Carbonation of $Mg(OH)_2$ in a pressurised fluidised bed for CO_2 sequestration

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Preface

The work presented in this thesis contains an attempt at tackling a small portion of a very large problem that is known as global climate change. It has been conducted at the Thermal and Flow Engineering Laboratory at Åbo Akademi University (ÅA). The work was mainly funded by the Academy of Finland as a part of the CARETECH project during the years 2008–2011. In addition, generous funding has been provided by KH Renlund foundation, the Finnish Foundation for Technology Promotion (TES), Walter Ahlströms foundation, Harry Elving's legacy and a scholarship by the Rector at Åbo Akademi University. Furthermore, Aalto University and Prof. Carl-Johan Fogelhom is also kindly acknowledged for financial support at a final stage of the making of this thesis.

Still, there is one person that I would like to thank especially. He is the "man behind the idea" and the key person responsible for initiating this work: Prof. Ron Zevenhoven. Ron has been an excellent supervisor throughout the whole thesis work (2007–2012) and it has been a pleasure to work with him and learn from him.

Naturally, there are a number of other persons that I would like to acknowledge and thank for their help during my time working on this thesis. Affi, our lab technician, has played an important role in the making of this thesis, especially in the early phase during the construction of the fluidised bed setup. He basically taught me (together with some theoretical studies of my own) to become an electrical engineer. Pekka, from the workshop at Axelia, is another person who deserves a big thank you for all his help (and patience) during the construction phase. I would also like to acknowledge Jimmy for some nice work with modifying the cyclone.

My fellow co-authors, Berndt and Stig from the inorganic chemistry department have kindly provided me with insights and working equipment at their lab. For this I am highly grateful. I would also like to thank my other co-authors and all the people at our lab, especially the "carbonation team". The working environment (with coffee breaks at 10 am and 2 pm) and support from my colleagues and friends have been more than important. A special thank you goes to Martin, H-P and Calle, who have all provided me with considerable help in a multitude of things. I also want to thank Inês and XP, who are in the same boat as I am, so to speak, for ideas and great discussions not only related to work. Thanks also to Thomas, for support at the end and great tips regarding Singapore.

In early 2011 I had the possibility to visit Singapore as part of an ongoing collaboration between ÅA and ICES-A*Star. This was indeed a valuable experience and although not everything went according to the plans, the trip was successful in many ways. Again, I would like to acknowledge Ron, together with my colleague and supervisor in Singapore, Dr. James Highfield, who made this trip possible. Also a special thanks goes to Kenneth and April in Singapore, who were more than helpful showing me around in the labs. On top of this, I also want to thank my wife's

supervisors Dr. Leena Hupa and Prof. Mikko Hupa at the Inorganic Chemistry Lab of ÅA for making it possible for her to join.

Due to the very close connection between this work and geology, parts of my studies have been performed at the Geology and Mineralogy department at ÅA. I would like to acknowledge Em. Prof. Carl Ehlers, Prof. Olav "Joffi" Eklund and Fredrik Strandman for their kind support and understanding of this special arrangement.

In addition to the very concrete help provided by many persons during my thesis work, a number of persons have contributed in less tangible ways, but nonetheless very significantly. My family have all believed in me and helped to keep my priorities straight. No matter how important your work is, there should always be time for family and friends.

Finally I would like to say that, although I have had the possibility to meet some wonderful people during my time as a doctoral student, the most important person in my life has been with me throughout the whole project, my wife. She has been the reserve energy when my own has depleted, she has given me confidence when my own has failed me and most importantly she has been there for me no matter what. Thank you Susanne, now I feel it is my turn to support you.

Svensk sammanfattning

Under de senaste 150 åren har atmosfärens koldioxidhalt ökat oroväckande snabbt och i god överensstämmelse med den industriella utvecklingen. I takt med den ekonomiska tillväxten har CO_2-utsläppen till atmosfären ständigt ökat, och utan kraftiga åtgärder kommer de att fortsätta att öka i allt snabbare takt. Konsekvenserna av en påtagligt förhöjd atmosfärisk CO_2-halt är fortfarande osäkra (men eventuellt katastrofala) och fenomenet går under namnet global uppvärmning eller klimatförändring.

De naturliga mekanismer (upptag av hav, fotosyntes, vittring) som strävar efter att minska den ökande atmosfäriska CO_2-koncentrationen är inte tillräckligt effektiva för gå jämsides med människans ”framsteg”. Däremot kunde det vara möjligt att snabba upp dessa naturliga mekanismer och i denna avhandling behandlas en dylik process, nämligen naturlig vittring av mineraler.

Naturlig vittring är en process som förenklat innefattar nedbrytningen av sten/berg (även känt som erosion) och de därpå följande reaktionerna med CO_2-mättat regnvatten. Som en följd av det svagt sura regnvattnet och fint fraktionerade stenmaterialet kan element som kalcium och magnesium frigöras från det fasta mineralgittret för att reagera vidare med karbonatjonerna i en vattenlösning. Slutresultatet är en utfällning av fasta mineraler som kalcium- och magnesiumkarbonat och den huvudsakliga drivkraften bakom denna process (och de facto alla andra processer) är entropi, som gynnas av bildningen av karbonater. I själva verket är reaktionen mellan en magnesium- eller kalciumrik bergart inte bara termodynamiskt fördelaktig, utan även exoterm (friger värme) under atmosfäriska förhållanden. Det återstående problemet är att snabba upp denna process, som i naturen är ytterst långsam, på ett ekonomiskt och miljömässigt fördelaktigt sätt.

Hittills har ett antal metoder för att påskynda naturlig vittring, eller med andra ord öka CO_2-upptagninsförmågan av olika mineraler föreslagits. De mera etablerade uttrycken (lånade från engelskan) talar om mineralkarbonatisering och CO_2-mineralisering. En kort litteraturöversikt över nyligen publicerade artiklar inom detta område, som är en del av ett antal olika koldioxidavskiljnings- och lagringsmetoder (eng. carbon dioxide capture and storage, CCS), ges i denna avhandling. Ett klart ökat intresse för mineralkarbonatisering kan påvisas redan enbart utifrån antalet aktuella publikationer inom området.

Till skillnad från många andra CO_2-mineraliseringsalternativ är det alternativ som behandlas i denna avhandling i hög grad baserat på möjligheten att utnyttja den värme som frigörs vid karbonatiseringen av magnesium. Med detta som utgångspunkt har processen i fråga delats in i tre steg, varav de två första är energikrävande. Det tredje steget i sin tur är ”energinegativt” och i teorin källan till den energi som krävs i de två första stegen. Tyvärr är dock energibehovet i de två första stegen, bestående av Mg-extraktion och $Mg(OH)_2$-produktion, (tillsvidare) mycket högre än vad som kan tillgodoses av det efterföljande $Mg(OH)_2$-karbonatiseringssteget. Det återstår dock fortfarande möjligheter att minska processens energibehov betydligt och även om en energineutral karbonatiseringsprocess kan vara svår att uppnå, kan energibehovet fortfarande göras industriellt acceptabelt (och jämförbart eller bättre än för övriga CCS alternativ).

Det huvudsakliga syftet med denna avhandling har varit att utveckla processens tredje steg, $Mg(OH)_2$-karbonatiseringen, som utförs med hjälp av en trycksatt fluidiserad bädd. Utan trycksättning skulle karbonatiseringen begränsas till en viss temperatur som avgörs av stabiliteten hos det bildade karbonatet. En ökning i CO_2-trycket (typiskt runt 20 bar) möjliggör således en ökning i temperaturen (kring 500 °C) som i sin tur leder till snabbare kemiska reaktioner.

Ökningen av reaktionshastigheterna som funktion av temperaturen är betydande, men uppenbarligen dehydroxyleras $Mg(OH)_2$ i högre utsträckning än $MgCO_3$ bildas, resulterande i ofullständig karbonatisering. Även om $MgCO_3$ är termodynamiskt mer stabilt än MgO under de flesta experimentella förhållanden som undersökts i denna avhandling, har bildningen av MgO inte kunnat undvikas. Dessutom har vi kunnat påvisa uppkomsten av en relativt ovanlig kristallin karbonatform: $MgO{\cdot}2MgCO_3$.

