Production of $Mg(OH)_2$ from Mg-silicate rock for CO_2 mineral sequestration

Experience Nduagu

Academic Dissertation

Thermal and Flow Engineering Laboratory

Department of Chemical Engineering

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Åbo Akademi University

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Abstract

Sequestration of carbon dioxide in mineral rocks, also known as CO_2 Capture and Mineralization (CCM), is considered to have a huge potential in stabilizing anthropogenic CO_2 emissions. One of the CCM routes is the *ex situ* indirect gas/sold carbonation of reactive materials, such as $Mg(OH)_2$, produced from abundantly available Mg-silicate rocks. The gas/solid carbonation method is intensively researched at Åbo Akademi University (ÅAU), Finland because it is energetically attractive and utilizes the exothermic chemistry of $Mg(OH)_2$ carbonation. In this thesis, a method for producing $Mg(OH)_2$ from Mg-silicate rocks for CCM was investigated, and the process efficiency, energy and environmental impact assessed. The $Mg(OH)_2$ process studied here was first proposed in 2008 in a Master's Thesis by the author. At that time the process was applied to only one Mg-silicate rock (Finnish serpentinite from the Hitura nickel mine site of Finn Nickel) and the optimum process conversions, energy and environmental performance were not known.

Producing $Mg(OH)_2$ from Mg-silicate rocks involves a two-staged process of Mg extraction and $Mg(OH)_2$ precipitation. The first stage extracts Mg and other cations by reacting pulverized serpentinite or olivine rocks with ammonium sulfate (*AS*) salt at 400 - 550 °C (preferably < 450 °C). In the second stage, ammonia solution reacts with the cations (extracted from the first stage after they are leached in water) to form mainly FeOOH, high purity $Mg(OH)_2$ and aqueous (dissolved) *AS*. The $Mg(OH)_2$ process described here is closed loop in nature; gaseous ammonia and water vapour are produced from the extraction stage, recovered and used as reagent for the precipitation stage. The *AS* reagent is thereafter recovered after the precipitation stage.

The Mg extraction stage, being the conversion-determining and the most energy-intensive step of the entire CCM process chain, received a prominent attention in this study. The extraction behavior and reactivity of different rocks types (serpentinite and olivine rocks) from different locations worldwide (Australia, Finland, Lithuania, Norway and Portugal) was tested. Also, parametric evaluation was carried out to determine the optimal reaction temperature, time and chemical reagent (*AS*). Effects of reactor types and configuration, mixing and scale-up possibilities were also studied. The $Mg(OH)_2$ produced can be used to convert CO_2 to thermodynamically stable and environmentally benign magnesium carbonate. Therefore, the process energy and life cycle environmental performance of the ÅAU CCM technique that first produces $Mg(OH)_2$ and the carbonates in a pressurized fluidized bed (FB) were assessed. The life cycle energy and environmental assessment approach applied in this thesis is motivated by the fact that the CCM technology should in itself offer a solution to what is both an energy and environmental problem.

Results obtained in this study show that different Mg-silicate rocks react differently; olivine rocks being far less reactive than serpentinite rocks. In summary, the reactivity of Mg-silicate rocks is a function of both the chemical and physical properties of rocks. Reaction temperature and time remain important parameters to consider in process design and operation. Heat transfer properties of the reactor determine the temperature at which maximum Mg extraction is obtained. Also, an increase in reaction temperature leads to an increase in the extent of extraction, reaching a maximum yield at different temperatures depending on the reaction time. Process energy requirement for producing $Mg(OH)_2$ from a hypothetical case of an iron-free serpentine rock is 3.62 GJ/t-CO_2. This value can increase by 16 - 68% depending on the type of iron compound (FeO, Fe_2O_3 or Fe_3O_4) in the mineral. This suggests that the benefit from the potential use of FeOOH as an iron ore feedstock in iron and steelmaking should be determined by considering the energy, cost and emissions associated with the FeOOH by-product. *AS* recovery through crystallization is the second most energy intensive unit operation after the extraction reaction. However, the choice of mechanical vapor recompression (MVR) over the "simple evaporation" crystallization method has a potential energy savings of 15.2 GJ/t-CO_2 (84 % savings). Integrating the $Mg(OH)_2$ production method and the gas/solid carbonation process could provide up to an 25% energy offset to the CCM process energy requirements. Life cycle inventory assessment (LCIA) results show that for every ton of CO_2 mineralized, the ÅAU CCM process avoids 430 - 480 kg CO_2.

The $Mg(OH)_2$ process studied in this thesis has many promising features. Even at the current high energy and environmental burden, producing $Mg(OH)_2$ from Mg-silicates can play a significant role in advancing CCM processes. However, dedicated future research and development (R&D) have potential to significantly improve the $Mg(OH)_2$ process performance.

Sammanfattning

Koldioxidlagring i mineralform, även känt som CO_2-avskiljning och mineralisering (CCM, från engelskans CO_2 capture and mineralization) anses ha stor potential att stabilisera antropogena CO_2-utsläpp. Ett CCM-alternativ utgörs av så kallad ”*ex situ*” indirekt gas/fast karbonatisering av olika reaktiva material, som $Mg(OH)_2$, som kan framställas av i naturen rikligt förekommande Mg-silikat bergarter. En sådan metod forskas det för tillfället intensivt om vid Åbo Akademi (ÅA). Metoden utgör ett energetiskt attraktivt alternativ och möjliggör tillvaratagande av den exoterma energi som frigörs vid $Mg(OH)_2$-karbonatisering. I denna avhandling undersöks en CCM-metod för att producera $Mg(OH)_2$ från Mg-silikat bergarter, och processens effektivitet, energibehov och miljöpåverkan utvärderas. $Mg(OH)_2$-produktionsprocessen som studeras här lyftes fram första gången år 2008 i en magistersavhandling av samma författare. Då tillämpades metoden endast på en typ av Mg-silikat bergart (finsk serpentinit från nickelgruvan i Hitura, Finn Nickels gruvområde) och de optimala process-, energi- och miljöförhållandena var inte kända.

Tillverkningen av $Mg(OH)_2$ från Mg-silikat bergarter består av två steg: extraktion av Mg och utfällning av $Mg(OH)_2$. I det första steget extraheras magnesium och andra katjoner genom att låta pulveriserad serpentinit eller olivin (ett slags Mg-silikat bergart) reagera med ammoniumsulfat (AS)-salt vid 400–550 °C (helst < 450 °C). I det andra steget reagerar katjonerna med en ammoniumlösning (extraherat från det första steget efter att de lakas i vatten) för att bilda huvudsakligen FeOOH, $Mg(OH)_2$ av hög renhetsgrad och AS (i vattenlösning). Produktionsprocessen av $Mg(OH)_2$ som beskrivs här utgör ett slutet system: gasformig ammoniak och vattenånga, som produceras vid extraktionssteget, återvinns och används vid utfällningssteget för att sedan åter utvinnas från vattenlösningen för användning i extraktionsteget.

Magnesiumextraktionssteget har fått en framträdande roll i denna avhandling eftersom den bestämmer konverteringsgraden samtidigt som det är det mest energikrävande steget i hela CCM- processen. Reaktiviteten och extraktionsbeteendet av olika bergarter (serpentinit och olivin) från olika geografiska områden (Australien, Finland, Litauen, Norge och Portugal) undersöktes. Dessutom utfördes en parametrisk undersökning för att bestämma den optimala reaktionstemperaturen, tiden och kemikaliehalten (AS). Utöver detta undersöktes också effekten av reaktortyp, konfiguration, omrörning och möjligheten för uppskalning av processen. Den producerade hydroxiden [$Mg(OH)_2$] kan användas för att omvandla CO_2 till termodynamiskt stabilt och miljövänligt magnesiumkarbonat. Därför har också hela CCM-processen vid ÅA, från Mg extraktionen till karbonatproduktionen, undersökts med hjälp av livscykelanalys, och dess

energi och miljöprestanda evaluerats. En livscykelanalys motiveras av det faktum att CCM-metoden i fråga bör erbjuda en helhetslösning på vad som är både ett energi- och miljöproblem.

Resultaten i denna studie visar att olika Mg-silikat bergarter reagerar olika och att olivin är betydligt mindre reaktivt än serpentinit. Sammantaget är reaktiviteten av olika Mg-silikat bergarter en funktion av både kemiska och fysikaliska egenskaper. Reaktionstemperaturen och uppehållstiden förblir två viktiga parametrar att beakta vid processens utformning och drift. Reaktorns värmeöverföringsegenskaper bestämmer temperaturen vid vilken maximal Mg-extraktion kan uppnås. Dessutom leder en ökning av reaktionstemperaturen till en ökning i extraktionsgraden upp till en punkt och olika resultat erhålls som funktion av uppehållstiden. Processenergibehovet för att producera $Mg(OH)_2$ i det hypotetiska fallet med järnfri serpentinitsten är 3,62 GJ/t-CO_2. Detta värde kan öka med 16–68% beroende på typen av järnförening (FeO, Fe_2O_3 eller Fe_3O_4) i mineralet. Detta tyder på att den potentiella användbarheten av FeOOH som råmaterial i järn- och stålproduktion bör övervägas med hänsyn till energin, kostnaderna och utsläppen som dess tillverkning kräver. Ammoniumsulfatåtervinning genom kristallisering är det näst mest energikrävande processteget efter extraktionssteget, men valet av en evaporator med mekanisk återkompression över "enkel avdunsting" som kristallisationsmetod kan medföra betydande exergibesparingar, upp till 15,2 GJ/t-CO_2 (84 % besparing). Integreringen av $Mg(OH)_2$-produktionsmetoden och det efterföljande (gas/fast) karbonatiseringssteget kan i sin tur reducera ÅA CCM-processens energibehov med 25 %. Resultaten från livscykelanalysen för ÅA CCM-processen visade att för varje ton mineraliserad CO_2 undviks 430–480 kg CO_2 utsläpp i atmosfären.

Den i denna avhandling undersökta $Mg(OH)_2$-processen har många lovande egenskaper. Även med processens relativt höga nuvarande energi-och miljöbelastning, kan produktionen av $Mg(OH)_2$ från Mg-silikater spela en viktig roll i påskyndandet av CCM-processer i allmänhet. Framtida forskning och utveckling har därmed potential att avsevärt förbättra $Mg(OH)_2$-produktionsprocessen.

Contribution of the author and list of publications

This thesis is based primarily on the below listed publications which will thereafter be referred to in the thesis by their Roman numerals. The thesis author is the main contributor in the publications.

Paper I: The author planned and performed the experiments with some assistance from Thomas Björklöf. The chemical modeling and kinetics study in this paper was done in collaboration with Prof. Johan Wärnå. The author interpreted the results, wrote the first draft of the manuscript and finalized it with the co-authors.

Paper II: The author planned and performed the experiments. The surface area and porosity measurements were performed by Ermei Mäkilä while the data modeling section was done by Thomas Björklöf. The author interpreted the results, wrote the first draft of the manuscript and finalized it together with the co-authors.

Papers III-VI: The author was responsible for most of the experiments. Modeling and simulations, process assessment, interpreting the results and writing the first draft of the paper were done by the author. Finalization of the papers was done together with the co-authors.

Paper I *Production of magnesium hydroxide from magnesium silicate for the purpose of* CO_2 *mineralization - Part 1: Application to Finnish serpentinite*

Nduagu, E., Björklöf T., Fagerlund, J., Wärnå, J., Geerlings, H., Zevenhoven, R.

Mineral Engineering 2012: 30, 75-87

DOI: 10.1016/j.mineng.2011.12.004

Paper II *Production of magnesium hydroxide from magnesium silicate for the purpose of* CO_2 *mineralization - Part 2: Magnesium extraction modeling and application to different Mg silicate rocks*

Nduagu, E., Björklöf, T., Fagerlund, J., Mäkelä, E., Salonen, J., Geerlings, H., Zevenhoven R..

Mineral Engineering 2012: 30, 87-94

DOI: 10.1016/j.mineng.2011.12.002

Paper III *Contribution of iron to the energetics of CO_2 sequestration in Mg-silicate-based rock*

Nduagu, E., Fagerlund, J., Zevenhoven, R.

Energy Conversion and Management 2012: 55. 178–186

DOI: 10.1016/j.enconman.2011.10.023

Paper IV *Life cycle assessment of Co_2 sequestration in magnesium silicate rock – A comparative study*

Nduagu, E., Bergerson, J., Zevenhoven, R.

Energy Conversion and Management 2012: 55. 116–126

DOI: 10.1016/j.enconman.2011.10.026

Paper V *Production of $Mg(OH)_2$ for CO_2 emissions removal applications: parametric and process evaluation*

Nduagu, E., Romão, I., Zevenhoven, R.

Proceedings of the 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS 2012), Perugia, Italy, June 26-29, 2012, paper 245

Paper VI *Performance assessment of producing $Mg(OH)_2$ for CO_2 mineral sequestration*

Nduagu, E., Romão, I., Fagerlund, J., Zevenhoven, R.

Applied Energy (Submitted August 2012).

Related publications not included in the thesis

- ***Carbonation of magnesium silicate mineral using a pressurised gas/solid process***

  Fagerlund, J., Teir, S., Nduagu, E., Zevenhoven, R.
  Energy Procedia 2009: 1(1). 4907–4914
  DOI: 10.1016/j.egypro.2009.02.321
  Presented at the 9th International Conference on Greenhouse Gas Technologies (GHGT-9), November 16–20, 2008, Washington DC, USA.

- ***Production of magnesium hydroxide from magnesium silicate for the purpose of CO_2 mineralisation and increasing ocean alkalinity: effect of reaction parameters***

  Nduagu, E., Zevenhoven, R.
  Proceedings of the 3rd International Conference on Accelerated Carbonation for Environmental and Materials Engineering (ACEME10), Turku Finland, Nov. 29 – Dec. 1, 2010, pages 31-40

- ***A stepwise process for carbon dioxide sequestration using magnesium silicates***

  Fagerlund, J., Nduagu, E., Romão, I., Zevenhoven, R.
  Front. Chem. Eng. China 2010: 4(2). 133–141
  DOI: 10.1007/s11705-009-0259-5
  Presented at 10th International Conference on Carbon Dioxide Utilization (ICCDU-X), May 17–21, 2009, Tianjin, China.

- ***CO_2 fixation using magnesium silicate minerals. Part 1: Process description and performance***

  Fagerlund, J., Nduagu, E., Romão, I., Zevenhoven, R.
  Energy (special edition: ECOS'2010) 2012: 41. 184-191
  DOI: 10.1016/j.energy.2011.08.032
  Presented at the 23rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS´2010), June 14–17, 2010, Lausanne, Switzerland.

- ***CO_2 fixation using magnesium silicate minerals. Part 2: Energy efficiency and integration with iron- and steelmaking***

  Romão, I., Nduagu, E., Fagerlund, J., Gando-Ferreira, L., Zevenhoven, R.

Energy (special edition: ECOS'2010) 2012: 41. 203-211
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Presented at the 23rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS´2010), June 14–17, 2010, Lausann, Switzerland.

- ***Recent developments in the carbonation of serpentinite derive $Mg(OH)_2$ using a pressurized fluidized bed***

  Fagerlund, J., Nduagu, E., Zevenhoven R.
  Energy Procedia 2011: 4. 4993–5000
  DOI: 10.1016/j.egypro.2011.02.470
  Presented at the 10th International Conference on Greenhouse Gas Technologies (GHGT-10), September 19–23, 2010, Amsterdam, The Netherlands.

- ***Integrated carbon capture and storage for an oxyfuel combustion process by using carbonation of $Mg(OH)_2$ produced from serpentinite rock.***

  Said, A., Eloneva, S., Fogelholm, C., Fagerlund, J., Nduagu, E., Zevenhoven, R.
  Energy Procedia 2011: 4. 2839-2846
  DOI: 10.1016/j.egypro.2011.02.189
  Presented at the 10th International Conference on Greenhouse Gas Technologies (GHGT-10), September 19–23, 2010, Amsterdam, The Netherlands.

- ***Carbonation of serpentinite rock from Lithuania and Finland***

  Stasiulaitiene, I., Fagerlund, J., Nduagu, E., Denafas, G., Zevenhoven, R.
  Energy Procedia 2011:4. 2963-2970
  DOI: 10.1016/j.egypro.2011.02.205
  Presented at the 10th International Conference on Greenhouse Gas Technologies (GHGT-10), September 19–23, 2010, Amsterdam, The Netherlands.

- ***Carbon dioxide storage by mineralisation applied to an industrial-scale lime kiln***

  Romão, I., Eriksson, M., Nduagu, E., Fagerlund, J., Gando-Ferreira, L., Zevenhoven, R.
  Proceedings of the 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (ECOS2012), Perugia, Italy, June 26-29, 2012, paper 226.

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Nomenclature

ÅAU	Åbo Akademi University
ARC	Albany Research Center (nowadays National Energy Technology Laboratory (NETL)), Albany, US.
AS	Ammonium sulfate salt
C	Carbon
CCGS	CO_2 capture and geological storage
CCM	Carbon dioxide capture and mineralization
CCS	Carbon dioxide capture and storage
CDR	carbon dioxide removal
CE	Climate engineering
C/GJ	Carbon per Gigajoule
CO_2e or CO_2eq	Carbon dioxide equivalent
$CO_2e/t\text{-}CO_2$	Carbon dioxide equivalent per ton CO_2 mineralized
E	Exergy, J
EDTA	Ethylenediaminetetraacetic acid
EJ	Exajoules, 10^{18} J
EOR	Enhanced oil recovery
EPA	Environmental Protection Agency
FB	Fluidized bed
Fe *ext*	Iron extraction
G	Gibbs free energy, J/mol
GE	Geoengineering
GJ	Gigajoule
$GJ/t\text{-}CO_2$	Gigajoule per ton CO_2
GHGs	Greenhouse gases
GWe	Gigawatt electricity
Gt	Gigatonne
Gt-C	Gigatonne carbon
GWP	Global warming potential
H	Enthalpy, J/mol
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
IEA	International Energy Association
IPCC	Intergovernmental Panel on Climate Change

kWh/t-CO_2	Kilowatt hour per ton CO_2
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle inventory assessment
MEA	Monoethanolamine
Mg ext	Magnesium extraction
Mg/Fe	Elemental Mg to Fe ratio of Mg-silicate rock
Mg-silicate	Magnesium silicate mineral.
MJ	Megajoule
MJ/t-CO_2	Megajoule per ton CO_2
MSWI	Municipal solid waste incinerator
MVR	Mechanical vapor recompression
MWh/t-CO_2	Megawatts-hour per ton CO_2
NETL	National Energy Technology Laboratory
NG	Natural gas
NGCC	Natural gas combined cycle
OTEC	Ocean thermal energy conversion
P	Pressure, atm
PCC	Precipitated calcium carbonate
Q	Heat, J
R&D	Research and development
S	Magnesium silicate mineral
S/AS	Mg-silicate to ammonium sulfate ratio
ΔS	Change in entropy, J/mol-K
SRM	Solar radiation management
T	Temperature, K
t	Time, s
UNFCCC	United Nations Framework Convention on Climate Change
XRD	X-ray diffraction
W	Work, J/s
Greek symbols	
Δ	Difference
$\sum$	Sum

1. Background

1.1. Anthropogenic carbon dioxide emissions and global warming

The Intergovernmental Panel on Climate Change (IPCC) concluded that global warming and climate change are strongly linked to anthropogenic long-lived greenhouse gases (GHGs), of which carbon dioxide (CO_2) is dominant (see Figure 1). Global warming as defined by Houghton (2005) is the effect on the climate of human activities, in particular the burning of fossil fuels (coal, oil and gas) and large-scale deforestation, which cause emissions to the atmosphere of large amounts of GHGs. The GHGs present in the atmosphere cause what is generally known as greenhouse gas effect – the formation of a blanket by the GHGs which absorbs a portion of the thermal infrared radiation from the earth surface that determines the thermal balance between the sun's radiation absorbed and radiated back to space.

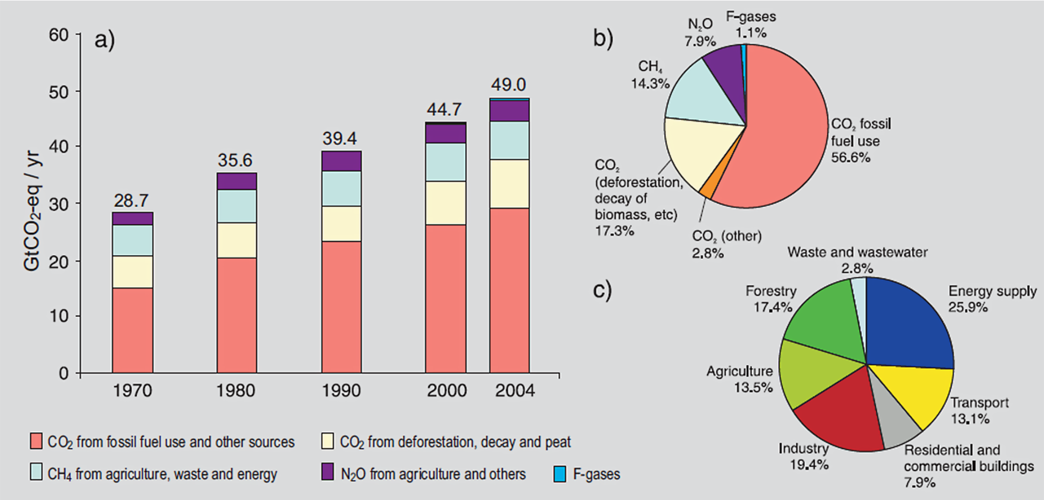

Figure 1 . (a) Global annual emissions of anthropogenic GHGs from 1970 to 2004. (b) Share of different anthropogenic GHGs in total emissions in 2004 in terms of CO_2-eq. (c) Share of different sectors in total anthropogenic GHG emissions in 2004 in terms of CO_2-eq. (Forestry includes deforestation) (IPCC, 2007b).

The term radiative forcing ($Wm^{-2}ppm^{-1}$) is used to show the measure of strength of externally imposed perturbation in the radiative energy budget of the Earth's climate system (Lashof and Ahuja, 1990). This variation in the radiative energy balance of the climate is caused by secular changes in the concentrations of radiatively active species (e.g., CO_2, aerosols, etc.), changes in the solar irradiance incident upon the planet, or other changes that affect the radiative energy absorbed by the surface (e.g., changes in surface reflection properties) (IPCC, 2001a). Apart from the radiative effects of GHG emissions on the atmosphere, their impacts are also time dependent. Radiative properties control the absorption of radiation per kilogram of gas present at any instant, but the lifetime controls how long an emitted kilogram of gas is retained in the atmosphere and hence is able to influence the thermal budget (IPCC, 2001a). Global warming potential (GWP) index, with units in carbon dioxide equivalent (CO_2eq. or CO_2e), was adopted in Kyoto (Kyoto Protocol, 1997) to account for a time-integrated radiative forcing effect of a GHG compared to that of a reference gas (usually CO_2). The GWP of the major GHGs are presented in Table 1.

Figure 1 shows that global GHG emissions due to human activities have grown since pre-industrial times, with an increase of 70% between 1970 and 2004. According to IPCC (2007a), based on the combined anthropogenic radiative forcing, it is extremely likely that since 1750 humans have exerted a substantial warming influence on the climate. More so, the rate of warming over the last 50 years is almost double that over the last 100 years (0.13°C ± 0.03°C vs. 0.07°C ± 0.02°C per decade) (IPCC, 2007b).

Table 1 Lifetime, cumulative forcing (Lashof and Ahuja, 1990) and 100-yr GWP (IPCC, 2007c) for various GHGs.

GHGs	**Residence time**(yr)	**Cumulative forcing** ($Wm^{-2}yrPg^{-1}$)	**GWP** (CO_2 eq.)
CO_2	230	0.42	1
CH_4	14.4	4.4	21
N_2O	160	77	310
HCFC-22	15	180	1500
CFC-11	60	540	3800
CFC-12	120	1600	8100

Associated with this warming are changes of climate (IPCC, 2001b, 2007a,b), some of which are unwanted and could portend deleterious environmental and socio-economic impacts. The possible impacts of climate change are well documented (IPCC, 2007b) but fall outside the scope of this thesis.

1.2. Alarming rise in atmospheric CO_2 concentrations

The use of fossil fuels as the primary energy source has attendant environmental implications (IEA, 2011, IPCC, 2007b). Figure 2 illustrates how CO_2 emissions from fossil-fuel burning, cement manufacture, and gas flaring and the atmospheric CO_2 concentrations strongly correlate and are both increasing at unprecedented levels. Current atmospheric CO_2 concentration is almost 395 ppm (Conway and Tans, 2012). Anthropogenic CO_2 emissions contribute significantly to the historic rise in atmospheric CO_2 concentrations.

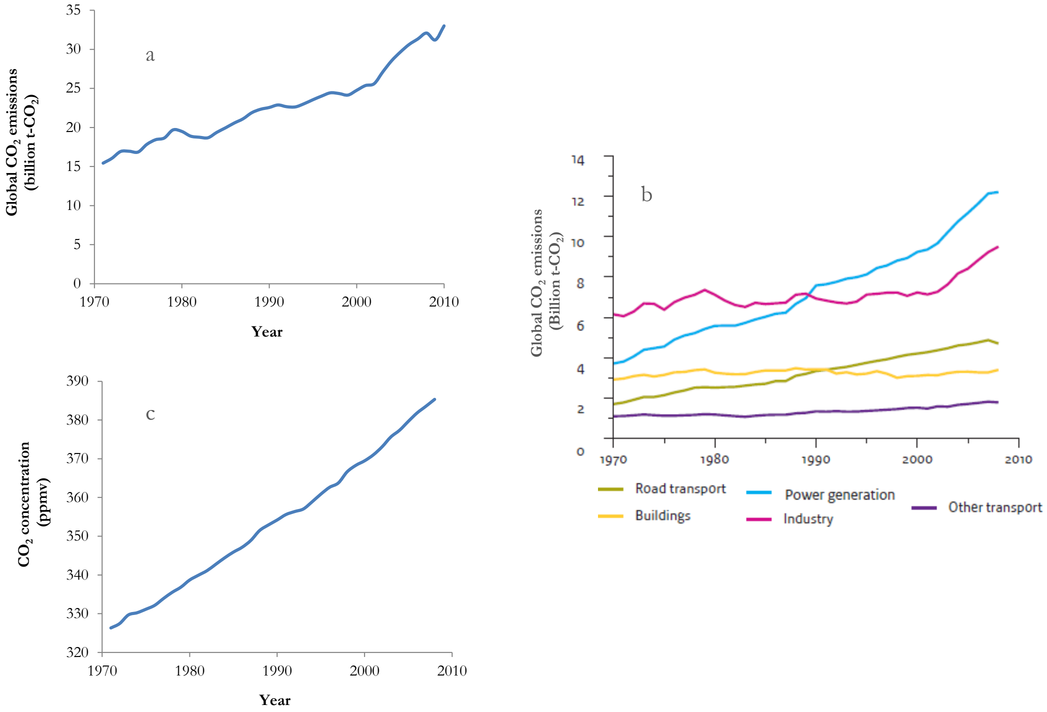

Figure 2. (a) Global CO_2 emissions from fossil-fuel burning, cement manufacture, and gas flaring (1970-2008 data is from Boden et al. (2011) while 2009-2010 data is from IEA (2012)); (b) Industry contribution to global CO_2 emissions (Redrawn from Olivie et al. (2011)) and (c) Mean atmospheric CO_2 concentrations(Data from Conway and Tans (2012)).

