimental tests show that its serpentinite material is suitable for the ÅA process [9].

1.2 – Process description

The serpentinite rock reacts with ammonium sulphate (AS) and water at 450°C and atmospheric pressure in order to produce XSO_4 salts ($\text{X}=\text{Mg},\text{Ca},\text{Fe}$), as first described by Nduagu [9-11]. During the reaction considerable amounts of NH_3 , SO_3 and water are released. The solids are put in water and the insoluble fraction (mainly unreacted serpentinite and SiO_2) is discarded. The NH_3 produced in the first step is used to raise the pH of the aqueous solution to ~8-9 in order to precipitate the iron and calcium in the form of hydroxides. These are separated and possibly redirected to the steelmaking industry creating the opportunity to reduce the net CO_2 emissions and replace raw materials [12]. Once more, using the NH_3 produced in the first step, the pH of the aqueous solution is raised to ~10-12 and the magnesium precipitates to form $\text{Mg}(\text{OH})_2$. AS is recovered from the residual solution and the $\text{Mg}(\text{OH})_2$ is carbonated at 500°C and 20 bar of CO_2 partial pressure, in a pressurised fluidised bed (PFB) reactor. The carbonation method is described in more detail by Fagerlund [13-15]. The gas entering the carbonator may be a pure stream of CO_2 but may also be the whole flue gas from a process. The heat released in the carbonation reactor may provide some of the energy needed to heat the serpentinite rock, aiming at an auto-thermal process.

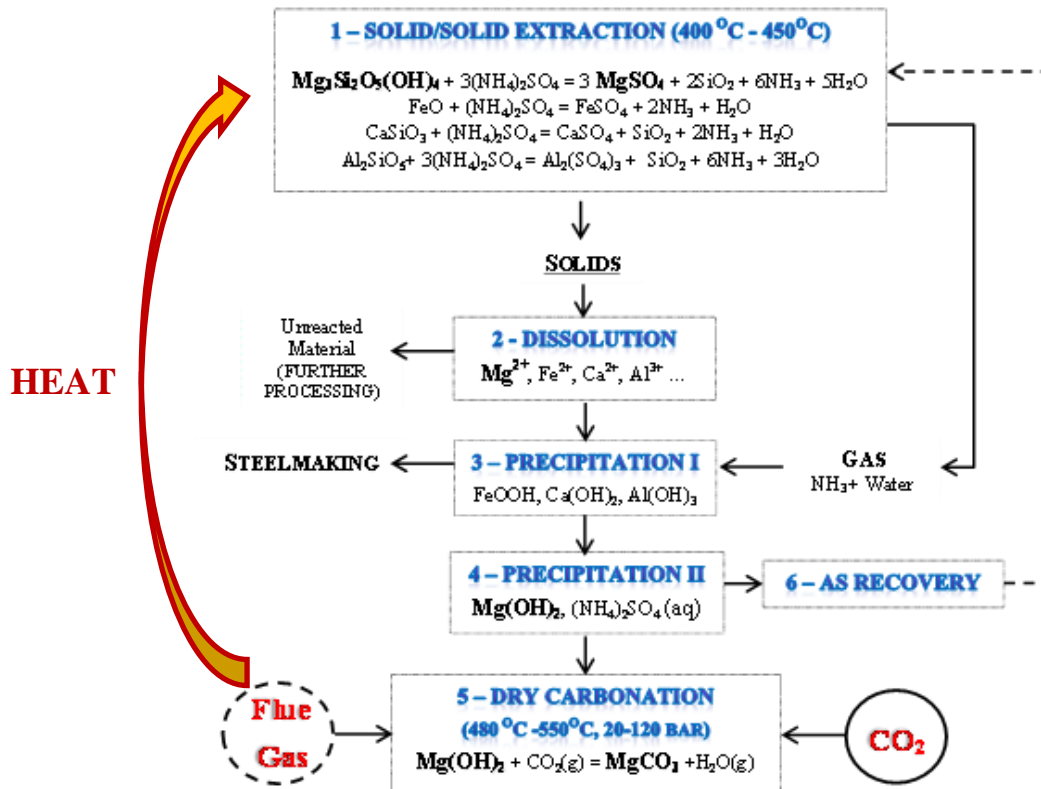


Fig. 1. Scheme and main reactions of the magnesium silicates' carbonation process. Adapted from [15]

2. Aspen Plus ® simulations – Mineralisation of serpentine with flue gas

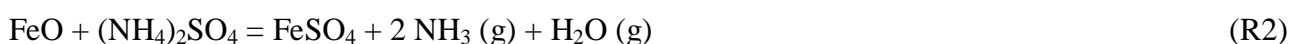
2.1. Aspen Plus ® model – Hitura's (Finland) serpentine

The ÅA CSM process was simulated using Aspen Plus® Software. The model follows the same scheme as the ones presented in earlier publications [12,16-17] but differs on the CO₂ inlet stream of the carbonation step and on the source of heat supplied to the endothermic stages.

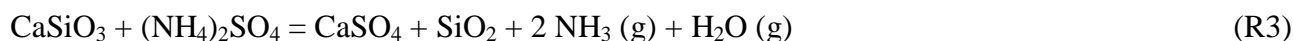
The S-DECOMP block represented in the Aspen Plus model (Figure 3) simulates the Solid/Solid extraction reactor. It operates at 440°C and atmospheric pressure. Experimental results, on Portuguese samples, show that the presence of water greatly enhances the rate of magnesium extraction and lowers the temperature by ≈50°C compared to reacting dry matter. [16-17].

In this block, AS is mixed with Hitura's serpentinite (86% Mg₃Si₂O₅(OH)₄, 13% FeO, 1% CaSiO₃) and water at a ratio of 3:2:1. In the simulations 80% of Magnesium¹, 60% of iron and 100% of calcium are assumed to be extracted.

It is expected that, under the referred operating conditions, the following reactions occur:



¹ Although experimental results with Hitura's samples so far had a maximum of 74% of Mg extraction.



As the large amounts of NH_3 and water released are cooled, the NH_3 dissolves in the water to produce a 30-40% solution of NH_4OH (Block TANK 1). A small make-up stream of NH_3 or NH_4OH will be necessary due to possible losses in the overall process. The appropriate temperature for this vessel depends on the amount of water present in the gases and, in this case, it was estimated to be $\sim 40^\circ\text{C}$ (roughly the boiling temperature of an aqueous solution with $\approx 30\%$ NH_3). The NH_4OH produced in this vessel is later used to cautiously raise the pH in both precipitation steps (blocks PPI and PPII). After cooling, the hot solid from the S-DECOMP block is dissolved in water (block DISSOLUT). Unreacted serpentine, iron oxide, wollastonite and insoluble reaction products (silica, e.g) settle and are separated, most likely by a filtration process, forming the RESIDUE. In the aqueous solution at $\sim 80^\circ\text{C}$, the XSO_4 salts formed in the first step are converted to X^{2+} species.

For the sequential precipitations, pH is the most important operation parameter. The solution must be rigorously kept at $\text{pH}=9-9,5$ (block PPI) so that only iron and calcium are precipitated and, consequentially, magnesium recovery is maximised in the second precipitation stage (block PPII) at a pH of $\sim 9,5-11,5$. This pH may slightly vary depending on the mineral and reaction conditions. The iron is precipitated in the form of FeOOH (goethite), (although in the simulation $\text{Fe}(\text{OH})_2$ is used due to some database problems in Aspen Plus®) calcium as $\text{Ca}(\text{OH})_2$ and magnesium as $\text{Mg}(\text{OH})_2$. The NH_3 present in the gases from the Solid/Solid Reactor may not be enough to increase the pH of the second precipitation stage to 11,5. For that reason it may be necessary to add NH_3 to the block PPII.

Although AS is a cheap chemical (cheaper than ammonia or sulphuric acid) its recovery is compulsory, not only for environmental reasons but also to make the process economically viable. After being separated from the precipitated $\text{Mg}(\text{OH})_2$, the AS is recovered from the aqueous solution through a concentration/crystallisation process (block EVAPORAT). The recovered wet AS is then fed back to S-DECOMP reactor, thereby closing the AS cycle and process loop.

The $\text{Mg}(\text{OH})_2$ is directly carbonated with flue gas from the limekiln, in a pressurised fluidised bed (block CARBONAT). In order to achieve a CO_2 partial pressure of ~ 20 bar, the flue gas, with $\sim 21\%$ -vol CO_2 , must be compressed to at least 80 bar. The block MSCOMPRESS (multistage compressor) represents a series of 6 polytropic compressors with 80% of efficiency. $\text{Mg}(\text{OH})_2$ reacts with gaseous CO_2 to form MgCO_3 and water vapour at 500°C and a total pressure of 80 bar. The stream leaving the CARBONAT reactor contains $\text{MgCO}_3(\text{s})$, $\text{H}_2\text{O}(\text{g})$, O_2 , N_2 and unreacted $\text{Mg}(\text{OH})_2(\text{s})$ and $\text{CO}_2(\text{g})$. The gases are separated from the solids (most likely) by a cyclone. The $\text{MgCO}_3/\text{Mg}(\text{OH})_2$ solid product mix may be re-circulated until the $\text{Mg}(\text{OH})_2$ content becomes sufficiently low (few %). Decompressing and cooling the gaseous stream leaving the separation unit allows for the recovery of some of the energy input for the initial flue gas compression. This stream contains water vapour, produced in the carbonation reaction.



In order to avoid the presence of a liquid phase inside the isentropic expansion turbine, the decompression cannot go under ~ 5.6 bar. The rest of stream's exergy/heat content is recovered in a heat exchanger. The main assumptions taken to design the Aspen model are summarized in Table 1.

In this simulation, the heat required for this process is provided by $\sim 10.3 \text{ m}^3\text{n}$ [7] of flue gases coming from the limekiln located in Pargas. Currently, the heat content of those gases is utilised to supply district heating for the city of Pargas. In the Aspen Plus® model the flue gas is defined as two different utilities. Utility FG500 is the flue gas leaving the limekiln at 500°C and is used to provide heat for the Mg, Ca and Fe elements extraction and to pre-heat the CO_2 rich gas entering the carbonator. After cooling to 440°C , the flue gas FG440 is then used to provide heat for the

(raw) materials pre-heating and AS recovery. The specifications for these two utilities are listed in Table 2.

Table 1. Main assumptions taken in the Aspen Plus ® model

Block	Assumption
S-SDECOM	Operating conditions: T= 440°C, P=1bar AS/S/W=3:2:1 Extraction %: Mg = 80%, Fe = 60%, Ca = 100%
DISSOLUT	T=80°C; Total conversion of XSO ₄ species to X ²⁺
TANK 1	T=40°C; Complete dissolution of NH ₃ into water producing a 30~40% solution of NH ₄ OH
PPI	Total precipitation of Fe and Ca as Fe(OH) ₂ and Ca(OH) ₂ pH =9-9.5; T=30°C
PPII	Precipitation of Fe and Ca as Fe(OH) ₂ and Ca(OH) ₂ pH =9.5-11.5; T=30°C
CRYST	Water is evaporated so that the recovered product has 75% -w/w of AS and 25 %-w/w of water.
CARBONAT	Carbonation with Flue Gas from the limekiln p _{CO2} ~20 bar, P=80 bar 90% of Mg(OH) ₂ carbonation according to reaction R4
MSCOMPRES	6 polytropic compressors with 80% efficiency and intercoolers
TURBINE	Isentropic; Decompression to ~5.6 bar

Table 2. Data for the limekiln's flue gas defined as a utility in the Aspen Plus ® model

Utility ID	Composition (mol %)	T _{IN} (°C)	T _{OUT} (°C)
FG500	H ₂ O 5.9	500	460
	CO ₂ 21.7		
FG440	O ₂ 6.9	440	350
	N ₂ 65.5		

2.2. Results – Mass and exergy

The aim of this simulation is to evaluate the performance of a pilot scale mineral carbonation plant running on waste heat from the limekiln. In order to process 600 kg/hr of flue gas (7 m³ at 500 °C and 80 bar) i.e., ~190 kg of CO₂, 500 kg/hr of serpentinite and 750 kg/hr (later recovered) of AS are required. The amounts of residue produced are quite significant, 298 kg/hr. However, this material is very rich in SiO₂ (>70%) making its future processing for Si recovery an auspicious possibility. Ideally, the ~36 kg/hr of iron and calcium hydroxide products are redirected to the steelmaking industry. Although this appears to be a modest quantity of by-product, note that, at a larger scale, the mineralisation of, e.g., all the CO₂ emissions of a single steel company operating in Finland (Ruukki), is enough to replace up to 18% of iron ore raw material with FeOOH [12].