De flesta av karbonatiseringsexperimenten har utförts med kommersiellt tillgänglig $Mg(OH)_2$ (Dead Sea Periclase Ltd., DSP), som är mycket mindre reaktivt än hydroxid som producerats från serpentinit (en vanligt förekommande Mg-silikatbergartstyp) i enlighet med de två första stegen av CO_2-mineraliseringsprocessen som tas upp i denna avhandling. Den låga reaktiviteten hos DSP-$Mg(OH)_2$ är inte bara en följd av dess relativt låga ytareal, men även av dess låga porositet, vilket av allt att döma förhindrar CO_2 från att tränga in i partikeln, men inte H_2O (som är mindre än CO_2) från att lämna den. Vattnets betydelse för karbonatiseringsreaktioner har bestyrkts och reaktiviteten mellan MgO och CO_2 är mycket låg om inte H_2O är inblandat. Det här är också en av orsakerna varför det är viktigt att kontrollera dehydroxyleringen av $Mg(OH)_2$.

I samband med modelleringen av reaktionerna som pågår i den fluidiserade bädden har det visat sig att det krävs en noggrann avvägning mellan de olika faktorer som påverkar $Mg(OH)_2$-reaktiviteten för att uppnå fullständig karbonatisering. Hittills har de mest lovande resultaten gett upphov till 65% karbonatisering under 15 minuter (540 °C, 50 bar CO_2) och kanske ännu mer lovande, 50% i fyra minuter vid endast 20 bar CO_2. Tyvärr kan inte resultatet direkt översättas till 100% karbonatisering i åtta minuter, för det förefaller som om karbonatiseringen hindras mera av diffusion än vad dehydroxyleringen gör och en jämvikt där ingen reaktivitet längre kan observeras uppnås innan fullständig karbonatisering har hunnit äga rum.

Sammanfattningsvis kan det nämnas att reaktiviteten för $Mg(OH)_2$ (dock inte DSP-$Mg(OH)_2$) är bra, men de exakta förhållandena för fullständig karbonatisering är ännu inte fastställda. Dessutom kan det konstateras att även om mineralkarbonatiseringsprocessen som utvecklats vid Åbo Akademi har betydande industriella tillämpningsmöjligheter, krävs det mer arbete både för att förbättra effektiviteten och minska energibehovet av magnesiumutvinningssteget.

Abstract

In the past 150 years, atmospheric carbon dioxide levels have increased alarmingly, correlating with the increasing anthropogenic (*i.e.* human) industrial activities. Elevated CO_2 levels lead to global warming, or more generally global climate change, with potentially devastating effects. The natural mechanisms (ocean uptake, photosynthesis, weathering) that reduce increasing atmospheric CO_2 levels are not able to keep up with human "progress", which results in excess atmospheric CO_2. Thus, it has been proposed that reducing CO_2 emissions could be achieved by mimicking natural processes, and in this thesis the process being mimicked is called natural weathering of minerals.

Basically, natural weathering is a process that involves breaking up of rock (also known as erosion) into smaller fractions that more easily react with (mildly acidic) CO_2 saturated rain water. As a result, elements such as calcium and magnesium can react with the dissolved CO_2 to form solid carbonates. The principal driving force behind this process (and in fact all other processes) is entropy, which increases in the direction of carbonate formation. In fact, forming carbonates from Mg or Ca-silicate rock is not only thermodynamically favourable, but also exothermic at atmospheric conditions. However, in nature the process is very slow, operating on geological time scales.

To date, a number of methods to accelerate natural weathering or in other words increase the CO_2 uptake rate of various minerals have been suggested; commonly this is known as mineral carbonation or CO_2 mineralisation. A brief literature review of recently published articles in this field is presented, showing that the interest in mineral carbonation is increasing. However, it should be noted that mineral carbonation is only one option in a larger portfolio of various carbon dioxide capture and storage (CCS) alternatives.

Unlike many other options, the CO_2 mineralisation option considered in this thesis is largely founded on the possibility to utilise the exothermic nature of magnesium carbonation and based on this notion, it has been divided into three steps. The first two steps are energy demanding, while the third step is energy "negative", and in theory, the source of the energy required in the first two steps. Unfortunately, however, the energy demanded by the first two steps, Mg extraction and $Mg(OH)_2$ production, is (currently) much higher than what could be generated by the subsequent $Mg(OH)_2$ carbonation step. Nevertheless, opportunities to reduce the energy intensity of the process in question are still being investigated, and while an energy-neutral carbonation process might be difficult to achieve, energy requirements can still be rendered industrially acceptable (and comparable to or even better than for other CCS methods).

The main focus of this thesis lies with the third step, $Mg(OH)_2$ carbonation, which is performed using a pressurised fluidised bed (PFB). The elevated CO_2 pressure conditions (typically ~20 bar) allow for the carbonation reaction to take place at higher

temperatures (typically ~500 °C) than otherwise due to thermodynamic constraints on carbonate stability. The increase in reaction rate as a function of temperature follows the Arrhenius equation of exponential increase, but unfortunately, $Mg(OH)_2$ dehydroxylation is also affected and seemingly to a higher extent than $MgCO_3$ formation. Although $MgCO_3$ is thermodynamically more stable than MgO at most of the conditions investigated for this thesis, the presence of MgO in the end product has not been avoided. In other words, not all the decomposing hydroxide is able to form carbonate and the formed MgO is unreactive towards CO_2 in the absence of steam. In addition, the formation of a comparatively rare crystalline carbonate form, referred to as oxymagnesite, has been detected over a range of dry or mildly dry carbonation conditions.

Most of the PFB carbonation experiments have been performed (for reasons of availability) using commercially available $Mg(OH)_2$ (Dead Sea Periclase Ltd., *i.e.* DSP), which is much less reactive than the hydroxide produced from serpentinite (a common Mg-silicate rock) according to the first two steps of the process addressed in this thesis. At similar conditions (< 15 min, 20 bar, 500 °C), the carbonation of serpentinite derived $Mg(OH)_2$ exceeds that of DSP-$Mg(OH)_2$ by 100%. The low reactivity of DSP-$Mg(OH)_2$ is not only a result of low surface area (~5.5 m^2/g), but also of low porosity (~0.024 cm^3/g), which apparently prevents CO_2 from entering the particle, but not H_2O (which is smaller than CO_2) from exiting. The importance of water for the carbonation reaction has been demonstrated, and the reactivity of MgO in the absence of H_2O is negligible even at comparatively high CO_2 pressures (20 bar). Thus it is important that excessive dehydroxylation, *i.e.* dehydroxylation without sequential carbonate formation, is prevented.

Preliminary kinetic modelling of the carbonation step, assuming an intermediate hydrated MgO-species is produced, showed that a delicate balance between the various factors (temperature, partial pressures, fluidisation velocity and particle properties) affecting $Mg(OH)_2$ carbonation in a fluidised bed is required to achieve complete carbonation. To date the best results show a 65% carbonation in less than 15 minutes, at relatively severe conditions (540 °C, 50 bar CO_2), but more impressive is 50% carbonation in four minutes at 20 bar CO_2. Unfortunately, carbonation seems to become hindered by diffusion, more so than dehydroxylation, which explains the lack of a clear correlation with reaction time, so that a 50% conversion in four minutes does not translate to 100% in eight minutes.

In summary, the reactivity of serpentinite-derived $Mg(OH)_2$ is certainly much better than that of the DSP material, but the exact conditions of complete carbonation within industrially feasible time scales have not yet been established. Furthermore, although the mineral carbonation process developed at Åbo Akademi University is theoretically sound, more work is required to improve the Mg extraction efficiency and reduce the energy requirements thereof as briefly addressed in this thesis.

Contribution of the author and list of publications

This thesis is based on a number of publications, which can be found at the end of this work, but the introduction of this thesis outlines a more general perspective of mineral carbonation than presented within the following list of included publications.

The author of this thesis is the main contributor in five of the below listed publications and the second author of a book chapter given here as Paper III. It should be noted that the book chapter is for a large part based on a literature review (2005–2007) by Sipilä *et al.* (see "List of related contributions"). Paper VI represents the second part of a two-part paper and is included here for the sake of clarity and continuity. Compared to the other papers listed below, the contribution of J. Fagerlund was minor for Paper VI. All experimental and most of the analytical work (comprising mainly of sample composition determination) related to the here presented pressurised fluidised bed setup, not to mention its construction, has been planned and performed by the author of this thesis.

The list has been arranged in chronological order and all references to these will hereafter be made in accordance with their respective Roman numerical.