The rising atmospheric concentrations of CO_2 present a serious long term threat to the environment. IPCC (2007b) points out that depending on the rate of change in greenhouse gas emissions, the global mean temperature will continue to rise between 1°C and 6°C as compared to 1990 – 2000 levels; the level of warming that may have deleterious ecological, agricultural and socio-economic consequences.

1.3. The need to reduce CO_2 emissions from energy use

Not all scientists agree that climate change exists, its causalities are traceable to human activities or possible magnitude and impact are as generally portrayed due to inherent uncertainties and complexity of the climate system (Heal and Kriström, 2002, New and Hulme, 2000, Reilly et al., 2001, Tol, 2003, Kellogg, 1991, Idso, 1998). Consequently, there have been doubts and skepticism about climate change in the public domain. More interesting is the fact that the lack of unanimity among the climate scientists has also created room for political debates on whether or not to take the climate change issue seriously in policy decisions.

Nonetheless, there seems to be a consensus to limit the increase in anthropogenic CO_2 emissions build-up in the atmosphere. Thus, the need to reduce CO_2 emissions from fossil sources and produce energy in a sustainable manner has become one of the most important energy and environmental challenges of the 21st century. The United Nations Framework Convention on Climate Change (UNFCCC), which was adopted in 1992, has an objective to stabilize GHG concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Later, an international legally binding commitment was made by developed countries to reduce GHG emissions worldwide by an average of 5% from 1990 levels over the period 2008 - 2012 (Kyoto Protocol, 1997). The European Union (EU), for example, committed to achieving a 20% reduction of its GHG emissions by 2020 as compared to 1990. In 2009, at the United Nations Climate Change Conference in Copenhagen through the Copenhagen Accord, developed and developing nations negotiated a deal to both contribute to emissions reduction and limit global warming to two degrees Celsius compared to pre-industrial times. Thus, commitments and efforts to reduce GHG emissions are being made, though these are too insignificant to make a difference when compared with the scope and magnitude of the problem.

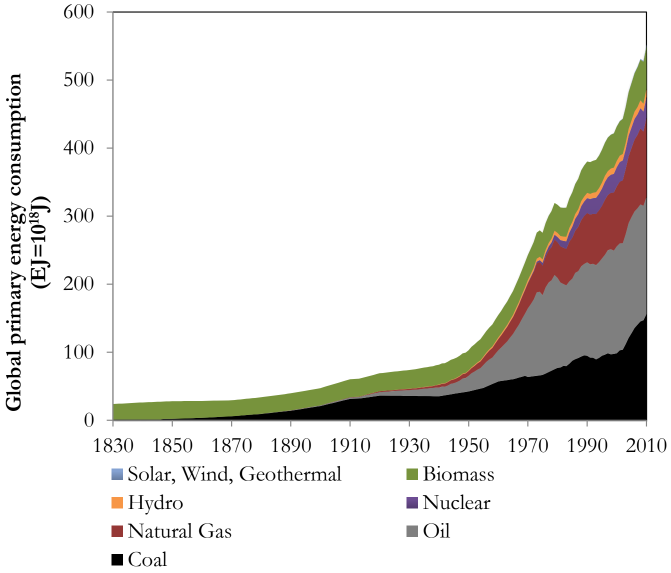

Figure 3. Global energy consumption in Exajoules (10^{18}J) from 1830 to 2010. Redrawn from Koppelaar (2012).

At the heart of the GHG emission reduction discussion is the need to reassess the ways the global energy demand is met. For many decades, the global demand for energy and associated services has increased dramatically (Fig. 3). Fossil fuels (coal, oil, natural gas *etc.*) have been the principal driver of the world's energy and economic engine since the beginning of the 20th century. Currently, the global primary energy consumption is over 500 exajoules (EJ=10^{18} J) annually. Fossil fuels provide over 80% of this energy, while the rest is provided for by bio-energy (mainly from wood combustion) 11.3%, nuclear 5.5%, hydro 2.2% and other renewable energy sources <0.4% (Koppelaar, 2012).

Regardless of the global awareness of threats of global warming, there seems to be no possible immediate or near term reversal of the disturbing trend. According to the International Energy Agency (IEA), by 2010 there was more than 1600 GWe of installed generation capacity of the global coal-fired power plant fleet, accounting for more than 8.5 Gigatonnes (Gt) of carbon dioxide (CO_2) emissions each year. This represents roughly one-quarter of the world's anthropogenic CO_2 emissions. A more astonishing fact is that coal-fired power generation is expanding faster than ever, with capacity additions experiencing a record growth of more than 350 GWe over the last five years (OECD/IEA, 2012). Forecasts indicate that fossil fuels will increase their global share of energy by ~5% by the middle of this century. This may be as a result of their relative low cost compared with nuclear and renewable energy, versatility of use and ease of storage.

Given the theoretical energy supply from non-fossil and renewable energy sources and the engineering options to decarbonize the global energy sector, it could be possible to stabilize atmospheric CO_2 concentrations at the current levels of emissions. However, significant investments must be made in the short term in research and development, demonstration and deployment of these alternative energy options.

1.4 Options for reducing CO_2 emissions and mitigating climate change

Significant reductions in CO_2 emissions from the global energy system are technically feasible over the course of the next century, using various combinations of low CO_2 energy technologies (Johansson et al., 1996). These options, which can reduce CO_2 emissions from the energy system and avoid the most severe impacts of climate change while still satisfying global demand for energy services, have been outlined and assessed (IPCC, 2007b). They include: energy conservation and efficiency improvements, fossil fuel switching, renewable energy, nuclear and carbon dioxide sequestration. The scale and timeframe required for CO_2 emissions reduction make it unlikely for one single technology to provide all of the mitigation potential in any of the CO_2 emitting sectors (IPCC, 2007b). Thus, a pragmatic approach would be to consider all options in view of their respective mitigation potentials, their contribution to sustainable development and all associated risks and costs (IPCC, 2011).

Energy conservation and efficiency improvements would play a leading role in meeting climate stabilization targets in the short term untill 2030 (IPCC, 2007b). Energy efficiency could in principle achieve large improvements (≥5-fold) through aggressive investments in R&D and the removal of market imperfections such as corporate subsidies (Huesemann, 2006). However, its contribution will be limited and time dependent, considering the scale of global economic expansion and rate of growth of developing economies. Over the next century, and as the emissions reduction targets become more ambitious, the importance of energy efficiency would be reduced as compared with options representing decarbonised energy supply, but it still remains very important (Ürge-Vorsatz and Metz, 2009).

Fossil fuel switching – substituting with low-carbon fossil fuels – is a viable option for reducing emissions because this could achieve as much as a 50% reduction in the fuel carbon intensity. Natural gas is the most favored fuel in this respect because it has the lowest specific

CO_2 emission rate of all fossil fuels at ~ 14 kg C/GJ compared to ~ 20 kg C/GJ for oil and ~ 25 kg C/GJ for coal (Johansson et al., 1996). The shift from coal to natural gas in power production is gaining attention because of both economic competitiveness and environmental benefits.

The renewable energy technologies assessed by IPCC (2011) as potentially able to contribute to low carbon transformation of the energy sector include bioenergy, geothermal energy, direct solar energy, hydropower, ocean (tidal, through ocean thermal energy conversion, OTEC) and wind energy. Most of these technologies are not as well established as their fossil counterparts while others are not fully deployed. However, the good news is that renewable energy technology development and deployment is gaining some momentum although its contribution in absolute terms remains limited. According to Olivie et al. (2011), the annual growth of renewable energy supply accelerated after 2003 from a few per cent to an average of 6% while the renewable energy's share of the global energy supply increased from 7% by 2004 to over 8% by 2010 (excluding traditional biofuels such as fuel wood and charcoal). The global technical potential for renewables is substantially higher than the global energy demand, with the technical potential for solar energy being the highest among the renewable sources (IPCC, 2011). However, technical limitations to full deployment of these technologies are also substantial. Some of these challenges include sustainability and intermittency concerns, public acceptance, system integration and economic competitiveness.

Due to its high energy density, remarkably low fuel requirements and the potential to deliver large amounts of energy without releasing significant quantities of greenhouse gases, nuclear energy is an attractive alternative to fossil fuel-derived energy in a carbon-constrained world. However, a handful of nuclear accidents, for example, the Three Mile Island, Chernobyl and more recently, the Fukushima nuclear disaster, engendered a negative public perception and consequently mired the deployment of more nuclear power plants especially in many western countries. For instance, the associated health and proliferation risks of nuclear plants have led countries like Austria, Sweden, Italy and Belgium to phase out nuclear power. More recently, after the Fukushima nuclear disaster, Germany announced the shutting down of all its seventeen nuclear stations by 2022. Even with the increasing negative perception and phasing out of nuclear power by a few countries, the share of nuclear power has remained constant at ~6 % of the global primary energy supply for many years, and currently at 13% of the world electricity generation (IEA, 2011, Olivie et al., 2011, Koppelaar, 2012). In a future with likely greater restrictions on CO_2-emitting fuels, it is anticipated that nuclear energy would at least maintain its current global energy share among the various energy options.

Carbon dioxide sequestration technology has a significant potential and could reduce overall mitigation costs while increasing flexibility; ensuring that both current and future energy demands are met in a carbon-neutral manner as we transition towards a decarbonized and mostly renewable energy economy (Lackner, 2003, IPCC, 2005b). A major component of CO_2 sequestration technology is carbon dioxide capture and storage (CCS).The other component involves improving the rate and capacity for terrestrial or marine photosynthesis. The IPCC characterized CCS as the capture of CO_2 emissions at source prior to potential release, transport and storage in: 1) deep oceans or geological media known as CO_2 capture and geological storage (CCGS) and 2) mineral rocks or waste products, also known as mineral carbonation or CO_2 mineralization. Of particular interest to this thesis is the mineral carbonation component of the CCS technology. This study is part of R&D efforts aimed at reducing GHG emissions by permanently binding CO_2 emissions to mineral substrates like magnesium (Mg) silicate-based rocks. The chapter on "CO_2 sequestration" will discuss the various sequestration options.

An emerging climate mitigation option gaining attention lately is geoengineering (GE). GE is defined as the intentional modification of the Earth's environment to promote habitability (EPA, 2009). Climate engineering (CE) is a more accurate term reflecting the broader implications of the most widely discussed concepts of modifying climate to curtail the harmful effects of global warming (Bickel and Lane, 2010). Although CE was not part of the mitigation portfolios considered by IPCC, there has been increased but controversial debate lately on what role, if any, that CE may play in mitigating climate change and if the technology should be developed.

According to The Royal Society (2009), two components of climate engineering considered are carbon dioxide removal (CDR) and solar radiation management (SRM). CDR approaches remove CO_2 from the atmosphere. The CDR approaches include, 1) air capture of $CO_{2,}$ 2) terrestrial and ocean CO_2 removal and storage as biotic carbon and 3) accelerated mineral weathering – similar to mineral carbonation. The main challenge for air capture is high costs (Holmes and Keith, 2012, American Physical Society, 2011, House et al., 2011, Lackner, 2010). However, its major advantages, should it be realized at cost-effective industrial scale include the following: 1) It allows one to apply industrial economies of scale to small and mobile emission sources—about 60 per cent of global carbon emissions—which enables a partial decoupling of carbon capture from the energy infrastructure. 2) It provides a route to managing carbon emissions in the transportation sector—where carbon mitigation costs are generally higher than in the electric sector—by enabling the generation of carbon-neutral hydrocarbons (Zeman and Keith, 2008). The other CDR approaches are discussed in Chapter 2.

On the other hand, SRM techniques would reflect a small percentage of the sun's light and heat back into space, offsetting the global warming effects of increased greenhouse gas concentrations by causing the Earth to absorb less solar radiation (The Royal Society, 2009, Keith et al., 2010). Keith et al. (2010) summed up the characteristics of SRM as cheap and fast but imperfect. The prevailing opinion is that large-scale intervention in the climate system would involve numerous side-effects and incalculable risks and that the option of drastically reducing emissions is preferable on all accounts (Rickels et al., 2011). GE techniques are unproven and are considered potentially dangerous (The Royal Society, 2009, Corner and Pidgeon, 2010). However, adherents of technology argue that CE should be researched and developed, and may become a viable remedy to climate emergency (The Royal Society, 2009, Keith et al., 2010).

1.5 Aims of this thesis

Mg-silicate minerals react naturally with atmospheric CO_2 at geological timeframes (over hundreds of thousands of years) to form environmentally benign and thermodynamically stable magnesium carbonate ($MgCO_3$) through a process called rock weathering (Lackner et al., 1995, Lackner, 2003). On the other hand, $Mg(OH)_2$ produced from Mg-silicate rocks react with CO_2 faster, in a few minutes. More so, $Mg(OH)_2$ reacts significantly faster than MgO, which has also been proposed as a potential material for CO_2 sequestration (Lackner et al., 1997, Lackner, 2002b, Zevenhoven et al., 2008a,b, Fagerlund and Zevenhoven, 2011, Fagerlund et al., 2009, 2011, 2012b).

Earlier attempts were made to produce $Mg(OH)_2$ for the same purpose but the processes proposed were expensive and/or required enormous amounts of energy for reagent regeneration; therefore, emitting more CO_2 than it sequesters (Lackner et al., 1995, 1997, Lin et al., 2008). In this thesis, a method for producing $Mg(OH)_2$ from Mg-silicate rocks for carbon dioxide capture and mineralization (CCM) was investigated, and the process efficiency, energy and environmental impact assessed. The $Mg(OH)_2$ process studied here was proposed (Nduagu, 2008) prior to this thesis; however, at that time the process was applied to only one Mg-silicate rock (Finnish serpentinite from the Hitura nickel mine site of Finn Nickel) and the optimum process conversions, energy and environmental performance were not known.

— Background—

In this thesis, producing $Mg(OH)_2$ from Mg-silicate rocks was investigated in order to design an effective mineral carbonation process that can store CO_2 emissions permanently and safely as magnesium carbonates. Process energy and life cycle assessments were carried out to determine the feasibility of producing $Mg(OH)_2$ from Mg-silicate rocks for CO_2 mineral sequestration. This research work expands further the work done by Nduagu (2008) and adds to the recent thesis of Fagerlund (2012).

2. CO_2 sequestration

CO_2 sequestration in its broadest sense is any technology that keeps CO_2 out of the atmosphere (Yegulalp et al., 2001). Carbon dioxide sequestration as a climate change mitigation strategy could happen by natural and/or engineered ways:

Table 2. Comparison of carbon dioxide sequestration methods in terms of their long term potential, stage of development, relative costs and potential risks. Modified from Huesemann (2008).

Mitigation technology	**Long-term potential***	**Stage of development**	**Relative cost**[a]	**Potential risks**	**Other issues**
Terrestrial	50 to 100 Gt-C.	Current technology.	Low.	None.	Competition with food, fibre and fuel wood.
Geological					
Coal seams, oil and gas fields.	10s to 100s Gt-C.	R&D, pilot study.	Medium to high.	Environmental health.	Leakage issues, public acceptance
Saline aquifers.	100s to 10000s Gt-C.	R&D, pilot study.	Medium to high.	Environmental health.	Leakage issues, public acceptance
Ocean					
CO_2 disposal.	1000s Gt-C	R&D, pilot stopped.	Medium to high	Acidification of marine biota.	Public resistance, legality.
Iron fertilization.	~0.2 Gt-C yr^{-1}.	R&D, pilot study	Low to Medium	Marine environment.	Public resistance, legality.
Mineral carbonation	10000s to 1000000 Gt-C.	R&D, pilot study.	Medium to high.	None.	Ecological issues of large-scale mining and processing of rocks.

*[a]The quantification of exact costs or cost ranges is difficult for the following reasons: (1) for many currently existing technologies, costs are expected to decrease substantially due to economies of scale if they were to be widely adopted; (2) for mitigation strategies that exhibit some type of saturation phenomenon (e.g. planting trees on limited land), marginal costs increase as opportunities for applying them decreases; (3) for technologies that are still in the research and development stage (e.g. geological sequestration, iron fertilization), costs are difficult to estimate because the final system or end-product is not yet known; (4) for technologies that transfer costs and risks to future generations (e.g. geological sequestration), present-day cost estimates may be significantly underestimated. * Orders of magnitude estimates for CO_2 storage capacity (Lackner, 2002a, Herzog, 2001, Huesemann, 2008).*

1) By improving the rate and capacity for terrestrial or marine photosynthesis, 2) Capture of CO_2 emissions at source prior to potential release, and storage in deep oceans or geological media and 3) Surface mineral carbonation. Options (2) and (3) are known collectively as carbon capture and storage, CCS. The capacity, stage of development, relative costs and potential risks of the different CO_2 sequestration methods are tabulated in Table 2.

2.1. CO_2 removal from air by enhanced photosynthesis

Terrestrial and marine photosynthesis involve the removal of CO_2 from the atmosphere and its subsequent long-term storage of the carbon-rich biomass (Bachu, 2008). As shown in Table 2, enhanced terrestrial photosynthesis, through reforestation, improved agricultural soil management, etc., has a long-term potential for CO_2 reduction of about 100 Gt-C (Gt-C=3.67 Gt-CO_2) while iron fertilization has an annual CO_2 reduction potential of 0.2 Gt-C yr^{-1}. Potential benefits from forestation and bioenergy practices aside CO_2 sequestration include restoring deforested land, managing water runoff and retaining soil carbon and adding value to rural economies (Huesemann, 2006). However, atmospheric biomass, soil and ocean are all limited in their uptake capacity in regards to the size of fossil fuel deposits (Huesemann, 2006, Lackner, 2002a). More so, the associated issues of public acceptance, legality and competition with agricultural land use for food, fibre and fuel wood production and negative biodiversity effects are important limitations (Bachu, 2008, Huesemann, 2006, 2008).

2.2. CO_2 capture and storage

As mentioned in Section 1.4, the goal of CCS is to achieve greenhouse gas emission reductions while allowing the continued use of fossil fuels. This aim has been criticized as a possible “excuse technology” to continue the reliance on fossil fuels, or as a deceptive “silver bullet” in solving the global warming problem, or as a detour to the development and deployment of more sustainable, zero carbon energy technologies. In addition, the uncertainties about capacity to store CO_2 safely and permanently in gigaton (Gt) scales, technological and safety issues due to CO_2 leakage, negative public perception and high costs are some of the reasons that are delaying the full scale development and commercial deployment of carbon capture and geologic storage (CCGS) options. Apart from the discussions on the potential CO_2 leakage risks of CCGS, there has been an active debate recently on the possible seismic hazards associated with large scale CCGS deployment. This debate ensued after Zoback and Gorelick (2012) argued that large scale CCGS is risky and has a high probability to trigger earthquakes through the injection of large volumes of CO_2 into the brittle rocks commonly found in continental interiors. However, it still remains a fact that if these issues are solved, given an appropriate legal and policy framework, CCS, energy efficiency and some other mitigation efforts are complementary measures and should form part of a broad mix of measures required for a successful CO_2 mitigation strategy (Praetorius and Schumacher, 2009).

2.2.1. CO_2 capture and geological storage (CCGS)

Potential sites for geological storage include active oil fields, deep coal seams, depleted oil and gas reservoirs, deep saline aquifers, and mined salt domes and rock caverns (IPCC, 2005a,b). CCGS is a CCS option whose techniques have been in commercial operation for many years. For example, enhanced oil recovery (EOR), where CO_2 is injected into oil or gas formations to increase production output, has been evaluated since the 1950s and deployed at full scale in the oil industry since the 1970s. There are five industrial-scale storage projects in operation today, each annually sequestering around 1 Mt-CO_2. These projects include the Sleipner project in an offshore saline formation in Norway, the Weyburn EOR project in Canada, the In Salah project in a gas field in Algeria (IPCC, 2005a) and more recently the Snøhvit project in Norway and Gorgon in Australia. EOR is not typically a CO_2 mitigation option. It is targeted at maximizing the output of oil from oil wells, and not necessarily at addressing issues like the long term fate and possible leakage of the injected CO_2 (Praetorius and Schumacher, 2009). EOR uses CO_2 to eventually produce more CO_2 which results from the additional oil output and use. This makes EOR counterintuitive as an environmental solution; it may make sense economically but not long term CO_2 reduction-wise, when considered on a life cycle perspective. Besides, most of the CO_2 injected during EOR is extracted from underground wells (Lackner, 2003). To be able to contribute to CO_2 emissions reduction, the CO_2 for EOR should be emission-derived or anthropogenic (Voormeij and Simandl, 2004). Nonetheless, a wealth of experience and transferrable knowledge gained from EOR is applicable to CO_2 geological storage.

The global carbon storage capacity is estimated to be tens to hundreds Gt-CO_2 for coal seams, hundreds to ten thousand Gt-C for saline aquifers, and several hundred Gt-C for depleted oil and gas fields (Herzog, 2001). Deep saline aquifers are the largest potential sink for CO_2 among the various geological storage options, but are dwarfed by the storage volume that CO_2 mineralization – to be discussed below – offers. Although the storage capacity of geologic formations is large, more development is required to address integrity issues of the injected CO_2 and the possible occurrence of seismic disasters. Aside from that, more technological development is needed to reduce the energy and costs of CO_2 capture which is ~80% of the total CCS costs. The current state-of-the-art of CO_2 capture technology has an energy requirement (mainly heat) of 3 - 4 GJ/t-CO_2 (Abanades et al., 2004, Blomen et al., 2009, Davison, 2007, Kothandaraman et al., 2009, Rao and Rubin, 2002, Rubin et al., 2007).

2.2.2. Ocean storage of CO_2

Oceans cover about 70% of the surface of the planet, and represent the largest potential sink for anthropogenic CO_2. It already contains an estimated 40,000 Gt-C compared with only 750 Gt-C in the atmosphere and 2200 Gt-C in the terrestrial biosphere (Herzog, 2001). Since pre-industrial times, the oceans have absorbed about a half of the CO_2 emissions produced from burning fossil fuels, cement manufacture *etc.* The aim of ocean disposal is to accelerate the transfer of CO_2 from the atmosphere to the deep ocean, a process which occurs naturally at an estimated annual rate of 2 Gt-C (Huesemann, 2006). However, the unprecedented increase in levels of carbon emissions from pre-industrial levels (~280 ppm) to today's level (~395ppm) has resulted in increasing levels of acidity of the ocean; thereby, making the ocean lose its capacity to remove atmospheric CO_2 at rates that were obtainable earlier.

Ocean storage could be accomplished by injecting and dissolving CO_2 into the water column (typically below 1,000 meters) or onto the sea floor at depths below 3,000 m, where CO_2 is denser than water and is expected to form a "lake" that would delay dissolution of CO_2 into the surrounding environment (IPCC, 2005a). Injecting CO_2 to the ocean would increase ocean acidity and further slowdown the natural processes that absorb CO_2 from the atmosphere. CO_2 pumped into the ocean bottom will return to the atmosphere in about hundreds to thousands of years. It could also trigger processes that alter the geochemical balance of the marine environment and result in adverse environmental consequences. Pumping CO_2 into the sea is seen as a potentially risky practice that could trade one environmental problem for another, and possibly transfer today's environmental problem to future generations.

2.2.3. Mineral carbonation

Mineral carbonation (also known as mineral sequestration) involves the reaction of CO_2 with metal oxide-bearing materials to form insoluble carbonates, with calcium and magnesium being the most attractive metals (IPCC, 2005b). Mineral carbonation attractiveness is based upon the fact that mineral resources (alkaline and alkaline-earth silicate mineral deposits) are abundant (e.g. over 300,000 Gt of Mg-based silicate minerals), widespread, easily accessible, and could in theory sequester the CO_2 from all available fossil fuel at a rate faster than CO_2 removal through natural weathering (Lackner, 2003, Lackner et al., 1995). Natural weathering of alkaline silicate plays a significant role in absorbing and storing atmospheric CO_2 as environmentally benign and thermodynamically stable carbonates (Kojima et al., 1997, IPCC, 2005b). However, rock weathering happens very slowly, at geological timeframes - several millions of years (Hilley and Porder, 2008).

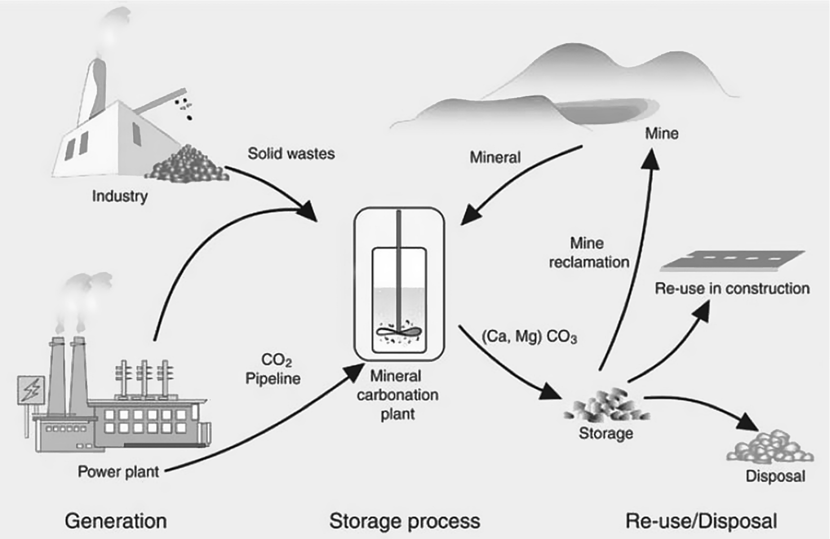

Figure 4. Material fluxes and process steps associated with the mineral carbonation of silicate rocks or industrial residues (IPCC, 2005b).

As illustrated in Fig. 4, mineral carbonation would require that the mineral rocks are mined, crushed and pulverized to required particle sizes. Depending on the design requirements, the processed mineral rocks would react with CO_2 separated from flue gases, or directly with CO_2-containing flue gases in a mineral carbonation plant. The location of the mineral would determine what material has to be transported to the mineral carbonation plant. Siting the mineral carbonation plant close to the CO_2 source would mean that the pulverized mineral rocks have to be transported (e.g. by lorry or train) to the mineral carbonation plant. Otherwise, the mineral carbonation plant can be sited close to the rock mining site. In this case the CO_2 or CO_2 containing gas would be transported via a pipeline or tankers.

Mineral carbonation, as a technological concept, is relatively new when compared to its geological storage counterpart. It was first proposed by Seifritz (1990) and later investigated by Lackner et al. (1995) in the U.S., and since around year 2000, also at many other locations like Finland. Mineral carbonation is still in the research phase, mostly done at laboratory scales, with a few pilot projects, about twenty-seven patents issued and an average of thirty-one publications annually (Torróntegui, 2010). The relatively slow pace of progress, delay in commercial deployment, and the associated leakage and seismic risks and economic issues associated with the more "popular" conventional geological storage (CCGS) seem to spur mineral sequestration research (Zevenhoven et al., 2011). A major advantage of mineral carbonation is that it avoids long term storage of CO_2 as a free phase (Lackner et al., 1997). The main products from mineral carbonation are thermodynamically stable solids; therefore, the sequestration of CO_2 is permanent and safe (Huijgen and Comans, 2005a). Mineral carbonation is even more attractive in countries like Finland and other places endowed with large amounts of magnesium silicates but without access to suitable sites for geological storage, offshore oil and gas fields or saline aquifers for CO_2 storage.