Out of the 500 kg/hr of processed serpentinite it is possible to produce 275.3 kg/hr of Mg(OH)₂. Assuming a 90% carbonation efficiency, 275 kg/hr of MgCO₃/Mg(OH)₂, with a content of 90%

MgCO₃, are produced. Figure 2 presents a schematic diagram of the process including mass balance results.

Table 3 presents the detailed exergy results for each block simulated in Aspen Plus®. Flue gas provides heat to all endothermic units (including AS recovery) making the process auto-thermal while not compromising the district heating supply to Pargas. Partly this is because the ÅA route generates itself significant amounts of low temperature heat suitable for district heating.

Clearly, the most energy intensive block is the extraction of the various (Mg, Ca, Fe...) elements from serpentinite. The heat needed for the Mg extraction is supplied by gas leaving the limekiln at 500°C. After this, the flue gas is further used to pre-heat (raw) materials and provide heat for the AS recovery.

The energy needed for crushing the rock was estimated using a Bond index of 19 kWh/t [18] and equation (1):

$$E_0 = W_i \cdot \left(\frac{\sqrt{F} - \sqrt{P}}{\sqrt{F}} \right) \cdot \sqrt{\frac{100}{P}} \quad (1)$$

where:

- E₀: energy required for pulverisation [kWh/t];
- W_i: work index [kWh/t];
- F: size of feed particles [µm], assumed to be 2 cm;
- P: size of the pulverized particles [µm], assumed to be the average particle size of the samples used in earlier experiments, 100 µm [8-10,14-16].

The main drawback in this process is the energy required for the flue gas compression, even though ~66% of this energy input may be recovered later on while decompressing gaseous products from the carbonator (CARBONAT), where the CO₂^{gas} is converted to H₂O^{vapor}. Table 2 presents the overall exergy input needed for flue gas compression and crushing of the serpentinite rock. The final value for the overall exergy input for this is 0.71MJ/kg CO₂ captured.

Table 2. Exergy input for the gases compression and raw materials crushing.

	MJ/hr	MJ/kg CO ₂
Compressor	280	1.52
Turbine	-185	-1.01
Crushing	35	0.19
Total	131	0.71

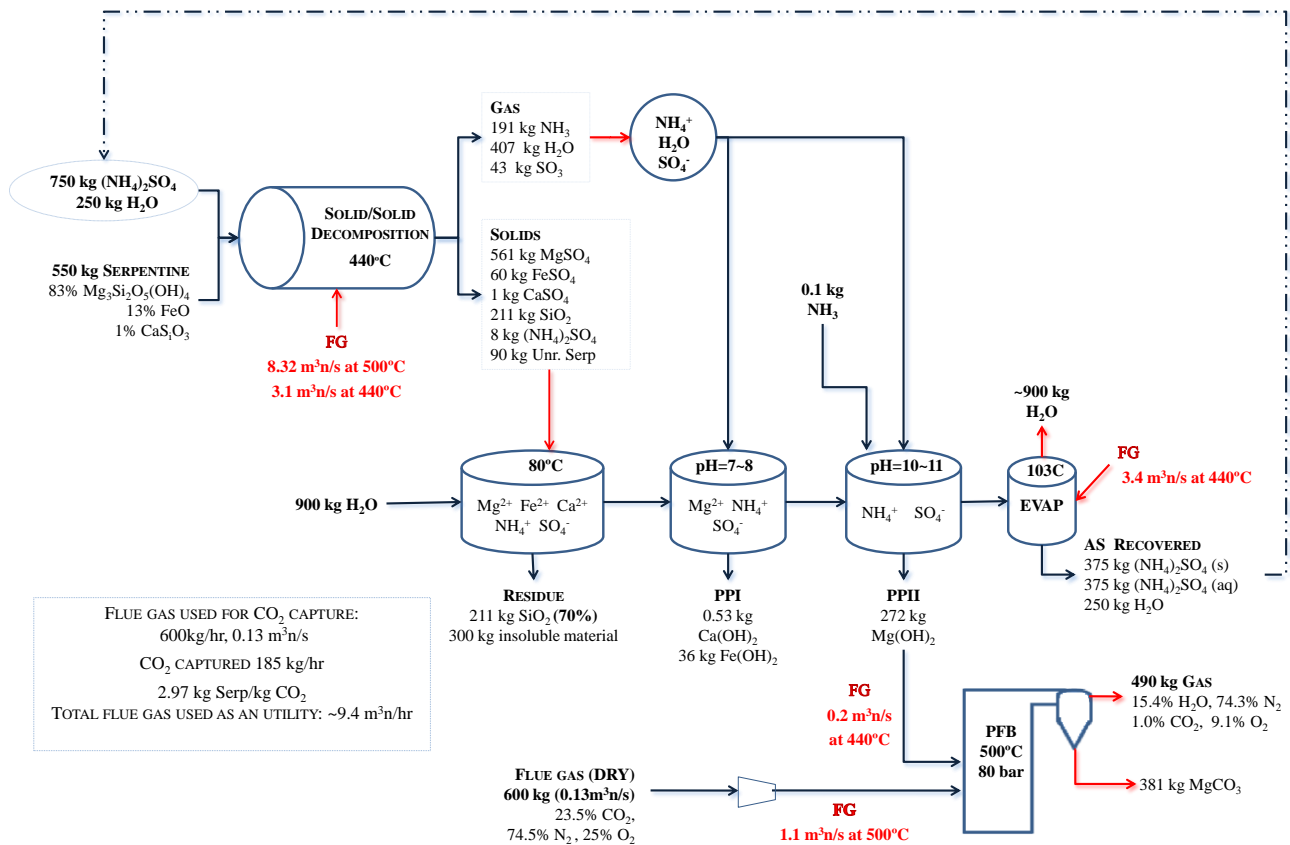


Fig. 2. Mass results for 80% magnesium extraction and 90% Mg(OH)₂ carbonation using Hitura nickel mine serpentinite rock (kg values are for one hour operation).

3. Mineralisation of diopside with flue gas

This section assesses the applicability of the ÅA process using the in-site available diopside as the metal oxide source, instead of nickel mine tailing from Hitura (500 km from Pargas). The Aspen Plus® model presented in section 2 simulates a case where serpentinite rock is used as the mineral source for Mg. An alternative would be to use a diopside material that is produced by Nordkalk as by-product from its limestone quarry. Therefore the reactivity of this material was assessed by the performing of some experimental tests using the same experimental procedure developed by Nduagu [9], before embarking on further Aspen Plus® simulations.

3.1. Diopside characterisation and experimental work.

A sample of diopside provided by the Nordkalk's facility located in Pargas, was ground to obtain a size distribution of 125-250 µm and analysed using X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). The results are reported in Table 4.

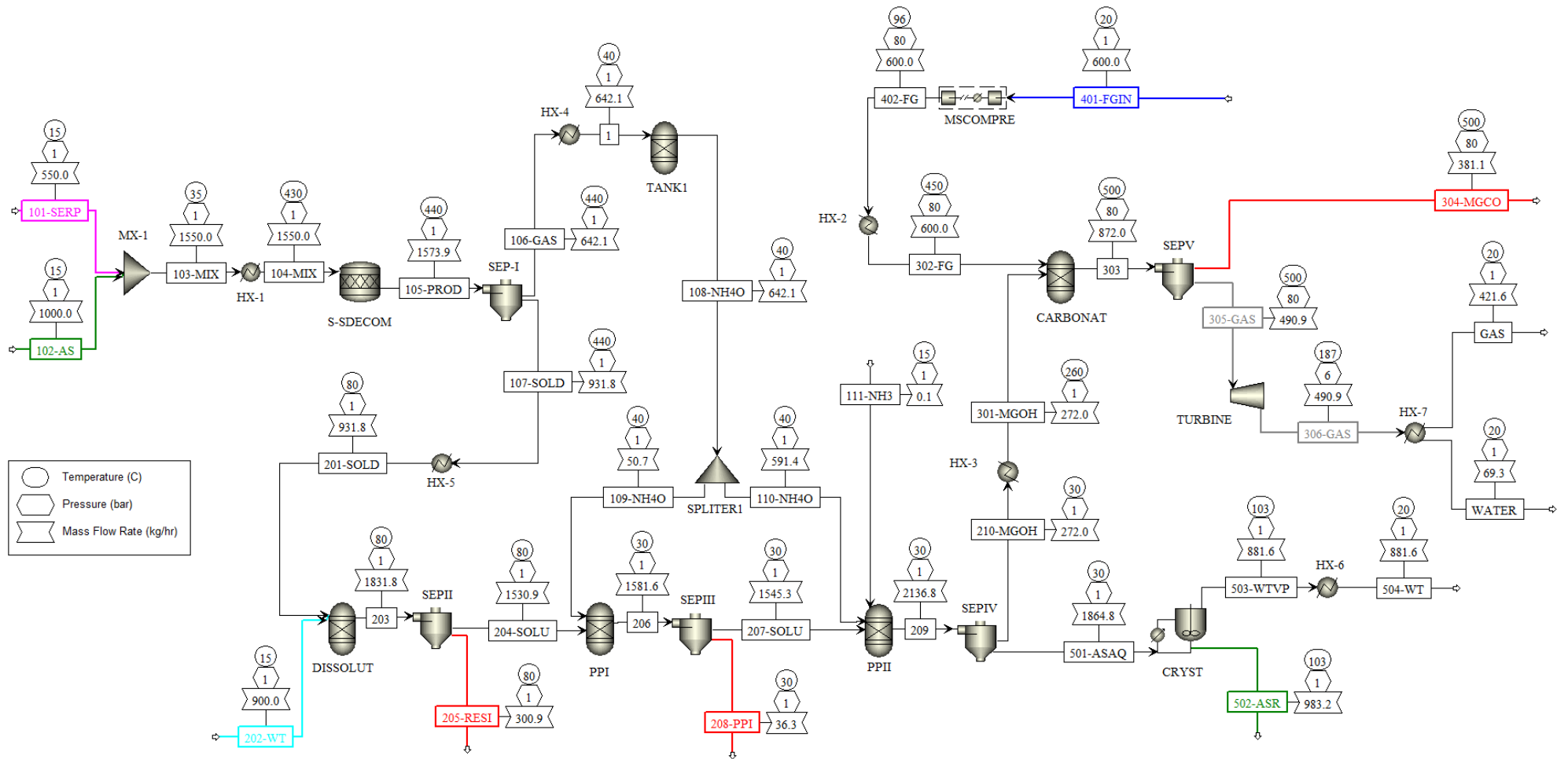


Fig 3- Aspen Plus® model

Table 3. Summary of the process' exergy.