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

II. **Gasometric determination of CO_2 released from carbonate materials**
J. Fagerlund, S.-G. Huldén, B. Södergård, R. Zevenhoven
J. Chem. Educ., 2010, 87(12), pp. 1372–1376
DOI: 10.1021/ed1001653

III. **Mineralisation of CO_2**
R. Zevenhoven, J. Fagerlund
Chapter 16 in: "Developments and innovation in CCS technology" M. Maroto-Valer (Ed.), Woodhead Publishing Ltd., Cambridge (UK), 2010, pp. 433–462

IV. **An experimental study of $Mg(OH)_2$ carbonation**
J. Fagerlund, R. Zevenhoven
Int. J. Greenhouse Gas Control, 2011, 5(6), pp. 1406–1412
DOI: 10.1016/j.ijggc.2011.05.039
Presented at the 5th Trondheim Conference on CO_2 Capture, Transport and Storage, 2009, June 16–17, Trondheim (Norway)

V. **CO_2 fixation using magnesium silicate minerals. Part 1: Process description and performance**
J. Fagerlund, E. Nduagu, I. Romão, R. Zevenhoven
Energy (special edition: ECOS'2010), accepted / in press,
DOI: 10.1016/j.energy.2011.08.032
Presented at ECOS´2010, 2010, June 14–17, Lausanne (Switzerland)

VI. **CO_2 fixation using magnesium silicate minerals. Part 2: Energy efficiency and integration with iron- and steelmaking**
I. Romão, E. Nduagu, J. Fagerlund, L. Gando-Ferreira, R. Zevenhoven
Energy (special edition: ECOS'2010), accepted / in press,
DOI: 10.1016/j.energy.2011.08.026
Presented at ECOS´2010, 2010, June 14–17, Lausanne (Switzerland)

VII. **Kinetic studies on wet and dry gas-solid carbonation of MgO and $Mg(OH)_2$ for CO_2 sequestration**
J. Fagerlund, J. Highfield, R. Zevenhoven
ChemSusChem, submitted (Dec. 2011)

List of related contributions

The following list includes publications in the field of mineral carbonation that are related to the work presented here. The order of the list is arbitrary.

- **Carbon dioxide sequestration by mineral carbonation: Literature review update 2005–2007**
  J. Sipilä, S. Teir, R. Zevenhoven
  Åbo Akademi University, Thermal and Flow Engineering Report 2008-1
  Turku (Finland), pp. 1–47 (+ appendix)
  ISBN 978-952-12-2036-4
  Available: http://users.abo.fi/rzevenho/MineralCarbonationLiteratureReview05-07.pdf

- **Ammonium salts as recyclable activators and carbonators of serpentine and model compounds via mechanochemistry**
  J. Highfield, H. Q. Lim, J. Fagerlund, R. Zevenhoven
  RSC Advances, submitted (Dec. 2011)

- **Contribution of iron to the energetics of CO_2 sequestration in Mg-silicates-based rock**
  E. Nduagu J. Fagerlund, R. Zevenhoven
  Energy Convers. Manage., accepted / in press,
  DOI: 10.1016/j.enconman.2011.10.023

- **CO_2 mineral sequestration - developments toward large-scale application**
  R. Zevenhoven, J. Fagerlund, J. Songok
  Greenhouse Gases: Science and Technology, 2011, 1(1), pp. 48–57
  DOI: 10.1002/ghg3.007

- **Recent developments in the carbonation of serpentinite derived $Mg(OH)_2$ using a pressurized fluidized bed**
  J. Fagerlund, E. Nduagu, R. Zevenhoven
  Energy Procedia, 2011, 4, pp. 4993–5000
  DOI: 10.1016/j.egypro.2011.02.470
  Presented at GHGT-9, 2008, November 16–20, Washington DC (USA)

- **Fixation of CO_2 into inorganic carbonates: The natural and artificial weathering of silicates**
  R. Zevenhoven, J. Fagerlund
  Chapter 14 in: "Carbon dioxide utilization", M. Aresta (Ed.) Wiley-VCH, Weinheim (Germany), 2010, pp. 353–379
  DOI: 10.1002/9783527629916

- **Production of reactive magnesium from magnesium silicate for the purpose of CO_2 mineralization. Part 1. Application to Finnish serpentinite**
  E. Nduagu, T. Björklöf, J. Fagerlund, J. Wärnå, H. Geerlings, R. Zevenhoven
  Min. Eng., accepted / in press 2012
  DOI: 10.1016/j.mineng.2011.12.004

- **Production of reactive magnesium from magnesium silicate for the purpose of CO_2 mineralization. Part 2. Mg extraction modeling and application to different Mg silicate rocks**
  E. Nduagu, T. Björklöf, J. Fagerlund, E. Mäkelä, J. Salonen, H. Geerlings, R. Zevenhoven
  Min. Eng., accepted / in press 2012
  DOI: 10.1016/j.mineng.2011.12.002

- **Carbonation of calcium-containing mineral and industrial by-products**
  R. Zevenhoven, A. Wiklund, J. Fagerlund, S. Eloneva, B. in 't Veen, H. Geerlings, G. van Mossel, H. Boerrigter
  Front. Chem. Eng. China, 2010, 4(2), pp. 110–119
  DOI: 10.1007/s11705-009-0238-x
  Presented at ICCDU X, 10th International Conference on Carbon Dioxide Utilization, May 17–21, 2009, Tianjin (China)

- **Carbonation of magnesium silicate mineral using a pressurised gas/solid process**
  J. Fagerlund, S. Teir, E. Nduagu, R. Zevenhoven
  Energy Procedia, 2009, 1(1), pp. 4907–4914
  DOI: 10.1016/j.egypro.2009.02.321
  Presented at GHGT-10, 2010, September 19–23, Amsterdam (The Netherlands)

In addition to the lists presented here, a number of non-refereed publications and contributions have been made by or in collaboration with the author of this thesis in the field of CO_2 sequestration, including conference proceedings, reports and other presentations.

List of abbreviations and symbols

ARC	Albany Research Center
CCGS, CGS	Carbon dioxide capture and geological storage
CCM	Carbon dioxide capture and mineralisation
CCS	Carbon dioxide capture and storage
CFC	Chlorofluorocarbon (also known as Freon)
CHP	Combined heat and power
CSM	Carbon dioxide storage by mineralisation
DSP	Dead Sea Periclase Ltd.
EOR	Enhanced oil recovery
FA	Fly ash
FB	Fluidised bed
GHG	Greenhouse gas
GHGT	Greenhouse Gas Control Technologies (conference)
IEA-GHG	International Energy Agency - Greenhouse Gas R&D Programme
IJGGC	International Journal of Greenhouse Gas Control
IPCC	Intergovernmental Panel on Climate Change
IR	Infrared
MWe	Megawatt electrical
MVR	Mechanical vapour recompression
NETL	National Energy Technology Laboratory
PFB	Pressurised fluidised bed
PTGA	Pressurised thermogravimetric analyser
SA	Surface area
SEM	Scanning electron microscope
XRD	X-ray diffraction
ÅA	Åbo Akademi University
ÅA CSM	Three step mineral carbonation process developed at Åbo Akademi University

AS	Ammonium sulphate
$CaCO_3$	Calcium carbonate (calcite, aragonite, limestone)
CaO	Calcium oxide (quicklime)
FeO	Iron oxide (mineral name: wüstite)
FeOOH	Iron hydroxide (mineral name: goethite)
$Mg(OH)_2$	Magnesium hydroxide (mineral name: brucite)
$(Mg,Fe)_2SiO_4$	Olivine (Mg end-member: Forsterite)
$Mg_3Si_2O_5(OH)_4$	Serpentine
$MgCO_3$	Magnesium carbonate (mineral name: magnesite)
MgO	Magnesium oxide (mineral name: periclase)
$MgO \cdot 2MgCO_3$	Oxymagnesite
$MgO \cdot H_2O$	Hydrated magnesium oxide
$(NH_4)_2SO_4$	Ammonium sulphate

c_i	Species concentration (kg/kg)
E_{heat}	Process heat requirement (kWh, MJ)
E_{power}	Process electricity requirement (kWh, MJ)
k_i	Rate coefficient (1/s)
K_p	Equilibrium constant
n_i	Exponential coefficient (-)
p_{eq}	Thermodynamic equilibrium pressure (bar)
p_k	Pressure coefficient (-)
R_{CO2}	Ratio of source material to sequestered CO_2 (kg/kg)
T	Temperature (°C, K)
T_{eq}	Thermodynamic equilibrium temperature (°C, K)
ε_{heat}	CO_2 emitted by heat generation process (kg CO_2/kWh)
ε_{power}	CO_2 emitted to produce power (kg CO_2/kWh)

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1. Background - Increasing atmospheric carbon dioxide levels

The main motivator for this thesis can be found in the constantly increasing atmospheric carbon dioxide (CO_2) levels, which have increased from around 280 ppmv (parts per million, volumetric) before industrialisation (IPCC, 2007b) to the current level of 389 ppmv (Tans and Keeling, 2011). Carbon dioxide is a so called greenhouse gas (together with methane, nitrous oxide, CFC's and many more, including water vapour) and thus responsible for keeping our planet's surface warm. Without greenhouse gases (GHG's), the average temperature of the earth's surface would be significantly colder and consequently, an increase of GHG's in the atmosphere has been attributed to causing an increase in the global mean temperature (IPCC, 2007b). In fact, the impact of CO_2 emissions is much larger than the impact of other GHG's as displayed in Figure 1.