Another motivation for mineral carbonation is that the reaction of all common calcium and magnesium minerals is exothermic and thermodynamically favorable under ambient conditions (Lackner et al., 1997). Carbonate products formed from the process have a lower energy state than CO_2. This means that, in principle, the carbonation of abundantly available Mg and Ca minerals should at least be self-sustaining energetically, if not energy-generating. However, due to slow kinetics of the mineral carbonation reactions, several pretreatment options have to be applied to improve its efficacy. Consequently, the energy and economic costs of the process are increased to levels that make commercial application impractical. Several process routes are now pursued in many laboratories around the globe, aiming at addressing the technical and economic issues facing mineral carbonation.

The variants of the mineral carbonation process routes are presented in detail in Chapter 3. The feasibility of such processes is evaluated based on the following minimum requirements (Gerdemann et al., 2004): 1) The resource used to store the CO_2 must be large enough to store significant amounts of the CO_2. 2) The mineral resource must be near the power plant to minimize transportation costs. 3) The reagents must be cheap, recoverable and recyclable. 4) The product formed from binding the CO_2 must be environmentally benign and thermodynamically stable. 5) The energy and economic costs for the process must be kept to a minimum.

Over the past three years, there has been a significant increase in the number of review papers and book chapters covering the field of mineral carbonation (also known as carbon dioxide capture and mineralization, here abbreviated as CCM). Table 3 presents the most important ones.

Table 3. Review papers in the field of CCM

Reference	**Topic**	**Major highlights and conclusions**
Pan et al. (2012)	CO_2 capture by accelerated carbonation of alkaline wastes: A review on its principles and applications	The review focused on the use of industrial alkaline wastes, mainly steelmaking slags and metalworking wastewater. Also, a brief discussion on the different routes for carbonating minerals. Proposed a mechanism of carbonation reaction of alkaline solid waste and evaluated the kinetics.
Bobicki et al. (2012)	Carbon capture and storage using alkaline industrial wastes	The review focused on the use industrial alkaline wastes, also covering different aspects of mineral carbonation. Carbon sequestration capacity results have been published in a variety of forms, which are not readily converted from one to another. Each waste has its own unique set of advantages and disadvantages. Carbonation of industrial wastes could help establish mineral carbon sequestration technology as their use may be a stepping-stone towards the development of economic CO_2 sequestration processes utilizing natural minerals.
Zevenhoven et al. (2011)	CO_2 mineral sequestration: developments toward large-scale application	Summarized the state-of-the-art of ongoing development work worldwide. Illustrated future prospects of CO_2 mineralization within a portfolio of CCS. Twenty years of R&D work in CCM has not yet resulted in mature technology that can be applied on a large scale in an economically viable way. Current developments include an increasing number of patents and patent applications and a trend towards scale-up and demonstration.
Torróntegui (2010)	Assessing the mineral carbonation science and technology	The review was CCM-specific and covered developments in CCM from 2008 - 2010. Noted decrease of interest in single-step gas processes, but more interest in multi-step processes and the use of flue gas. The single step, direct aqueous carbonation with minerals is still the predominant investigated route with no major breakthrough. Comparative assessment of the different CCM options is difficult because all the work done is still at laboratory stages.

Stephens and Keith (2008)	Assessing geochemical carbon management	Described niche opportunities for using CaO- and MgO-rich industrial waste steams to sequester carbon. Considered application options for steel and iron slag and concrete, proposed possible carbonation schemes and estimated costs.
Sipilä et al. (2008) note: J Sipilä is nowadays J Fagerlund.	Carbon dioxide sequestration by mineral carbonation – Literature review Update 2005–2007	A CCM-specific review. Main routes for CCM were by direct aqueous, where an additive is used to achieve the required chemical reaction rate, or indirect aqueous, where extraction and carbonation of Mg or Ca are separate process steps optimised independently. Carbonation has gained attention and is studied by researchers in the US, Japan, the Netherlands, Finland, Canada, Switzerland, Lithuania, South Korea, Italy, Norway, Estonia and Greece.
Huijgen and Comans (2005a)	Carbon dioxide sequestration by mineral carbonation: Literature review update 2003-2004	A CCM-focused review. Some processes identified by the same authors in an earlier preliminary review (Huijgen and Comans, 2003) have been dropped. More research attention was focused on more promising aqueous processes. Considerable breakthroughs are required to make any of the processes viable. From an economical and practical point of view, possibilities for carbonation of industrial waste were emerging.
Voormeij and Simandl (2004)	Geological, ocean, and mineral CO_2 sequestration options: A technical review	Presented an overview of various CCS options with particular focus on application in Canada. The costs of CCM could be higher than for the injection of CO_2 into oil and gas reservoirs or deep coal seams.
Huijgen and Comans (2003)	Carbon dioxide sequestration by mineral carbonation	A CCM-focused review. Major improvements of the conversion rates were achieved by developing various process routes; the most promising being the direct aqueous route. Major setbacks to CCM at the time (and still now) are process energy consumption, the reaction rates and the environmental impact.
Herzog (2002)	Carbon sequestration via mineral carbonation: Overview and assessment	A CCM-specific review. Identified carbonation kinetics as a major challenge to CCM, noting that the environmental issues of a large mining operation seem manageable. Compared to other sequestration options, mineral sequestration should be viewed as longer-term and higher risk option because it still requires some key

		fundamental advances.
Lackner (2002a)	Carbonate chemistry for sequestering fossil carbon	A CCM-specific review. The only comprehensive theoretical review of CCM concept, covering also experimental work done at that period at Albany Research Center, (ARC), Albany, USA and cost estimates for CCM components. Identified heat treatment step for mineral ore as the most difficult challenge, raising the cost of the process to unacceptable levels.

Recent research interests involve exploring the possibility to sequester CO_2-containing flue gases directly; thereby, avoiding the expensive CO_2 capture step. This has raised hope of achieving an economically feasible mineral carbonation process. This process can be applied to flue gases from power plants, cement production plants, lime kiln processing plants (Khoo et al., 2011, Zevenhoven et al., 2012, Reddy et al., 2010, Romão et al., 2012a). More so, one key development during the last decade is that carbonation of waste materials, ashes, and industrial byproducts is rapidly expanding, with the benefit of binding significant amounts of CO_2 and/or producing a (valuable) carbonate material (Zevenhoven et al., 2011). Although the CO_2 sequestration potential for these waste products (at several 100 Mt CO_2/a) is limited when compared to Mg silicates, the overall benefit would then be the development of technical infrastructure for CO_2 mineralization. Progress in CO_2 sequestration in waste products could act as an 'icebreaker' for increased public acceptance of this inherently safe and environmentally benign CCS method (Zevenhoven and Fagerlund, 2010a).

3. CO_2 capture and mineralization (CCM)

Mineral rocks as well as industrial residues (or by-products) are potential materials for CCM. The type of material determines the type of processing required (Fig. 5). Alkaline as well as alkaline earth-based minerals can be carbonated, though alkaline earth metals especially those of calcium (Ca) and magnesium (Mg) are preferred. The high solubility of products of alkaline metals carbonation makes them unsuitable for safe and permanent CO_2 disposal. However, Ca- and Mg-carbonates produced from the mineral carbonation are thermodynamically stable and environmentally benign solids suitable for above ground disposal. Ca-based minerals (e.g. Wollastonite – $CaSiO_3$) suitable for carbonation are less reactive and less abundant than Mg-based minerals. The abundance of Mg-silicate rocks, for example, peridotite and serpentinite having 35 - 40%-wt. MgO content makes Mg-based rocks more attractive as carbonation candidates than their Ca-based mineral counterparts. The abundant calcium silicates contain only about 12 -15%-wt. CaO (Yegulalp et al., 2001).

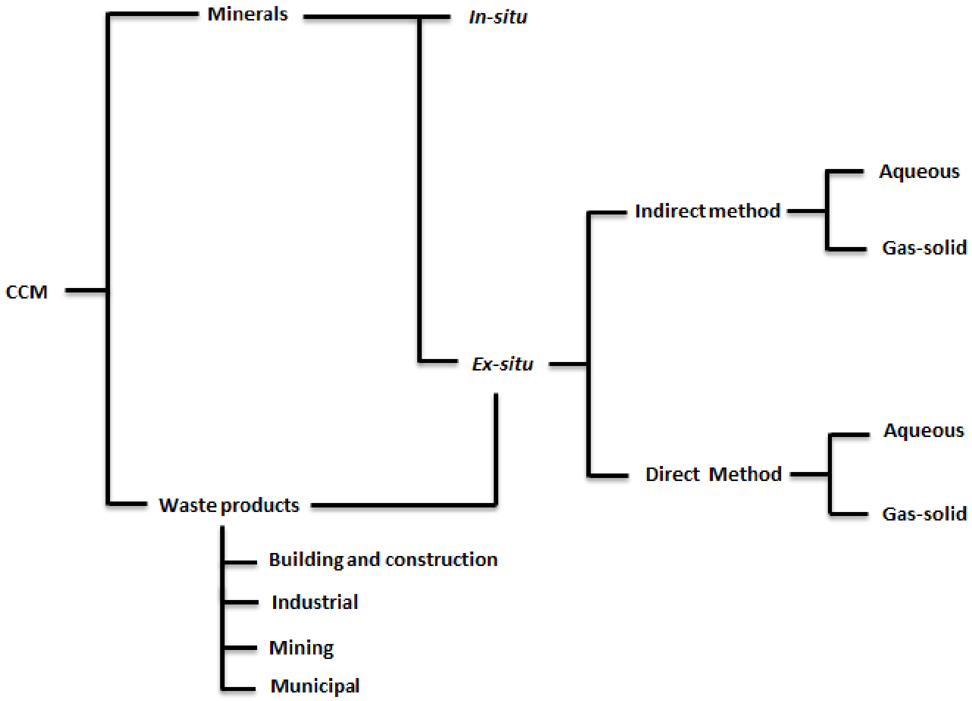

Figure 5. Carbon capture and mineralization processes and routes.

Waste products (especially industrial residues and by-products) are potential sources of alkalinity for CO_2 sequestration. Carbonation of waste products are mainly done *ex-situ* - above ground in a traditional chemical processing plant while carbonation of minerals can be applied either *in-situ* - CO_2 injection underground into geologic formations, and subsequently the host rock traps CO_2 to form carbonate minerals (Gerdemann et al., 2004) or *ex-situ*.

3.1 Carbonation of waste products

Alkaline waste residues from thermal processes or from construction and demolition activities are alternative feedstock for mineral carbonation (Costa et al., 2007). Among the waste products considered for carbonation, steelmaking slags (Eloneva et al., 2011a,b, 2008, Mattila et al., 2012, Watkins et al., 2010, Huijgen and Comans, 2005b, c, Doucet, 2010, Chang et al., 2011), cement and concrete wastes (Huntzinger et al., 2009a, Huntzinger et al., 2009b, Venhuis and Reardon, 2001, Walton et al., 1997), mining and mineral processing wastes (Pronost et al., 2011, Wilson et al., 2009, Akorede et al., 2012, Power et al., 2009, 2011), combustion waste and fly ashes (Montes-Hernandez et al., 2009, Uliasz-Bocheńczyk et al., 2009), alkaline paper mill wastes (Watkins et al., 2010, Perez-Lopez et al., 2008, Montes-Hernandez et al., 2009) and municipal wastes (Costa et al., 2007, Jianguo et al., 2009, Li et al., 2007, Bertos et al., 2004, Baciocchi et al., 2009) feature prominently.

The typical storage time of most of the CO_2 currently used by industrial processes is from days to months (IPCC, 2005b). This reduces the capacity of the carbon stored in waste products to contribute meaningfully to climate change mitigation, as it degrades to CO_2 and is re-emitted to the atmosphere in a short time. However, Bobicki et al. (2012) are of the opinion that carbonation of industrial wastes could help establish mineral carbon sequestration technology as their use may be a stepping-stone towards the development of economic CO_2 sequestration processes utilizing natural minerals.

Industrial residues and wastes are carbonated mostly via direct methods (either "dry" gas-solid or aqueous route). The aqueous processes have better carbonation kinetics and attain higher conversions than the dry processes, but large volumes of reactants (because of the introduction of large amounts of water) are processed. Consequently, bigger and probably more expensive reactors are needed for the aqueous than the dry processes. In addition, aqueous carbonation does poorly in energy economy; recovering the exothermic heat produced from carbonation is difficult because of dilution and a relatively low temperature. Direct aqueous carbonation of waste products is actively investigated as compared to only very few research projects (Prigiobbe et al., 2009, Baciocchi et al., 2006, Larachi et al., 2010, Reddy et al., 2010) focused on dry gas-solid carbonation.

The differences in compositions of the industrial residues make it difficult to generalize the process conditions for all wastes, demonstrating the importance of varying reaction conditions against different residue types (Torróntegui, 2010). However, there is a greater pace of progress of R&D in carbonating wastes when compared to carbonating natural minerals. The reason is that wastes are more reactive, achieving good carbonation kinetics and conversions without the need for activation. A major benefit of carbonating wastes is that value added products are made from seemingly useless and unwanted (some are even hazardous) products from a wide range of industries while also improving its environmental properties as well as sequestering CO_2. For example, carbonation neutralizes and stabilizes the high alkalinity of municipal solid waste incinerator (MSWI) ash, and reduces the mobility of heavy metals and sequesters CO_2 generated by incineration (Bobicki et al., 2012). Also worth mentioning is the production of precipitated calcium carbonate (PCC – a high quality, commercially attractive product for the pulp and paper-making industry) from steelmaking slags, a research subject that now receives a great amount of attention and is in the process of demonstration. The prospects mentioned above make carbonation of waste products economically and environmentally attractive.

3.2. *In-situ* carbonation of minerals

In-situ mineral trapping was suggested by Bachu et al. (1994) as one of the mechanisms of precipitating carbonate minerals when CO_2 is injected into basic siliciclastic aquifers. Yegulalp et al. (2001) also suggested an approach where concentrated CO_2 is injected into underground formations like limestone or silicate rock reservoirs, potentially forming bi-carbonates or carbonates. Recognizing that the cost for the *ex-situ* process of the Department of Energy's ARC, Albany, USA (now National Energy Technology Laboratory, NETL), were prohibitive, Rush et al. (2004) investigated the *in-situ* storage of CO_2 in geological formations. They tested the injection of CO_2 in deep brackish to saline non-potable aquifers, and the formation of secondary carbonate minerals over time within these aquifers. They showed through laboratory experiments with an autoclave reactor that the formation of secondary carbonate minerals are possible through the release of Mg, Ca and Fe(II) cations into the solution.

The CarbFix project is another example of *in-situ* mineral carbonation pilot study. The CarbFix project tests the feasibility of fixing CO_2 by carbonation in basaltic rocks via injection of CO_2

charged waters into basaltic rocks in SW Iceland through laboratory experiments, natural analogues and geochemical modeling (Gislason et al., 2010). The study is aimed at sequestering CO_2 emission of magmatic CO_2 from the geothermal power plant at Hellisheidi Iceland (60,000 tons/year) which would take about 200 years to fill the available pore space. It is expected that forming carbonates by underground CO_2 injection is advantageous as it would solve the problem of long-term stability (Yegulalp et al., 2001). If the carbonates are formed, the CO_2 can no longer escape to the surface.

Another *in-situ* approach, as proposed by Kelemen and Matter (2008), involves increasing CO_2 uptake by accelerating the natural carbonation of mantle peridotite in the Samail ophiolite, in the Sultanate of Oman and other large massifs through hole-drilling and hydraulic fracturing. They showed that the carbonation rate could be increased further by a factor of $\sim 10^6$ by raising the temperature of the peridotite, injecting CO_2-rich fluids and managing the conditions within the optimal reaction temperature for peridotite carbonation. However, field and laboratory observations suggest that the stress induced by rapid precipitation may lead to fracturing and subsequent increase in pore space. Carbonation of olivine resulted in ~44% increase in the solid volume, which can lead to enormous stresses that may be relieved by cracking and additional expansion (Matter and Kelemen, 2009).

In principle, an *in-situ* process has a simpler design and is expected to be more economical than an *ex-situ* process. The *in-situ* process would require no chemical plant infrastructure; the reactor itself being the natural geologic formation where CO_2 is injected. Nevertheless, these proposed *in-situ* processes still face similar uncertainties of integrity of the injected CO_2, leakage and monitoring issues associated with geological storage. Consequently there are only a few studies focused on carbonation of minerals via the *in-situ* approach.

3.3. *Ex-situ* carbonation of minerals

Ex-situ mineral carbonation processes, on the other hand, are more complicated and costly than *in-situ* processes due to the many processes involved: mining, pulverization, activation, carbonation and disposal of products. Even with a significant improvement in the reaction rate, the quantity of mineral ore mined would be significantly more than the quantity of coal being burned (Gerdemann et al., 2004). These processes would potentially increase plants' energy requirements, capital and operating costs; yet, it is still the preferred process route for most researchers in the field of mineral carbonation. The advantages of the above ground, *ex-situ* process include permanence of storage of CO_2 as thermodynamically stable carbonates and reduced uncertainties. Rather than relying on circumstantial evidence that the carbonate indeed has been formed or will form in the foreseeable future as in the case *in-situ* processes, the product formed by *ex-situ* processes is handy, and its quality can be determined immediately (Yegulalp et al., 2001)

The *ex-situ* processes can be further divided into direct or indirect routes. The direct method is simple and typically involves one step reaction of gaseous or pressurized CO_2 with pulverized rocks. In contrast, the indirect method is multi-staged: activating/leaching the active cation (Mg or Ca) in the mineral followed by its reaction with CO_2 or precipitation of Mg/Ca carbonates.

3.3.1. Direct carbonation method

The direct method is the simplest *ex-situ* mineral carbonation technique. It takes place in a single step. This method is further divided into the gas-solid "dry" and the aqueous "wet" routes. While the gas-solid "dry" method involves the direct reaction of Ca- or Mg-mineral ore with gaseous (or pressurized) CO_2, the direct aqueous "wet" method extracts the Ca or Mg cations into a solution and subsequently carbonates it in a single reactor.

Direct gas-solid carbonation route

The thermodynamics of the direct gas-solid reaction of Ca- and Mg-(hydro)oxides (a more detailed study on forsterite, Mg_2SiO_4) and gaseous CO_2 was studied by Lackner et al. (1995). Later, Zevenhoven et al. (2002) investigated the direct gas-solid reaction of serpentinite with pressurized CO_2. The equations and thermodynamics of some direct gas-solid reactions are presented in Eq. 1-5.

$$CaO\ (s) + CO_2\ (g) \leftarrow \rightarrow CaCO_3\ (s),\ \Delta H = -179\ kJ/mole \quad (1)$$

$$MgO\ (s) + CO_2\ (g) \leftarrow \rightarrow MgCO_3\ (s),\ \Delta H = -118\ kJ/mole \quad (2)$$

$$CaSiO_3\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + SiO_2\ (s),\ \Delta H = -90\ kJ/mol \quad (3)$$

$$Mg_2SiO_4\ (s) + 2CO_2\ (g) \rightarrow 2MgCO_3\ (s) + SiO_2\ (s),\ \Delta H = -95\ kJ/mole \quad (4)$$

$$Mg_3Si_2O5(OH)_4\ (s) + 3CO_2\ (g) \rightarrow 3MgCO_3\ (s) + 2SiO_2\ (s) + 2H_2O\ (g),\ \Delta H = -64\ kJ/mole \quad (5)$$

The direct gas-solid method, at first sight, looks promising and straightforward given its simplicity of design and potential to recover and use the exothermic heat of carbonation. The exothermic carbonation chemistry of Mg/Ca silicates potentially allows for a process with a zero or negative overall energy input (Lackner et al., 1995). However, it is impractical due to slow kinetics and low conversions. These are the major setbacks to the direct gas-solid carbonation of the abundant minerals like olivine and serpentinite that have the potential for large CO_2 reductions. Most reviews on CCM, for example, Huijgen and Comans (2003, 2005a) and Sipilä et al. (2008) came to the same conclusion that direct gas-solid carbonation of minerals is unviable for industrial purposes and has been abandoned. Therefore, many researchers moved on to investigate the more promising aqueous or indirect, multi-step gas-solid carbonation options.

Direct aqueous carbonation route

The direct aqueous route was also studied by Lackner et al. (1995) alongside the dry route. The authors suggested a process where, for example, Mg is extracted from serpentine, $Mg_3Si_2O_5(OH)_4$ in an acidic aqueous environment. Examples are decomposing mineral in hydrochloric acid or in carbonic acid produced from dissolving CO_2 in water. This is subsequently followed by precipitating magnesite ($MgCO_3$) in the same reactor after introducing CO_2 into the solution and adding an alkalinity source. The reactions exhibit faster kinetics in an aqueous environment than in the dry route. However, opposing reaction conditions are required for the extraction of Mg/Ca cations (acidic, low pH conditions) and the precipitation of their carbonates (alkaline, high pH conditions). That means that conditions favoring Mg/Ca cation extraction limit precipitation of carbonates and *vice versa*; therefore, an optimum condition will strike a balance between extraction and carbonate precipitation.

Extractants or chemical additives used aside HCl acid (Lackner et al., 1995, 1997) are NH_4Cl/EDTA (Goldberg et al., 2001), $NaCl/NaHCO_3$ (Fauth et al., 2000, O'Connor et al., 2002) and $KHCO_3$ (McKelvy et al., 2006). Prominent among the direct aqueous routes was the process developed by the ARC in the 1990s which was considered to be the state-of-the-art until lately when other process routes began to match it (Fagerlund, 2012). At optimized conditions of grinding, heat pre-treatment (615 – 630°C for serpentine) and solution chemistry (using 0.64 M $NaHCO_3$ and 1 M NaCl), a 65% conversion was obtained after 1 h and 80% conversion within ½ h at 185°C/150 bar for olivine, 155°C/115 bar for heat-treated serpentine or 40 bar/100°C for wollastonite (O'Connor et al., 2005, Gerdemann et al., 2007). Another promising result of 63 % carbonation conversions were obtained (for olivine carbonation) by adding a solution of 5.5 $KHCO_3$ in water into a stirred batch autoclave reactor at 185 ºC and CO_2 partial pressures of 135 atm for 1 hr (McKelvy et al., 2006). Apparently, the chemical additives are mostly unrecoverable, making the environmental impact and costs of the process prohibitive.

Apart from introducing additives (chemical treatment), pre-treatment methods - mechanical and thermal activation (McKelvy et al., 2004, 2006, Park and Fan, 2004, Zhang et al., 1997, Alizadehhesari et al., 2011, Kim and Chung, 2002, Maroto-Valer et al., 2005) - have been applied to the direct aqueous route in order to overcome the limiting step, the dissolution or extraction of Mg/Ca cations from the feedstock. The high energy requirements of mechanical attrition and thermal pretreatment pose significant energy penalties. The direct aqueous route also suffers from poor energy integration. Poor energy economy comes from the loss (i.e. failing to recover) of potentially useful energy that would have been recovered from the exothermic nature of the carbonation chemistry. Pre-treating the mineral, adding chemical activators and separating the process into two or more steps make the aqueous route essentially a multi-step “indirect” route. Investigation on this route has strongly declined, especially for carbonation of Mg-silicate minerals as not many papers were found for the years 2008 and onwards. The research focus tilted more to the indirect methods.

3.3.2. Indirect carbonation method

The indirect method of mineral carbonation receives far greater research attention than the direct methods. This method is usually multi-staged, involving most of these steps: activation, leaching/extraction, pH swing, carbonation and separation of products. The indirect method can be categorized into aqueous “wet” or gas-solid “dry” routes.

Indirect aqueous carbonation route

A lot of R&D effort during the last decade focused on methods of extracting Mg or Ca from minerals or industrial byproducts and wastes using strong or weak acids, alkali solutions or ligands (Zevenhoven et al., 2011). In indirect aqueous carbonation routes, both acids and alkaline solutions have been used to extract Mg/Ca cations from the feedstock. Different acids ranging from mild acids, like acetic acid (Kakizawa et al., 2001), to strong acids, like sulfuric acid (Maroto-Valer et al., 2005, Teir et al., 2007, Alexander et al., 2007), have been tested and their kinetics studied. For example, at room temperature (20 °C), < 30% Mg extraction was obtained with H_2SO_4 being the most efficient at extracting Mg from serpentinite, followed by HCl, HNO_3, HCOOH and CH_3COOH (Teir et al., 2007). With increasing temperatures H_2SO_4, HCl, HNO_3 achieved almost > 90% conversion. Additionally, Teir et al. (2007) used a range of common bases and ammonium salts (NaOH, KOH, NH_3, NH_4Cl, $(NH_4)_2SO_4$, and NH_4NO_3) to extract

Mg from serpentinite in an aqueous media. However, bases and ammonium salts were not as strong as acids in extracting Mg from serpentinite. Costs for producing the bases needed to raise pH levels in the solutions as to allow for carbonate precipitation would make these routes too expensive.

Carbonation or carbonate precipitation follows extraction of cations. However, the extraction solution is usually acidic and not suitable for dissolving CO_2; so a base is usually introduced to make the solution alkaline in order to promote carbonate precipitation. Increasing the pH from acidic to alkaline before or during carbonation, a process referred to by some researchers as pH swing, could consume large amounts of bases. While excess acid can be recycled by distillation, the portion of the acid that is converted to intermediate salt products is spent in the process (Teir et al., 2007). Reagent losses, costs and CO_2 emissions arising from recovering and recycling chemicals are the major setbacks to most of the indirect, multi-stage aqueous carbonation routes. Lackner et al. (1995) rightly noted that a major requirement for a feasible chemically activated process is that the agent used to extract the Mg or Ca from the mineral must be easily recoverable at the end of the process, and because of inevitable losses, it must not be expensive. No major breakthrough has been made in regards to solving the problem of reagent recovery. However, additive-free alternatives are in general not able to match the additive-enhanced methods in reactivity (Zevenhoven et al., 2011).

Recent trends in indirect aqueous route point towards improving process efficiency, solving the problems associated with chemical reagents recovery as well as mineralizing flue gases directly and removing the expensive CO_2 separation step from the mineral carbonation process chain (Zevenhoven and Fagerlund, 2010b, Zevenhoven et al., 2011, Torróntegui, 2010). These have led to increasing the number of process steps. Examples of these indirect aqueous processes are tabulated in Table 4.

Table 4. Promising aqueous multi-step process routes for mineralizing CO_2 from flue gases.

Process (Ref.)	**Description**	**Highlights and comments**
Chilled ammonia-water-metal silicate slurry mixture for CO_2 scrubbing from flue gas (Hunwick, 2008).	The process involves three stages: 1) Producing ammonia-water-metal silicate slurry. 2) The slurry is sprayed to scrub CO_2 from flue gas stream. 3) The reactive slurry containing absorbed CO_2 is passed through a reactor at controlled reaction conditions to promote carbonate formation. Increase in reactor temperature and pressures are necessary to enhance carbonation reaction. The ammonia reagent is recoverable.	A promising method that can be applied directly to a flue gas. However, a proof of concept and a process energy evaluation are necessary to determine the process feasibility.
Recoverable ammonium salts for capturing CO_2 directly from flue gases and carbonating extracted Mg (from serpentinite) (Sanna et al., 2012a, Wang and Marota-Valer, 2011, 2011a, b).	The process has about five steps: 1) Ammonia is used to scrub CO_2 from flue gases to form ammonium (bi)-carbonate. 2) Precipitation of hydromagnesite by reacting ammonium (bi)-carbonate and $MgSO_4$ extracted from serpentinite. 3) Extraction of $MgSO_4$ with ammonium bi-sulfate in aqueous solution. 4) pH swing, and 5) Regeneration of reagents.	Total CO_2 captured from the process is ~63% and the reagents are recoverable. Process energy requirements especially those of reagent recovery have not been adequately assessed.
Direct flue gas CO_2 mineralization using activated serpentine (Verduyn et al., 2009, Werner et al., 2011)	The process steps are: 1) Serpentine activation, 2) Serpentine dissolution, 3) CO_2 dissolution and 4) Carbonate precipitation.	Experimental results are sketchy. No process performance results were presented.