EQUIPMENT	Energy	T	Exergy as heat		Flue Gas (kg/hr)		Flue Gas NTP (m ³ n/s)		
	Q (J/s)	(°C)	(MJ/hr)	MJ/kgCO ₂	FG500	FG440	FG500	FG440	
SS DECOMPOSITION	463146	450	1003	5.44	37442		8.32		
DISSOLUTION	-52259	80	-35	-0.19		11235		3.40	
PPI	-52455	30	-9	-0.05	4992		1.11		
PP2	-14218	30	-3	-0.01		13723		3.08	
TANK 1	-82000	40	-137	-0.74		891		0.20	
EVAPORAT	630066	103	532	2.88					
CARBONATOR	-5500	500	-12	-0.07					
HX-1 (S+AS+WT pre-heat)	434378	430	923	5.01					
HX-2 (FG pre-heat)	65050	450	141	0.76					
HX-3 (Mg(OH)₂ pre-heat)	27517	260	46	0.25					
HX-4 (Gaseous Products)	-472663	440	-1014	-5.50					
HX-5 (solid Products)	-93161	440	-200	-1.08					
HX-6 (wt from AS recovery)	-612765	103	-517	-2.80					
HX-7 (gas from turbine)	-73507	187	-99	-0.54					
Utilities Multistage Compressor (Water [15–90] °C)									
stage 1	-30105	90	-22	-0.12					
stage 2	-23328	90	-17	-0.09					
stage 3	-23512	90	-18	-0.09					
stage 4	-23878	90	-18	-0.10					
stage 5	-24599	90	-18	-0.10					
Total Exergy Process ²			525	2.85	Total	42434	24958	9.42	6.65
Exergy provided by the FG ³			2645	14.34					
Exergy Process + FG ⁴			-2120	-11.49					

² Total exergy as heat (120–450°C) needed to run the process, without integration with flue gas. ³ Exergy that the flue gas provides to the endothermic blocks. ⁴ Total exergy of the process when flue gas provides heat to all the endothermic stages. This final value may lead to the erroneous conclusion that the heat content of the flue gas is enough to process more serpentine. This “surplus” of exergy comes from streams at T ≤ 400°C making its heat content unsuitable for the processing of rock material at ~440°C. On the other hand this heat is appropriate for district heating.

Table 4. Elemental and XRD analysis of the diopside sample.

Elemental Analysis (%)									Structural Analysis (XRD)
CaO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	Others	
15.6	50.9	0.4	12.2	4.5	4.9	3.1	2.1	6.3	Hedenbergite, Orthoclase, Albite (Calcium), Muscovite, Clinochlore

A total of twelve experiments were done in order to determine the reactivity of the rock. The diopside (D) was mixed with solid ammonium sulphate (D:AS=2g:3g) and placed in an oven at different temperatures, 250-500°C, for 30 minutes. The products of this extraction step were dissolved in water and the concentrations of magnesium, iron, aluminium, calcium, sodium, potassium and sulphur in the solution were measured by an ICP-OES analysis. In six of the experiments, the influence of water was studied by adding 3 ml of water to the diopside/AS mixture (D:AS:W=2g:3g:1ml).

3.2 Experimental results

À priori, the composition of the diopside does not seem to be very suitable for direct application of the ÅA procedure mainly due to its dramatically low content of MgO, but also due to its high percentage of aluminium and other alkaline elements. In earlier experiments [16] the increase of aluminium content did not appear to favour the extraction reactions.

Disappointingly, also the extraction results are very discouraging. Besides its low Mg content, the diopside's reactivity is extremely low making the upgrading of this material doubtful. Water does not appear to play a key role on the materials reactivity. In fact, contrary to what occurs with the serpentine minerals [17], the evolution of the extraction rates with temperature is quite similar both in the presence and absence of water.

Even if it was possible to extract all the X elements of the rock material, the applicability of the ÅA route presents several challenges. The extraction of all the magnesium is energy consuming due to the presence (in greater percentages) of other elements (mainly Al, Fe, Na, K, and Ca). In fact, a quick calculation allows for concluding that only 1/4 of the overall reactions' heat is used for Mg extraction. A successful extraction of Ca would imply a second carbonation stage (probably in an aqueous solution). And finally, the presence of alkali metals (which are highly water soluble and do not precipitate) would make the AS recovery very difficult implying the application of extra separation stages to preclude the recirculation/accumulation of those unwanted elements. In Table 5 a brief comparison of the pros and cons of using serpentinite vs diopside for CO₂ mineralisation is presented.

As these results show that the diopside seems not to be a suitable material, no Aspen Plus simulations were made for that.

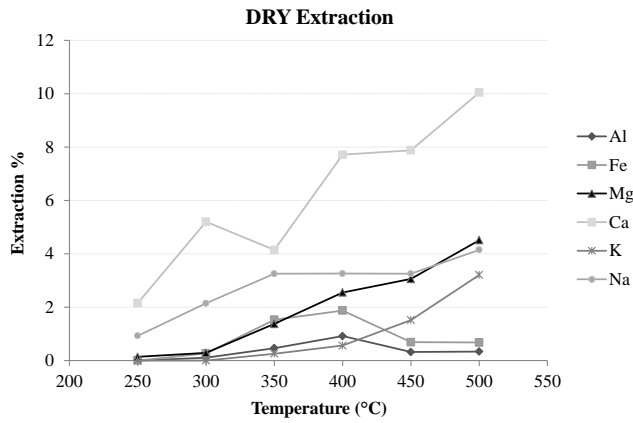


Fig.4 Experimental results concerning the extraction of six X elements from the diopside material in absence of water.

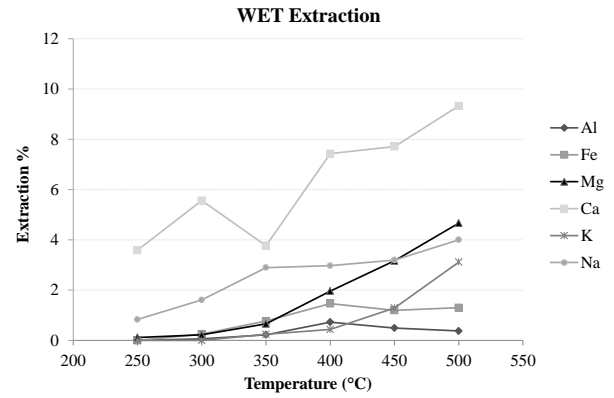


Fig.5 Experimental results concerning the extraction of six X elements from the diopside material in presence of water.

Table 5 – Pros and cons of utilising serpentinite or diopside as raw materials in the ÅA CSM process.

	Serpentinite	Diopside
Availability	Must be purchased (500 km away)	Available at the plant site
Extraction temperature	~400 – 440 °C	≥ 500°C making the use of waste heat questionable.
Reactivity	Good reactivity (So far ~60 – 70 % of Mg extraction but with good potential for 80%)	Very low reactivity (<5% of Mg extraction)
Iron/Calcium/Aluminium by-product	Low content of Al hydroxides Suitable for the steel-making industry.	High content of Al making it unsuitable to the steel making industry. An extra carbonation step needed to carbonate the by-products coming from the first precipitation stage.
Mg(OH)₂ product	~0.5kgMg(OH) ₂ /kg of serpentinite processed (89% Mg extraction) Crushing energy is ~12% of the exergy input (as electricity): 0.19MJ/kgCO ₂ captured	~0.087 kgMg(OH) ₂ /kg of diopside processed (if 100% Mg extraction is achieved) To produce an equal amount of Mg(OH) ₂ (as when serpentine is used) it's necessary to process at least 5.75x more rock. Excessive energy consumption for milling the raw materials which escalates to 1.09MJ/tCO ₂ (~73% of the exergy input as electricity) In this case, the waste heat available from the limekiln will be insufficient to achieve an auto-thermal process while processing such amounts of rock in the solid/solid decomposition stage.

AS recoveryFinal solution contains
 NH_4^+ , SO_4^{2-} and waterPresence of alkali elements (Na^+ & K^+) in
the remaining solution make the AS recovery
and recycling problematic.

4. Conclusions

The waste heat available from a limekiln located at Pargas, Southwest Finland is enough to process 550 kg/hr of serpentinite coming from Hitura, (western central Finland) with a capture potential of ~190 kg/hr of CO_2 , for 80% of Mg extraction and 90% of $\text{Mg}(\text{OH})_2$ carbonation. Even though the integration with flue gas allows for an auto-thermal process, a total of 0.71 MJ/kg CO_2 captured is needed, as an electrical input, for materials crushing/grinding and compression of gases.

Although it would be interesting to carbonate the diopside (by-product from the limestone quarry) available at Pargas, this material does not possess the required composition and reactivity to apply the ÅA CSM route. The content of Mg and Ca in the material make it unsuitable for CO_2 mineralisation in general because the large amounts of material needed will give rise to excessive crushing and grinding costs.

The energy penalty on the district heating supply, which arises from CO_2 capture, may be reduced by running this during low demand hours, for example during the summer. The same integration concept may be applied to other industries, making use of steam, at the right temperature, from a steam cycle of a power plant or some other nearby process which could supply most of the heat needed for CSM.

5. Acknowledgements

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6. Nomenclature

AS – Ammonium Sulphate

CCS – Carbon Capture and Storage

CSM – Carbon storage by Mineralisation

D – Diopside

 E_0 – Energy required for pulverisation [kWh/t]F – Size of feed particles [μm]

MC – Mineral Carbonation

PFB – Pressurised Fluidised Bed (reactor)

P – Size of the pulverized particles [μm]

W – Water

 W_i – work index [kWh/t]

X – Mg, Ca, Fe, Al, Na, K

7. References

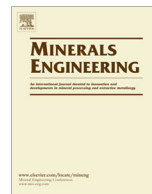
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PAPER VI

Minerals Engineering

(2013)



Technical note

Combined extraction of metals and production of $Mg(OH)_2$ for CO_2 sequestration from nickel mine ore and overburden



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ABSTRACT

Carbon storage by mineralisation (CSM) is an option for CO_2 emissions mitigation that has been under intensive study at Åbo Akademi (ÅA), Finland. Magnesium from silicate rocks is extracted with recoverable ammonium salts at 250–500 °C. The extracted elements are separated by selective precipitation and Mg is subsequently carbonated in a pressurised fluidised bed. This work studies the applicability of the process for co-extraction of Ni, Cu, Fe and Mg from nickel ore and nickel mine waste rock (overburden). The rock samples were collected from the Hitura Nickel mine, Finland. The results show that it is possible to co-extract the listed elements and integrate CSM (by the ÅA process) with steelmaking and Ni production industries.

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1. Introduction

At Åbo Akademi University (ÅA), in Finland, a process route for carbon storage by mineralisation (CSM) (IPCC, 2005; Zevenhoven et al., 2011) is being developed towards industrial application. The process starts with the extraction of magnesium from silicate rocks (such as serpentines and olivine) by reaction with (recoverable and cheap) ammonium salts at 250–500 °C. The solid products are dissolved in water and the species aimed at (Mg, Fe, Ca, etc.) are selectively precipitated in the form of hydroxides (Nduagu, 2012). The $Mg(OH)_2$ is carbonated in a pressurised fluidized bed (PFB) at ~500 °C and 20–30 bar CO_2 partial pressure (Fagerlund, 2012).

So far, the Finnish Hitura nickel mine waste (overburden) rock has been most used at ÅA (see Fig. 1) to study the optimum conditions for magnesium extraction (Nduagu, 2012). This paper explores the possibility to expand the use of the ÅA route to the mine's ore itself, studying the simultaneous extraction of Mg (for CSM purposes) and other valuable elements such as Fe, Ni and Cu. While it results in one process serving a double purpose, it might open a window towards making low grade and otherwise unfeasible ores economically attractive, driven by the EU's mine waste directive (EC, 2006).

The nickel recovery at Hitura is typically low (~66.5%) and becomes even lower if higher nickel grade concentrates are produced

(Meriläinen et al., 2012). The fineness of the grind is around $60\% < 74 \mu m$.

2. Experimental work – methods and results

2.1. Mineralogical characterization of the samples

The rock samples were crushed and ground to obtain three size fractions of 125–250 μm , 74–125 μm and $< 74 \mu m$, respectively. The compositions of the three different rock materials used in the experiments, the nickel ore and overburden were determined by X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES) after the rock's digestion. The results are shown in Table 1.

The Ni percentage in the ore (0.77–0.83 wt.%) is consistent with the values reported by Belvedere (2013).