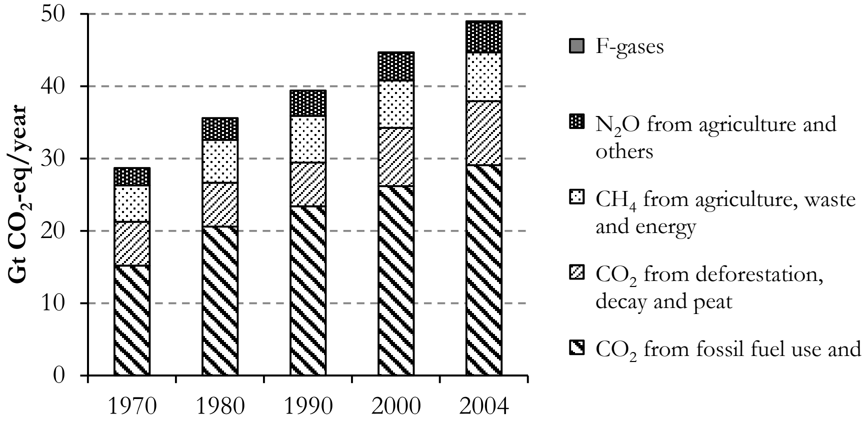

Figure 1. Annual levels of greenhouse gases represented as CO_2-equivalent emissions[1] (IPCC, 2007a, topic 2).

The principal mechanism behind the so called greenhouse effect is that the radiant energy from the sun can penetrate earth's atmosphere more easily than the long-wavelength infrared (IR) radiation that is emitted back from the earth's surface. In other words, earth's atmosphere works in a way similar to a window glass of a greenhouse, which allows for visible light and short-wave (< 4 μm) thermal radiation to enter, but prevents longer wave (> 4 μm) thermal radiation from exiting, causing the greenhouse to warm. This is a very simplistic description of the system in question, but an in-depth analysis of the mechanisms that govern earth's climate are outside the scope of this thesis. It is sufficient to say that our planet is a very complex dynamic system and many factors affect its climate and how it would change.

While an overwhelmingly large number of scientists are convinced that the perceived increase in global mean temperature is caused by human activities, a number

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[1] *"CO_2-equivalent emission is the amount of CO_2 emission that would cause the same time-integrated radiative forcing, over a given time horizon, as an emitted amount of a long-lived GHG or a mixture of GHGs" (IPCC, 2007a, topic 2)*

of sceptics still exist (Sudhakara Reddy and Assenza, 2009). This, however, does not change the fact that human activities have caused major detrimental changes to the environment (if not the climate) in the past and a consequence of the climate change research and discussion is an increased environmental awareness. In the author's opinion, this awareness, the "precautionary principle"[2] and the fact that legislators are paving the way for CO_2 emission taxation are more than sufficient reasons to motivate the carbon dioxide capture and storage (CCS) research considered in this thesis.

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[2] *"In order to protect the environment, the precautionary approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation." (UNCED, 1992)*

2. Introduction to carbon dioxide capture and storage

Carbon dioxide sequestration is a commonly used term when discussing climate change mitigation and according to the Oxford English Dictionary, to sequester means to set aside or to separate. Hence, carbon dioxide sequestration is another way of saying carbon dioxide capture and storage (CCS). The concept of CCS involves capturing (or separating) CO_2 from a flue gas (or some other CO_2 containing source) and storing it in a way that prevents it from entering the atmosphere. The principal ways of accomplishing this are carbon dioxide capture and underground storage (CCGS or CGS)[3], ocean storage and carbon dioxide storage by mineralisation (CSM). The option that has received and continues to receive the most attention is CCGS, while ocean storage is often cited as being too uncertain from an environmental perspective (Pires *et al.*, 2011) or that more research is needed before large-scale employment can be justifiable (Li *et al.*, In Press 2011). Similarly, it can be concluded that more research on various mineral carbonation options is still required. Based on Figure 2, however, mineral carbonation research has in fact been increasing notably during the past ten years.

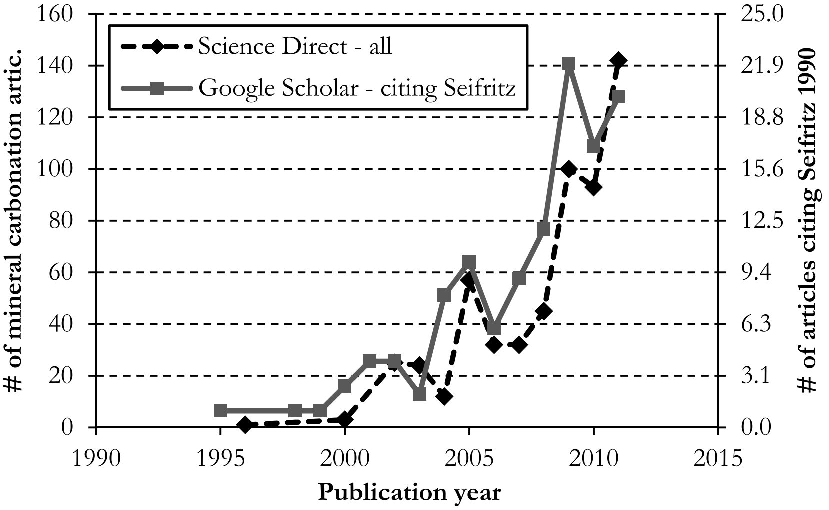

Figure 2. An indication of the number of articles published in the field of mineral carbonation since its initiation in 1990.

While the number of articles published in the field of mineral carbonation is comparatively small, it is still difficult to track down all of them, but based on the two lines in Figure 2 a clear trend can be seen. The lines represent the number of articles found using the Science Direct (SD) database and a more general search tool aimed at finding scientific work, called Google Scholar. Using SD with the keywords "carbon dioxide sequestration" and "mineral carbonation" resulted in 567 hits (6 October

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[3] *G standing for geological. Instead of CCGS or CGS, the recent EU-directive (EC, 2009) ignores other CCS alternatives and defines CCS to be carbon dioxide capture, transport and underground storage.*

2011), whereas, searching for material citing Seifritz (the person who in 1990 first mentioned mineral carbonation as a way to tackle increasing CO_2 levels) using Google Scholar resulted in 123 hits (6 October 2011). Arranging this data by year of publication reveals remarkably similar trends (although different scales), suggesting that mineral carbonation research is receiving more and more attention. However, compared to CO_2 sequestration in general (SD, using the keywords "carbon dioxide sequestration": 12 716 hits) or even CCGS (SD, using additionally "geological storage": 2697) the research efforts are still small. Also in Finland, where work on mineral carbonation started in the year 2000, motivated by large resources of magnesium silicates and absence of storage sites for CCGS, the funding of CSM has been much smaller than that for other CCS options.

2.1. Mineral carbonation

Mineral carbonation is a relatively new concept and was first mentioned by Seifritz (1990). Gradually, this idea started to spread and more and more research effort has been invested in it ever since (see Figure 2), as can also be seen from a number of literature reviews in the field (Huijgen and Comans, 2003; Huijgen and Comans, 2005; Sipilä *et al.*, 2008; Torróntegui, 2010). Until around 2000, published research on mineral carbonation was mainly developed in the USA. Halfway through the decade, teams from other countries joined in, mainly focusing on Ca-based wastes and by 2009 quite a number of groups had started to investigate various mineral carbonation options.

Carbon dioxide capture and mineralisation, CO_2 storage by mineralisation (CSM), mineral carbonation or CO_2 mineralisation are all names for the same concept and the principal topic of this thesis. Similarly to CO_2 sequestration in general, mineral carbonation can also be divided into multiple options, but the basic concept is the same, to form a carbonate from CO_2.