Indirect gas-solid carbonation route – Process of interest in this thesis.

The potential benefit, in terms of energy recovery, of the gas-solid carbonation route makes it a more attractive option than the aqueous route. The exothermic carbonation heat can be recovered for use in the earlier steps of the process, thereby, reducing the overall energy input of the process. The indirect gas-solid carbonation route was performed by the ARC research group, who studied the carbonation of pure oxides and hydroxides of Mg and Ca (Lackner et al., 1997, Butt et al., 1996). They reported that the carbonation of CaO and $Ca(OH)_2$ progresses rapidly (completion can be in minutes) at elevated temperature and pressures. They also reported that the carbonation of MgO was very slow compared with $Mg(OH)_2$. This result was later confirmed by Zevenhoven et al. (2006). Although the results from carbonation of CaO and $Ca(OH)_2$ were very promising, these materials or the minerals from which they can be produced (e.g. wollastonite) are less abundant compared with the capacity required to considerably reduce CO_2 emissions. Promising carbonation results were obtained in the case of $Mg(OH)_2$ carbonation. This led to proposing a reaction scheme to produce $Mg(OH)_2$ from the abundant Mg-silicate minerals (Lackner et al., 1995). However, carbonation of $Mg(OH)_2$ obtained at near atmospheric conditions were not good enough; therefore, the carbonation results needed improvement. One suggestion to improve it was by increasing the temperature and pressure conditions. It was noted that the carbonation of $Mg(OH)_2$ consisted of a dehydroxylation-rehydration reaction, a reversible reaction converting $Mg(OH)_2$ to MgO (and *vice versa*), and carbonation of MgO to form $MgCO_3$ (Béarat et al., 2002, McKelvy et al., 2001). The dehydroxylation-rehydration and carbonation reactions are shown in Eq. 6 and Eq.7 respectively.

$$Mg(OH)_2\ (s) \leftarrow\rightarrow MgO\ (s) + H_2O\ (g) \quad (6)$$

$$MgO\ (s) + CO_2\ (g) \leftarrow\rightarrow MgCO_3\ (s) \quad (7)$$

Fargerlund (2012a), however, proposed that the dehydroxylation of $Mg(OH)_2$ (see Eq.6) proceeds through an intermediate, $MgO*H_2O$. More so, Béarat et al. (2006) and Zevenhoven et al. (2006) showed that the gas-solid carbonation of $Mg(OH)_2$ kinetics is fast but becomes rate-limited by the formation of a carbonate layer/coating. This limitation can be avoided with good gas-solid mixing, improving the heat transfer and removing the carbonate layer through attrition. Attrition is a result of collision of the solids.

Research on the indirect gas-solid carbonation started in Finland since 2000, focusing on ways to effectively carbonate MgO or $Mg(OH)_2$ and to maximally utilize the carbonation heat

(Zevenhoven et al., 2006, 2008a, Zevenhoven and Teir, 2004). Initial studies in Finland tested the carbonation of $Mg(OH)_2$ in a pressurized thermobalance, with humid CO_2, from 1 to 35 bar pressure (Zevenhoven and Teir, 2004). Also, Zevenhoven and Teir (2004) tested $Mg(OH)_2$ and MgO carbonation in an atmospheric bubbling fluidized bed batch reactor. They found that increased pressure levels in the pressurized thermobalance did not give the expected increase in MgO carbonation rate. A more interesting finding from that study was that attrition, abrasion *etc.* continuously removed small amounts of material from the particles' surface. The fine particles produced from collision of solid particles with each other and with the walls of the reactor show higher levels of carbonation than (larger) particles sampled from the bed. The preliminary results and observations from these tests motivated the use of a fluidized bed (FB) (Zevenhoven et al., 2006, 2008b).

Gas-solid carbonation of $Mg(OH)_2$ using pressurized fluidized bed (FB)

Pressurized FB carbonation of $Mg(OH)_2$ has been intensively researched by Fagerlund and co-workers (Fagerlund and Zevenhoven, 2011, Fagerlund et al., 2009, 2010, 2011, 2012b), with a doctor thesis (Fagerlund, 2012) produced on the subject. As mentioned above, the motivation for using a pressurized FB is the beneficial collision, attrition and abrasion effects associated with continuous movement of the particles in a FB. The particles inside a bed are constantly colliding with each other and the reactor walls, and the force of these impacts is the cause of particle attrition and/or abrasion (Fagerlund et al., 2012b). Consequently, these collisions wear off the rate-limiting carbonate layer/coating formed, thus, exposing the unreacted inner (core) materials to CO_2. Another benefit of the fluidized bed is the good heat distribution that allows for homogenous conditions inside the reactor (Fagerlund et al., 2012b).

The studies at ÅAU centered on improving the gas-solid carbonation of $Mg(OH)_2$. This means that the optimal conditions were investigated with the aim of obtaining a maximum reaction conversion in the shortest possible reaction time. Some of the parameters investigated include temperature, pressure, time, fluidization velocity, particle size, $Mg(OH)_2$-type and wet/dry conditions (Fagerlund, 2012). In order to achieve this goal, a small electrically heated, pressurized fluidised bed (height 0.5 m, diameter 0.014 m) setup (Fig. 6) was used.

The FB setup is made up of the following main parts:

1) A horizontally placed gas preheater, ensuring that the right temperature is maintained inside the FB.

2) A vertically placed fluidized bed, facilitating fluidization of $Mg(OH)_2$ particles.
3) A cyclone, separating the solid particles from the gas.

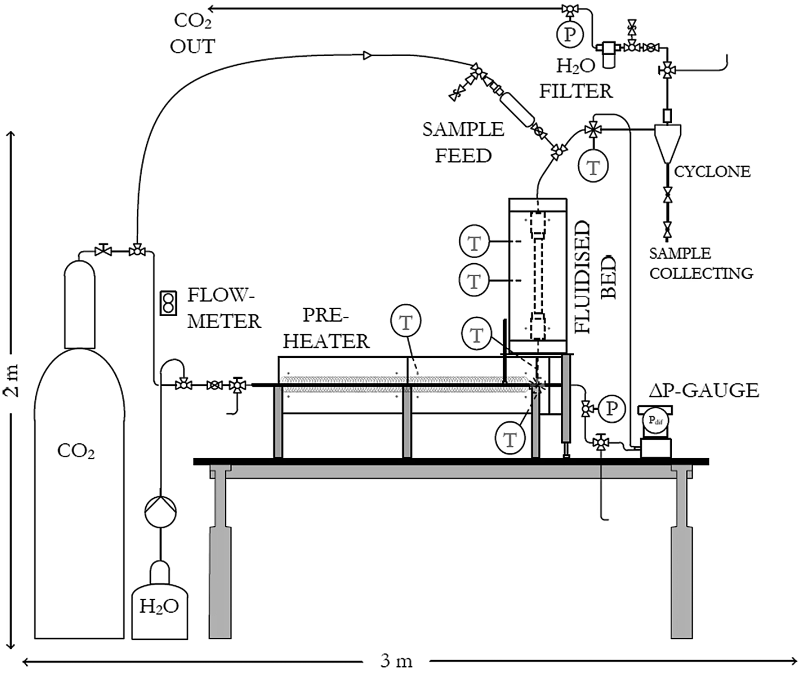

Figure 6. Schematic illustration of the fluidized bed setup used for $Mg(OH)_2$ carbonation. Adapted from Fagerlund et al. (2012b).

The procedure involved testing at different pressures and temperatures up to the supercritical pressure of CO_2 (>7.4MPa). For a given pressure, the temperatures typically selected are taken to be equal to $T = 0.95 \cdot Teq$ (K), where Teq is the equilibrium temperature for the $Mg(OH)_2$ carbonation reaction, which allows for some driving force (*i.e.* $-\Delta G/T$) for the chemistry (Fagerlund et al., 2009, Zevenhoven et al., 2008b). The reactions taking place during carbonation of $Mg(OH)_2$ are presented in Eqs. 6 and 7. The particles are separated from the gas after the reaction using a cyclone while very small particles that escape the cyclone are collected by a filter (Fig. 6). Product samples received from the cyclone are collected for carbonate analysis. Details of the concept and methods of FB carbonation of $Mg(OH)_2$ are available in the literature (Fagerlund and Zevenhoven, 2011, Fagerlund et al., 2009, 2010, 2011, 2012a,b, Fagerlund, 2012)

Most of the tests with the FB were performed with synthetic $Mg(OH)_2$ produced by Dead Sea Periclase Ltd. A few tests were also done with $Mg(OH)_2$ produced from serpentinite rocks using the process described in this thesis (see $Mg(OH)_2$ production process description in Chapter 4). Besides being more reactive than the original mineral (Mg-silicates) from which $Mg(OH)_2$ is made, carbonating $Mg(OH)_2$ in lieu of the serpentinite mineral significantly reduces pressure drop in the reactor because only the reactive material is fluidized (Fagerlund, 2012).

Fagerlund (2012) made the following major findings and conclusions from the pressurized fluidized FB studies of $Mg(OH)_2$ carbonation.

- More than 50% carbonation was achieved in 15 min at 20 bar and 500 °C with serpentinite-derived $Mg(OH)_2$ particles of 250 μm – 425 μm. This is a much faster kinetics than what other currently considered mineral carbonation routes offer.
- Carbonation proceeds to a maximum and levels off in few minutes prior to complete carbonation and would not go to completion even after long reaction times. The reactivity of $Mg(OH)_2$ at high temperatures and long reaction times (> 1 h) do not favor the formation of $MgCO_3$ at elevated temperatures, where $Mg(OH)_2$ is thermodynamically unstable.
- While carbonate layer build-up and slow flow conditions might be the inhibiting factors at low temperatures, higher temperatures and flow rates result in a highly dehydroxylated product with considerably reduced carbonation reactivity. $Mg(OH)_2$ produced from Mg-silicates is more reactive than the synthetic $Mg(OH)_2$ from Dead Sea Periclase Ltd. (This may be because the serpentine-derived $Mg(OH)_2$ has a ~9 times larger specific surface of ~45 m^2/g vs. ~5 m^2/g.) The properties of the $Mg(OH)_2$ particles, for example, porosity, surface area and particle size, play a critical role in determining the final outcome of FB carbonation. This could imply that the carbonation of the synthetic $Mg(OH)_2$ may be limited by its comparatively small pore size. Worst still, the pore size is further reduced by an increase in solid material volume due to carbonate formation, and in the absence of cracking, or other particle breaking effects, pore volume decreases as a function of carbonation degree until the pores are filled.
- Adding small amounts of water (0–3%-vol H_2O in CO_2) does not result in any significant changes to the product. However, with steam amount up to 15% H_2O in CO_2 the dehydroxylation rate was considerably reduced while the carbonate conversion remained unchanged. It was found that the intrinsic water in $Mg(OH)_2$ is what makes its reactivity with CO_2 different from that of MgO. Results showed that

steam enhanced the reactivity of MgO, while $Mg(OH)_2$ is enhanced by the presence of intrinsic H_2O (Fagerlund et al., 2012a).

- Increase in both the reaction temperature and pressure promotes the carbonation of $Mg(OH)_2$ until a point where thermodynamic restrictions set in, necessitating a right balance between these operating conditions. Increase in temperature must accompany an equivalent increase in pressure (and *vice versa*) in order to avoid calcination of the carbonate product (if temperature is too high) or low conversion (if pressure is too low).
- The fluidizing motion of the particles must be sufficient to remove the limiting carbonate layer; otherwise, low levels of collisions are experienced, resulting in low carbonation levels. A relatively high fluidization velocity is preferable, keeping in mind that dehydration is also enhanced. Velocities just above the minimum fluidization velocity appear to improve reactivity the most, with little benefit achieved from additional velocity increase.
- Adding an inert material such as SiO_2 into the FB improves fluidisation, increases attrition between particles, but also adds thermal inertia to the system and makes separation of products difficult.

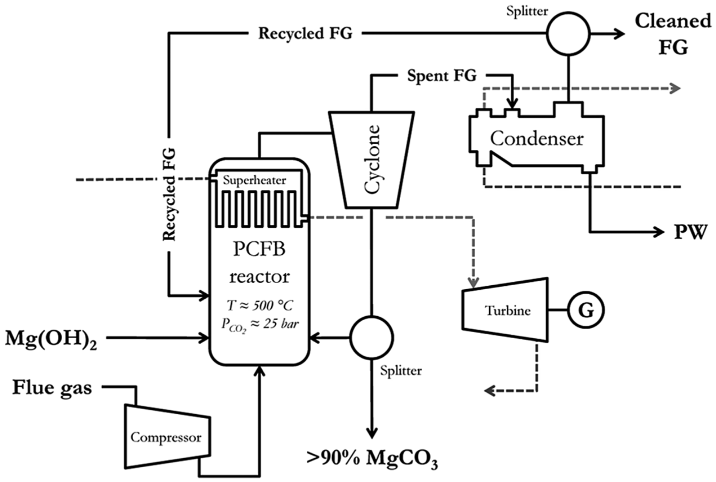

Figure 7. Schematic of a carbonation reactor operating on CO_2-rich flue gas, the dotted lines indicating possible major heat recovery systems. PCFB = pressurised circulating fluidised bed, PW = process water. Source: Fagerlund (2012).

An emerging interest, as pointed out in Chapter 3, is the mineralization of flue gases directly. The preliminary testing of this concept (illustrated in Fig. 7) has been carried out at ÅAU, using $Mg(OH)_2$ to mineralize a gas stream containing CO_2, O_2 and SO_2 (Zevenhoven et al., 2012). The same concept has also been investigated for application to flue gases from lime kiln (Romão et al., 2012a).

In the mineralization of flue gas both SO_2 and CO_2 are captured and mineralized in a single reactor, thus, presenting a possibility to replace a conventional flue gas desulphurisation unit with a combined CO_2 and SO_2 scrubber. Results from initial tests found that the reactivity of $Mg(OH)_2$ towards SO_2 in the presence of CO_2 at pressurized conditions is significant even under low SO_2 partial pressures (Zevenhoven et al., 2012). Initial process evaluation results show that mineralizing lime kiln flue gases using $Mg(OH)_2$ produced from serpentinite would provide significant energy savings that could make the ÅAU process industrially attractive.

4. Production of $Mg(OH)_2$ from Mg-silicate rocks for CCM

The $Mg(OH)_2$ carbonation process studied by Fagerlund (2012) is the third and last stage in the CCM process investigated in the thesis. Before carbonation takes place, $Mg(OH)_2$ must first be produced, preferably from the most abundant Mg-silicate rocks: serpentinite and olivine. Thus, the first two stages of the CCM process deal with $Mg(OH)_2$ production. Though Mg, itself as an element, is abundant in several compounds on Earth and in the sea, MgO or $Mg(OH)_2$ is comparatively scarce in nature. Thus, naturally occurring MgO or $Mg(OH)_2$ cannot be used to remarkably reduce CO_2 emissions. It was noted in Section 3.2.2.2. that $Mg(OH)_2$ is more reactive than MgO, and that CaO-based minerals are limited in abundance. That is the reason this study focuses on the production of $Mg(OH)_2$ from the most abundant Mg-silicate rocks, serpentinite and olivine (Lackner et al., 1997, 1995, Butt et al., 1996, Zevenhoven and Teir, 2004, Zevenhoven et al., 2002, 2006).

Production of $Mg(OH)_2$ from Mg-silicate rocks is not straightforward, however. Extraction of Mg from Mg-silicate minerals and its subsequent conversion to $Mg(OH)_2$ suffer from low conversion, high energy and chemical costs and significant environmental burden (Lackner et al., 1997, Lin et al., 2008). In this chapter, a novel method of processing Mg-silicate minerals, producing a more reactive material - $Mg(OH)_2$ - from Mg-silicate rocks is described. This method aims at addressing the inherent drawbacks in the previous methods, some of which include low reaction conversion degree and rate, high energy and chemical costs and loss of reagents.

The $Mg(OH)_2$ method, which was reported in Paper I (initially proposed in Nduagu (2008)), is a closed loop process involving a staged reaction of serpentine and ammonium sulfate (*AS*) followed by precipitation of $Mg(OH)_2$ and *AS* recovery/looping. The method comprises two stages: i) Mg extraction - achieved through the solid stage reaction of pulverized Mg-silicate rocks and *AS* salt (discussed more in Section 4.1) and ii) $Mg(OH)_2$ precipitation and reagent recovery - presented in Section 4.2. Section 4.3 describes various integration options with carbonation of $Mg(OH)_2$ produced from Mg-silicates while Section 4.4 applies process engineering and environmental concepts, techniques and tools to evaluate the energy requirements and life cycle environmental impacts of the CCM process.

4.1. Mg & Fe extraction from Mg-silicate rocks

Paper I investigated a method for extracting Mg (including Fe and other cations) from Finnish serpentine from the Hitura nickel mine site (of Finn Nickel) by using equilibrium thermodynamics and laboratory methods. Thermodynamic equilibrium calculations were done with HSC software (v.5.11) for Gibbs energy minimization (Roine, 2002). The laboratory tests performed involved the reaction of an Mg-silicate rock (mainly serpentinite or olivine) with *AS* within the temperatures range 270 - 600 °C. Paper II extended the application of this extraction method to different serpentinite and olivine rocks from other locations like Lithuania, Australia and Norway. The application of this method was further extended to other rocks by performing eighty-four tests with thirteen different Mg-silicate minerals (nine serpentinite and four olivine rocks) at different reaction conditions of temperature, time, serpentine to ammonium sulfate mass ratio (*S/AS*) (see Paper V). In Paper VI additional tests were performed to conclusively determine the effects of extraction parameters, including reactor type and configuration.

Serpentinite rock contains serpentine mineral (represented here as $Mg_3Si_2O_5(OH)_4$, but $3MgO*2SiO_2*2H_2O$ is also used in the literature), iron ore (in forms of $FeO/Fe_2O_3/Fe_3O_4$), wollasonite ($CaSiO_3$) and other minute compounds. Serpentinite rocks with chemical compositions: 19 - 23 %-wt. Mg, 12 - 20 %-wt. Si, 5 - 12 %-wt. Fe and 0 - 1 %-wt Ca and olivine rocks with chemical compositions: 3 - 30 %-wt. Mg, 18 - 23 %-wt. Si, 8 - 13 %-wt. Fe, 0 - 6 %-wt Ca and 0 - 9 %-wt. Al were tested in the laboratory. For example, the Finnish serpentinite (tailings from the Hitura nickel mine), the most tested rock sample in this study, contains ~ 83%-wt. serpentine and 14%-wt. magnetite (Fe_3O_4). Most of the compounds in the rock react with *AS* to form their corresponding sulfates. In Section 5.1 the equilibrium products formed by reacting *AS* with serpentine and magnetite are shown. Equation 8 represents the global equation for the reaction of serpentine and *AS*.

$$Mg_3Si_2O_5(OH)_4\,(s) + 3(NH_4)_2SO_4\,(s) \rightarrow 3MgSO_4\,(s) + 2SiO_2\,(s) + 5H_2O\,(g) + 6NH_3\,(g) \qquad (8)$$

Besides producing sulfates, which are soluble in water, the extraction reaction also produces SiO_2, H_2O vapor and recoverable gaseous NH_3. (A more detailed presentation of the extraction reactions, mechanisms and thermodynamics can be found in Papers I-III.) Mg/Fe/Ca-sulfates obtained from the extraction reaction are leached in water at room temperature and pressure conditions. The elemental amounts of Mg, Fe and Ca and other metals extracted were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis.

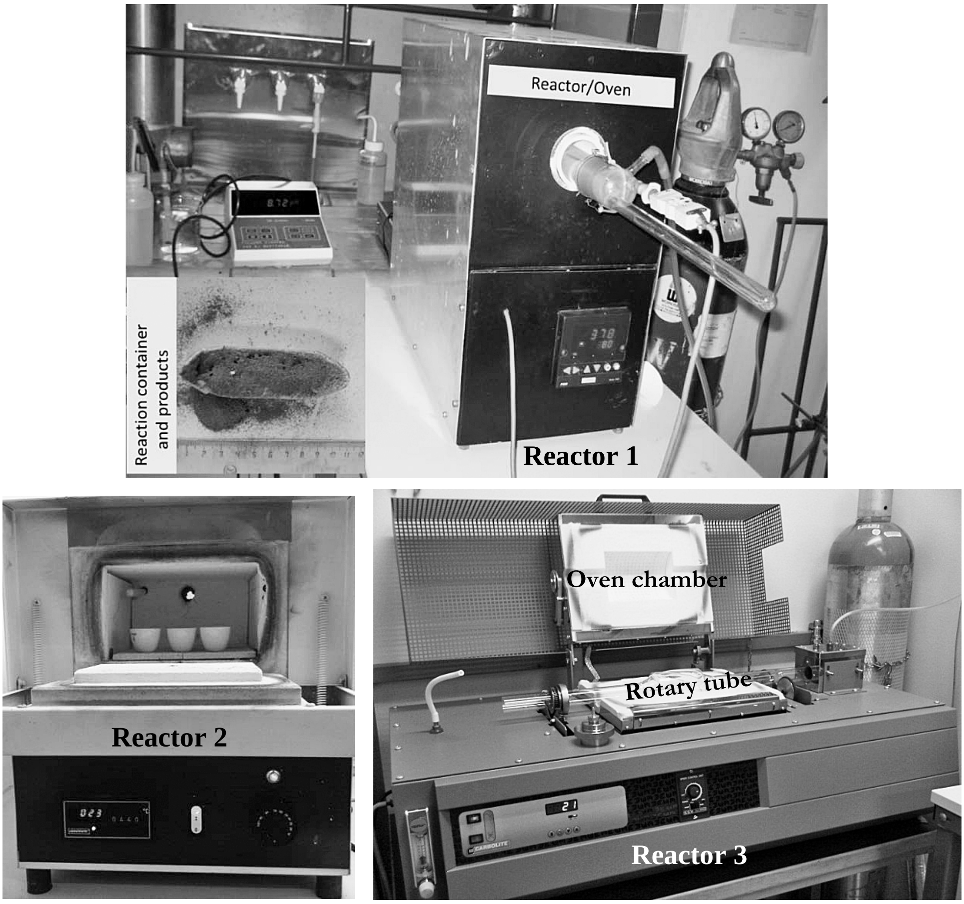

Figure 8. Reactor types used for extraction reaction. An aluminum foil cup is used in *Reactor* 1, a porcelain crucible in *Reactor* 2 and a quartz rotary tube in *Reactor* 3.

The extraction reaction takes place in a reactor or oven. Different reactor types (*Reactors* 1-3), shown in Fig. 8 have been used and their effects on extraction studied. The reagent containers used in the tests include a boat-like shape cup folded from thin aluminum foil (a sample loaded with reaction products is shown besides *Reactor* 1 in Fig. 8), a porcelain crucible (inside *Reactor* 2) and a rotating quartz tube (*Reactor* 3). The details of the configuration of the reactors are presented in Paper VI.

As reported in Paper V, several tests were carried out to study the effects of reaction parameters on the extraction reaction. The following reaction parameters were investigated, applying standard experimental design, laboratory, statistical and graphical approaches:

i. Mg to Fe mass ratio of the rock, also written as *Mg/Fe*. Several serpentinite and olivine rocks of different chemical properties were tested and the individual results interpreted in relation to their *Mg/Fe* ratios (Papers II & V).

ii. Mg-silicate to ammonium sulfate mass ratio reacted, represented as *S/AS*. This study aimed to maximize this parameter; meaning that the *AS* amount is minimized. The less the *AS* reacted, the lower the reagent costs, recovery energy use and environmental impact (Papers I, II, V & VI).
iii. Temperature (*T*). Different reaction temperatures ranging from 270 to 600 °C were tested (Papers I, V & VI).
iv. Time (*t*) - reaction times ranged from 10 - 120 min (Papers I, V & VI).
v. Interaction effects of the above listed parameters (Paper V).
vi. Reactor type and configuration. The effect of the type and configuration of the reactors was investigated in Paper VI using three reactors: *Reactors* 1, 2 & 3, with different heat up rate of the reactor and their contents.
vii. Scalability, mixing and moisture addition. A rotary tube furnace (*Reactor* 3) was used to test scalability and mixing (Paper VI).
viii. Particle size of mineral. Using Australian serpentinite and *Reactor* 1, tests were performed to understand the effects of serpentinite grain size on Mg extraction.

4.2. $Mg(OH)_2$ production and *AS* salt recovery

Precipitation of hydroxides or oxy-hydroxides from the (Mg/Fe/Ca)-sulfates-rich solution is achieved by increasing the pH of the solution by adding ammonia solution. A schematic of the complete extraction and precipitation stages of the process is shown in Fig. 9.

The recovered ammonia from the extraction reaction can be used. Fe is precipitated as goethite (FeOOH) at pH 8 - 9 and Mg as $Mg(OH)_2$ at pH 11 - 12 (Paper I). The $Mg(OH)_2$ produced from this method can be used to convert CO_2 to magnesium carbonate. After filtering precipitated Fe/Ca /Mg (oxy)-hydroxides from the solution, *AS* salt is then recovered via crystallization. Two major crystallization techniques were evaluated in Paper III; they are complete evaporative and mechanical vapor recompression (*MVR*) crystallization. This work focused on *MVR* as applied in Papers III - VI.

A very interesting feature of the $Mg(OH)_2$ method is the closed loop nature of the process. It has a prospect of recovering the chemical reagents as well as separating by-products in potentially useful forms. However, the $Mg(OH)_2$ process equally has significant setbacks; the extraction and reagent recovery appear to be energy-intensive and nearly complete conversion (> 90%) has not yet been realized (as discussed in the later sections).

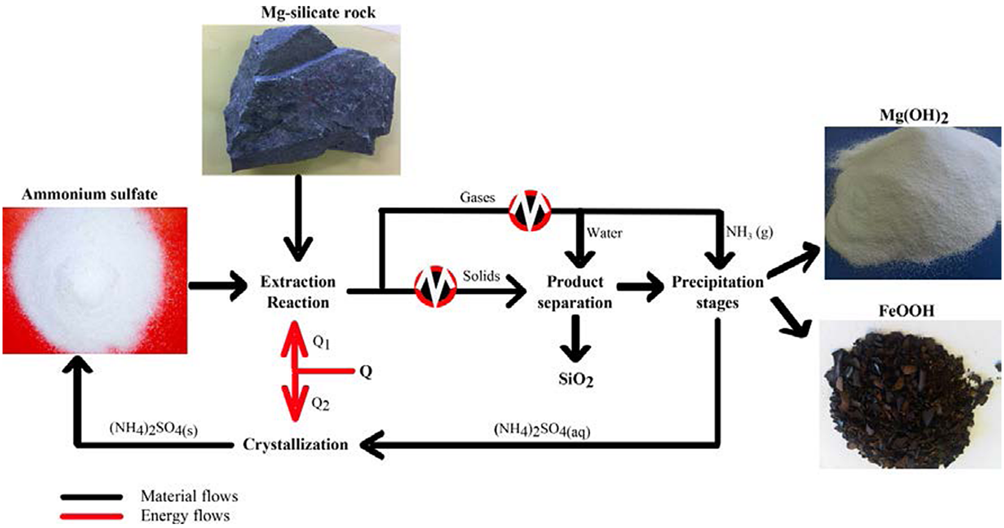

Figure 9. Schematic of a closed loop process of producing $Mg(OH)_2$ from Mg-silicate rock

4.3. Integrated $Mg(OH)_2$ production and carbonation process

The $Mg(OH)_2$ thus produced can be used to sequester CO_2 through many routes (see also Fig. 10):

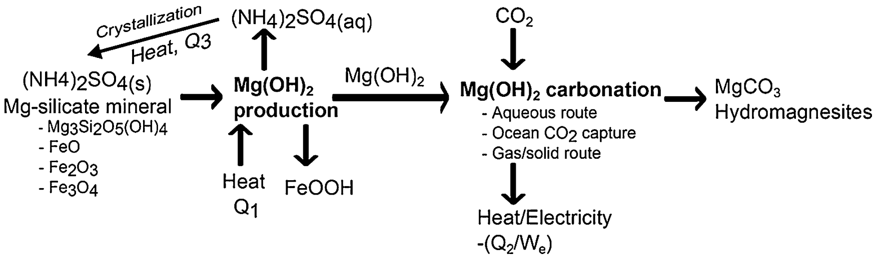

Figure 10. Process integration possibilities of $Mg(OH)_2$ production and carbonation (Paper III)

(i) Dry or aqueous reaction with CO_2 from air at ambient conditions (Zhao et al., 2009).