2.2. Experimental method

- (1) Ore 1 material (size fraction 125–250 μm) was mixed with ammonium sulphate (AS) at a constant mixture mass ratio of 2:3 in a container reactor (ceramic pot) and placed in a rectangular oven for 30 min at several temperatures: 300, 350, 400, 450 and 500 °C. In some experiments 3 ml of water were added and these will be referred as the “Wet” experiments, while those performed in the absence of water will be mentioned as “Dry” experiments. The solid products were dissolved in water and the insoluble fraction separated from

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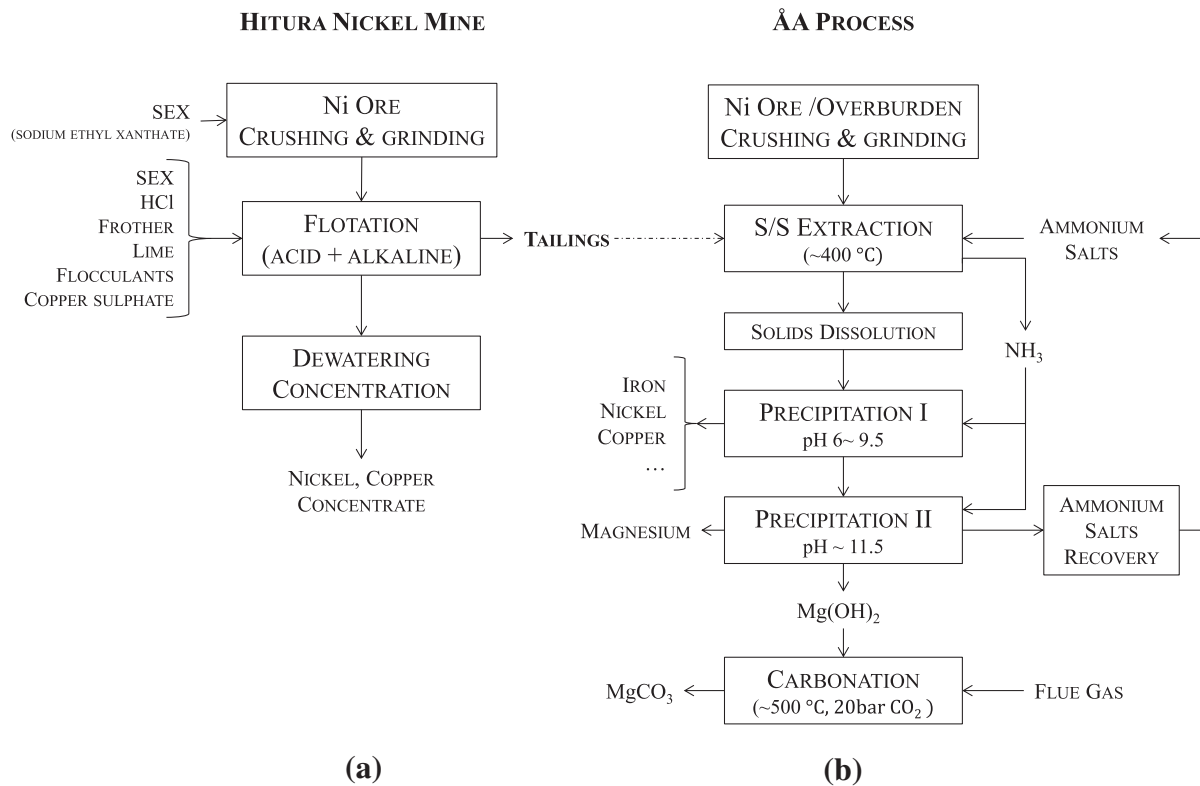


Fig. 1. (a) Simplified scheme for Ni ore beneficiation at Hitura site (adapted from Meriläinen et al., 2012; EC, 2004). (b) Ni ore processing via ÅÅ process (Romão et al., 2012).

the solution by vacuum filtration. The concentration of the different species in solution was determined by ICP-OES analysis.

- (2) Ore 2 material (size fraction 125–250 μm) was reacted with ammonium bisulphate (ABS) at a constant mixture mass ratio of 3:4 following a similar procedure to experiments set 1).
- (3) Ore 2 material (size fraction of 60 wt.% < 4 μm , 40 wt.% 74–125 μm) was reacted with ABS at a constant mixture mass ratio of 3:4 following the procedure described in experiments set 1).
- (4) The overburden material (size fraction 74–125 μm) was reacted both with either AS or ABS with mixture ratios of 2:3 and 3:4, respectively. The experimental procedure is to that for experiments set 1).

Although Ores 1 and 2 were collected at a different time and place, the chemical analyses show, as expected, that they are very similar thus representing the same material. Therefore each sample was tested with only one of the ammonium salts.

2.3. Experimental results – discussion

The calculation for the extraction results were based on the rock's composition given by the ICP-OES analysis, and are shown in Fig. 2a–h.

It was found to be possible to simultaneously extract Ni, Cu, Fe and Mg from all the tested materials. The best extraction results are summarised in Table 2. In general ABS provides the best extraction rate (a combination of kinetics, mass transfer and mixing conditions) and the presence of water enhances the extraction yields for both AS and ABS as the flux salt. As expected, in general a smaller particle size improves the extraction results. The optimum conditions for a maximum extraction rate for Ni are the reaction of Ni ore with a particle size <125 μm , with ABS at 450 °C, whereas for Mg extraction the presence of water seems to be more favourable giving an unexpected extraction yield of circa 65% already at 250 °C.

Concerning Cu, the improved extraction rates with ABS (60–75% at lower temperatures) is quite significant compared to the extractions with AS (~40% at 450 °C). For the overburden there was no Cu

Table 1
Nickel ore and mining overburden composition from Hitura nickel mine, Finland.

Sample		Al (%)	Ca (%)	Cr (%)	Cu (%)	Fe (%)	Mg (%)	Ni (%)	Si (%)
Ore 1 ^a	(XRF)	1.07	0.42	0.34	0.34	11.13	17.19	0.77	15.84
Ore 1	(ICP-OES)	0.89	0.47	0.32	No data	14.26	20.37	0.82	16.42
Ore 2 ^b	(ICP-OES)	0.14	0.23	0.20	0.18	12.11	21.39	0.83	8.07
Overburden ^c	(ICP-AES)	0.02	0.34	0.01	<0.01	10.10	21.80	0.02	11.60
Overburden ^c	(XRF)	0.37	0.38	0.34	0.08	10.71	24.10	0.28	19.23

^a Collected from Hitura nickel mine site in 2011.

^b Collected from Hitura nickel mine site in 2013.

^c Teir et al. (2007).

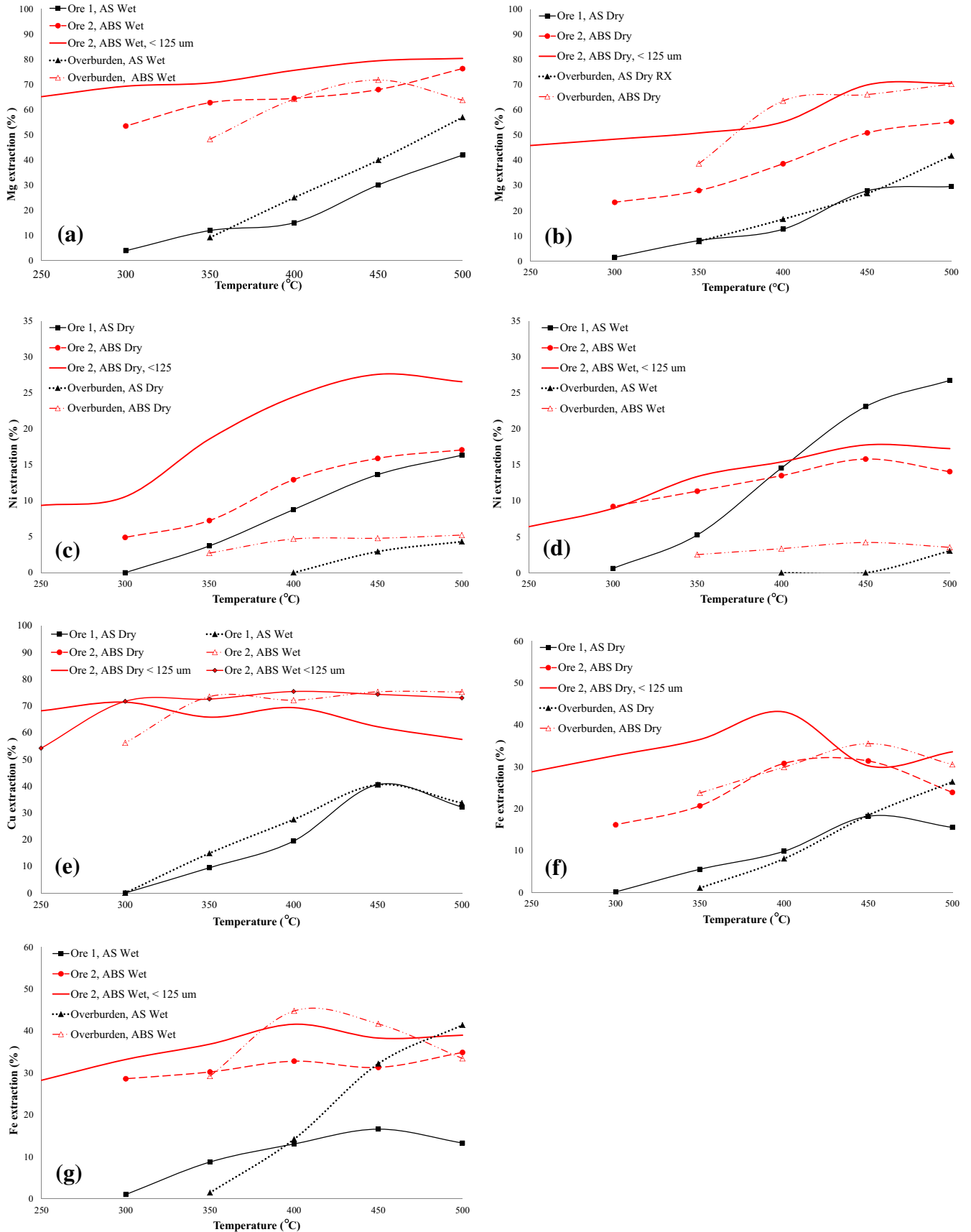


Fig. 2. Extraction results for (a) Mg in the absence of water. (b) Mg in the presence of water. (c) Ni in the absence of water. (d) Ni in the presence of water. (e) Cu in the absence and presence of water. (f) Fe in the absence of water. (g) Fe in the presence of water. AS – ammonium sulphate, ABS – ammonium bisulphate.

Table 2
Experimental results: range of extractions and best experimental conditions.

	Mg (%)		Fe (%)		Ni (%)		Cu (%)	
Ore 1 + AS	3.7–26.8	500 °C Wet 125–250 μm	0.2–18.2	450 °C Dry 125–250 μm	3.7–26.8	500 °C Wet 125–250 μm	0.0–40.5	450 °C Wet & Dry 125–250 μm
Ore 2 + ABS	23.4–80.4	500 °C Wet <125 μm	16.2–43.1	450 °C Dry <125 μm	4.9–27.6	450 °C Dry <125 μm	37.3–75.4	400 °C Wet <125 μm
Over Burden + AS/ABS	7.8–71.8	450 °C ABS Dry 125–250 μm	1.1–44.8	400 °C AS Wet 125–250 μm	2.7–5.2	500 °C ABS Dry 125–250 μm	–	–

detected in any of the solutions. The presence of water or the particle size does not seem to play a role in the reaction rate for Cu. As for iron the extraction rates with AS were consistent with those reported by Nduagu (2012). ABS greatly enhances the Fe extraction especially at lower temperatures.

After its extraction, the selective recovery of the Ni, Cu, Fe and Mg is a challenge. Currently the ÅA process includes two precipitation stages at a pH of 6–9.5 and ~11.5 to recover Fe and Mg as Fe(OH) and Mg(OH)₂, respectively. In order to produce pure Ni and Cu output streams as well, other options must be considered, for example the use of chelated ion exchange resins (Ferreira et al., 2011). This is part of ongoing work.

3. Conclusions

It is possible to extract Ni, Cu and Mg by reacting Ni ore with ammonium salts while extracting Mg for subsequent CO₂ sequestration. This would allow for the integration of CSM with steelmaking (using the iron by-product from rock processing) and Ni production making the overall process economically attractive.