Mineral carbonation derives from the fact that many naturally occurring minerals have a tendency to form carbonates in the presence of CO_2 (Seifritz, 1990). The problem, however, is that the natural process is too slow to prevent the atmospheric CO_2 concentration from rising. Natural weathering is a process where magnesium, calcium or some other element capable of forming carbonates is released from its host rock, for instance by rainwater streaming down a mountain wall. CO_2, being present in the atmosphere, dissolves in water and becomes available for reacting with these metal (Mg, Ca, …) elements resulting in carbonates of the same. As an example, the reaction between magnesium and CO_2 is exothermic and spontaneous; moreover, the reaction between CO_2 and any Mg-silicate rock is exothermic and spontaneous, which means that carbonates are in fact more stable (from a thermodynamic point of view) than the initial solid material and CO_2. Thus, it should be possible to create a process that accelerates natural weathering of rock and thereby prevents CO_2 from entering the atmosphere (and at the same time generate a useful heat or work effect). This is one of the drivers for R&D work on CSM in Finland and a schematic image of such a process can be seen in Figure 3.

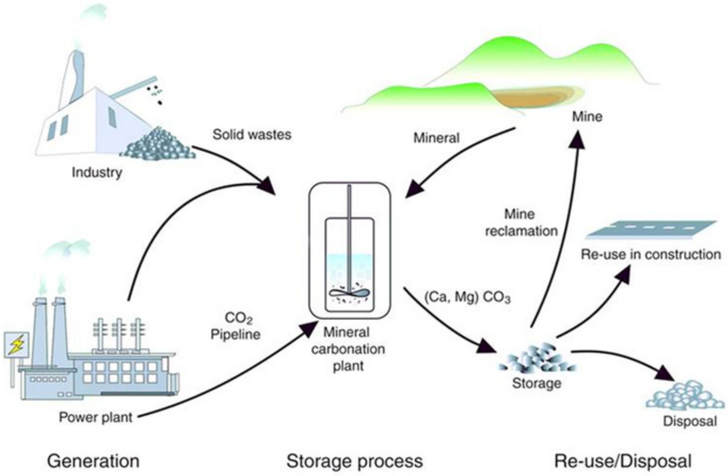

Figure 3. A schematic overview of a generic mineral carbonation process (IPCC, 2005).

The principal idea of an industrial mineral carbonation process and the material streams involved are given in Figure 3. Carbon dioxide is supplied from a source emitting a relatively high concentration of CO_2. This can either be further concentrated or used as such[4], depending on the type of mineral carbonation process considered. In addition to CO_2, a source of magnesium or calcium is required and that can be supplied from a mine or alternatively from an industrial side/waste product rich in either Ca or Mg.

The primary reason for magnesium and calcium being the main elements discussed for mineral carbonation is availability. Magnesium-containing minerals are abundant[5] and often found more concentrated in nature, more so than calcium-containing minerals (Lackner *et al.*, 1997a), and unlike many Ca containing minerals, not already present as carbonates. The worldwide (accessible) reserves of suitable Mg-rich silicates have been estimated to significantly exceed even the global coal reserves (~10 000 Gt) (Lackner *et al.*, 1995). Thus, Mg containing minerals are the only minerals with the potential to sequester globally significant amounts (Gt/yr) of CO_2. Calcium, however, is sometimes found concentrated in industrial residues and the option for using a such waste stream to sequester CO_2 is very promising. Not only is calcium usually more readily available for extraction in waste streams than natural minerals, but the prospect of utilising an otherwise worthless industrial side-stream is also a strong driving force. The realisation that industrial waste streams could be used for CSM purposes could actually pioneer the way for the less developed carbonation processes based on

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[4] *As of 2009, there is a trend to focus on direct gas treatment. No separate capture step needed → the new abbreviation introduced: carbon dioxide storage by mineralization (CSM)*

[5] *Even conservative estimates (mining depth < 35 m, 10% suitable for CO_2 sequestration) of mineral availability show vast capacity: 750 years of global CO_2 emissions in 2006 could be sequestered (Zimmerman et al., 2011).*

magnesium silicates, accelerating the introduction of large-scale Mg carbonation projects. Additional benefits of calcium carbonation can be received from achieving a high-purity end product. For instance, pure precipitated calcium carbonate (PCC) is a valuable product to the paper industry (Eloneva *et al.*, 2008; Teir *et al.*, 2007). Magnesium carbonate also has its uses, but if one considers the scale of a significant (Mt/yr) mineral carbonation plant, all current markets for this product would quickly be saturated (Zevenhoven *et al.*, 2006a). Thus mine reclamation, use in construction and even land reclamation[6] needs to be seriously investigated.

Considering the scale of mineral carbonation, a ton of CO_2 would require at least two tons of rock material and very likely somewhat more. Goff and Lackner (1998) introduced the concept of R_{CO2}, which represents the minimum amount of rock material required to sequester a unit mass of CO_2. For example the R_{CO2} value for pure serpentine is 2.1, meaning that it requires 2.1 t of pure serpentine (or around 2.5 t of serpentinite rock) for every one ton of CO_2 sequestered. The amounts required and scale of operation is undoubtedly large, but no larger than many typical mining activities today, ranging from a few Mt/yr (Nickel-mine, Kevitsa, Finland) to several hundreds of Mt/yr (Copper mine, Escondida, Chile) (InfoMine, 2012). Another revealing example is that of oil sand processing in Alberta, Canada, where more than one million ton of material is processed every day (Kunzig, 2009).

2.1.1. Direct versus indirect mineral carbonation

The simple direct approach of grinding a magnesium containing rock and exposing it to CO_2, under elevated pressure and temperature conditions, does not enhance carbonation significantly (Lackner *et al.*, 1997a), but there are alternatives that do. However, there are a few things that should be considered before attempting to create a new mineral carbonation process:

- Process energy requirements[7] have to be minimal so as to maximise the overall CO_2 sequestration efficiency (= CO_2 avoided/CO_2 captured)
- Using chemicals to enhance reactivity can only be done if (near to) complete chemical recovery is achieved.
- The reactions need to be "sufficiently fast" (< 1 h (Lackner *et al.*, 1997a)) for an industrially viable process to minimise reactor sizes, and consequently, costs.

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[6] *Recently Singapore has shown interest in large-scale mineral carbonation due to its plans to expand the usable land area. A goal of 1 km^2 new land area per year by 2020 would offer a very large market for mineral carbonation end product use.*

[7] *For instance, processes using electrolysis are unlikely to provide an energy efficient way of accelerating carbonation (more CO_2 will be emitted for power generation than can be sequestered) (Björklöf and Zevenhoven, Revised Dec. 2011)*

- The possibility to scale up should be addressed at an early stage. Is the process feasible on large-scale? (We need large-scale to tackle the large-scale CO_2 emissions.)
- Stability[8] of carbonate produced.
- Can the process work directly with flue gases or does it need concentrated pure CO_2?

The above-mentioned points should be fairly obvious, but still suggestions of processes that do not address these fundamental issues have been (for examples, see section 3.1, p. 13) and perhaps are still made.

Mineral carbonation processes can be divided into two subcategories, direct and indirect. Direct mineral carbonation is a process where everything happens in the same reactor, *i.e.* the extraction of magnesium or calcium and carbonation take place simultaneously. This is a simple approach, but it suffers from the fact that extraction and carbonation prefer different conditions. As a result, better alternatives can be found under the group of indirect carbonation methods.

Indirect carbonation includes a variety of options, but they all have in common the use of multiple steps that allow for the optimisation of each stage involved separately. Nevertheless, a direct carbonation method developed at the Albany Research Center (ARC, currently: NETL Albany) (O'Connor *et al.*, 2000; 2001; Gerdemann *et al.*, 2007) was for a long time considered state-of-the-art and has only recently been matched by other options (as discussed in section 2.1.2). Originally, the process developed at ARC consisted of using a solution of 0.64 M $NaHCO_3$ and 1 M NaCl in water at 150 bar and 150 °C (for heat treated serpentine) or 185 °C (for olivine), depending on the mineral used. Because this process has been extensively investigated and reported, it continues to serve as a benchmark for other process.

2.1.2. From lab-scale to demonstration projects

Recently, a number of processes have emerged with potential for moving from laboratory and pilot-scale to the demonstration phase. This is not surprising considering the number of publications, especially patents authored in recent years.