(ii) To increase ocean alkalinity, thereby enhancing the capacity of oceans to capture more atmospheric CO_2 (Lackner, 2002a, Kheshgi, 1995).

(iii) Gas-solid reaction with CO_2 or CO_2-containing (flue) gases. This thesis will focus on carbonating the $Mg(OH)_2$ produced by this route. The integration of the $Mg(OH)_2$ production process with the carbonation process using CO_2 separated from power plants was modeled in Papers III - VI. The application of CO_2 mineralization to flue (or other CO_2-containing) gases directly were also briefly discussed in Paper VI.

The various options for integrating $Mg(OH)_2$ production process with other units in the process chain were identified. However, more emphasis was given to the gas-solid reaction of $Mg(OH)_2$ with pressurized flue gas-derived CO_2 in a FB reactor. In the following sections (also reported in Papers III - VI), the process energy and life cycle environmental assessments are evaluated.

4.4. Process evaluation

The extraction reaction of serpentinite and *AS* is considered as the most energy intensive, and the limiting reaction in $Mg(OH)_2$ production process chain. A breakthrough in the extraction reaction will result in the largest impact on the process energy and environmental performance of the overall CCM process. Thus, a greater attention was given to extracting Mg efficiently than to the other processes.

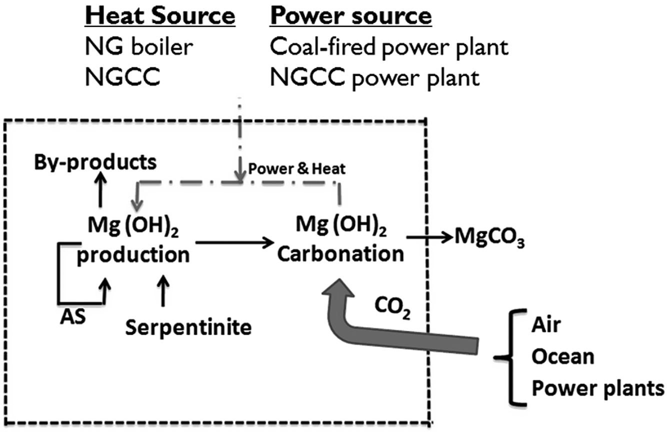

Figure 11. Options for energy integration for the CCM process.

The energy requirements of a standalone $Mg(OH)_2$ production process as well as that of an integrated $Mg(OH)_2$ production-carbonation process were evaluated. As illustrated in Fig. 11, the major ways the process energy requirement can be sourced were identified and evaluated. The energy sources include coal-fired power plants, natural gas combined cycle (NGCC) or a natural gas boiler.

The three stages of the CCM process: Mg extraction, $Mg(OH)_2$ precipitation (including the *AS* recovery) and $Mg(OH)_2$ carbonation were simulated using Aspen Plus® software. A comprehensive description and discussion of the methods, process models and results are presented in Papers III & V.

Exergy analysis was applied in evaluating the CCM process using the material and energy balance results extracted from process simulation studies. Process exergy calculations were implemented in Papers III & V. At any specified surrounding temperature (here taken to be T_0 = 15 °C = 288 K), using exergy provides a standard basis for calculating the amount of valuable energy (Kotas, 1985) that can be extracted from a heat stream and comparing heat with power input requirement P, for which the exergy Ex(P) = P. Exergy is a Second law of thermodynamics concept, which is superior to the energy analysis based on the First law of thermodynamics. For example, if the extraction reaction requires ~ 9.1 Gt/t-CO_2 of heat at 400 °C (~ 623 K) (see Paper V), this corresponds to an exergy equal to $Ex(Q) = (1\text{-}T_0/T)\cdot Q = (9.1 - 4.2)$ GJ/t-CO_2. The term $(T_0/T)\cdot Q$ is the exergy destruction, E_D. Equation 9 represents the exergy destruction of a system - the amount by which the value of the resource is consumed or degraded while Eq. 10 shows the exergy flow.

$$E_D = T_0(S - S_0) = T_0 \sum \Delta S \tag{9}$$

$$E = (H - H_0) - T_0 \sum \Delta S = \Delta H - E_D \tag{10}$$

where *$(S - S_0)$* is the entropy change, *T_0* is the ambient temperature and *$(H - H_0)$* the enthalpy change. Details of exergy analysis concept (Szargut et al., 1988) and how it was applied to the CCM process can be found in Papers III - VI.

In Paper V, pinch analysis was used for energy targeting and to ensure efficient thermal design and integration (Kemp, 2007). The pinch method enables the plotting of composite and grand composite curves using temperature versus enthalpy axes (Linnhoff, 1993). These curves provide an insight on the process heat availability and requirements.

4.5. Life cycle assessment (LCA)

Life cycle assessment (LCA) is a standardized methodology that accounts for the environmental effects of all the activities that make up the process chain of a product from the raw material extraction "cradle" to the disposal "grave". LCA, also known as "life cycle analysis", "life cycle approach", "cradle to grave analysis" or "Ecobalance", represents a rapidly emerging family of tools and techniques designed to help in environmental management and, longer term, in sustainable development (Jensen et al., 1997).

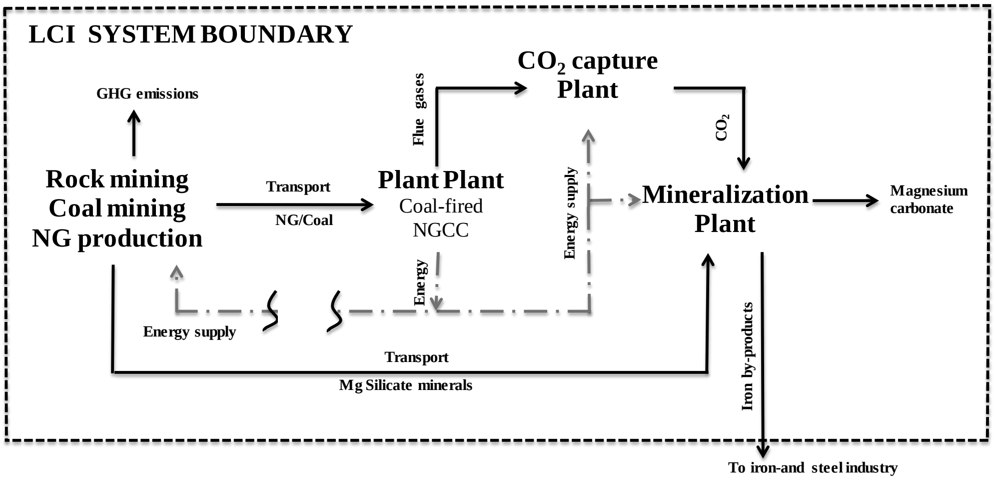

Figure 12. System boundary for the life cycle inventory analysis (LCI). NG in the figure represents natural gas.

LCA consists of four major elements (ISO 14040):

1) Goal and scope definition stage. One way to identify the scope of an LCA is through the system boundary (Fig. 12 is the illustration of a system boundary for the CCM process studied here)
2) Inventory analysis stage, also known as life cycle inventory analysis (LCIA). This involves compilation of data, energy and material balance calculations and emissions inventory.
3) Impact assessment stage – potential impacts associated with the identified forms of resource use and environmental emissions are assessed.
4) Interpretation stage. The results obtained from the earlier stages are interpreted in relation to the objectives of the study.

The LCA methodology was applied to the CCM process (Papers IV & VI). In Paper IV, an accounting type LCA of the CCM process studied at ÅAU was presented and the results were compared with the process developed at the National Energy Technology Laboratory (NETL), formerly ARC, Albany, US. The LCA models reported in Paper IV assumed that the CCM processes of ÅAU and NETL sequestered CO_2 produced from a coal-fired power plant. On the other hand, the LCI model in Paper VI focused on the ÅAU CCM process while assuming that the process sequestered CO_2 from a NGCC power plant. More so, Paper VI also investigated the environmental impact of losses or inefficient recovery of *AS* reagent.

The system boundary (Fig. 12) of the process includes the following: (i) serpenitinite rock mining, pulverization and transport, (ii) $Mg(OH)_2$ production and carbonation, and Fe-byproduct use, (iii) *AS* production to make-up for losses, (iv) NG production or coal mining, fuel transport and combustion, (v) material, fuel and energy input requirements of the power plant, (vi) CO_2 processing capture unit and (vii). transport of materials (chemical reagents). LCI models in Papers IV & VI were built on a functional unit based on the GHG emissions associated with the CCM process when 1 t-CO_2 is sequestered in serpentinite rock. Therefore, the LCI results are presented as kg CO_2e/t-CO_2.

5. Key findings and discussion

5.1. Mg & Fe extraction from Mg-silicate rocks

The reaction of serpentine and *AS* is thermodynamically favorable at 200 °C and above, almost coming to completion at 250 °C (see Figure 13). The equilibrium products formed by reacting *AS* with Finnish serpentinite above 200 °C are dominated by the solid products: $MgSO_3$ (Fig. 13a) and $FeSO_4$/$Fe_2(SO4)_3$ (Fig. 13b).

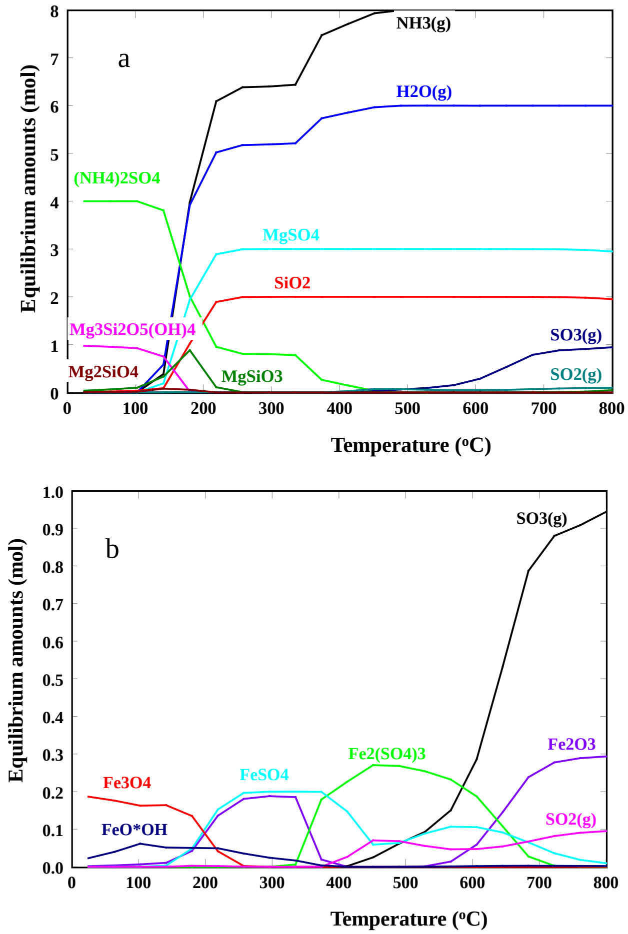

Figure 13. Thermodynamic compositions of products of the reaction of 4 mole AS, 1 mole serpentine and 0.2 mole magnetite a) Mg-species. b) Fe-species. The difference in the compositions of the Mg and Fe species can be seen from the y-axis scales of the above figures.

Aside from these, other products of interest are silica (SiO_2), ammonia gas and water vapor. The thermodynamic equilibrium calculation (Gibbs energy minimization) results are quite interesting, and show that the formation of Mg- and Fe-sulfates should not be thermodynamically inhibited at moderately elevated temperatures. Tests results showed that some limitations exist, however.

Laboratory results showed that the extraction reaction does not proceed significantly until 400 °C (Papers I, II & V) but tends to decline at a temperature higher than this, depending on the heat transfer properties of the reactor (Paper VI). Several tests were carried out in order to study the reaction parameters that affect the extraction reaction.

While a detailed analysis of the parametric effects can be found in Papers V &VI, the key findings about the effects of reaction parameters on Mg and Fe extraction are given below.

5.1.1. Reactivity of rocks - *Mg/Fe* mass ratio of the rocks

Paper II suggested that the reactivity of an Mg-silicate rock is determined by an interplay of both the chemical and physical properties of the rock. The *Mg/Fe* ratio as well as the specific surface area and porosity play complementary roles in determining the extent of the extraction reaction, and consequently $Mg(OH)_2$ production.

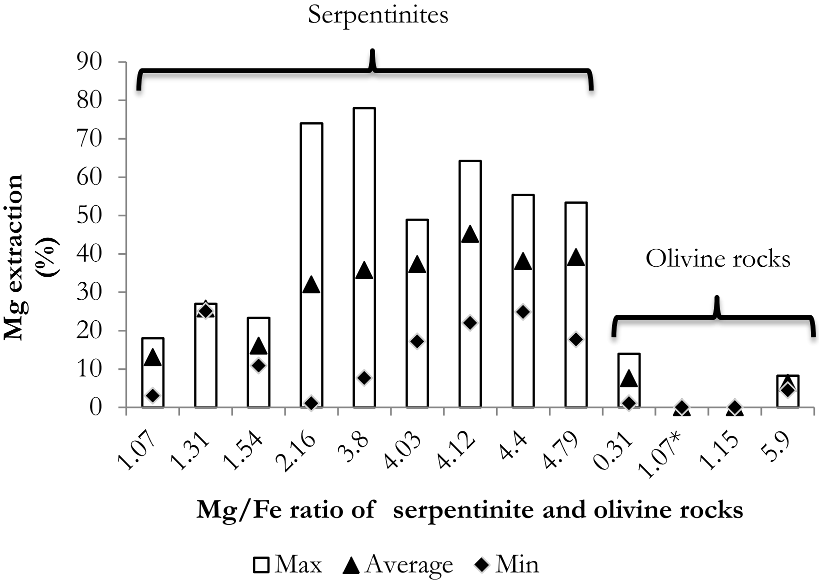

Figure 14. Effect of Mg/Fe ratio of Mg-silicate rock on Mg extraction

With results obtained from tests performed with five Mg-silicate rocks (two olivine and three serpentinite rocks), Paper II argued that the serpentinites are more reactive than the olivine rocks. The low reactivity of olivine rocks was attributed to their low specific surface area and pore volume. For example, Åheim olivine had the highest *Mg/Fe* ratio (5.9 kg/kg) but also had the lowest specific surface area and pore volume. As a result, its reactivity was the least of the five rocks tested. On another hand, even with good physical properties, rocks with low *Mg/Fe* ratios are not very reactive. An example is the Lithuanian serpentinite, though with desirable physical properties (high specific surface area and pore volume) had the lowest *Mg/Fe* ratio, and consequently was the least reactive among the serpentinite rocks tested in Paper II.

Paper V evaluated the results of more tests covering a broader range of Mg-silicates (four olivine and nine serpentinite rocks). A huge difference in reactivity of serpentinite and olivine rocks was observed. Based on maximum extraction values obtained for each mineral type, serpentinite is about five times as reactive as olivine. The results confirmed previous results reported in Paper II. This implies that olivine rocks may not be suitable for Mg extraction using the method studied in this thesis. Serpentinite rocks with an *Mg/Fe* ratio ≥ 2.16 show an exceptionally (>2 times) higher % *Mg ext* than others (Fig. 14). This shows that among the serpentinites, the effect of the rock chemical composition on Mg extraction may be significant until a certain *Mg/Fe* value when it matters no more. It is possible that the serpentinite rocks having an *Mg/Fe* ratio ≥ 2.16 also have similar physical properties.

5.1.2. *S/AS* mass ratio.

As mentioned earlier, the goal here is to minimize the amounts of *AS* used in excess of stoichiometric amounts. Paper I identified two distinct extraction patterns when the variation of *S/AS* ratio is plotted against temperature (see Fig. 15). It found that *S/AS* ratios above 1 g/g produced an Mg extraction pattern lower than that obtained from reacting *S/AS* ratios below 1 g/g. For Fe extraction, a similar pattern was obtained, though the *S/AS* ratio demarcation point in this case is at 2 g/g (Fig. 15). According to the general reaction equation for Mg extraction from serpentine, 3 moles of *AS* are needed for 1 mole of Mg in serpentine (with 83%-wt serpentine in the Finnish serpentinite), corresponding to a *S/AS* mass ratio equal to (277/(3×132))/0.83 = 0.85 kg S/kg *AS*.

Each data point in Fig. 15 represents the average value obtained at plotted temperatures and *S*/*AS* mass ratio ranges. The vertical lines in Fig. 15 (range plot) link the minimum and maximum Mg extraction values obtained at the same temperature for each of *S*/*AS* ranges.

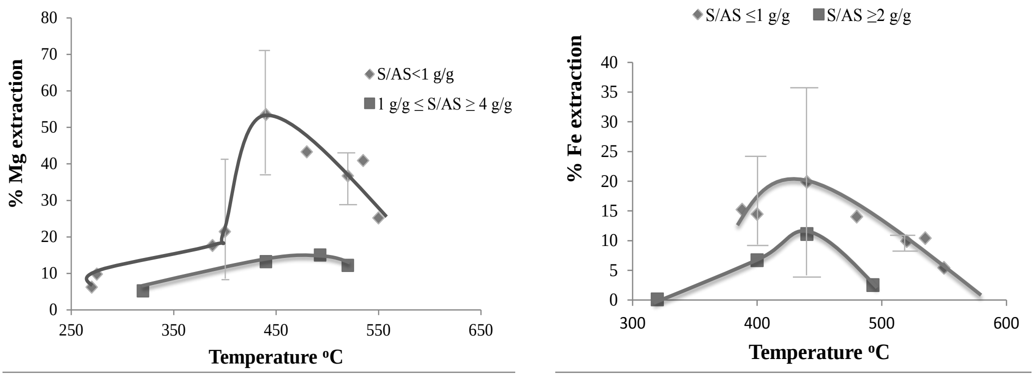

Figure 15. The effect of S/AS mass ratio on Mg extraction (left figure) and Fe extraction (right figure). Tests were done with *Reactor* 1. Modified from Paper I.

The significance of the results is that optimum Mg or Fe extraction results are obtainable within a certain range of *S*/*AS* ratio, preferably < 1g/g. Although this finding does not resolve the issue of minimizing *AS* reagent, it helped to identify a range that subsequent tests can focus on. In Paper V, this range was further reduced by varying the *S*/*AS* ratio of the tests between ≤0.67 g/g and ≤1 g/g and its effect on the extent of Mg extraction evaluated. The results showed that at 95 % ($\alpha = 0.05$) significance level, *S*/*AS* ratio has a significant positive effect on Mg extraction only at reaction times less than 60 min. At 60 min and above, the *S*/*AS* ratio has no effect.

5.1.3. Temperature (T).

Being an endothermic reaction, it is expected that an increase in temperature will increase the extent of extraction. The same conclusion was arrived at in this study (in Papers I, II, V & VI). However, at some point, a deviation from this was observed. It was found that depending on the heat transfer properties of the reactor, an increase in temperature of reactor increases the extraction extent to a certain point beyond which a decline in extraction sets in. A more pronounced decline is observed with Fe extraction than with Mg extraction. (The effects of reaction temperature can be observed in Figs. 15 and 16, which show the results of extraction reaction using two different reactors, *Reactor* 1 and *Reactor* 2 respectively. The types of reactors used and their effects on extraction are discussed below.)

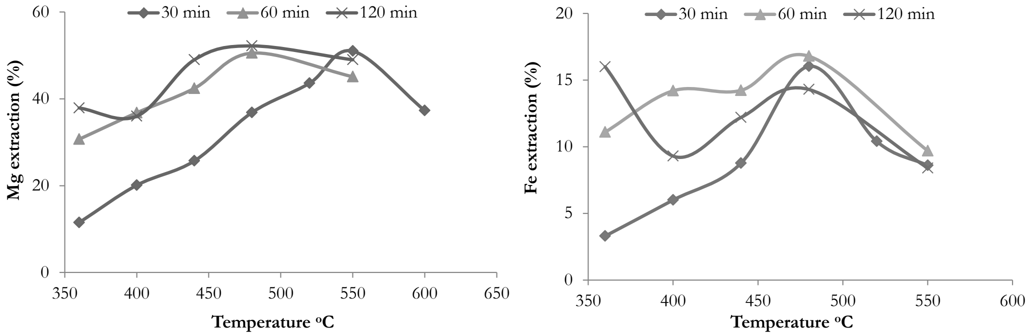

Figure 16. Effect of reaction temperature and time on Mg extraction (left figure) and Fe extraction (right figure). Adapter from Paper VI.

Factors identified to cause the decline in extraction after a maximum extraction is attained are decomposition of *AS* and formation of Mg & Fe compounds that are insoluble in water (Papers I, V & VI). The onset of production of SO_2/SO_3 above 400 °C (see Fig. 13) could signify the complete decomposition (and loss) of *AS*. The interaction effects of temperature and time is evident (see Fig. 16), especially for Mg extraction. A higher reaction temperature is required at a reaction time of 30 minutes to be able to attain similar maximum Mg extraction reached at 60 min. It can be further observed that the reaction temperature positively affects Mg extraction, reaching a maximum yield at different temperatures depending on the reaction time.

5.1.4. Time (t)

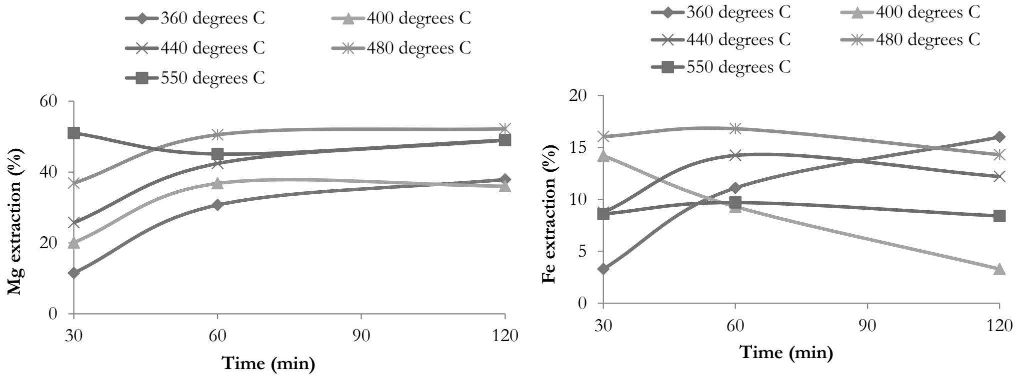

Figure 17. Effect of reaction time on Mg extraction (left figure) and Fe extraction (right figure).

An important finding from the results presented in Paper VI is that although an increase in reaction time from 30 min to 60 min favors extraction, reaction times longer than 60 min do not lead to a significant increase in either Mg or Fe extraction (see Fig. 17).

Actually, in the case of Fe extraction a sharp decline is observed. This decline could be associated with thermal decomposition of soluble $Fe_2(SO_4)_3$ formed to Fe_2O_3 (see Figure 13). This happens if the products formed are exposed to high temperatures for a longer reaction time. On the other hand, longer extraction times seem to favor Fe extraction at 360 °C.

5.1.5. Interaction effects of the above parameters

The interaction effects of *Mg/Fe* - *S/AS* ratios and *T* - *t* were significant at 95 % significance level. Increasing the reaction time above 25 min levels increases the Mg extraction by 30 % points if the reaction temperature is kept below 480 °C. Above this temperature, no increase in Mg extraction is possible, for reasons explained above. On the other hand, no matter the value of the *Mg/Fe* ratio of the rock, reacting *S/AS* ratio ≤1 g/g leads to a significant increase in *Mg* extraction. However, the % *Mg ext* values obtained with *Mg/Fe* (>2.16 g/g) are higher.

5.1.6. Reactor type and configuration

The effect of reactor properties and reactant containers on the extraction behavior can be observed from Fig. 18. At *t* < 30 min and *S/AS* ratios between 0.5 and 0.76 g/g, *Reactor 1* attained maximum *Mg ext* at a temperature lower than that of *Reactor 2* (480 °C against 550 °C).

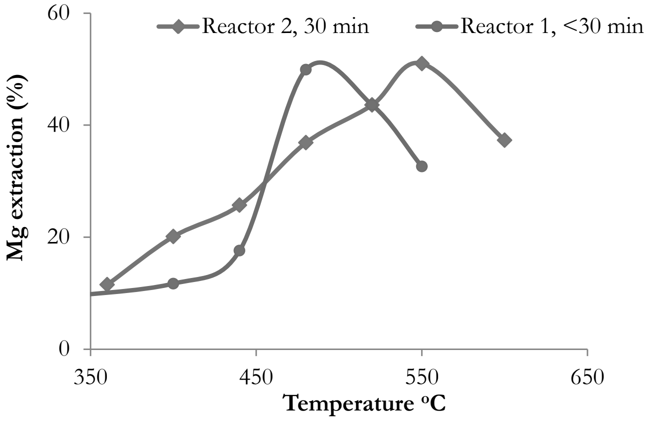

Figure 18. Mg extraction results from *Reactor 1* (*S/AS* = 0.5 - 0.76 g/g and *t* <30 min) compared to those from *Reactor 2* (*S/AS* = 0.4 g/g and *t* =30 min).

Note that the *Reactor 2* was operated at seemingly better reaction conditions (*t* = 30 min and *S/AS* = 0.4 g/g) than *Reactor 1* (*t* <30 min and *S/AS* = 0.5 - 0.76 g/g). With respect to the observed decline in *Mg ext*, *Reactor 1* shows that the decline starts at ~500 °C while the same occurrence is observed from *Reactor 2* at 550 °C. Using a micro-scale reactor (Thermogravimetry coupled to Fourier-Transform Infrared Spectroscopy) the decline in Mg extraction was shown to begin already at 400 °C (Highfield et al., 2012). This means that the reactor properties and the quantity of the reactants impose some heat and mass transfer limitations that affect the extraction behavior. As described in Paper VI, *Reactor 1* has better heat transfer properties than *Reactor 2*; thus, the more promising extraction results.

5.1.7. Scalability, mixing and moisture addition

Reactors 1 and *2* used only few grams (in most tests a total of <10 g) of materials, but *Reactor* 3 reacted a total of 100 g serpentinite and *AS,* with mixing. It took 40 - 60 min to heat up the oven to the set point and equilibrium temperatures, and the measured temperature was ~ 15 °C below than the set point temperature (Fig. 19).