The purpose of this work was not to replace the current Ni extraction method as the AS/ABS process does not appear to be the best route since it extracts only 1/3 of the Ni content of the ore.

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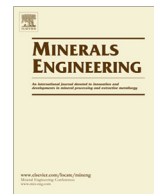
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PAPER VII

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Separation and recovery of valuable metals extracted from serpentinite during the production of $\text{Mg}(\text{OH})_2$ for CO_2 sequestration



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ABSTRACT

Amongst the several options for CO_2 storage, mineral carbonation presents the highest capacity for CO_2 fixation. Besides providing for a permanent (CO_2 leakage free) storage option, it is also directly applied to flue gases avoiding the expensive CO_2 capture processes. This paper focuses on the Åbo Akademi (ÅA) University route where suitable Mg rich silicate rocks are reacted with recoverable/recyclable ammonium salts (at ~ 400 – 450 °C) to produce mainly MgSO_4 . This is converted to $\text{Mg}(\text{OH})_2$ which reacts with a flue gas in a pressurised fluidized bed, at 20 bar CO_2 partial pressure and 500 °C to produce MgCO_3 . At some extent, a lot of the metals that compose the rock (Fe, Ni, Cr, Cu, etc.) will be co-extracted along with the Mg. Being so, this work aims to recover those (valuable) metals through a combination of selective precipitation and ion-exchange technology. It was found that 1 ton of the Portuguese serpentinite used in this work has the potential of capturing 270 kg of CO_2 while producing 517 kg of MgCO_3 , 75 kg of $\text{Fe}(\text{OH})_3$, 24 kg of $\text{Ca}(\text{OH})_2$ and 1.6 kg of Ni. This is equivalent to 1/3 of the nickel production per ton of nickel ore at the Hitura nickel mine in Finland.

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1. Introduction

Since 1940, measurements showed a continued rise of CO_2 levels in the earth's atmosphere. Hence the need of developing strategies to reduce the GHG emissions: use of energy efficiency improvements, the switch to less carbon-intensive fuels, nuclear power, renewable energy sources, enhancement of biological sinks, and reduction of non- CO_2 greenhouse gas emissions (IPCC, 2005). But the reality is that the known proven reserves of fossil fuels combined with profitable heat, power and transport technology, are enough to provide energy for at least another 100 years. Mineral carbonation is a carbon capture, utilisation and storage strategy that aims at binding CO_2 in a solid (e.g. MgCO_3) form to enable the continued use of fossil fuels without increasing the CO_2 levels in the atmosphere. It can be applied to any industrial process producing a CO_2 containing gas, provided that economy of scale, the avoided costs of CO_2 emissions and revenues from solid products make it economically viable.

At Åbo Akademi University (ÅA), in Finland, a process route for carbon storage by mineralisation (CSM) is being developed towards industrial application (Slotte et al., 2013). The process

(Fig. 1) starts with the extraction of magnesium from abundant silicate rocks, such as serpentinites and olivine, by reaction with (recoverable and cheap) ammonium salts (AS) at 350–500 °C. The metals and earth-alkali metals are extracted as sulphates and readily soluble in water at room temperature. The selective precipitation of Mg, Fe, Ca, Ni, Cr, Al in the form of hydroxides is achieved by raising the pH of the solution using the $\text{NH}_3(\text{g})$ released in the solid/solid reaction (Nduagu et al., 2012c). The produced $\text{Mg}(\text{OH})_2$ is carbonated in a pressurised fluidised bed (PFB) at ~ 500 °C and 20 bar CO_2 partial pressure (Fagerlund and Zevenhoven, 2011; Fagerlund et al., 2012).

Ultramafic and basaltic rocks are identified as the most suitable silicate mineral source due to their high content of Mg/Ca. Typical compositions of serpentinites (the most investigated minerals for mineral carbonation) are presented in Table 1. The first goal of the ÅA process is to maximise the extraction of Mg but reaction of AS with the minerals is not perfectly selective and other elements are co-extracted, e.g., Fe, Ni, Cr, Al, Ca (Romão et al., 2014; Nduagu et al., 2012c; Stasiulaitiene et al., 2011). Hence, the need for at least two precipitation stages to obtain a pure $\text{Mg}(\text{OH})_2$ suitable for carbonation in the pressurised fluidised bed (PFB). Per kg of $\text{Mg}(\text{OH})_2$ obtained, ~ 1.9 kg of rock must be processed. As a consequence, this route gives significant amounts of by-products: (i) a residue rich in (up to 80%) silica and (ii) an iron product. In a typical experiment this product consists in a mixture of goethite,

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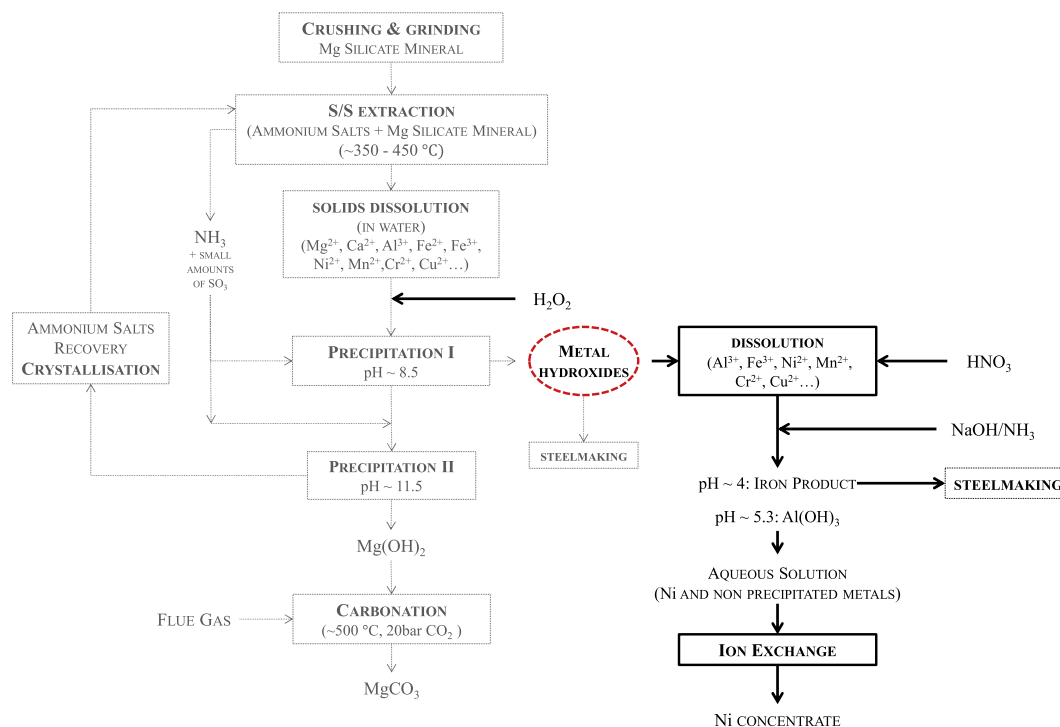


Fig. 1. AA mineral carbonation route (grey) and recovery of valuable metals through a combination of selective precipitation and ion exchange techniques (thick black). H_2O_2 is used to oxidise all the Fe^{2+} to Fe^{3+} which precipitates at a pH ~ 4.0 (instead of $FeOOH$ at pH $\sim 8-9$ as it is typical for the AA process). Ideally all the SO_x stays in the solid product bound to Mg, Fe, etc., to form the soluble sulphates. In reality some of it is released (Nduagu et al., 2014) but this will be again collected with the NH_3 , into the aqueous solutions in which the precipitates are formed.

Table 1
Elemental and structural composition of serpentinites.

Mg-silicate rock	Composition of atoms (wt%)								
	Mg	Fe	Si	Ca	Mn	Cr	Cu	Ni	Al
Donai serp. (Portugal) ^a	22.66	5.93	12.89	1.57	0.08	0.25	<LOQ	0.23	0.46
Åheim olivine (Norway) ^b	29.55	5.03	19.49	0.14	0.07	<LOQ	<LOQ	0.24	2.79
Hitura nickel mine ore (Finland) ^c	21.39	12.11	8.07	0.34	<LOQ	0.20	0.18	0.83	0.14
Varena serp. (Lithuania) ^b	18.94	12.30	15.89	0.86	0.04	<LOQ	0.01	0.01	0.12
ICP-OES LOD (mg/L)	0.0300	0.0046	0.0120	0.0100	0.0014	0.0071	0.0054	0.0150	0.0280
Structural analysis (XRD + polarizing microscope)									
Donai serp. (Portugal)	Antigorite, talc, lizardite, chrysotile, olivine, carbonates, iron oxides, bastites, tremolite								

<LOQ = below the limit of quantification.

LOD = limit of detection.

^a Determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

^b Nduagu et al. (2012).

^c Romão et al. (2013).

hematite and magnetite but, under controlled conditions of precipitation, – temperature, oxidation rate, pH and addition of alkaline together with stirring speed, – it is possible to favour magnetite formation which finds application in the steelmaking industry (Koivisto, 2013; Romão et al., 2012). Also, the separation scheme developed in this work removes undesirable contaminants (Al, K, Na^1) in a blast furnace thus avoiding further processing of this by product. So far the other co-extracted metals are flushed out of the process along with this iron rich product. The potential use of ammonium salts to extract Ni from low grade ore was earlier studied by Romão et al. (2013) and Liu et al. (2012).

This work focuses on the possibility of recovering those valuable metals that are already available in aqueous solution. Difficulties arise from the fact that the amount of water used to dissolve the solids must be minimised, otherwise the energy

penalty for the downstream AS recovery through a crystallisation process will make the AA route economically unviable. This results in a solution with a complex mixture of metals and a wide range of concentrations (45 mg/L for Ni to 16280 mg/L for Mg). A combination of selective precipitation coupled with filtration and ion exchange techniques may offer a method for the recovery of the valuable metals.

The use of resins to concentrate/recover metal ions from aqueous solutions is a common method that has been widely used and proven to selectively recover metals even in lower concentration solutions and with low energy requirements (Schoeman et al., 2012). In a follow up of experiments on Cu and Cr adsorption by chelating resins (Gando-Ferreira et al., 2011), the affinity of Ni towards the relatively new ion-exchange resin Diaion CR-11 was first tested. The poor experimental results lead to the selection of Amberlite IR-120 for this study, as it already exhibited good affinity towards the several divalent metals typically present in

¹ Al^{3+} is separated/recovered as $Al(OH)_3$ and Na^{2+} and K^+ stay in solution.

serpentinites (Jha et al., 2009; Luan et al., 2013; Valverde et al., 2006; Demirbas et al., 2005; Alguacil et al., 2004; Kocaoba, 2007). Also the recovery of cobalt and nickel from laterites using resins is described by (Christian et al., 1972).

2. Experimental procedure

2.1. Materials and reagents

The serpentinite rock samples were collected at the Donai quarry, Portugal, and were crushed and ground to obtain a size fraction <125 μm . The composition of the rock was determined by inductively coupled plasma optical emission spectrometry (using a PerkinElmer Optima 5300DV ICP-OES) after the rock's digestion. The structural analysis was determined by X-ray diffraction (XRD) using a Philips PW 3710 X-ray diffractometer, with a Cu tube, at 40 kV and 20 nA and the APD 3.6J software for mineralogical identification. The XRD was complemented with the observation of thin sections with Nikon polarizing microscope coupled with a Nikon digital camera. The results of these analyses are given in Table 2.

A stock solution with 1500 mgNi/L was prepared by dissolution of an appropriate amount of a nickel salt ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in distilled water. The solutions with lower concentrations needed for the experiments were prepared by dilution of the stock solution. The pH of the solutions was adjusted with HNO_3 and NaOH .²

Amberlite IR-120 (Na^+ form) was provided by Dow Chemical Company. It is a gel type strongly acidic cation exchange resin of the sulfonated polystyrene type. In the Na^+ form it is suitable for water softening while the H^+ form is well suited for demineralisation of water. The general properties and characteristics of the resin are presented in Table 2. Prior to the experiments, the resin was conditioned in a fixed column with cyclic washings of 2 M NaOH and 2 M HCl solutions to remove impurities and other preparation chemicals. The last conditioning step consisted of percolating the HCl solution through the resin to convert all the active groups to the H^+ form.