The list of patents is already quite extensive, but many of the patents do not give enough evidence of actual performance. USA-based companies such as Calera Corporation and Skyonic (and Cuycha Innovation Oy in Finland) have high-profile projects with patents backing them up (US 20110059000, US7727374 and US 20110083555 respectively). Still, the patents leave room for considerable doubt when it comes to industrial feasibility (Zimmerman *et al.*, 2011). However, there are other

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[8] *Hydrocarbonates are less attractive, while routes that give CO_2 bound in bicarbonate ions (HCO_3^-, dissolved in water) are altogether a less well understood "sequestration" option (Lackner, 2002)*

processes that appear fairly promising (is listed in a recent review article by Zevenhoven *et al.*, 2011):

- A process by Hunwick (2008) that eliminates the need for a separate CO_2 capture step, utilising ammonia or ammonium salts that can be recycled in conjunction with the carbonation step that would use preferably serpentinite as Mg source. Unfortunately, no “proof of concept” data is available in the public domain.
- A process (Verduyn *et al.*, 2011; Werner *et al.*, 2011) that utilises grinding to enhance the contact between the magnesium source, olivine or serpentinite (requires thermal activation), and CO_2. After the grinding/leaching step, the slurry is heated up for precipitation. It could work with seawater as the carrier solution.
- A process that has advanced to the demonstration scale (Reddy *et al.*, 2011) works by simultaneously capturing Hg, SO_2 and CO_2. As source material any alkaline waste material (*e.g.* fly as from a coal-fired power plant) is sufficient. The process can work directly on flue gases.
- A process (Wang and Maroto-Valer, 2011a; 2011b) that utilises recoverable ammonia in different forms for capturing CO_2 directly from the flue gas and reacting it with extracted magnesium (from serpentinite). The main question remains the energy penalty of regenerating ammonia (salts) from an aqueous solution.
- The process considered in this thesis: extraction of Mg from Mg-silicates, conversion to $Mg(OH)_2$ and gas-solid carbonation of $Mg(OH)_2$ in a pressurised fluidised bed. Experimental verification of both high extraction yields (> 90%) and high carbonation (> 90%) degrees are still required.

This list is by no means complete and more processes will probably appear in the near future, accelerated by the fact that mineral carbonation may sooner or later appear to be the least controversial[9] option of the CCS alternatives.

2.2. Other CCS options

Alternatives to mineral carbonation are (as mentioned) carbon dioxide capture and underground storage and ocean storage. The concept of CCGS is straight forward and in fact is being demonstrated on Mt-scale on four different locations worldwide (Herzog, 2011) at a total CCS capacity of around 5 Mt/yr. Firstly, CO_2 is separated from a point source (*e.g.* from the flue gas of a power plant), secondly, the pure CO_2 is pressurised and transported (for example via pipelines) to a suitable storage location

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[9] *Both CCGS (especially on-shore) and ocean storage suffer from public acceptance issues (Ashworth et al., 2010). The uncertainty of the permanency of both options and in the case of ocean storage, the negative influence on marine life is still being debated (Israelsson et al., 2010).*

and thirdly, the CO_2 is pumped into the selected storage site (*e.g.* a used oil field or a saline aquifer) (IPCC, 2005 chapters 4,5). The concept of ocean storage is similar, only the storage location is considered to be an ocean. One option considered is to inject CO_2 at great depth (> 3 000 m), where CO_2 becomes denser than water and accumulates on the ocean floor (IPCC, 2005, chapter 6).

Although a literature survey of other CCS alternatives than mineral carbonation (CSM) is outside the scope of this thesis, some of the major features can easily be compared (see also IPCC, 2005, chapter 7). The three key attributes of mineral carbonation are: inherently safe and leakage-free long-term storage in the form of carbonates, abundant mineral resources available world-wide and the possibility of utilising the exothermic nature of the carbonation reaction. Besides this, land reclamation and other uses for the solid products are being considered (Zimmerman *et al.*, 2011).

In comparison, none of the above-mentioned aspects apply to CCGS, although the technology of pumping CO_2 into underground formations has existed for some time (a lot of experience was obtained via enhanced oil recovery, EOR). Assessments of CCGS capacity have been very inconsistent and considerably overestimated in the early research phase and suitable locations are not available everywhere (Bradshaw *et al.*, 2007). Storing the CO_2 underground will require monitoring and it is uncertain how this monitoring should be performed over very long time frames (centuries to millennia)[10] (IPCC, 2005, chapter 5). Studies have argued that CCGS does not require long-term monitoring in some cases (several decades is usually considered to be enough - see also EC, 2009) because the CO_2 will eventually form carbonates within the injected formation (White *et al.*, 2011). Still, uncertainties in these studies (and the existing negative public perception of CCGS (*e.g.* Goerne, 2007)) justify the research of other CO_2 sequestration alternatives, such as mineral carbonation.

Another comparatively popular option of CCS is that of “air capture” (Lackner, 2003; Lackner *et al.*, 1999; Mahmoudkhani and Keith, 2009), a method where CO_2 is separated directly from air. The obvious benefit of such an option (assuming that the energy to drive the unit is CO_2 neutral or very low) is that the sequestration plant is not limited to any particular location and in large enough numbers could actually reduce the atmospheric concentration of CO_2. However, the captured and concentrated CO_2 would still require disposal, but overall “air capture” provides an interesting option for so called geo-engineering.

2.3. Alternatives to CCS

Carbon dioxide capture and storage could be seen as a bridging technology that allows for the continued use of fossil fuels until the use of carbon-free renewable energy

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[10] *The reader most certainly recognises parallels with nuclear waste storage.*

sources has become wide-spread and large-scale. At the same time this is one of the reasons why CCS is a less popular option than for instance solar power and commonly seen as a method that hinders the development of truly sustainable energy and power options (IPCC, 2005, chapter 5).

At this point it should be noted that it is unlikely that "any single technology option will provide all of the emissions reductions needed" (IPCC, 2005, technical summary), which is why research of all possible CO_2 emission mitigation options should be considered. This is evident if one considers the scale of current CO_2 emissions and the projected future emissions for a business-as-usual approach. Currently, global CO_2 emissions are around 30 Gt CO_2/yr and have increased with more than 200% since 1960[11].

The annual CO_2 emissions of ~30 Gt translate into the burning of roughly 8 Gt of carbon per year (in the form of petroleum, coal and natural gas). In order to offset the burning of fossil fuels a number of alternative energy generation systems have to be further developed, most notably solar, wind and hydroelectric power systems. Currently (2008 data) these three account for only a small fraction (~2.6%) of the total energy supply, as seen in Figure 4, but especially solar and wind power systems are growing rapidly (REN21, 2011). Both solar and wind power have significant potential for further development considering the vast theoretical amounts of energy available in wind and in solar radiation. According to one estimate (Jacobson and Delucchi, 2009), wind power generation could readily be increased to between 40–85 TW, while solar power could provide up to 580 TW, excluding inaccessible regions such as open seas and high mountains. These numbers are much higher than the current-level (2009) global power consumption estimate of around 12.5 TW (1 TW = 10^{12} W).

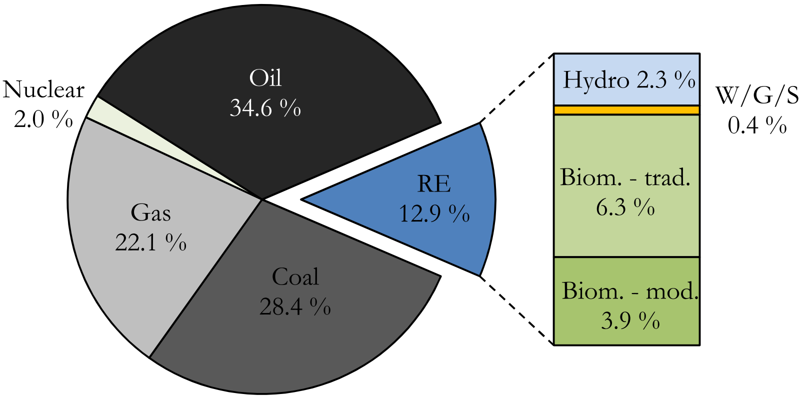

Figure 4. Distribution of world primary energy supply in 2008 (IPCC, 2011, technical summary). RE stands for renewable energy technologies, biom. is short for biomass and W/G/S means wind, geothermal and solar. Traditional biomass incorporates mainly cooking and heating applications in developing countries.