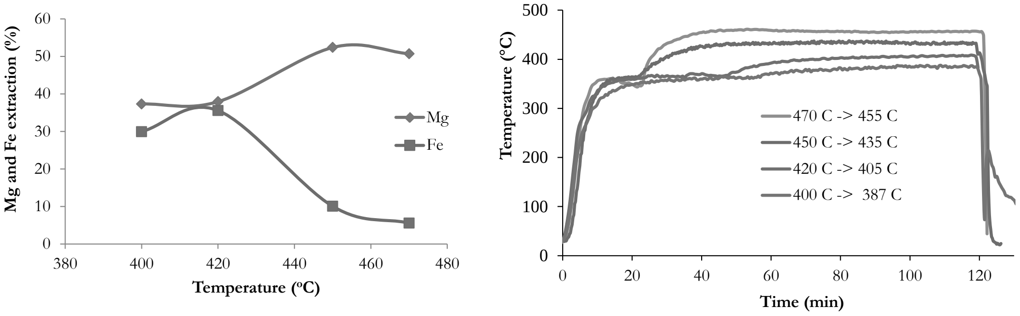

Figure 19. Mg and Fe extraction results from the rotary kiln (*Reactor* 3). Unwashed serpentinite samples (particle size fraction 125 – 250 µm) were used. The heating profiles of the kiln are shown on the right (the arrow in the legend points from the set point to the measured temperature inside the reactor).

A maximum Mg extraction result of 53 % was obtained at 450 °C, 2 hr. (including 40 min heat up time), *S/AS* 0.4 g/g and particle size fraction 125 – 250 µm with serpentinite rock. Although the results do not seem very promising given the "reaction time" of 2 hr. plus mixing, they show that scaling up above a few grams of reactants is possible. Worthy to note is that the particle size fraction, used in *Reactor 3* is larger than that used in the other reactors (125 – 250 µm vs. 75 - 125 µm). Figure 19 shows an unusual degree of decline in the Fe extraction trend starting already at

420 ºC. As shown in Fig. 13, the decline in Fe extraction could be as a result of the transformation of the water-soluble iron compounds (iron sulfates) to a less soluble one (e.g. hematite). This was confirmed as the appearance of a mixture of the extraction products in water became increasingly muddy-brown with increase in reaction temperatures of tests.

Adding water as part of the extraction reagents has been suggested to be beneficial in reducing the *AS* recovery energy requirement as well as increasing reactivity (Romão et al., 2011). However, more experiments are needed to determine if the observed effects are applicable to different serpentinite and olivine rocks.

5.1.8. Particle size

The particle size fraction ranges tested were 0 - 74 µm, 75 - 124 µm, 125 - 211 µm, 212 - 249 µm, 250 - 299 µm and 300 - 425 µm, with all experiments done under the same conditions (500 °C, 20 min, *S*/*AS* = 2 g/4 g). Reactor 1 was used here.

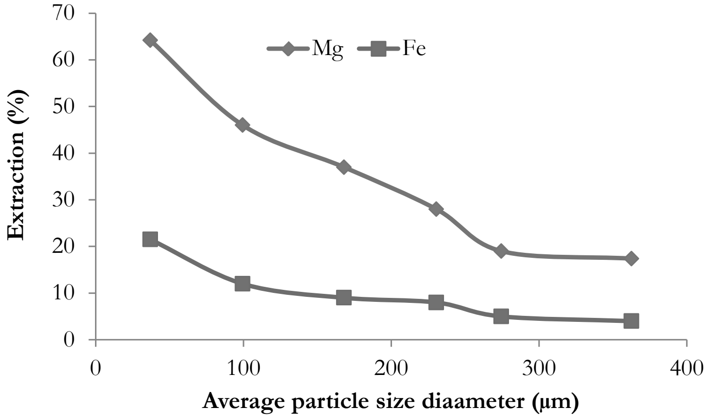

Figure 20. Effect of particle size on the extraction of Mg and Fe. The size ranges are represented by their respective average size. All experiments were done under the same conditions: 500 °C and 20 min with 2 g Australian serpentinite and 4 g AS (Data by T. Björklöf).

The results were not surprising as it is expected that the smaller the grain size the better the extraction conversion of both Mg and Fe (Fig. 20). Experimental results showed a minimum and maximum Mg extraction of 17.4 % and 64.2 % with particle sizes 300 - 425 µm and 0 - 74 µm respectively.

5.2. $Mg(OH)_2$ production and *AS* salt recovery

A two stage precipitation is carried out to separately produce Fe- and Mg- hydroxides (Paper I). In the first stage, the pH of the extraction filtrate (also referred to as $MgSO_4$-rich solution) is increased by adding aqueous ammonia solution. This precipitates goethite (FeOOH) at pH between 8 and 10 (Eq. 11).

Table 5. Chemical reactions and thermodynamics of the precipitation stage

Eq.#	Precipitation reactions	ΔHr (T=40 °C)
11	$Fe_2(SO_4)_3(s) + 6NH_3(g) + 4H_2O\ (l) \rightarrow 2FeOOH(s) + 3(NH_4)_2SO_4(aq)$	-720 kJ/mol Fe
12	$MgSO_4(s) + 2NH_3(g) + 2H_2O\ (l) \rightarrow Mg(OH)_2(s) + (NH_4)_2SO_4(aq)$	-85 kJ/mol Mg

The pH of precipitation of the FeOOH-rich product affects its chemical properties as well as the amount of $Mg(OH)_2$ that is subsequently produced in the next precipitation step. If the precipitation pH is too high, some Mg^{2+} would precipitate and contaminate the FeOOH by-product. At a lower pH, however, some Fe cations would not have precipitated but would precipitate in the next stage, contaminating the $Mg(OH)_2$ product. Therefore, a good pH regulation is required for an optimized precipitation process.

$Mg(OH)_2$ precipitates when the solution's pH is further increased to 11 - 12. Complete conversion of $MgSO_4$ to $Mg(OH)_2$ is possible at this stage. ICP-OES and XRD analysis performed (reported in Paper I) on the samples showed that high quality $Mg(OH)_2$ was produced. Equations 11 & 12 show that *AS* is a product from the precipitation stages. However, the *AS* formed is in aqueous form (in solution) but is needed in solid form for the extraction reaction. Therefore, *AS* salt must be crystallized out of the solution. Experimental results showed that *AS* is recoverable; the extent of the recovery depends mainly on the loss of *AS* from thermal decomposition during the extraction reaction, and the amount of ammonia solution used during precipitation (Paper I). The loss of the *AS* reagent is also a function of the temperature of the extraction reaction. This is because the decomposition of *AS* is a function of the reaction temperature; the higher the temperature, the greater the loss/degradation of the *AS* reagent. A maximum *AS* recovery of 72% was achieved for only one batch of tests performed to recover *AS* salt. However, this value may be much higher if the process is operated on a larger scale where some losses experienced in the experiments can be avoided (simply because large losses are unacceptable).

Both Mg extraction and *AS* salt crystallization require energy. Providing this energy through the conventional fossil energy sources results in CO_2 and other (pollutants) emissions. The following sections (Sections 5.3 and 5.4) explore the methods to integrate $Mg(OH)_2$ production and carbonation processes and to provide for the process energy requirements, and evaluate the process energy requirements as well as the GHG impact (or GWP) of the process.

5.3. Integrated $Mg(OH)_2$ production and carbonation process.

CO_2 reacts with $Mg(OH)_2$ at suitable conditions to form $MgCO_3$ and superheated steam. Sequestration of CO_2 using the gas-solid carbonation provides utilizable energy at high temperature (480 - 550 °C, $\Delta H \sim -59.5$ kJ/mol Mg) and pressure conditions. Pressures can vary from 20 bar to 80 bar depending on the concentration of CO_2 – pure and concentrated or in flue gas stream (Romão et al., 2012a, Zevenhoven et al., 2012). In Papers III & V, an integrated $Mg(OH)_2$ production and carbonation process was modeled.

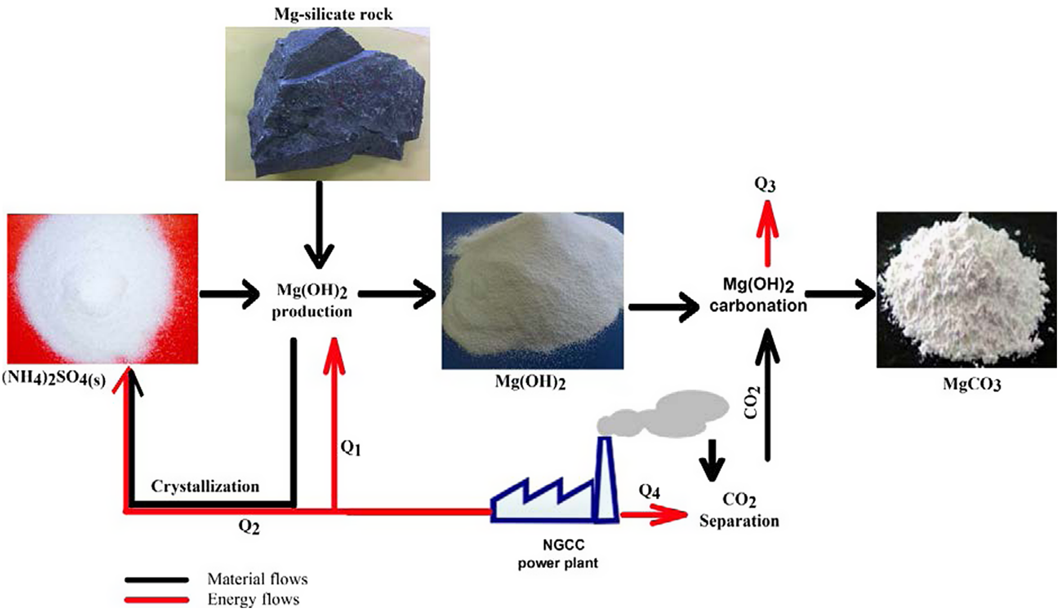

Figure 21. Schematic of CO_2 sequestration in Mg-silicate rock. While process heat and power are provided by the NGCC plant, the CO_2 from the power plant reacts with $Mg(OH)_2$ to produce $MgCO_3$ (Q=heat) (Paper VI).

Results presented in Paper V show that the exothermic heat from carbonation could increase the temperature of products by 15 °C. This energy is also sufficient to heat up the reactants

($Mg(OH)_2$ and CO_2) and as well provide energy to the process (heat or power depending on what it is designed to achieve). With the focus of this study on carbonation of CO_2 separated from fossil fuel power plants, it is necessary that the CO_2 be captured and compressed. Therefore, CO_2 processing is incorporated as part of the process chain. The CCM process can be illustrated using Fig. 21 where NGCC power plant provides for the energy requirement of the process while its CO_2 emissions are in turn sequestered using serpentinite rock (Paper VI).

The reboiler heat duty for solvent regeneration in CO_2 capture using Monoethanolamine (MEA) solvent varies between 3 - 4 GJ/t-CO_2 (Zahra, 2009) while compression power can be estimated at 0.1 MWh/t-CO_2 (Göttlicher and Pruschek, 1997). The costs and emissions from supplying heat and power for CO_2 capture and compression are part of the overall costs and emissions of the CCM process.

5.4. Process evaluation

Iron oxide by-product from the CCM process is a useful raw material for the iron- and steelmaking industry (Romão et al., 2012b, Lackner et al., 2008). However, Paper III reports that the presence of Fe during the extraction reaction constitutes an additional energy penalty. The extent of this energy penalty depends on the form in which Fe exists in the mineral rock. Figure 22 shows the energy requirements for the extraction reactions (mostly from sensible heat and reaction enthalpies), the net energy requirement for the $Mg(OH)_2$ process and that of *AS* recovery (using mechanical vapor recompression (*MVR*) technique).

The use of exergy as a metric for process energy evaluation is a reliable way to add together values of different grades of heat and power. It is not correct to add up heat amounts of two or more streams having different temperatures. Likewise, the values of heat and power cannot simply be summed up to a single value unless by using exergy. This is because heat has a lower quality than power; the former is converted to the latter at a limited thermodynamic efficiency (usually far less than 100%), and results in inevitable waste heat generation. Because electric power is a higher quality energy form, it costs more.

Exergy analysis results show that the extraction reactions have a heat requirement of 4.7 - 6.8 GJ/t-CO_2. The range of energy values (see Fig. 22) is a result of the different types of iron compounds (FeO, Fe_2O_3 and Fe_3O_4) that may be present in the mineral ore. The results presented here were obtained for Finnish serpentinite with 10-wt.% Fe. An additional energy of ~1.2 GJ/t-CO_2 is required as compression power (in *MVR*) for *AS* recovery. However, as seen from Eq. 11 & 12, the precipitation reactions are exothermic and could generate recoverable heat, albeit at low temperatures. The quality of this heat at 40 °C does not make it useful for many industrial applications. However, carrying out precipitation at higher temperatures up to 60 °C could – while making heat recovery easier – produce a quality of heat useful for district heating in winter seasons. With heat recovery using heat exchangers, and combining the energy values of all the unit operations, the net energy requirements for producing $Mg(OH)_2$ is 4.0 - 5.8 GJ/t-CO_2.

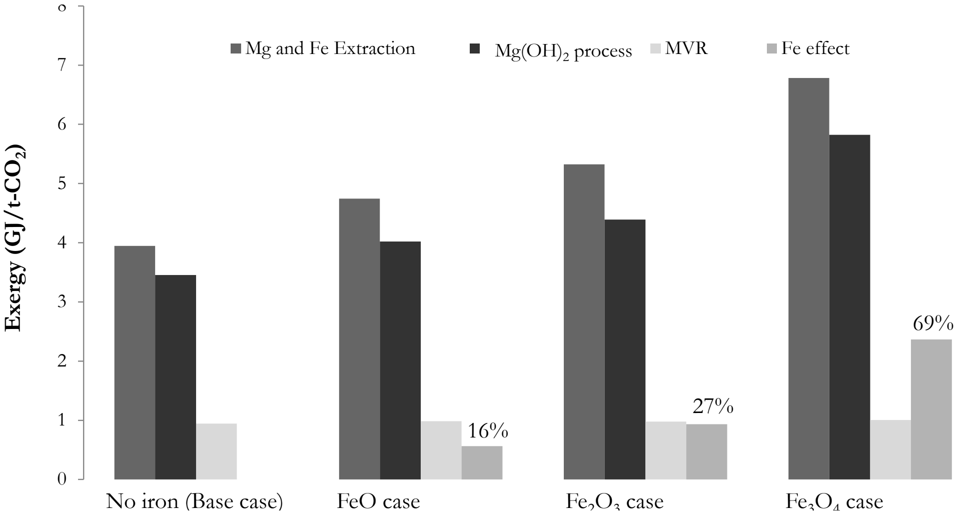

Figure 22. Energy input requirements as a function of the Fe compound in serpentinite. The percentage values indicated on the chart shows the percentage increase in energy requirement due to FeO, Fe_2O_3 or Fe_3O_4 as compared to the "no iron" base case.

The results presented in Fig. 22 also show that the contribution of iron to the energy requirement of producing $Mg(OH)_2$ from serpentinite rocks increases by 69%, 27% and 16% points for serpentinite rocks containing Fe as Fe_3O_4, Fe_2O_3 and FeO compounds, respectively, as compared to an iron-free rock. By implication, while integrating the steel industry's CO_2 emissions with the CCM process would result in emissions reduction and in the replacement of raw materials (iron ore); a significant energy penalty is incurred by processing Fe together with Mg.

Integrating the gas/solid carbonation and the $Mg(OH)_2$ production processes reduces the $Mg(OH)_2$ process energy requirements due to the high grade steam produced from the high temperature gas-solid carbonation of $Mg(OH)_2$. Exergy analysis shows that at complete conversion, the carbonation of $Mg(OH)_2$ could be self-sustaining as well as offset 0.82 GJ/t-CO_2 (14 - 23%) of the $Mg(OH)_2$ production process energy requirements.

Papers III & V evaluated the two major crystallization techniques for *AS* recovery. The results obtained showed that from an energy economy standpoint, the *MVR* technique is preferred over the complete evaporative method. The benefit from this technique comes from recovery of the latent heat of vaporization of the water vaporized from the crystallizer which is used to heat up the crystallizing liquor. This would have been impractical given that saturated steam at slightly above 100 °C cannot be used to vaporize (saturated) water at temperatures close to 100 °C. Heat transfer is only possible if a temperature driving force, ΔT exists.

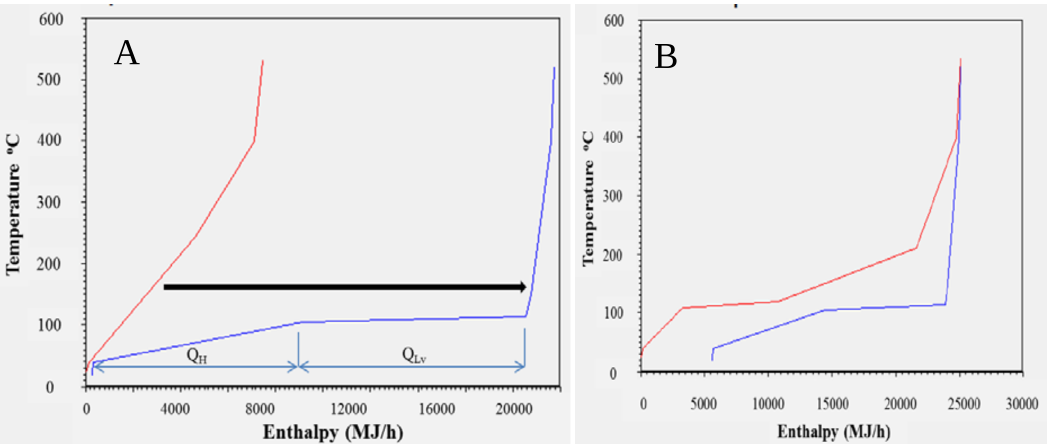

Fig 23. Hot and cold composite curves of the process shown in red and blue colors respectively. *A* represents a process with “evaporation only” crystallization while *B* represents a process with *MVR* (Paper V).

Without *MVR*, almost all the water in the crystallizing liquor stream is evaporated with virtually no heat recovery. This is more clearly illustrated using the results from pinch analysis shown using composite curves (Fig. 23). The thick black arrow in Figure 23A pointing from hot to cold composite curves indicates the possible amount of energy losses with “evaporation only” crystallization. Most part of that heat is represented in Fig. 23A as Q_{Lv} (~ 9.4 GJ) while Q_H is the value of other low temperature heat lost. The gap between the hot and cold steams needs to be closed. To achieve that, the temperature and the enthalpy of the hot stream must be such that allow for a heat transfer to the cold stream (saturated water at about 100 °C) while maintaining a minimum ΔT of typically 10 °C. The application of *MVR* crystallization closes that gap, with a compressor work penalty of ~1.2 GJ/t-CO_2. (~330 kWh/t-CO_2), however. Let us assume that

that the compression work is produced from a coal-fired or NGCC-fired power plant at 30% or 50% thermal efficiencies respectively. In these cases, the compression work of ~1.2 GJ/ton CO_2 translates to ~ 4 GJ/t-CO_2 and ~2.4 GJ/t-CO_2 heat (or steam) produced from coal-fired and NGCC-fired power plants respectively. Thus, an energy saving of 12 - 13.6 GJ/t-CO_2 can be realized.

Compressing the water vapor stream from 1 to 2 bar increases the enthalpy as well as the temperature of the stream to a level at which it can transfer heat to saturated liquid water at 100 ºC. This modification also changes the pinch point of the process from 40 - 50 ºC to 400 - 410 ºC (Fig. 23), and reduces the hot utility requirements from 12290 MJ to 93 MJ (more details are presented in Paper V).

5.5. Life cycle analysis

The LCA studies presented in Papers IV evaluated three possible allocation scenarios for the Fe/Ca by-products. Case A allocated all the CCM process emissions to the $Mg(OH)_2$ product. Case B considered that the possible use of the Fe/Ca (oxy)-hydroxides by-products warrants allocating some CCM process emissions to these by-products. As a result, mass allocation was applied in Case B. For 1325 kg $Mg(OH)_2$ needed for sequestering 1 t-CO_2 through the CCM process, 457 kg by-products (FeOOH and $Ca(OH)_2$) are produced alongside. Thus, 74% of the CCM process emissions was allotted to the $Mg(OH)_2$ product while 26% was assigned to the Fe/Ca (oxy)-hydroxides by-products. The Mg-carbonate and silica, which are major products from the CCM process, were not allocated any emissions in any of the cases. The other approach (Case C) allocated emissions to the by-products according to how much emission reductions are possible from their use in iron-and steelmaking. Results presented in Paper IV show that the use of the by-products would result in an 8% emission reduction of the sinter plant. This translates to a 13 % reduction (half of what is obtained from mass allocation) of the CCM process.

A monetized allocation method can be applied in future studies, if markets for the products and by-products are identified and their monetary values quantified. This may provide the needed boost to CCM processes given that research on the possible uses and values of by-products of mineral carbonation seems to have begun (Sanna et al., 2012b, Brent et al., 2011). Opportunities for using the Mg-carbonate product (~ 2 t/t-CO_2) as cement additives, fillers or for land reclamation, and the Fe/Ca (oxy)-hydroxides as iron ore feedstock may be dwarfed in magnitude compared with the scale of CO_2 emissions (Sanna et al., 2012b). However, producing high-value products like silica, nickel, chromium *etc.* as CCM by-products could be the key to cost competiveness of mineral carbonation processes.

The serpentinite ore used in the LCI calculation of Paper IV was modeled after the Finnish serpentinite containing 82 %-wt. serpentine, 14 %-wt. Fe_3O_4 and the rest being $CaSiO_3$ and impurities. The process energy requirements for $Mg(OH)_2$ production and carbonation, as reported in Paper III, were used to calculate the life cycle GHG inventory of the ÅAU process. In Paper IV, the heat requirements are provided by an industrial gas-fired furnace while a coal-fired power plant provided for the power requirements for both the ÅAU and the NETL processes. The CCM processes in turn sequester CO_2 from the coal-fired power plant.

The LCIA results show that process heat and power use and mineral mining, transport and processing are the major contributors to the GWP of the $Mg(OH)_2$ process. Assuming 100% efficiencies of the $Mg(OH)_2$ production and *AS* recovery processes, LCI results show that the GHG emissions associated with a standalone $Mg(OH)_2$ production process are in the range of 456 – 618 kg/t-CO_2. With mass allocation, the process GHG emissions burden is made up of 55% heat and 38% power requirements and 7% upstream processes (mineral mining, transport and processing).

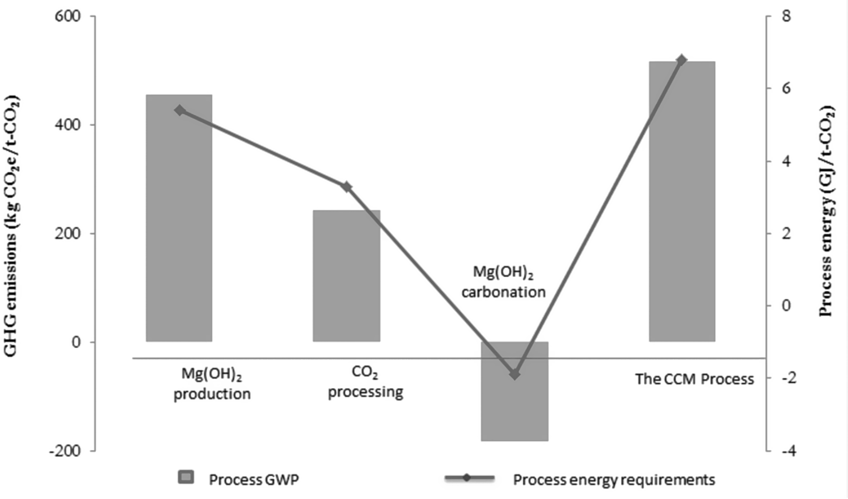

Figure 24. Process energy requirements and life cycle emissions for sequestering CO_2 from coal power plant in Finnish serpentinite rock (82 %-wt. serpentine, 14 %-wt. Fe_3O_4 and the rest are $CaSiO_3$ and impurities) with the ÅAU process. Mass allocation scenario was implemented.

Integrating the $Mg(OH)_2$ carbonation with the $Mg(OH)_2$ production process provides heat (1900

MJ/t-CO_2) and electricity (80 kWh/t-CO_2) that can partly drive the $Mg(OH)_2$ process. The GHG emissions from CO_2 processing, which includes capture from the coal power plant and compression to pipeline pressures is 240 kg CO_2e/t-CO_2 while the $Mg(OH)_2$ carbonation unit provides a GHG emissions offset of 180 kg CO_2e/t-CO_2 (27 – 35%). This means that the net CCM process emissions are 60 kg CO_2e/t-CO_2 greater than the life cycle GHG emissions for the $Mg(OH)_2$ production process. The impact of Mg extraction and carbonation conversion inefficiencies was addressed using sensitivity analysis (see Papers IV and VI).

The NETL process energy and life cycle performance were also evaluated and compared with those of ÅAU process (Paper IV). The NETL process preheats the pulverized mineral ore at 630 °C, adding buffer solutions (0.64 M $NaHCO_3$ and 1 M NaCl) to form 30 %-wt. solid slurry. Pure and pressurized CO_2 stream is afterwards reacted with the slurry at temperature of 185 °C, CO_2 partial pressure of 150 atm and water partial pressure of 6.5 atm. Dissolution of serpentinite and precipitation of $MgCO_3$ take place in a single unit. Detailed process description of the NETL process can be found elsewhere (Gerdemann et al., 2004, 2007, O'connor et al., 2005). The NETL and the ÅAU process are alike in some regards: similar upstream rock mining and fuel processing; uses the same mineral ore, i.e. serpentine (antigorite); CO_2 processing – capture and compression – is applied in both processes. The processes are also different in many ways, however.

(i) The NETL process has a simple, one stage reactor which could make its design, construction and operation easier and more economical than the more complex, multi-staged reactor configuration of the ÅAU process.
(ii) Different process energy requirements. The energy requirement for the NETL process as calculated in Paper IV is 3.4 GJ/t-CO_2 while that of the ÅAU process is 3.6 GJ/t-CO_2.
(iii) The NETL process requires high temperature pre-treatment (at ~630 °C) of the mineral ore whereas the ÅAU process does not need thermal pre-treatment but requires heat at reaction temperatures of 400 - 500 °C (preferably < 450 °C).
(iv) Difference in composition and value of by-products. While the use of iron by-products from both the ÅAU and the NETL processes in iron- and steelmaking could eliminate CO_2 emissions associated with mining virgin raw materials, only those of the ÅAU process can reduce CO_2 emissions of the sinter plant. The iron and calcium by-products of the NETL process still require the conventional raw material pre-treatment stage, resulting in 1 ton of CO_2 emissions for every 3.3 tons of Fe_3O_4 and 0.3 ton $CaCO_3$ fed to

the sinter plant.

(v) The chemical reagents added to the NETL process are mostly unrecoverable whereas that of the ÅAU process is recoverable.

By implementing exergy analysis in the LCI model, it was found that the GWP of the NETL process is 683 kg CO_2e/t-CO_2 (Paper IV). If the method applied in a previous LCA study (Khoo and Tan, 2006), where the energy requirements (heat and power) were lumped together into a single value is applied, the process GWP becomes significantly higher (1270 - 2170 kg CO_2e/t-CO_2) than it should be. Paper IV, therefore argued in favor of exergy analysis as reliable concept for process energy evaluation, especially when different grades of heat and power are to be added together. The ÅAU process was found to give a 170 kg CO_2e/t-CO_2 lower GWP than the NETL process (Paper IV). This value remains fairly constant at varying process heat requirements of the processes. A major reason for the lower GHG emissions burden of the ÅAU process is the recoverable *AS* reagent used in the ÅAU process compared with the non-recoverable reagents (NaCl and $NaHCO_3$) applied in the NETL method. Other factors include the lower thermal treatment temperature at 400 °C (which may also make it possible to use renewable energy sources like solar thermal energy), the CO_2 reduction potential of the Fe/Ca by-products and the heat recovery potential from the carbonation reaction.