2.2. Procedures

2.2.1. Preparation of the rock derived solution (from serpentinite rock)

Following the experimental procedure optimised by Nduagu (2012) and Romão et al. (2014), the Portuguese crushed rock material, with a particle size of <125 μm , was reacted with a mixture of ammonium salts: 50/50-w% of ammonium sulphate (Emsure[®], $\geq 99.5\%$) and ammonium bisulphate (Fluka[®], $\geq 98\%$) and water, at a mass ratio of 2:3:1, and placed in a rectangular oven at 450 $^\circ\text{C}$ for one hour.³ After cooling down, the solid products were dissolved in water (a minimum of 10 ml of water per 1 g of reacted rock material⁴) at room temperature for one hour. The residue (insoluble fraction rich in silica) was separated from the 'leaching solution' by vacuum filtration and discarded. The same type of filter

² The reaction of ammonium (bi-)sulphate with rocks releases considerable amount of NH_3 that (in theory) is enough for complete Fe and Mg precipitation. In excess of NH_3 Ni forms a blue soluble complex precluding a total Ni precipitation. Therefore, for this work, it was decided to use NaOH to increase pH. In an industrial process a rigorous control of the leachate concentration combined with pH control would be necessary to prevent the formation of that complex and maximise Ni recovery.

³ The optimum experimental conditions (temperature, reactor type, presence of water, time of reaction and other factors) were studied in a different paper (Romão et al., 2014). Iron extraction is favoured at lower temperatures (~ 300 $^\circ\text{C}$) while Ni and Mg are favoured at >400 $^\circ\text{C}$. This is why we used only the 450 $^\circ\text{C}$ for the extraction reaction.

⁴ The volume of water needed might be higher in order to completely break and dissolve small pieces of sintered solid product.

Table 2
Properties of the resin.

Item	Property
Functional group	Sulfonic acid
Matrix	Styrene divinylbenzene copolymer
Ionic form	Na^+
Apparent density (g dry resin cm^{-3})	0.91
Wet density (g wet resin cm^{-3})	1.57
Moisture content (%)	42.4
Wet particle porosity	0.632

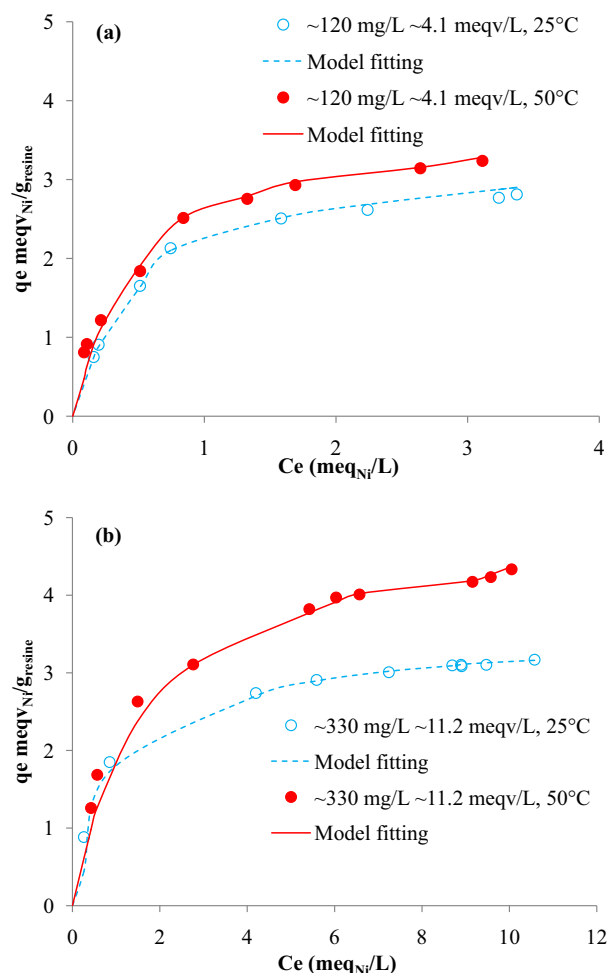


Fig. 2. Model fitting to the experimental data obtained; effect of temperature and initial concentration at: (a) initial concentration ~ 120 mgNi/L and (b) ~ 330 mgNi/L. q_e – equilibrium adsorption capacity (mg/g); C_e – equilibrium concentration of the adsorbate in the aqueous phase (mg/L).

was used for all the filtration steps: Whatman fibre glass filter, Grade GF/F: 0.7 μm .

The amount of $\text{Fe}^{2+}/\text{Fe}^{3+}$ present in the solution is always uncertain. Therefore, a few drops of H_2O_2 were added to the 'leaching solution' to oxidise all the Fe^{2+} to Fe^{3+} which precipitates at a pH ~ 4.0 (instead of FeOOH at pH $\sim 8-9$ as it is typical for the ÅA process).

The pH of the leachate typically lies in the range of 1.5–2.5 depending on the A 1M solution of NaOH was then added to increase the pH to $\sim 8.0-8.2$ in order to convert all the metals in solution to insoluble hydroxides. These were separated by vacuum filtration and the solution containing Ca and Mg ('Mg rich solution')

Table 3
experimental conditions and equilibrium parameters of Eq. (6) for the binary system $\text{Ni}^{2+}/\text{H}^+$. q_{max} – total operating capacity of the resin; $K_{\text{M,H}}$ – separation factor.

Run	Initial conditions			Parameters calculated	
	pH	Concentration (mgNi/L)	Temperature (°C)	q_{max} (meqv g ⁻¹)	$K_{\text{M,H}}$
1	5.58	120	25	3.04	4.81
2	5.63	330	25	3.24	4.81
3	5.58	120	50	3.42	7.52
4	5.63	330	50	4.60	7.52

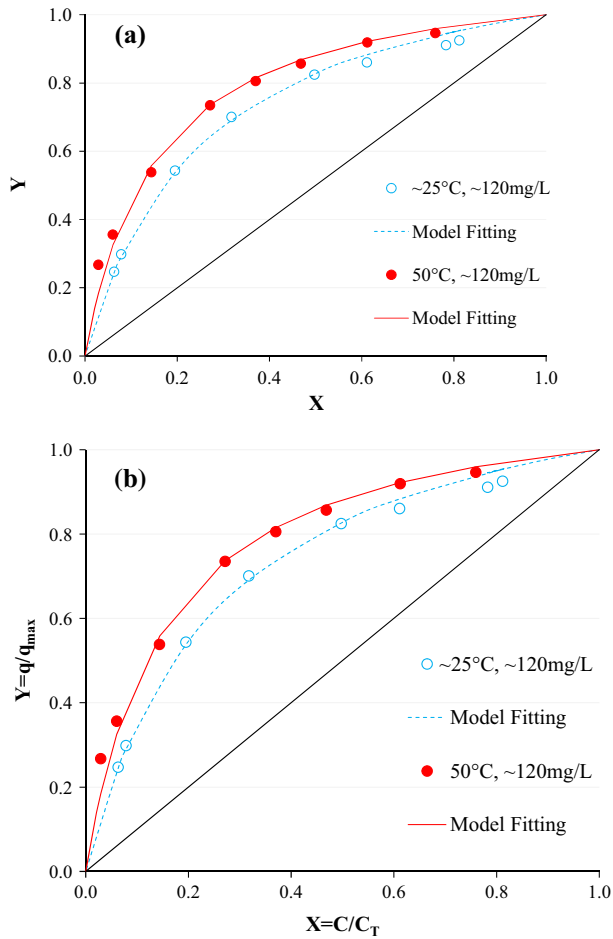


Fig. 3. Effect of temperature on ionic fraction of metal in the solid phase as a function of the ionic fraction observed in the liquid phase in the system $\text{Ni}^{2+}/\text{H}^+$ at: (a) initial concentration ~ 120 mgNi/L and (b) ~ 330 mgNi/L.

was put aside. The solid product was then washed and re-dissolved in water. Nitric acid solution was used to lower the pH until complete dissolution of the solid fraction was achieved (typically when $\text{pH} = [1.00\text{--}1.15]$).

This was followed by a staged precipitation of Fe^{3+} at $\text{pH} \sim 4.0$ and Al^{3+} (in the form of a white $\text{Al}(\text{OH})_3$ gel) at $\text{pH} \sim 5.35$. Both products were separated from the solution by vacuum filtration. Further pH elevation with NaOH solution did not result in visible formation of $\text{Ni}(\text{OH})_2$, thus this final ‘rock derived solution’, which also contains traces of some of the other metals extracted from the rocks, was used in the ion exchange experiments with the Amberlite IR-120 resin as it is illustrated in Fig. 1 (right side).

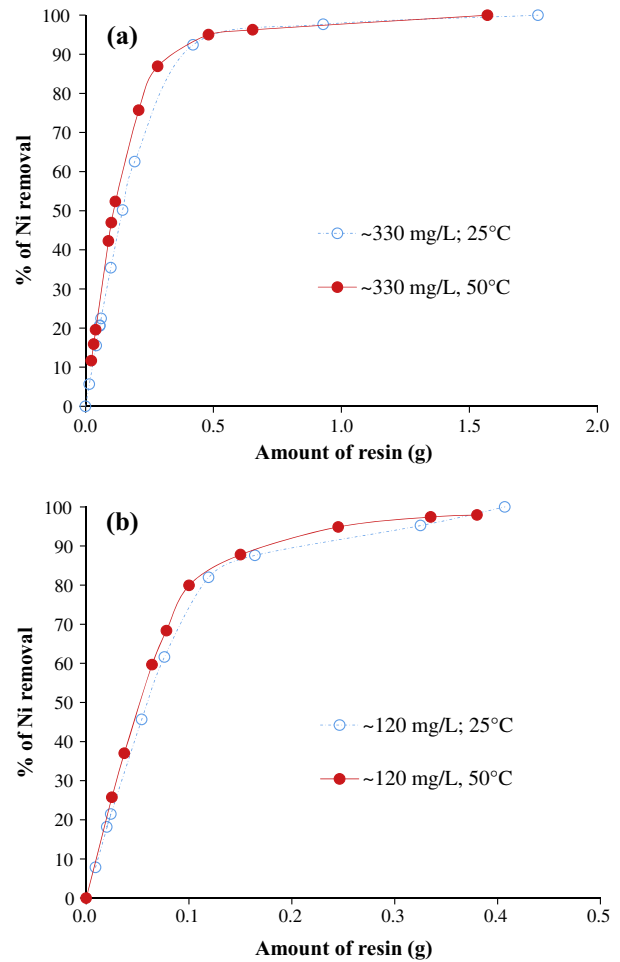


Fig. 4. Effect of resin dosage on the Ni^{2+} uptake on Amberlite IR-120: amount of resin 0.01–1.80 g; volume of sorption medium 75 ml; initial pH 5.58. (a) Initial concentration ~ 330 mgNi/L and (b) ~ 120 mgNi/L.

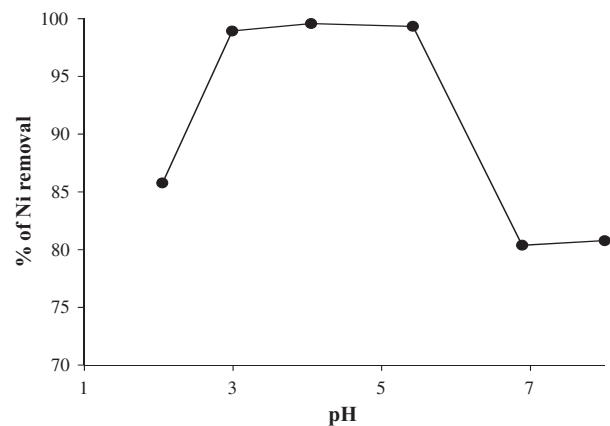


Fig. 5. Initial pH effect on the exchange capacity of the resin: $\text{Ci} \sim 100$ mgNi/L, 0.2 g of resin, 80 ml of sorption medium.