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[11] *http://lgmacweb.env.uea.ac.uk/lequere/co2/carbon_budget.htm and refs within.*

It is clear that renewable energy systems have the potential to replace conventional fossil fuel based energy and power sources. However, for (political and financial) reasons outside the scope of this thesis, deployment of such systems is comparatively slow; comparatively to the continued global increase in energy and power demand that is. Thus, CCS should be seen as an additional method to cut CO_2 emissions together with, and not instead of, the development of other climate change mitigation options.

3. Mineral carbonation options

There are several different alternatives for mineral carbonation and recent literature reviews (Huijgen and Comans, 2003; Huijgen and Comans, 2005; Sipilä *et al.*, 2008; Torróntegui, 2010; Zimmerman *et al.*, 2011) have established a basic overview of the processes in the form of a tree-diagram as seen in Figure 5.

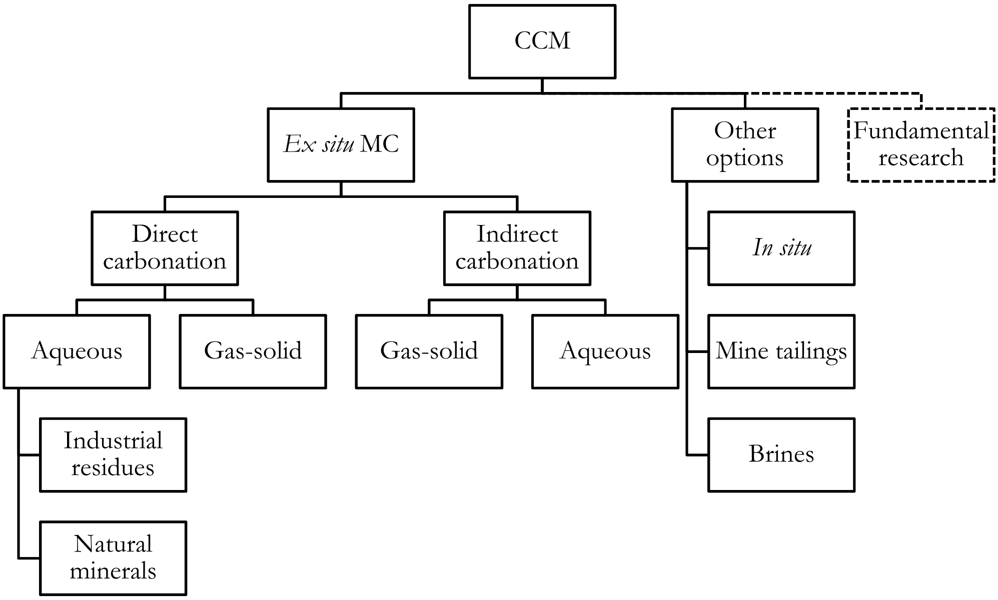

Figure 5. Currently studied mineral carbonation options tree-diagram (mod. from Torróntegui, 2010)

One of the most recent literature reviews in the field of mineral carbonation (Torróntegui, 2010) concludes that direct carbonation routes are gradually making way for more complex multi-step processes. In addition, a clear trend in recent years has been to move away from using pure CO_2 to the direct use of flue gases. This would be very beneficial considering that CO_2 capture is still very problematic and costly (both energetically and economically), but at the same time, it could instead require the transportation of an Mg or Ca source to the CO_2 emission source. Or, for "green field" processes: install the CO_2-producing unit at or near a suitable mineral deposit .

It seems, similarly to what Torróntegui (2010) concluded, that a comparison between different mineral carbonation routes is very difficult as there are no actual demonstration projects yet to compare to. That is to say, many projects are still in research phase and critical information about some aspects of the processes in question is still missing. In the following section, however, short presentations of the different routes, together with the latest[12] publicly available research information are given. (More detail, covering the situation until 2010 is given in the enclosed book chapter, Paper III.)

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[12] *Literature published between April 2010 and September 2011*

3.1. Recent publications

Figure 2 indicates that the number of publications in the field of CSM is increasing and a similar conclusion was reached by Torróntegui (2010). Since that review (including literature until March 2010), a number of new studies, including reviews (and patents), have been published on mineral carbonation. Although the number of papers is considerable, the fundamental aspects of CSM remain the same: Costs (both energetic and economic) should be reduced and special attention should be given to chemical additives consumption. However, (as also noted by Zevenhoven *et al.*, 2011) there are already process routes that seem to be moving rapidly towards commercialisation.

3.1.1. Direct carbonation - Aqueous

Based on recently published mineral carbonation studies, direct aqueous carbonation continues to receive a considerable amount of attention in the field of CSM. The likely reason for the high interest is the fact that this route offers a relatively simple method for carbonating various materials, ranging from industrial residues to abundant naturally occurring minerals. However, as pointed out earlier (Torróntegui, 2010), one issue that requires more consideration is the necessity to recycle the process water used.

The study of direct aqueous carbonation of natural minerals has decreased considerably, especially if one considers studies aiming principally at *ex situ* processes. However, the number of studies considering mineralisation at geological conditions (usually around 80 bar, 100 °C) has increased together with studies using industrial residues.

There are a multitude of industrial residues that could be and are considered for use as raw material for mineral carbonation. Table 1 presents only the most recent residues of interest. Some of the materials have low carbonation potential (*e.g.* 5.3 g CO_2/100 g red mud[13]), but being residues, all options for utilisation can be considered.

Table 1. Industrial residues investigated for direct aqueous mineral carbonation purposes during 2010–2011.

Residue	CO_2 source	Ref.	Comments
BA[a] from RDF[b]	Pure CO_2	(Baciocchi *et al.*, 2010)	No large-scale assessment made, but potential as a BA stabilisation technique.
APC[c] residue from MSWI[d]	Pure CO_2	(Cappai *et al.*, In Press 2011)	Carbonation times around 3 h, only preliminary estimates of capacity (200 g/kg APC residue)
Coal FA[e] (brine impacted)	Pure CO_2	(Nyambura *et al.*, 2011)	Elevated pressure (10–40 bar) conditions (2 h), small potential, but possibility to utilise two wastes (brine and FA) for sequestration

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[13] *Red mud is the alkaline waste sludge that results from aluminum production. Roughly, 1 to 1.5 t of red mud is produced for every 1 ton of alumina (Yadav et al., 2010).*

Lignite FA[e]	Partial CO_2	(Bauer *et al.*, 2011)	2 h reaction time, incomplete carbonation (53%) and ambient temperature.
Steel-making slags	Partial CO_2	(van Zomeren *et al.*, 2011)	Different temperatures (< 100 °C) primarily for 24 h, V leaching increased.
Steel-making slags	Pure CO_2	(Chang *et al.*, In Press 2011)	Comparatively long (12 h) reaction times, and high CO_2 pressures (> 48 bar) and temperatures (160 °C) were studied
FA[e] from MSWI[d]	Simulated FG	(Sicong *et al.*, 2011)	SO_2 in FG affected the stability of the carbonated samples negatively
Residue from acetylene prod.	Atmospheric CO_2	(Morales-Flórez *et al.*, 2011)	Artificial pools, small overall potential (800 t CO_2/yr of one plant).
Cement waste	Simulated FG	(Uliasz-Bocheńczyk and Pomykala, 2011)	Elevated pressure conditions (9–10 bar) and ambient temperature, reaction times measured in days.
Steel-making slags	Pure CO_2	(Chang *et al.*, 2011)	Shrinking core type kinetics, 72% conversion in 1 h at 60 °C.
Red mud	Pure CO_2	(Yadav *et al.*, 2010)	CO_2 (3.5 bar), room temperature, reaction time measured in hours. Low capacity: 5.3 g CO_2/100 g red mud at best
Mg-rich wastewaters (or seawater)	Pure CO_2, partial CO_2	(Mignardi *et al.*, 2011; Wang *et al.*, 2011)	Large raw material potential. Mg-concentrations (7–32 g/l) (lower for seawater, also Ca) was carbonated into for example nesquehonite. pH adjusted with ammonia.

[a] Bottom ash, [b] refuse-derived fuel, [c] air pollution control, [d] municipal solid waste incineration and [e] fly ash.

The increasing interest in carbonating various industrial residues can be seen from Table 1. Perhaps the strongest incentive to this is in the fact that an otherwise useless (or even harmful) residue might be refined into something useful, while simultaneously reducing CO_2 emissions. Improving the residue quality has been the principal purpose of some recent studies (Cappai *et al.*, In Press 2011; Sicong *et al.*, 2011; van Zomeren *et al.*, 2011) and it can be concluded that while carbonation generally lowers the leaching of elements compared to the raw material, not all elements present the same behaviour. For instance, vanadium leaching was found to increase considerably for carbonated rapid air-cooled basic oxygen furnace steel slag (van Zomeren *et al.*, 2011). In another case (Sicong *et al.*, 2011), SO_2 in the carbonation gas (simulated flue gas) was found to increase the leaching for most of the elements. In other words, while carbonation is generally considered to improve the properties of waste materials, care should be taken to ensure that this actually is the case.