Paper VI assessed the life cycle GHG emissions of the ÅAU process applied to sequester CO_2 emissions from a 555 MWe NGCC power plant. Unlike in Paper IV where the Finnish serpentinite ore used had Fe_3O_4 as the form of Fe in the rock, Finnish serpentinite ore used here contains Fe_2O_3 as the iron compound. Also, the $Mg(OH)_2$ production and carbonation energy requirements reported in Paper V were used to calculate the ÅAU process life cycle inventory in Paper VI. In Paper VI, both the heat and power requirements are provided by the NGCC power plant whose CO_2 emissions are sequestered in serpentinite.

The process GHG emissions of the ÅAU process in Paper VI are comparable in many respects with those of Paper IV. Both show that the process heat and power use, mineral mining, transport and processing are the major contributors to the GWP of the $Mg(OH)_2$ production and mineralization processes. However, the process environmental performance is slightly better in Paper VI. This is due to the fact that a low intensity fuel (NG) was used to provide for both the process heat and power requirements. Also, the serpentinite rock used in Paper VI contains a Fe compound requiring lesser energy during extraction reaction.

At 100% conversion and recovery of reagent, the CO_2 mineralization process has a life cycle

GWP of 433 kg $CO_2e/t\text{-}CO_2$. This value increases by 82, 7 and 0.4 $CO_2e/t\text{-}CO_2$ for every %-point efficiency loss of *AS* recovery, $Mg(OH)_2$ production and $Mg(OH)_2$ carbonation respectively. For example, Table 6 shows a drastic increase in the GHG emissions of the ÅAU process for a 1% inefficiency in *AS* recovery.

Table 6. Summary of the life cycle material, energy GHG inventory for mineral sequestration of CO_2 from a NGCC power plant (Paper IV).

100% conversion of $Mg(OH)_2$ production and carbonation and 99% recovery of *AS*						
Material (*t/t-* CO_2)	Input	Output	Energy/GHG emissions	Input	Output	GWP*
Serpentinite	2.53		Rock processing (*kWh/t-*CO_2)		42.4	23
AS salt make-up	0.04		Heat (*GJ/t-*CO_2)	2.94	0.55$^{\#}$	106
Water	0.4		Electricity (*kWh/t-*CO_2)	327	66$^{\#}$	84
Silica	0.92		Production of *AS*			82
FeOOH & $Ca(OH)_2$		0.46	Rock transport			22
$MgCO_3$		1.92	MEA and *AS* transport			12
			Total GHG emissions			329
CO_2 Capture with MEA						
Material (*kg/t-*CO_2)	Input	Output	Energy/GHG emissions	Input	Output	GWP*
MEA make-up	1.5		Reboiler Heat (*GJ/t*CO_2)	3.5		156
			Production of MEA			4
			CO_2 (*t-*CO_2*/hr*)	202.6	20.46	
			Total GHG emissions			160
CO_2 compression						
Material (*t/t-* CO_2)	Input	Output	Energy/GHG emissions	Input	Output	GWP*
CO_2 (*t-*CO_2)	1	1	Power (*kWh/t-*CO_2)	120		38
Gross amount of GHGs from the CO_2 mineral sequestration process 527						
NGCC power plant						
Material	input		Energy/GHG emissions	w/o CCM		w/CCM
NG (*t/hr*)	75.90		Gross power (*MWe*)	564.2		564.2
Air (*t/hr*)	3155		Auxiliary load (*MWe*)	9.62		214.3
CO_2 in NG (*t/hr*)	201.1		Net Power (*MWe*)	555.08		340.8
CO_2 in Air (*t/hr*)	1.573		GWP (CO_2e/MWh)	386		193
CO_2 (*t-*CO_2*/hr*)	202.6					
Water use (*t/hr*)	228					

GWP presented as kg* $CO_2e/t\text{-}CO_2$ *stored safely in serpentinite. w/o CCM – without* CO_2 *mineral sequestration. w/CCM – with* CO_2 *mineral sequestration.* $^{\#}$*Heat and power output from the carbonation reaction.*

When applied to the 555 MW NGCC plant, the ÅAU reduces its net plant efficiency from 50.2% to 30.8% but avoids 52% of CO_2/MWh emissions to the atmosphere. Paper VI also evaluated the effect of inefficiencies in $Mg(OH)_2$ production and carbonation (see Table 7). LCI results show that up to 733 kg CO_2e/t-CO_2 could result from a low efficiency $Mg(OH)_2$ production while the energy penalty from low efficiency $Mg(OH)_2$ carbonation could exert a GWP of 42 kg CO_2e/t-CO_2.

Table 7. Life cycle GHGs (kg CO_2e/t-CO_2) associated with the CO_2 mineralization process at different conversion efficiencies

Mg extraction	$Mg(OH)_2$ carbonation efficiency					
efficiency	100%	90%	80%	60%	40%	20%
100%	433	437	441	450	458	466
90%	448	452	456	465	473	481
80%	468	472	476	485	493	501
60%	529	533	537	546	554	562
40%	652	656	660	669	677	685
20%	1020	1024	1028	1037	1045	1053

6. Conclusions and suggestions for future work

This thesis contributes towards finding carbon sequestration solutions that could stabilize the unprecedented increasing anthropogenic CO_2 emissions and mitigate climate change. Carbon sequestration is considered a viable technological approach through which deep reductions in global CO_2 emissions can be realized. Carbon sequestration could ensure that both current and future energy demands are met in a less carbon intensive way and pave way for a decarbonized or renewable energy systems future. Carbon dioxide capture and mineralization (CCM), which is part of the carbon sequestration technology family, involves a geochemical binding of CO_2 emissions to abundantly available mineral rocks and waste products for permanent and safe storage as solid carbonates. Research interest in CCM has continuously increased, although technical and economic setbacks, such as inefficient chemical conversions, slow chemical kinetics, high energy and costs requirements, identified over a decade ago are yet to be addressed.

This thesis studied the *ex situ* indirect gas/solid carbonation method of CCM whereby $Mg(OH)_2$ is produced from Mg-silicates and is later carbonated in a pressurized fluidized bed (FB). The gas/solid carbonation method is intensively researched at ÅAU because it is attractive in terms of energy usage and recovery. The energy from the exothermic chemistry of $Mg(OH)_2$ carbonation is utilized. Here, the first stages of the ÅAU process, which involve the production of $Mg(OH)_2$ from Mg-silicates (serpentinite and olivine rocks) are investigated . The last stage of the ÅAU process - carbonation $Mg(OH)_2$, was addressed in another study but is included in this thesis for purposes of process performance assessment.

This study has shown that $Mg(OH)_2$ can be produced from serpentinite and olivine rocks through a staged process of Mg extraction followed by precipitation of $Mg(OH)_2$. Mg extraction is achieved by reacting pulverized serpentinite or olivine rocks with ammonium sulfate (*AS*) salt at temperatures 270 - 600 °C (preferably < 450 °C). Mg extraction is the conversion-determining and the most energy-intensive step of the entire CCM process chain. This study shows that different Mg-silicate rocks react differently. For example, there is a huge difference in reactivity of serpentinite and olivine rocks, with the former reacting almost five times more than the latter. Different serpentinite rocks react differently too. The reactivity of serpentinite and olivine rocks is interdependent and complementary on both their chemical and physical properties. Rocks with desirable chemical compositions, having a high Mg to Fe (*Mg/Fe*) ratio, have a high reactivity if they also have a high surface area and porosity. More so, serpentinite rocks with an

Mg/Fe ratio ≥ 2.16 kg/kg react remarkably better than those with an *Mg/Fe* ratio <2.16 kg/kg. Therefore, in considering the suitability of a mineral as raw material for the production of $Mg(OH)_2$ for CCM, the combination of *Mg/Fe* ratio, specific surface area and porosity are important factors to consider.

Reaction temperature and time are parameters of interest. An increase in reaction temperature results in an increase in the extent of extraction, reaching a maximum yield at different temperatures depending on the reaction time. However, the heat transfer properties of the reactor also play a role in Mg extraction; optimal extraction yield and conditions reported for different reactors differ. It can be inferred from the results that reaction temperatures 400 - 480 °C and time 30 - 60 min suffice for Mg extraction from the serpentinite rocks tested. Within this range of reaction conditions, 65% Mg extraction has been obtained for Finnish serpentinite. Reaction condition beyond the upper range of the reaction conditions results in a decline in both Mg and Fe extraction.

Using a newly acquired rotary reactor, scalability and mixing were studied with a larger amount of serpentinite (40 g instead of the usual 2 - 8 g) and larger serpentinite grain size (125 – 250 μm) than that (75-125 μm) mostly used in other reactors. The tests achieved 53% maximum Mg extraction at 450 °C and 2 hr (including 45 min heat up time). While the results obtained from this first batch of tests with the rotary reactor may not be considered as very promising, it demonstrates that scale-up is feasible. The knowledge that is gained from operating the rotary reactor will be relevant in designing a future pilot reactor which may not be very different in configuration. Therefore, more research is needed to improve the performance of the rotary reactor. An interesting parameter to assess in future tests should be the introduction of moisture in the rotary reactor.

The $Mg(OH)_2$ process is closed loop in nature as the gaseous ammonia and water vapour products of the extraction stage are recoverable, and can be used as reagent for the precipitation stage. FeOOH, high purity $Mg(OH)_2$ and aqueous AS are produced from the next stage – precipitation reactions. Recovery of the *AS* reagent via crystallization closes the process loop. The closed loop method of producing $Mg(OH)_2$, meaning that all reagents are potentially recoverable, makes this process attractive. Besides this, the *AS* salt reagent used for extracting Mg from the minerals is relatively cheap, and is a product and by-product of several chemical processes. More so, the FeOOH and $Ca(OH)_2$ are considered valuable by-products and may be useful raw materials replacing feedstock of the sinter plant of the iron and steelmaking industry.

Opportunities for using the Mg-carbonate product (~ 2 t/t-CO_2) as cement additives, fillers or for land reclamation, and the Fe/Ca (oxy)-hydroxides as iron ore feedstock may be dwarfed in magnitude compared with the scale of CO_2 emissions. However, producing high-value products like silica, nickel, chromium etc. alongside the FeOOH, carbonate products may become a game changer that can render mineral carbonation cost competitive.

Notwithstanding its promising potential, the energy required for reacting large amounts of minerals and *AS* salt at 400 - 480 °C makes the $Mg(OH)_2$ process energy intensive. In addition, *AS* recovery through crystallization also exerts a substantial energy burden. However, the choice of *MVR* over the "evaporation only" crystallization methods has a potential energy savings of 15.2 GJ/ton CO_2 (84 % savings). Results show that the presence of Fe during the extraction reaction constitutes an additional energy penalty, the extent of which depends on the form in which Fe exists in the mineral rock. The implication is that given the significant energy penalty connected to iron compounds, proportionate energy, cost and CO_2 emission penalties should be allocated to the FeOOH by-product. The benefit of the potential use of FeOOH as an iron ore feedstock in iron and steelmaking can only be correctly quantified when also considering these trade-offs.

Integrating the $Mg(OH)_2$ production method and the gas/solid carbonation process adds an energy benefit to the CCM process; up to 25% of the energy requirements of the $Mg(OH)_2$ process is offset by the carbonation process, however. More so, this benefit reduces if carbonation efficiency is not close to 100%. By implication, going forward, the exothermic carbonation energy should not be relied upon as a source of significant offset to the energy requirements of the upstream $Mg(OH)_2$ process. Rather, producing $Mg(OH)_2$ efficiently at a low energy requirement would be the key to the success of the CCM process. If the carbonation efficiency is not sufficient to provide a significant part of exothermic carbonation heat, a more efficient aqueous carbonation of $Mg(OH)_2$ would become a viable alternative. An even more attractive, although controversial and probably risky option, would be the application of $Mg(OH)_2$ to oceans to boast oceans capacity to directly remove atmospheric CO_2 and at the same time reduce the escalating ocean acidification problem.

The process performance of the CCM process was assessed using a combination of process evaluation and life cycle analysis approaches to determine the process energy and GHG burden of the entire CCM process. This is a reasonable approach since CCM technology should in itself offer a solution to what is both an energy and environmental problem. Although serpentinite rocks occur in thick layers with usually a small overburden compared to coal seams, the application of CCM requires a greater mining effort (>2.5 t/t-CO_2). The mining requirements together with the location of the energy source, the CO_2 source, and the CO_2-type, whether processed or unprocessed (direct mineralization of flue-gases) are ultimately important factors to consider in front-end engineering design and siting of the CCM plant. The process energy (and of course costs) and environmental impact associated with any CCM process are dependent on these.

The first LCI case studied in this thesis determined, among other things, the net GHG emissions burden associated with sequestering coal-derived CO_2 in serpentinite mineral ore, the priorities and opportunities for energy and GHG reduction, and compared LCA results of ÅAU mineralization process with that of NETL Albany. In the first case an industrial gas burner provided the heat requirements of the CCM processes while a coal-fired power plant, whose CO_2 emissions were mineralized, provided for the process power requirements. The LCIA results showed that for every ton of coal power plant derived CO_2 mineralized, the ÅAU CCM process avoids 483 kg CO_2 while the NETL CCM process avoids 317 kg CO_2e. It was found that although the energy intensities of both processes are in the same range (3.4 - 3.6 GJ/t-CO_2), the ÅAU process has considerably lower environmental impact than the NETL process. The reasons for the lower GWP of the ÅAU process were identified as: the recoverability of the chemical reagent, lower thermal treatment temperature (at 400 °C), which may also make it possible to use renewable energy sources like solar thermal energy, the CO_2 reduction potential of the Fe/Ca by-products and the heat recovery potential of the carbonation reaction. However, an economic evaluation would be required to conclude on the feasibility of or comparison of the viability of these CCM processes.

The possibility of generating both power and heat using either low intensity fuels or solar thermal sources would reduce the ÅAU process GWP. The second LCI case was modeled to sequester CO_2 emissions from a 555 MW NGCC power. The NGCC provides for both the heat and power requirements of the ÅAU process. Results showed that a 100% efficient ÅAU process coupled to a NGCC power plant has a life cycle GHG emissions of 235 kg CO_2e/t-CO_2 from $Mg(OH)_2$ production and 433 kg CO_2e/t-CO_2 from the entire mineral carbonation process. Process inefficiencies, especially those of *AS* recovery and $Mg(OH)_2$ would exert an enormous burden on the CCM process. In both LCI cases, CO_2 capture using MEA reagent and CO_2 compression contribute significantly to the emissions burden of the CCM process. Storage of 90% of the CO_2 emissions captured from a 555 MW NGCC power plant in serpentinite rock reduces the net power efficiency by ~ 20% but avoids 52% of its life cycle CO_2 emissions. It can be deduced from the LCIA that the ÅAU process could become a viable CO_2 mitigation route if it is applied to flue gases directly, avoiding the energy and environmental penalty from CO_2 capture. In addition, another attractive integrating option involves sequestering CO_2 emissions from waste-heat generating sources that could provide this heat for the $Mg(OH)_2$ production process. It is important to note that the LCA studies did not consider uncertainties resulting from the use of processes that are still at a laboratory scale to represent large-scale industrial applications. Scaling up of processes does not necessarily follow a linear pattern, as has been applied in this work. Ongoing and future work involves exploring the technical, energy and economic uncertainties of process scale-up.

In short, producing $Mg(OH)_2$ from serpentinite rocks for CCM, as described and evaluated in this thesis, has many attractive features that make the process look promising. Nonetheless, it currently has a high energy and environmental burden which represents a considerable setback to large-scale implementation. It is the opinion of the author that more research on this process could lead to a significant improvement of process efficiency, and a reduction of process energy requirements and environmental impact.

References

ABANADES, J. C., RUBIN, E. S. & ANTHONY, E. J. 2004. Sorbent cost and performance in CO_2 capture systems. *Industrial & Engineering Chemistry Research,* 43**,** 3462-3466.

AKOREDE, M. F., HIZAM, H., AB KADIR, M. Z. A., ARIS, I. & BUBA, S. D. 2012. Mitigating the anthropogenic global warming in the electric power industry. *Renewable and Sustainable Energy Reviews,* 16**,** 2747.

ALEXANDER, G., MERCEDES MAROTO-VALER, M. & GAFAROVA-AKSOY, P. 2007. Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation. *Fuel,* 86**,** 273-281.

ALIZADEHHESARI, K., GOLDING, S. D. & BHATIA, S. K. 2011. Kinetics of the Dehydroxylation of Serpentine. *Energy & Fuels,* 26**,** 783-790.

AMERICAN PHYSICAL SOCIETY 2011. Direct air capture of CO_2 with chemicals. *Assessment for the APS Panel on Public AffairsTechnology.* New York, USA.: American Physical Society.

BACHU, S. 2008. CO_2 storage in geological media: Role, means, status and barriers to deployment. *Progress in Energy and Combustion Science,* 34**,** 254-273.

BACHU, S., GUNTER, W. & PERKINS, E. 1994. Aquifer disposal of CO_2: Hydrodynamic and mineral trapping. *Energy Conversion and Management,* 35**,** 269-279.

BACIOCCHI, R., COSTA, G., DI BARTOLOMEO, E., POLETTINI, A. & POMI, R. 2009. The effects of accelerated carbonation on CO_2 uptake and metal release from incineration APC residues. *Waste management,* 29**,** 2994-3003.

BACIOCCHI, R., POLETTINI, A., POMI, R., PRIGIOBBE, V., VON ZEDWITZ, V. N. & STEINFELD, A. 2006. CO_2 sequestration by direct gas-solid carbonation of air pollution control (APC) residues. *Energy & Fuels,* 20**,** 1933-1940.

BÉARAT, H., MCKELVY, M. J., CHIZMESHYA, A. V. G., GORMLEY, D., NUNEZ, R., CARPENTER, R. W., SQUIRES, K. & WOLF, G. H. 2006. Carbon Sequestration via Aqueous Olivine Mineral Carbonation: Role of Passivating Layer Formation. *Environmental Science & Technology,* 40**,** 4802-4808.

BÉARAT, H., MCKELVY, M. J., CHIZMESHYA, A. V. G., SHARMA, R. & CARPENTER, R. W. 2002. Magnesium hydroxide dehydroxylation/carbonation reaction processes: implications for carbon dioxide mineral sequestration. *Journal of the American Ceramic Society,* 85**,** 742-748.

BERTOS, M. F., LI, X., SIMONS, S., HILLS, C. & CAREY, P. 2004. Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO2. *Green Chem.,* 6**,** 428-436.

BICKEL, J. E. & LANE, L. 2010. Climate Engineering. *In:* LOMBORG, B. (ed.) *Smart solutions to climate change.* Cambridge, NY, USA and Cambridge, UK.: Cambridge University Press.

BLOMEN, E., HENDRIKS, C. & NEELE, F. 2009. Capture technologies: Improvements and promising developments. *Energy Procedia,* 1**,** 1505-1512.

BOBICKI, E. R., LIU, Q., XU, Z. & ZENG, H. 2012. Carbon capture and storage using alkaline industrial wastes. *Progress in Energy and Combustion Science,* 38 302-320.

— References —

BODEN, T., MARLAND, G. & ANDRES, B. 2011 Global CO_2 emissions from fossil-fuel burning, cement manufacture, and gas flaring: 1751-2008 *In:* CARBON DIOXIDE INFORMATION ANALYSIS CENTER, O. R. N. L., OAK RIDGE, TENNESSEE, US. (ed.).

BRENT, G. F., ALLEN, D. J., EICHLER, B. R., PETRIE, J. G., MANN, J. P. & HAYNES, B. S. 2011. Mineral Carbonation as the core of an industrial symbiosis for energy-intensive minerals conversion. *Journal of Industrial Ecology,* 16**,** 94-104.

BUTT, D. P., LACKNER, K. S., WENDT, C. H., CONZONE, S. D., KUNG, H., LU, Y. C. & BREMSER, J. K. 1996. Kinetics of thermal dehydroxylation and carbonation of magnesium hydroxide. *Journal of the American Ceramic Society,* 79**,** 1892-1898.

CHANG, E., PAN, S. Y., CHEN, Y. H., CHU, H. W., WANG, C. F. & CHIANG, P. C. 2011. CO_2 sequestration by carbonation of steelmaking slags in an autoclave reactor. *Journal of Hazardous Materials,* 195**,** 107–114.

CONWAY, T. & TANS, P. 2012. Globally averaged marine surface monthly mean carbon dioxide data. *In:* NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION, E. S. R. L. (ed.). www.esrl.noaa.gov/gmd/ccgg/trends/.

CORNER, A. & PIDGEON, N. 2010. Geoengineering the climate: the social and ethical implications. *Environment: Science and Policy for Sustainable Development,* 52**,** 24-37.

COSTA, G., BACIOCCHI, R., POLETTINI, A., POMI, R., HILLS, C. D. & CAREY, P. J. 2007. Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues. *Environmental monitoring and assessment,* 135**,** 55-75.

DAVISON, J. 2007. Performance and costs of power plants with capture and storage of CO2. *Energy,* 32**,** 1163-1176.

DOUCET, F. J. 2010. Effective CO_2 specific sequestration capacity of steel slags and variability in their leaching behaviour in view of industrial mineral carbonation. *Minerals Engineering,* 23**,** 262-269.

ELONEVA, S., MANNISTO, P., SAID, A., FOGELHOLM, C. J. & ZEVENHOVEN, R. 2011a. Ammonium salt-based steelmaking slag carbonation: Precipitation of CaCO3 and ammonia losses assessment. *Greenhouse Gases: Science and Technology,* 1**,** 305–311.

ELONEVA, S., SAID, A., FOGELHOLM, C. J. & ZEVENHOVEN, R. 2011b. Preliminary assessment of a method utilizing carbon dioxide and steelmaking slags to produce precipitated calcium carbonate. *Applied Energy,* 90**,** 329–334.

ELONEVA, S., TEIR, S., SALMINEN, J., FOGELHOLM, C. J. & ZEVENHOVEN, R. 2008. Steel converter slag as a raw material for precipitation of pure calcium carbonate. *Industrial & Engineering Chemistry Research,* 47**,** 7104-7111.

EPA 2009. Economics of climate change. Http:/yosemite.epa.gov/ee/epa/eed.nsf/webpages/ClimateEconomics.html: National Center for Environmental Economics.

FAGERLUND, J. 2012. *Carbonation of $Mg(OH)_2$ in a pressurised fluidised bed for CO_2 sequestration.* Dr. Tech., Åbo Akademi University, Finland.

FAGERLUND, J., HIGHFIELD, J. & ZEVENHOVEN, R. 2012a. Kinetics studies on wet and dry gas-solid carbonation of MgO and $Mg(OH)_2$ for CO_2 sequestration. *RSC Advances,* 2, 10380-10393.

FAGERLUND, J., NDUAGU, E., ROMÃO, I. & ZEVENHOVEN, R. 2010. A stepwise process for carbon dioxide sequestration using magnesium silicates. *Frontiers of Chemical Engineering in China,* 4**,** 133-141.

FAGERLUND, J., NDUAGU, E., ROMÃO, I. & ZEVENHOVEN, R. 2012b. CO_2 fixation using magnesium silicate minerals. Part 1: Process description and performance. *Energy – the Int. J. (special edition ECOS2010),* 41**,** 184-191.

FAGERLUND, J., NDUAGU, E. & ZEVENHOVEN, R. 2011. Recent developments in the carbonation of serpentinite derived $Mg(OH)_2$ using a pressurized fluidized bed. *Energy Procedia,* 4**,** 4993-5000.

FAGERLUND, J., TEIR, S., NDUAGU, E. & ZEVENHOVEN, R. 2009. Carbonation of magnesium silicate mineral using a pressurised gas/solid process. *Energy Procedia,* 1**,** 4907-4914.

FAGERLUND, J. & ZEVENHOVEN, R. 2011. An experimental study of $Mg(OH)_2$ carbonation. *International Journal of Greenhouse Gas Control,* 5**,** 1406-1412.

FAUTH, D. J., JONES, J. R., KNOER, J. P. & SOONG, Y. 2000. Binding carbon dioxide as carbonate minerals. 17th Annual Int. Pitt. Coal Conference, Sep. 11–15 2000 Pittsburgh, PA, USA.

GERDEMANN, S. J., DAHLIN, D. C., O'CONNOR, W. K., PENNER, L. R. & RUSH, G. 2004. Ex-situ and in-situ mineral carbonation as a means to sequester carbon dioxide. 21st Annual International Pittsburgh Coal Conference, Sept. 13-17, 2004 Osaka, Japan. Albany Research Center (ARC), Albany, NY, paper 47-5.

GERDEMANN, S. J., O'CONNOR, W. K., DAHLIN, D. C., PENNER, L. R. & RUSH, H. 2007. Ex situ aqueous mineral carbonation. *Environ. Sci. Technol,* 41**,** 2587-2593.

GISLASON, S. R., WOLFF-BOENISCH, D., STEFANSSON, A., OELKERS, E. H., GUNNLAUGSSON, E., SIGURDARDOTTIR, H., SIGFUSSON, B., BROECKER, W. S., MATTER, J. M. & STUTE, M. 2010. Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *International Journal of Greenhouse Gas Control,* 4**,** 537-545.

GOLDBERG, P., CHEN, Z. Y., O'CONNOR, W., WALTERS, R. & ZIOCK, H. 2001. CO_2 mineral sequestration studies in US. *J Energy Environ Res,* 1**,** 117-126.

GÖTTLICHER, G. & PRUSCHEK, R. 1997. Comparison of CO_2 removal systems for fossil-fuelled power plant processes. *Energy Conversion and Management,* 38**,** 173-178.

HEAL, G. & KRISTRÖM, B. 2002. Uncertainty and Climate Change. *Environmental and Resource Economics,* 22**,** 3-39.

HERZOG, H. 2002. Carbon sequestration via mineral carbonation: Overview and assessment. http://sequestration.mit.edu/pdf/carbonates.pdf: Massachusetts Institute of Technology.

HERZOG, H. J. 2001. Peer reviewed: What future for carbon capture and sequestration? *Environmental Science & Technology,* 35**,** 148-153.

HIGHFIELD, J., LIM, H., FAGERLUND, J. & ZEVENHOVEN, R. 2012. Activation of serpentine for CO_2 mineralization by flux extraction of soluble magnesium salts using ammonium sulphate. *RSC Advances* 2**,** 6535-6541.

HILLEY, G. E. & PORDER, S. 2008. A framework for predicting global silicate weathering and

CO_2 drawdown rates over geologic time-scales. *Proceedings of the National Academy of Sciences,* 105**,** 16855-16859.

HOLMES, G. & KEITH, D. W. 2012. An air–liquid contactor for large-scale capture of CO_2 from air. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 370**,** 4380-4403.

HOUGHTON, J. 2005. Global warming *Rep. Prog. Phys. ,* 68**,** 1343.

HOUSE, K. Z., BACLIG, A. C., RANJAN, M., VAN NIEROP, E. A., WILCOX, J. & HERZOG, H. J. 2011. Economic and energetic analysis of capturing CO_2 from ambient air. *Proceedings of the National Academy of Sciences,* 108**,** 20428-20433.