2.2.2. Ion exchange experiments

The equilibrium isotherms for the synthetic Ni^{2+} solution were determined in batch operation where 50 ml of solution and a variable amount of pre-conditioned resin (0.01–2 g) were mixed in 100 ml flasks. These were sealed and placed in a water bath with agitation at constant temperature of 25 °C or 50 °C for seven hours to reach equilibrium (experiments performed by Demirbas et al.,

2005) showed that equilibrium is attained in less than four hours. When necessary, the initial pH was pre adjusted by addition of HNO₃ or NaOH.

The equilibrium isotherms for the ‘rock derived solution’ were determined also in batch operation with 30 ml of solution and a variable amount of pre-conditioned resin (0.01–12 g) at 25 °C or 50 °C and pH 5.65. The composition of the final solutions was determined by ICP-OES and the percentage of the elements removal calculated from the final ‘rock derived solution’.

3. Results and discussion

3.1. Synthetic solution of Ni²⁺

3.1.1. Ion-exchange equilibrium studies – Effect of temperature and initial concentration

The uptake of Ni²⁺ is dependent on the solution’s initial concentration (see Fig. 2) suggesting that ion exchange is the phenomenon governing the retention of nickel.

The experimental data was treated following the same methodology used by Gando-Ferreira et al. (2011). In short, the chemical reaction of exchange is:



Considering that the activity coefficients for both phases are equal to unity (assuming ideality), the equilibrium constant can be written as:

$$K_{M,H} = \frac{[RHM^+][H^+]}{[RH_2][M^{2+}]} \quad (2)$$

Also, the equivalent fractions for each species in solid phase, Y_i, and liquid phase, X_i, can be defined as:

$$Y_i = \frac{q_i}{q_{max}} \quad (3)$$

$$X_i = \frac{C_i}{C_T} \quad (4)$$

$$(i = 1 \text{ for M, 2 for H}), C_T = C_H^+ + C_M^{2-} \quad (5)$$

where q_i is the amount of metal ion exchanged (meqvg⁻¹_{resin}), q_{max} the total operating capacity of the resin (meqvg⁻¹_{resin}), C_{M²⁺} and C_{H⁺} are the concentrations of metal and hydrogen ion in solution expressed in meqv L⁻¹. Since the summations of the equivalent fractions of the metal and hydrogen in the solution and resin phases are both equal to unity, Eq. (2) becomes:

$$Y_M = \frac{K_{M,H}X_M}{1 + (K_{M,H} - 1)X_M} \quad (6)$$

The starting conditions for each experiment (pH and metal concentration), the temperature (kept constant during the experiment) and the equilibrium parameters (q_{max} and K_{M,H}) are shown in Table 3. The parameters q_{max} and K_{M,H} were determined by fitting the equilibrium model, Eq. (2), to the experimental data by shifting them iteratively in order to minimize the average deviation, AD(%), calculated according to the equation:

$$AD = \frac{1}{N} \sum_{i=1}^N \frac{Y_M^{exp,i} - Y_M^{cal,i}}{Y_M^{exp,i}} \times 100 \quad (7)$$

where Y_{Mⁱ}^{exp,i} and Y_{Mⁱ}^{cal,i} are the experimental and calculated ionic fractions of metal in the solid phase, respectively. The deviations were

Table 5
composition of the ‘rock derived solutions’ used in the equilibrium studies.

‘Rock derived solution’	Al mg/L	Ca mg/L	Cr mg/L	Mg mg/L	Mn mg/L	Ni mg/L
A	4	136	–	553	81	275
B	10	41	–	265	37	105
C	3	116	3	1073	47	74

Table 4
Extraction results (from a total of three tests) for the reaction of Portuguese serpentinite with ammonium salts.

	Al	Ca	Cr	Fe	Mg	Mn	Ni	Si
Extraction (%)	64 ± 9	67 ± 19	47 ± 5	70 ± 4.8	71 ± 4	74 ± 13	67 ± 4	0.8 ± 0.4
Leaching solution (mg/L)	193–289	609–932	61–109	1911–4376	7668–16280	29–56	68–153	32–124

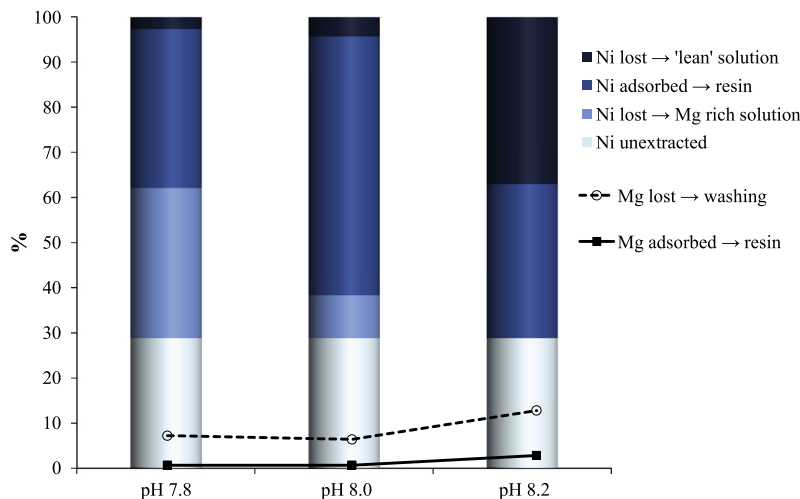


Fig. 6. Influence of the pH (of the first precipitation stage) on the recovery and losses of Ni and Mg. The ‘lean’ solution is the remaining solution when the equilibrium with the resin is reached. At this point, the losses of Ni are indirectly due to the undesired conversion of Mg to Mg(OH)₂ as a consequence of the higher precipitation pH in the first precipitation stage. All the Mg²⁺ converted to Mg(OH)₂ will end up in the ‘rock derived solution’ used in the ion exchange experiments and most of it will be adsorbed by the resin reducing its capacity for adsorbing Ni²⁺.

less than 9% leading to a satisfactory fit of the equilibrium data to the model as shown in Fig. 2.

Ion exchange reactions are known to be endothermic (Demirbas et al., 2005; Singare et al., 2009) and indeed higher temperatures clearly favour Ni retention as shown in Figs. 2 and 3.

The separation factor $K_{M,H}$ increased 1.56 times when the temperature rose from 25 °C to 50 °C. The enthalpy of exchange (ΔH°) can be estimated by integration of the thermodynamic (van't Hoff) relationship:

$$\frac{d \ln K_{M,H}}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (8)$$

with R being the universal gas constant (8.314 J/mol K) and T the temperature in Kelvin. Assuming that ΔH° is independent of temperature gives:

$$\ln K_{M,H} = C^{\text{ast}} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (9)$$

and the fitting the experimental data to Eq. (9) allows for the estimation of a $\Delta H^\circ = 1.46$ kJ/mol (valid for the average value of the concentrations range covered in this work).

On the other hand, higher metal concentration does seem to play a role on the metal uptake by the resin. Yet, what stands out from Fig. 2 is the synergetic effect that both temperature and concentration have on the uptake of Ni: at 50 °C and 330 mgNi/L the equilibrium adsorption capacity (q_e) increases significantly. For this reason the equilibrium studies with the 'rock derived solution' were run at 50 °C.

3.1.2. Effect of resin dosage

As expected, the sorption density increases with the resin amount (Fig. 4). Using more resin results in higher surface area and sorption sites and further in a decrease of the contact time needed to reach equilibrium. A complete adsorption of Ni was achieved with 6.7 g resin/L for the solution with 120 mgNi/L and 20 g resin/L for the 330 mgNi/L solution.

3.1.3. Effect of initial pH

The effect of initial pH on the adsorption of nickel was studied in batch experiments with a fixed amount of resin. Although Amberlite IR-120 is a strong cationic resin, which means that it can operate in wide pH range, from Fig. 5 it is seen that the uptake of Ni is strongly affected by the initial pH. The best result was obtained at pH 4 with 99.6% of Ni removal and the resin is effective over a pH range 3–6. Outside this, Ni uptake decreases significantly at low pH due to competition of sorption sites between Ni^{2+} and H^+ while at higher pH it is most likely due to Ni partial conversion to $\text{Ni}(\text{OH})_2$.⁵

3.2. Rock derived solution – Selective precipitation

The serpentinite material was reacted with a mixture of 50/50-w% of ammonium sulphate/bisulphate and the solid product was dissolved in water. After separating the unreacted solid fraction, by vacuum filtration, a "leaching solution" remains, containing all the soluble elements (Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Mn^{2+} , Cr^{3+} , etc.) and with the average concentrations described in

Table 4. The Ni extraction levels are unexpectedly high when compared to those obtained with the Finnish Hitura nickel mine ore rock material (Romão et al., 2013).

As it can be seen from Table 4, the range of metals' concentration is quite wide and dependent on both the extent of the solid/solid extraction reaction and amount of water used for dissolution. Often the solid product contains small pieces of sintered solid product. It is unclear why in some experiments (in the same operation conditions) there is the formation of this sintered product. Extra addition of water facilitates its dissolution/breakage. Hence the difference in the leachate solution's concentration. On the other hand, the recovery of the elements present in the leaching solution is strongly influenced by the efficiency of the selective precipitation and filtration steps.

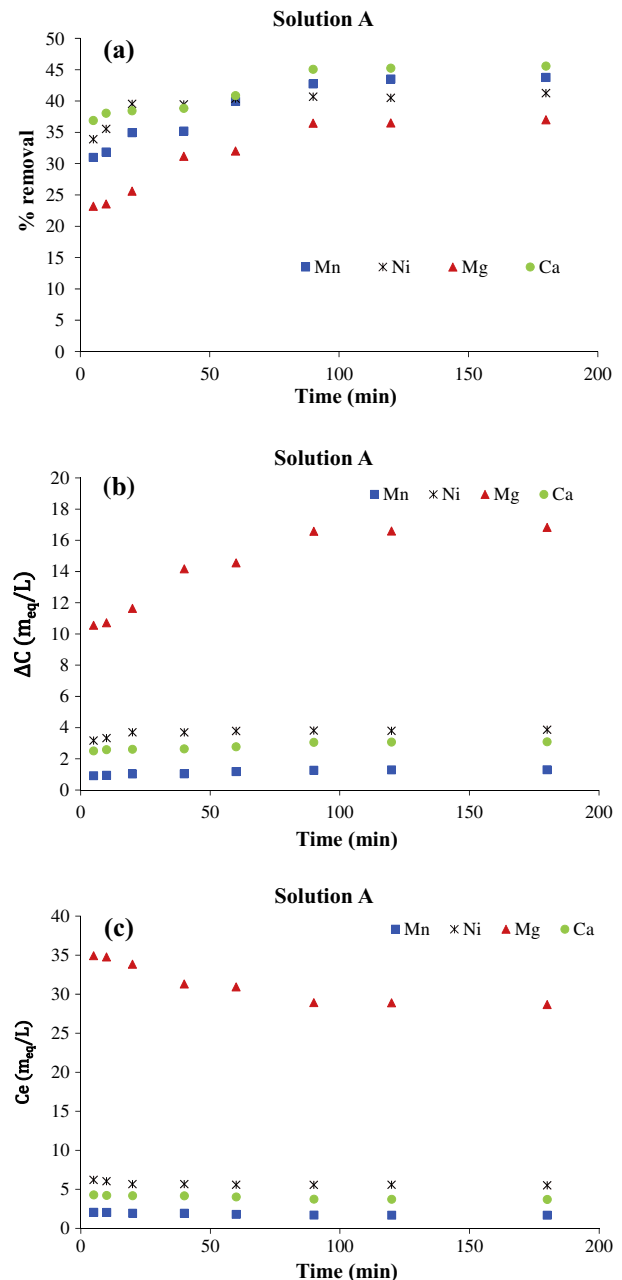


Fig. 7. Effect of contact time on the uptake of the metals in solution A ($S/L = 0.1$ g_{res}/L): (a) % metal removal; (b) amount of metal adsorbed and (c) equilibrium concentration. C_e – equilibrium concentration of the adsorbate in the aqueous phase (mg/L). The composition of solution A is given in Table 5.

⁵ The ICP analyses on the samples are performed some time (often days) after the experimental work. This sometimes leads to formation of precipitates in the samples, especially when the concentration of metals is higher. Because of this issue, the ICP operator did two analyses per sample: one of the sample's 'overflow' and one after addition of one drop of acid. In the case of the pH experiments, only those at higher pH showed a difference between both cases (with and without addition of acid). Thus we concluded that during the ion exchange experiments at higher pH likely there is precipitation of Ni which becomes unavailable for the ion exchange process.

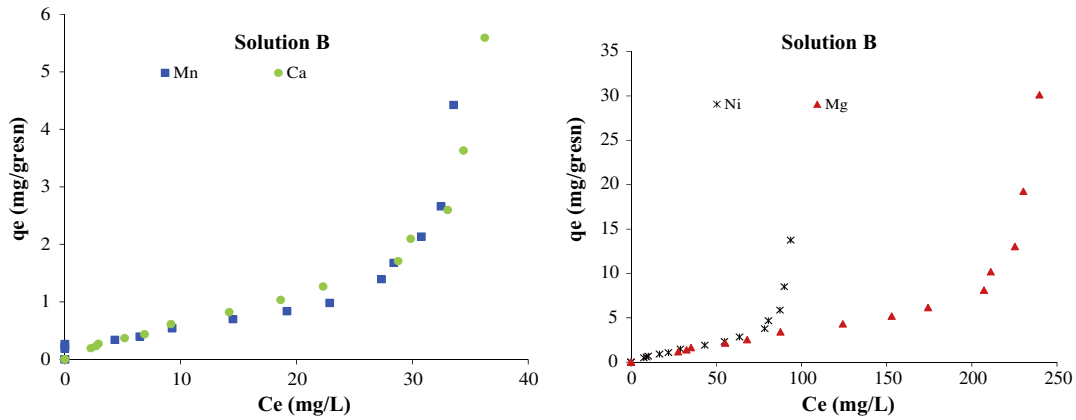


Fig. 8. Ion exchange equilibrium for the solution B at 50 °C. q_e – equilibrium adsorption capacity (mg/g); C_e – equilibrium concentration of the adsorbate in the aqueous phase (mg/L). The composition of solution B is given in Table 5.

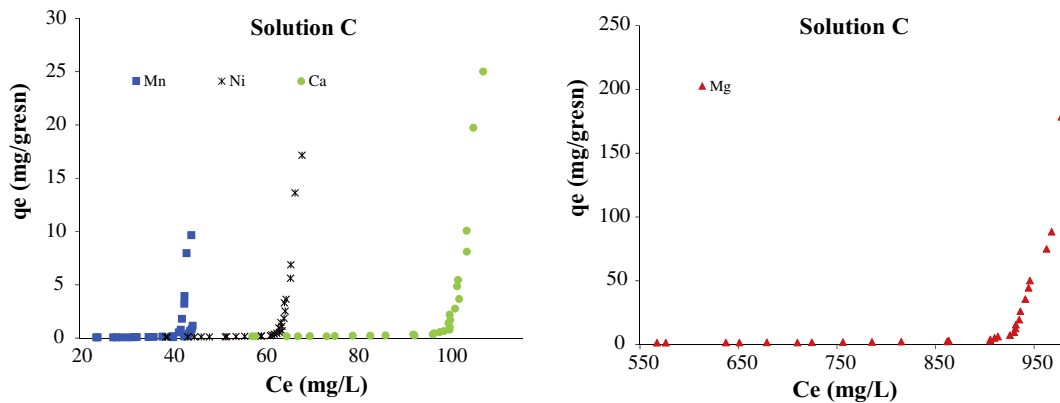


Fig. 9. Ion exchange equilibrium for solution C at 50 °C. q_e – equilibrium adsorption capacity (mg/g); C_e – equilibrium concentration of the adsorbate in the aqueous phase (mg/L). The composition of solution C is given in Table 5.

The pH of the leaching solution was then raised by addition of NaOH. The aim was to convert all the metals in solution into hydroxides. After this the Mg/Ca rich solution is separated from the metal hydroxides by vacuum filtration.

ICP analyses on the rich Mg/Ca solution confirm that at a pH of 8.2 all the metals will be in the form of insoluble hydroxides (Fe rich product) but at the cost of losing ~10% of the extracted Mg.⁶ It was found that this lost Mg is mainly retained by the Fe rich product. In our opinion this is due to two reasons: (1) the iron-rich product is extremely viscous and its filtration with a traditional vacuum filtration system is difficult and rather inefficient. The Fe rich cake will thus retain considerable amounts of Mg and Ca. This was minimised with several washing cycles; (2) due to the high concentration of Mg^{2+} its co-precipitation is inevitable. All the Mg^{2+} converted to $Mg(OH)_2$ will end up in the 'rock derived solution' used in the ion exchange experiments and most of it will be adsorbed by the resin. Co-precipitation mechanisms are usually complex and their study is outside of the scope of this work. After this, the solids were re-dissolved in water with HNO_3 being added until their complete dissolution.

The iron was completely converted to $Fe(OH)_3$ along with the chromium at pH 4 (by addition of NaOH). Compared to the exploitation of chromium ore, the amounts recovered in this process are irrelevant. Chromium is a particular by-product from the Portuguese serpentinite while in the case of Finnish serpentinite,

for example, it is copper. In this particular case, its simultaneous precipitation with the iron makes this by-product more valuable for application to the steelmaking industry for special steel products. The Al^{3+} was recovered as $Al(OH)_3$ at pH ~ 5.35 in the form of a white gel. The nearly complete recovery (>98%) of Al is very fortunate because resins tend to have more affinity to ions with higher valence (Silva, 1999; HDR Engineering Inc., 2002).

The results in Section 3.1 show that a pH ~ 5.35 is favourable for Ni retention, thus the ion exchange tests proceeded without further pH adjusting and at 50 °C.

Fig. 6 presents an overview of the influence of pH on the amount of Ni and Mg converted to hydroxides and "lost" in the sequential steps of the process. The losses of Ni are the result of three different processes:

- (1) The solid/solid reaction: Ni not extracted from the rock is considered here a loss.
- (2) The first precipitation step (pH ~ 7.8–8.2): the Ni that is not converted to $Ni(OH)_2$ (along with the iron-rich solid product) is discarded with the magnesium rich solution.
- (3) The ion exchange process: Ni that is not adsorbed by the resin and thus remains in the final "lean" solution.

The losses of Mg occur during:

- (1) The first precipitation step (pH ~ 7.8–8.2): Mg that is converted to $Mg(OH)_2$ will end up in the solution used for the ion exchange experiments. Part of it will be taken up by the resin and the rest will remain in the "lean" solution.

⁶ Co-precipitation of Mg is highly undesirable as the main purpose of the process is to use the Mg to bind CO_2 as $MgCO_3$ and small losses will result in several more kilos of rock to be processed, compromising the process' economics.

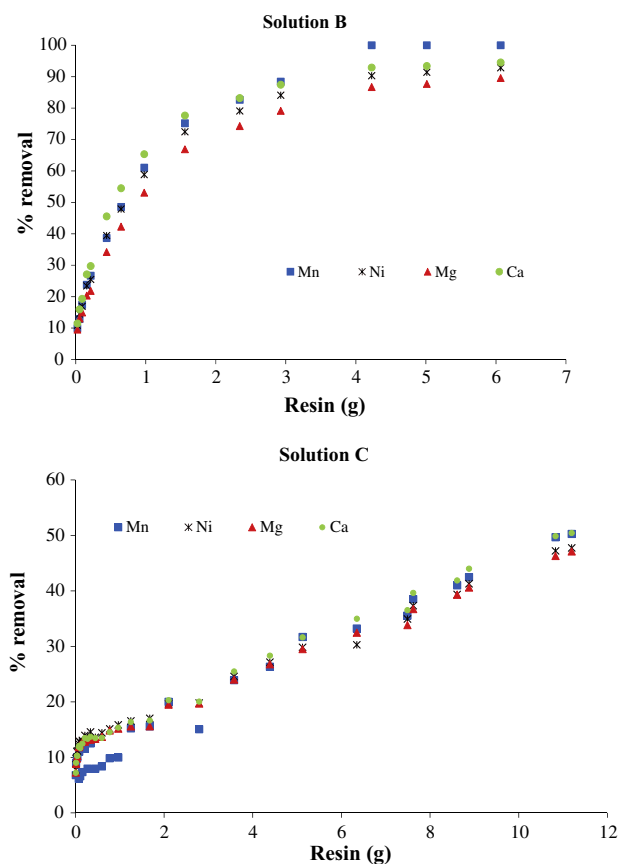


Fig. 10. Percentage of metals removal for solutions B and C. The composition of solutions B and C are given in Table 5.

- (2) The washing of the iron-rich product which is quite viscous and retains a lot of moisture.

3.3. Rock derived solution – Equilibrium studies

The ion exchange equilibrium studies include three different solutions, derived from the Portuguese serpentinite rock material, with concentrations listed in Table 5.

The Solutions A, B and C have different concentrations because the amount of water used in the dissolution of the iron product was different. This was done on purpose in order to infer the influence of the elements concentration on the uptake of metals by the resin.

This study does not include any kinetic evaluation of the adsorption process. It is however observed that the adsorption equilibrium is reaching a plateau after 100 min, as shown in Fig. 7. From the experimental data it is not possible to infer on the selectivity of the resin due to the different initial concentrations of the adsorbed ions. It is however reasonable to assume that the uptake of metals is directly related to their initial concentration.

From Figs. 8–10 it becomes clear that the presence of earth-alkali elements strongly influences the adsorption of Ni and Mg. It was expected that the capacity of the resin for the uptake of Ni would decrease with higher concentration of Mg and Ca. In a recent paper Cheng et al. (2014) discuss the formation of Ca^{2+} and Mg^{2+} hydrates with positive charges that, when adsorbed by a chelating sponge, increase repulsive forces between the sponge and the metal ions. As future work it might be useful to investigate how the concentration of earth-alkali ions affects the ion exchange reactions because for the ÅA process, these ions will inevitably be

present in the “rock derived solutions”. Also, a chelant resin selective for Ni will be more suitable for the process.

The regeneration of resin was not considered in the work. In general, there are two options for recovery of the metals: regeneration with a concentrated solution of HCl (the most common method) or, in case the metals are strongly fixed, incineration of the resin.

Based on the experimental results reported, from 1t of powdered serpentinite rock material it is possible to produce ~360 kg of $\text{Mg}(\text{OH})_2$ (with a CO_2 capture potential of ~270 kg of CO_2), ~517 kg of MgCO_3 , ~75 kg of $\text{Fe}(\text{OH})_3$ (with ~2.6 kg of Cr), 24 kg of $\text{Ca}(\text{OH})_2$, 1.6 kg of Ni. This amount of Ni may seem modest but it has substantial potential for partially replacing nickel ore mining activities. For example, the Hitura nickel mine in Finland processes ore containing ~0.82% of nickel with a typical recovery of 66.5% (Belvedere, 2012). Thus, 1 ton of ore produces ~4.8 kg of nickel. The experimental results in this work suggest that, per ton of rock, the recovery of the Ni co-extracted from the Portuguese serpentinite tested for the ÅA mineral carbonation process produces the equivalent to 1/3 of the Hitura nickel mine production activity, thus confirming that it may be advantageous to integrate mineral carbonation with mining activities (Romão et al., 2013)

4. Conclusions

The first step of the ÅA mineral carbonation process successfully co-extracts valuable metals (especially Ni, besides Cr and Cu) usually present in the Mg rich silicate rocks suitable for the process. The co-precipitation of metals due to the wide range of concentrations and pH sensitivity is the main cause for Ni losses. As it seems to be intangible to prepare a Mg/Ca free solution for the ion exchange step, it would be wise to choose a chelant resin selective for Ni. Still the experimental results here presented show that the recovery of Ni, as a by-product of the ÅA mineral carbonation route has substantial potential for partially replacing nickel ore mining activities.

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