HUESEMANN, M. H. 2006. Can advances in science and technology prevent global warming? *Mitigation and Adaptation Strategies for Global Change,* 11**,** 539-577.

HUESEMANN, M. H. 2008. Ocean fertilization and other climate change mitigation strategies: an overview. *Mar. Ecol. Prog. Ser.* 364, 243-250.

HUIJGEN, W. & COMANS, R. 2003. Carbon dioxide sequestration by mineral carbonation. Literature review.: Energy research Centre of the Netherlands (ECN).

HUIJGEN, W. & COMANS, R. 2005a. Carbon dioxide sequestration by mineral carbonation: Literature review update 2003-2004. Energy Research Centre of the Netherlands (ECN).

HUIJGEN, W. & COMANS, R. 2005b. Mineral CO_2 sequestration by carbonation of industrial residues. The Netherlands: Energy Research Centre of the Netherlands (ECN).

HUIJGEN, W. J. J. & COMANS, R. N. J. 2005c. Mineral CO_2 Sequestration by Steel Slag Carbonation. *Environmental Science & Technology,* 39**,** 9676-9682.

HUNTZINGER, D. N., GIERKE, J. S., KAWATRA, S. K., EISELE, T. C. & SUTTER, L. L. 2009a. Carbon Dioxide Sequestration in Cement Kiln Dust through Mineral Carbonation. *Environmental Science & Technology,* 43**,** 1986-1992.

HUNTZINGER, D. N., GIERKE, J. S., SUTTER, L. L., KAWATRA, S. K. & EISELE, T. C. 2009b. Mineral carbonation for carbon sequestration in cement kiln dust from waste piles. *Journal of Hazardous Materials,* 168**,** 31-37.

HUNWICK, R. J. 2008. *System, apparatus and method for carbon dioxide sequestration.* WO patent application B01D 53/62; C01B 31/20; C01B 31/24; C01B 33/20.

IDSO, S. B. 1998. CO_2-induced global warming: a skeptic's view of potential climate change. *Climate Research,* 10**,** 69-82.

IEA 2011. *Key world energy statistics*, IEA, Paris.

IEA 2012. *Indicators for CO_2 emissions*, IEA, Paris.

IPCC 2001a. Chapter 6: Radiative forcing of climate change. *In:* JOOS, F. & J., S. (eds.) *Climate Change 2001: The Scientific Basis. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change.* United Kingdom and New York, NY, USA.: IPCC.

IPCC 2001b. Climate Change 2001: The Scientific Basis. *In:* DING, Y., GRIGGS, D.J, NOGUER, M., VAN DER LINDEN, P.J, DAI, X., MASKELL, K. AND JOHNSON, C.A. (ed.) *Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change.* United Kingdom and New York, USA: IPCC.

IPCC 2005a. Carbon dioxide capture and storage. Summary for policymakers. *A Special Report of*

Working Group III of the Intergovernmental Panel on Climate Change. United Kingdom and New York, NY, USA.: IPCC.

IPCC 2005b. IPCC special report on carbon dioxide capture and storage. . *In:* METZ, B., DAVIDSON, O., DE CONINCK, H. C., LOOS, M. AND MEYER, L. A. (ed.) *Prepared by Working Group III of the Intergovernmental Panel on Climate Change.* Cambridge, United Kingdom and New York, NY, USA.: IPCC.

IPCC 2007a. Changes in atmospheric constituents and in radiative forcing. *In:* SOLOMON, S., D. , QIN, M., MANNING, Z., CHEN, M., MARQUIS, K. B., AVERYT, M. T. & MILLER, T. A. H. L. (eds.) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* United Kingdom and New York, NY, USA.: IPCC.

IPCC 2007b. Climate Change 2007: Synthesis Report. *In:* ABDELKADER ALLALI, R. B., SANDRA DIAZ, ISMAIL ELGIZOULI, DAVE GRIGGS, DAVID HAWKINS, OLAV HOHMEYER, BUBU PATEH JALLOW, LUC4KA KAJFEZ4-BOGATAJ, NEIL LEARY, HOESUNG LEE, DAVID WRATT (ed.) *Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* United Kingdom and New York, NY, USA.: IPCC.

IPCC 2007c. Climate change 2007: The physical science basis. *In:* SOLOMON, S., D. QIN, M. MANNING, Z. CHEN, M. MARQUIS, K.B. AVERYT, M.TIGNOR AND H.L. MILLER (ed.) *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* United Kingdom and New York, NY, USA: IPCC.

IPCC 2011. Summary for Policymakers. *In:* EDENHOFER, O., PICHS-MADRUGA, R., SOKONA, Y., SEYBOTH, K., MATSCHOSS, P., KADNER, S., ZWICKEL, T., EICKEMEIER, P., HANSEN, G., SCHLÖMER, S., VON STECHOW, C. (ed.) *IPCC Special Report on renewable energy sources and climate change mitigation.* United Kingdom and New York, NY, USA.: IPCC.

JENSEN, A. A., HOFFMAN, L., MØLLER, B. T., SCHMIDT, A., CHRISTIANSEN, K., ELKINGTON, J. & VAN DIJK, F. 1997. Life cycle assessment (LCA) - a guide to approaches, experiences and information sources. *Environmental Issues Series, no.6.* European Environment Agency (EEA).

JIANGUO, J., MAOZHE, C., YAN, Z. & XIN, X. 2009. Pb stabilization in fresh fly ash from municipal solid waste incinerator using accelerated carbonation technology. *Journal of Hazardous Materials,* 161**,** 1046-1051.

JOHANSSON, T., WILLIAMS, R., ISHITANI, H. & EDMONDS, J. A. 1996. Options for reducing CO_2 emissions from the energy supply sector. *Energy Policy,* 24**,** 985-1003.

KAKIZAWA, M., YAMASAKI, A. & YANAGISAWA, Y. 2001. A new CO_2 disposal process via artificial weathering of calcium silicate accelerated by acetic acid. *Energy,* 26**,** 341-354.

KEITH, D. W., PARSON, E. & MORGAN, M. G. 2010. Research on global sun block needed now. *Nature,* 463**,** 426-427.

KELEMEN, P. B. & MATTER, J. 2008. In situ carbonation of peridotite for CO_2 storage. *Proceedings of the National Academy of Sciences,* 105**,** 17295.

KELLOGG, W. W. 1991. Response to skeptics of global warming. *Bulletin of the American Meteorological Society,* 72**,** 499-511.

KEMP, I. C. 2007. *Pinch analysis and process integration: a user guide on process integration for the efficient use of energy,* Oxford, UK., Butterworth-Heinemann.

KHESHGI, H. S. 1995. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy,* 20**,** 915-922.

KHOO, H. & TAN, R. 2006. Life cycle evaluation of CO2 recovery and mineral sequestration alternatives. *Environmental progress,* 25**,** 208-217.

KHOO, H. H., SHARRATT, P. N., BU, J., YEO, T. Y., BORGNA, A., HIGHFIELD, J. G., BJÖRKLÖF, T. G. & ZEVENHOVEN, R. 2011. Carbon capture and mineralization in Singapore: Preliminary environmental impacts and costs via LCA. *Industrial & Engineering Chemistry Research,* 50**,** 11350-11357.

KIM, D. J. & CHUNG, H. S. 2002. Effect of grinding on the structure and chemical extraction of metals from serpentine. *Particulate science and technology,* 20**,** 159-168.

KOJIMA, T., NAGAMINE, A., UENO, N. & UEMIYA, S. 1997. Absorption and fixation of carbon dioxide by rock weathering. *Energy Conversion and Management,* 38**,** 461-466.

KOPPELAAR, R. 2012. *World energy consumption - beyond 500 exajoules* [Online]. http://www.energybulletin.net/stories/2012-02-16/world-energy-consumption-beyond-500-exajoules: Energy Bulletin. Available: http://www.energybulletin.net/stories/2012-02-16/world-energy-consumption-beyond-500-exajoules [Accessed 29 August 2012 2012].

KOTAS, T. J. 1985. *The exergy method of thermal plant analysis,* Stoneham, MA, US., Butterworth Publishers.

KOTHANDARAMAN, A., NORD, L., BOLLAND, O., HERZOG, H. J. & MCRAE, G. J. 2009. Comparison of solvents for post-combustion capture of CO_2 by chemical absorption. *Energy Procedia,* 1**,** 1373-1380.

KYOTO PROTOCOL 1997. United Nations framework convention on climate change. *Kyoto Protocol, Kyoto.* United Nation Framework Convention on Climate Change (UNFCCC).

LACKNER, K. 2002a. Carbonate chemistry for sequestering fossil carbon. *Annu. Rev. Energy Environ.,* 27**,** 193–232.

LACKNER, K. 2003. Climate change: a guide to CO2 sequestration. *Science,* 300**,** 1677.

LACKNER, K. 2010. Washing Carbon Out of the Air. *Scientific American Magazine,* 302**,** 66-71.

LACKNER, K., DOBY, P., YEGULALP, T., KREVOR, S. & GRAVES, C. 2008. Integrating Steel Production with Mineral Carbon Sequestration. New York, NY: Columbia University, Department of Earth and Environmental Engineering, New York, NY.

LACKNER, K. S. 2002b. Carbonate Chemistry for sequestering fossil carbon. *Annual Review of Energy and the Environment,* 27**,** 193-232.

LACKNER, K. S., BUTT, D. P. & WENDT, C. H. 1997. Progress on binding CO_2 in mineral substrates. *Energy Conversion and Management,* 38**,** 259-264.

LACKNER, K. S., WENDT, C. H., BUTT, D. P. & JOYCE, E. L. 1995. Carbon dioxide disposal in carbonate minerals. *Energy,* 20**,** 1153-1170.

LARACHI, F., DALDOUL, I. & BEAUDOIN, G. 2010. Fixation of CO_2 by chrysotile in low-pressure dry and moist carbonation: Ex-situ and in-situ characterizations. *Geochimica et Cosmochimica Acta,* 74**,** 3051-3075.

LASHOF, D. A. & AHUJA, D. R. 1990. Relative contributions of greenhouse gas emissions to global warming. *Nature,* 344**,** 529 - 531.

LI, X., BERTOS, M. F., HILLS, C. D., CAREY, P. J. & SIMON, S. 2007. Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste management,* 27**,** 1200-1206.

LIN, P. C., HUANG, C. W., HSIAO, C. T. & TENG, H. 2008. Magnesium hydroxide extracted from a magnesium-rich mineral for CO_2 sequestration in a gas–solid system. *Environmental Science & Technology,* 42**,** 2748-2752.

LINNHOFF, B. 1993. Pinch analysis: a state-of-the-art overview: Techno-economic analysis. *Chemical engineering research & design,* 71**,** 503-522.

MAROTO-VALER, M., FAUTH, D., KUCHTA, M., ZHANG, Y. & ANDRÉSEN, J. 2005. Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. *Fuel Processing Technology,* 86**,** 1627-1645.

MATTER, J. M. & KELEMEN, P. B. 2009. Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nature Geoscience,* 2**,** 837-841.

MATTILA, H. P., GRIGALIŪNAITĖ, I. & ZEVENHOVEN, R. 2012. Chemical kinetics modeling and process parameter sensitivity for precipitated calcium carbonate production from steelmaking slags. *Chemical Engineering Journal,* 192**,** 77-89.

MCKELVY, M. J., CHIZMESHYA, A. V. G., DIEFENBACHER, J., BÉARAT, H. & WOLF, G. 2004. Exploration of the Role of Heat Activation in Enhancing Serpentine Carbon Sequestration Reactions. *Environmental Science & Technology,* 38**,** 6897-6903.

MCKELVY, M. J., CHIZMESHYA, A. V. G., SQUIRES, K., CARPENTER, R. W. & BEARAT, H. 2006. A novel approach to mineral carbonation: Enhancing carbonation while avoiding mineral pretreatment process cost. Available at http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=895921: Arizona State University, Center for Solid State Science, Science and Engineering of Materials Graduate Program, and Department of Mechanical and Aerospace Engineering.

MCKELVY, M. J., SHARMA, R., CHIZMESHYA, A. V. G., CARPENTER, R. & STREIB, K. 2001. Magnesium hydroxide dehydroxylation: In situ nanoscale observations of lamellar nucleation and growth. *Chemistry of materials,* 13**,** 921-926.

MONTES-HERNANDEZ, G., PEREZ-LOPEZ, R., RENARD, F., NIETO, J. & CHARLET, L. 2009. Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly-ash. *Journal of Hazardous Materials,* 161**,** 1347-1354.

NDUAGU, E. 2008. *Mineral carbonation: preparation of magnesium hydroxide [$Mg(OH)_2$] from serpentinite rock.* M.Sc. (Eng.) MSc. (Eng) Thesis, Åbo Akademi University, Finland.

NEW, M. & HULME, M. 2000. Representing uncertainty in climate change scenarios: a Monte-Carlo approach. *Integrated Assessment,* 1**,** 203-213.

O'CONNOR, W. K., DAHLIN, C. L., RUSH, G. E., GERDEMANN, S. J., PENNER, L. R. & NILSEN, D. N. 2005. Aqueous mineral carbonation.: Albany Research Center (ARC), Albany, NY.

O'CONNOR, W. K., DAHLIN, D. C., NILSEN, D. N., GERDEMANN, S. J., RUSH , G. E., PENNER, L. R., WALTERS, R. P. & Turneand, P.C. Continuing studies on direct aqueous mineral carbonation for CO_2 sequestration. Proc. 27th Int. Tech. Conf. on Coal

Util. & Fuel Syst., March 4-7 2002 Clearwater, FL, USA 819–830.

OECD/IEA 2012. CCS Retrofit - Analysis of the globally installed coal-fired power plant fleet. International Energy Agency, Paris.

OLIVIE, J. G. J., JANSSENS-MAENHOUT, G., PETERS, J. A. H. W. & WILSON, J. 2011. Long-term trend in global CO_2 emissions. 2011 report. The Hague: PBL/JRC: PBL Netherlands Environmental Assessment Agency and the Institute for Environment and Sustainability (IES) of the European Commission's Joint Research Centre (JRC).

PAN, S. Y., CHANG, E. & CHIANG, P. C. 2012. CO_2 Capture by accelerated carbonation of alkaline wastes: A review on its principles and applications. *Aerosol and Air Quality Research,* 12, 770–791.

PARK, A. H. A. & FAN, L. S. 2004. CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process. *Chemical Engineering Science,* 59**,** 5241-5247.

PEREZ-LOPEZ, R., MONTES-HERNANDEZ, G., NIETO, J., RENARD, F. & CHARLET, L. 2008. Carbonation of alkaline paper mill waste to reduce CO_2 greenhouse gas emissions into the atmosphere. *Applied Geochemistry,* 23**,** 2292-2300.

POWER, I. M., DIPPLE, G. M. & SOUTHAM, G. 2009. Bioleaching of ultramafic tailings by Acidithiobacillus spp. for CO_2 sequestration. *Environmental Science & Technology,* 44**,** 456-462.

POWER, I. M., WILSON, S. A., SMALL, D. P., DIPPLE, G. M., WAN, W. & SOUTHAM, G. 2011. Microbially Mediated Mineral Carbonation: Roles of Phototrophy and Heterotrophy. *Environmental Science & Technology,* 45**,** 9061-9068.

PRAETORIUS, B. & SCHUMACHER, K. 2009. Greenhouse gas mitigation in a carbon constrained world: The role of carbon capture and storage. *Energy Policy,* 37**,** 5081-5093.

PRIGIOBBE, V., POLETTINI, A. & BACIOCCHI, R. 2009. Gas-solid carbonation kinetics of air pollution control residues for CO_2 storage. *Chemical engineering journal,* 148**,** 270-278.

PRONOST, J., BEAUDOIN, G., TREMBLAY, J., LARACHI, F., DUCHESNE, J., H BERT, R. & CONSTANTIN, M. 2011. Carbon sequestration kinetic and storage capacity of ultramafic mining waste. *Environmental Science & Technology,* 45**,** 9413–9420.

RAO, A. B. & RUBIN, E. S. 2002. A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environmental Science & Technology,* 36**,** 4467-4475.

REDDY, K. J., WEBER, H., BHATTACHARYYA, P., MORRIS, A., TAYLOR, D., CHRISTENSEN, M., FOULKE, T. & FAHLSING, P. 2010. Instantaneous capture and mineralization of flue gas carbon dioxide: Pilot scale study. *Nature Precedings* Available at <http://dx.doi.org/10.1038/npre.2010.5404.1>.

REILLY, J., STONE, P. H., FOREST, C. E., WEBSTER, M. D., JACOBY, H. D. & PRINN, R. G. 2001. Uncertainty and climate change assessments. *Science(Washington),* 293**,** 430-3.

RICKELS, W., KLEPPER, G., DOVERN, J., BETZ, G., BRACHATZEK, N., CACEAN, S., GÜSSOW, K., J., H., HILLER, S., HOOSE, C., LEISNER, T., OSCHLIES, A., PLATT, U., PROELß, A., RENN, O., SCHÄFER, S. & M., Z. 2011. Large-scale intentional interventions into the climate system? Assessing the climate engineering debate. Scoping report conducted on behalf of the German Federal Ministry of Education and Research (BMBF). Kiel Earth Institute, Kiel.

ROINE, A. 2002. Outokumpu HSC Chemistry for Windows Version 5.11. *Outokumpu Research Oy, Pori, Finland.*

ROMÃO, I., ERIKSSON, M., NDUAGU, E., FAGERLUND, J., GANDO-FERREIRA, L. & ZEVENHOVEN, R. 2012a Carbon dioxide storage by mineralisation applied to a lime kiln. 25th International Conference on Efficieny, Costs, Optimisation, Simulation and Environmental Impact of Energy Systems (ECOS 2012). 26-29 June, 2012 Perugia, Italy., paper 226.

ROMÃO, I., GANDO-FERREIRA, L., MORAIS, I., SILVA, M. D., FAGERLUND, J. & ZEVENHOVEN, R. 2011. CO_2 sequestration with Portuguese serpentinite and metaperidotite. *11th International Conference on Enegy for a Clean Environment.* Lisbon, Portugal.

ROMÃO, I., NDUAGU, E., FAGERLUND, J., GANDO-FERREIRA, L. M. & ZEVENHOVEN, R. 2012b. CO_2 Fixation Using Magnesium Silicate Minerals. Part 2: Process Energy Efficiency and Integration with iron-and steelmaking. *Energy – the Int. J. (special edition ECOS2010),* 41 203-211

RUBIN, E., CHEN, C. & RAO, A. 2007. Cost and performance of fossil fuel power plants with CO2 capture and storage. *Energy Policy,* 35**,** 4444-4454.

RUSH, G. E., O'CONNOR, W. K., DAHLIN, D. C., PENNER, L. R. & GERDEMANN, S. J. 2004 Laboratory tests of mafic, ultra-mafic, and sedimentary rock types for in-situ applications for carbon dioxide sequestration. Proc. 29th International Technical Conference on Coal Utilization and Fuel Systems, 2004 Coal Technology Association, Clearwater, FL., USA., Medium: ED.

SANNA, A., DRI, M. & MAROTO-VALER, M. 2012a. Carbon dioxide capture and storage by pH swing aqueous mineralisation using a mixture of ammonium salts and antigorite source. *Fuel,* In press.

SANNA, A., HALL, M. & MAROTO-VALER, M. 2012b. Post-processing pathways in carbon capture and storage by mineralisation towards the introduction of carbon neutral materials. *Energy Environ. Sci.*

SEIFRITZ, W. 1990. CO_2 disposal by means of silicates. *Nature,* 345, 486.

SIPILÄ, J., TEIR, S. & ZEVENHOVEN, R. 2008. Carbon dioxide sequestration by mineral carbonation Literature review update 2005–2007. Available at http://users.abo.fi/rzevenho/MineralCarbonationLiteratureReview05-07.pdf: Åbo Akademi University, Turku, Finland

STEPHENS, J. C. & KEITH, D. W. 2008. Assessing geochemical carbon management. *Climatic Change,* 90**,** 217-242.

SZARGUT, J., MORRIS, D. R. & STEWARD, F. R. 1988. Energy analysis of thermal, chemical, and metallurgical processes. New York: Hemisphere Publishing Co.

TEIR, S., REVITZER, H., ELONEVA, S., FOGELHOLM, C. & ZEVENHOVEN, R. 2007. Dissolution of natural serpentinite in mineral and organic acids. *International Journal of Mineral Processing,* 83**,** 36-46.

THE ROYAL SOCIETY 2009. *Geoengineering the climate: science, governance and uncertainty,* London, UK, The Royal Society.

TOL, R. S. J. 2003. Is the uncertainty about climate change too large for expected cost-benefit analysis? *Climatic Change,* 56**,** 265-289.

TORRÓNTEGUI, M. D. 2010. *Assessing the Mineral Carbonation Science and Technology.* MSc. Thesis, Swiss Federal Institute of Technology, Zürich, Switzerland.

ULIASZ-BOCHEŃCZYK, A., MOKRZYCKI, E., PIOTROWSKI, Z. & POMYKAŁA, R. 2009. Estimation of CO_2 sequestration potential via mineral carbonation in fly ash from lignite combustion in Poland. *Energy Procedia,* 1**,** 4873-4879.

ÜRGE-VORSATZ, D. & METZ, B. 2009. Energy efficiency: how far does it get us in controlling climate change? *Energy Efficiency,* 2**,** 87-94.

VENHUIS, M. A. & REARDON, E. J. 2001. Vacuum Method for Carbonation of Cementitious Wasteforms. *Environmental Science & Technology,* 35**,** 4120-4125.

VERDUYN, M., BOERRINGTER, H., OUDWATER, R. & VAN MOSSEL, G. 2009 A novel process concept for CO_2 mineralization; Technical opportunities and challenges. 5th Trondheim Conference on CO_2 Capture, Transport and Storage, 2009 Trondheim.

VOORMEIJ, D. A. & SIMANDL, G. J. 2004. Geological, ocean, and mineral CO_2 sequestration options: A technical review. *Geoscience Canada,* 31**,** 11-22.

WALTON, J. C., BIN-SHAFIQUE, S., SMITH, R. W., GUTIERREZ, N. & TARQUIN, A. 1997. Role of Carbonation in Transient Leaching of Cementitious Wasteforms. *Environmental Science & Technology,* 31**,** 2345-2349.

WANG, X. & MAROTA-VALER, M. 2011. *Improvements in or relating to capture of carbon dioxide.* Great Britain patent application GB2010/052118.

WANG, X. & MAROTO-VALER, M. 2011a. Integration of CO2 capture and storage based on pH-swing mineral carbonation using recyclable ammonium salts. *Energy Procedia,* 4**,** 4930-4936.

WANG, X. & MAROTO-VALER, M. M. 2011b. Dissolution of serpentine using recyclable ammonium salts for CO2 mineral carbonation. *Fuel,* 90**,** 1229-1237.

WATKINS, G., MAKELA, M. & DAHL, O. 2010. Innovative use potential of industrial residues from the steel, paper and pulp industries–a preliminary study. *Progress in Industrial Ecology, An International Journal,* 7**,** 185-204.

WERNER, M., VERDUYN, M., VAN MOSSEL, G. & MAZZOTTI, M. 2011. Direct flue gas CO_2 mineralization using activated serpentine: Exploring the reaction kinetics by experiments and population balance modelling. *Energy Procedia,* 4**,** 2043-2049.

WILSON, S. A., DIPPLE, G. M., POWER, I. M., THOM, J. M., ANDERSON, R. G., RAUDSEPP, M., GABITES, J. E. & SOUTHAM, G. 2009. Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: Examples from the Clinton Creek and Cassiar chrysotile deposits, Canada. *Economic Geology,* 104**,** 95-112.

YEGULALP, T. M., LACKNER, K. S. & ZIOCK, H. J. 2001. A review of emerging technologies for sustainable use of coal for power generation. *International Journal of Surface Mining, Reclamation and Environment,* 15**,** 52-68.

ZAHRA, A. 2009. *Carbon dioxide capture from flue gas: Development and evaluation of existing and novel process concepts.* PhD Thesis PhD Thesis, TU Delft, Delft University of Technology.

ZEMAN, F. S. & KEITH, D. W. 2008. Carbon neutral hydrocarbons. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 366**,** 3901-3918.

ZEVENHOVEN, R., ELONEVA, S. & TEIR, S. 2006 A study on MgO-based mineral carbonation kinetics using pressurised thermogravimetric analysis. 8th International Conference on Greenhouse Gas Control Technologies, June 2006 Trondheim, Norway. 19-22.

ZEVENHOVEN, R. & FAGERLUND, J. 2010a. Fixation of Carbon Dioxide into Inorganic Carbonates: The Natural and Artificial "Weathering of Silicates". *In:* M, A. (ed.). Germany.: Wiley VCH Verlag.

ZEVENHOVEN, R. & FAGERLUND, J. 2010b. Mineralization of CO_2. *In:* MAROTA-VALER, M. (ed.) *Developments and innovation in CCS technology.* Cambridge: Woodhead Publishing Ltd.

ZEVENHOVEN, R., FAGERLUND, J., BJÖRKLÖF, T., MÄKELÄ, M. & EKLUND, O. 2012. Carbon dioxide mineralisation and integration with flue gas desulphurisation applied to a modern coal-fired power plant. 25th International Conference on Efficieny, Costs, Optimisation, Simulation and Environmental Impact of Energy Systems (ECOS 2012), 26-29 June 2012 2012 Perugia, Italy. paper 179.

ZEVENHOVEN, R., FAGERLUND, J. & SONGOK, J. K. 2011. CO_2 mineral sequestration: developments toward large scale application. *Greenhouse Gases: Science and Technology,* 1**,** 48-57.

ZEVENHOVEN, R., KOHLMANN, J. & MUKHERJEE, A. 2002 Direct dry mineral carbonation for CO_2 emissions reduction in Finland. 27th International Technical Conference on Coal Utilization & Fuel Systems., March 4-7, 2002 Clearwater, Florida, USA., 743-754.

ZEVENHOVEN, R., SIPILÄ, J. & TEIR, S. 2008a Motivations for carbonating magnesium silicates using a gas-solid process route. *In:* BACIOCCHI RENATO, C. G., POLETTINI ALESSANDRA, POMI RAFFAELLA, ed. 2nd International Conference on Accelerated Carbonation for Environmental and Materials Engineering (ACEME08), 1-3 October 2008 Rome, Italy. University of Rome "La Sapienza", 45-54.

ZEVENHOVEN, R. & TEIR, S. 2004 Long term storage of CO_2 as magnesium carbonate in Finland. 3rd Annual Conference on Carbon Capture and Sequestration, May 3-6 2004 Alexandria, Virginia 3-6.

ZEVENHOVEN, R., TEIR, S. & ELONEVA, S. 2008b. Heat optimisation of a staged gas-solid mineral carbonation process for long-term CO_2 storage. *Energy,* 33**,** 362-370.

ZHANG, Q., SUGIYAMA, K. & SAITO, F. 1997. Enhancement of acid extraction of magnesium and silicon from serpentine by mechanochemical treatment. *Hydrometallurgy,* 45**,** 323-331.

ZHAO, L., SANG, L., CHEN, J., JI, J. & TENG, H. H. 2009. Aqueous carbonation of natural brucite: Relevance to CO_2 sequestration. *Environmental Science & Technology,* 44**,** 406-411.

ZOBACK, M. D. & GORELICK, S. M. 2012. Earthquake triggering and large-scale geologic storage of carbon dioxide. *Proceedings of the National Academy of Sciences,* 109**,** 10164-10168.

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