Another aspect that also requires additional attention is the industrial-scale feasibility of the processes studied. Little or no consideration to energy input requirements and cost issues is given in the above mentioned literature, although all process descriptions aim at industrial scale CO_2 sequestration.

Besides industrial residues, the only recent direct aqueous carbonation study of natural minerals (Ryu *et al.*, 2011) suggested a simple process for potentially reducing the hazardous nature of fibrous tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$), while simultaneously binding some CO_2. The elevated pressure (P_{CO2} = 5 bar) and temperature (290 °C) conditions (5 h) did not, however, affect the tremolite crystal structure, and only the morphology was changed, but again, no scale-up feasibility was mentioned.

3.1.2. Direct gas-solid carbonation

Direct gas-solid carbonation represents perhaps the simplest approach to *ex situ* mineral carbonation: solid Ca or Mg bearing material is subjected (usually at elevated temperatures) to CO_2 to promote carbonate formation. Although it appeared, from a previous literature review (Torróntegui, 2010), that direct gas-solid carbonation has almost been abandoned, a number of recent studies (see Table 2) in the field are presented here.

Table 2. Different raw materials investigated for direct gas-sold mineral carbonation purposes during 2010–2011.

Resource	CO_2 source	Ref.	Comments
Olivine	Flue gas	(Kwon *et al.*, 2011a; 2011b)	Elevated temperature (150–200 °C), capacity up to 0.14 g CO_2/g of olivine, kinetic modelling in (Kwon *et al.*, 2011b).
$Ca(OH)_2$	Pure CO_2	(Montes-Hernandez *et al.*, 2010)	Demonstration of method (30–300 °C) and carbonation mechanisms of $Ca(OH)_2$.
FA[a]	Flue gas (real)	(Reddy *et al.*, 2011)	FB at mild temperature and pressure conditions, ~50 °C and ~1 bar. Fast initial CO_2 (and SO_2) capture, diminishes gradually after 10 minutes
Steel slags (BOF[b] and EAF[c])	Partial CO_2	(Yu and Wang, 2011)	EAF better, 30% of Ca carbonated within 20 minutes in 10% CO_2 and 550 °C.

[a] *fly ash,* [b] *basic oxygen furnace and* [c] *electric arc furnace*

Although direct carbonation of olivine using flue gas has great potential, the issue with kinetics or reaction extent is still the largest obstacle as also admitted in recent studies by Kwon *et al.* (2011a; 2011b). Another study that has already moved from laboratory scale into pilot scale is that of fly ash (FA) carbonation in a fluidised bed using flue gas from a coal combustion plant (Reddy *et al.*, 2011). The advantages, despite marginal overall capture capacity, are the possibility to reduce the harmfulness of the flue gas (SO_2, Hg removal) and the possibility to use flue gas and FA from the same location.

3.1.3. Indirect aqueous carbonation

The realisation that aqueous carbonation could be improved by dividing the process into a separate dissolution and carbonation step has resulted in a considerable amount of studies. Clear benefits include controllability and the option to produce pure (hydro)carbonates (disposal cost of 30–50 €/ton if no use for it can be found

(Zimmerman *et al.*, 2011)). Table 3 gives a brief overview of what has been studied in recent years in the field of indirect aqueous mineral carbonation.

Table 3. Different raw materials investigated for indirect aqueous mineral carbonation during 2010–2011.

Resource	CO_2 source	Ref.	Comments
Industrial wastes (steel slag and concrete)	Pure CO_2	(Kunzler *et al.*, 2011)	Chemical consumption: used HCl for extraction and bases for precipitation.
Serpentinite	Pure CO_2	(Orlando *et al.*, 2011)	Long reaction times (16 h), H_2SO_4 for dissolution and elevated T and P for carbonation
Steel slag	Pure CO_2	(Sun *et al.*, 2011)	Dissolved using NH_4Cl (recovery not fully addressed), 96% purity PCC.
Mg-silicates	Flue gas	(Verduyn *et al.*, 2011; Werner *et al.*, 2011)	A continuous process has been demonstrated: Mg-silicate (heat treated serpentinite) carbonation by wet-grinding and leaching, precipitation at elevated temperature.
Wollasonite	Pure CO_2	(Baldyga *et al.*, 2011)	Acetic acid and two dicarboxylic acids, succinic and adipic studied. Succinic acid most effective. 812 g acid and 1 kg wollastonite per 325 g CO_2. Energy costs and acid recovery experimentally not verified.
Red mud	Pure CO_2	(Sahu *et al.*, 2010)	Ambient conditions, CO_2 bubbled trough stirred solution cyclically for 3x5 h. Cost of this process roughly 147 $US/t CO_2. Sequestration in the form of Na_2CO_3, $NaHCO_3$, and H_2CO_3.
Steel (converter) slag	Partial CO_2	(Eloneva *et al.*, In Press 2011)	A previously studied (*e.g.* Teir *et al.*, 2007) process for PCC production was studied. Conclusion: clear potential for scale-up.
Phosphogypsum waste	Pure CO_2	(Cárdenas-Escudero *et al.*, In Press 2011)	The method requires the use of NaOH (2.34 g/ 5 g waste) and evaporation steps. No assessment of energy costs is given
Oil shale ash	Pure CO_2	(Uibu *et al.*, 2011)	Ambient conditions, theoretical capacity: ~35 g CO_2/100 g ash, experiments 9 g CO_2/100 g ash
Oil shale ash (leachate)	Pure CO_2 (FG considered)	(Velts *et al.*, In Press 2011)	96% purity PCC, oil shale ash leachate in Estonia roughly 10–15 million m^3. Currently 1 m^3 of ash leachate could sequester at least 1.3 kg of CO_2 resulting in 3 kg PCC.
Serpentinite	Flue gas	(2011b; Wang and Maroto-Valer, 2011a)	Complete dissolution of Mg was achieved in 3 h using 100 °C and 1.4 M NH_4HSO_4. Recovery of chemicals needs to be energetically assessed.

It is evident from Table 3 that aqueous indirect carbonation is considered a promising route, especially considering precipitated calcium carbonate (PCC) production, with steelmaking slags as the most widely studied raw materials. The possibility to produce a product of high commercial value, such as high-purity PCC, allows for some flexibility regarding process costs and energy requirements, especially if flue gases can be used as CO_2 source. Thus, it can be concluded that indirect carbonation routes aiming towards PCC production are good candidates for being among the first commercially viable CSM routes. However, "truly" large-scale sequestration (> 0.1 Mt/yr) requires the use of natural minerals and among such processes the one that appears to have advanced the furthest has been suggested by Shell Global Solutions, as discussed by Werner *et al.* (2011) and Verduyn *et al.* (2011).

One issue that was recently addressed by Eloneva *et al.* (2010), and also addressed above under the topic "Direct aqueous carbonation routes", is the effect of carbonation on the residue. For the case of indirect steel slag carbonation it was noted that both Cr and V solubility increased considerably compared to the raw material, which could shift its status from by-product to (hazardous) waste. This is perhaps a drawback of processes that aim to extract cations from the slag instead of directly carbonating the entire raw material. Similarly, Navarro *et al.* (2010) concluded that direct carbonation of steel slags reduces the leaching of both alkaline earth metals and harmful trace elements and it should not be confused with indirect carbonation of steel slags that removes Ca from the slag for subsequent precipitation in a separate process step.

3.1.4. Indirect gas-solid carbonation - Main focus of this thesis

The motivation for using a gas-solid route for mineral carbonation is based on the fact that carbonation reactions are generally exothermic (even at high temperatures). In other words, a properly optimised carbonation process could in theory be energy-neutral or even negative (Zevenhoven *et al.*, 2008). Currently the most studied indirect gas-solid carbonation route is the one being developed at Åbo Akademi University (ÅA) (Fagerlund *et al.*, In Press 2011; 2011; Nduagu, 2008; In Press 2012a; In Press 2012b; Romão *et al.*, In Press 2011; Stasiulaitiene *et al.*, 2011), while no other recent studies on the topic were found. It should also be noted that the ÅA process route combined with an oxyfuel plant was investigated by Said *et al.* (2011). The conclusion was that this process route provides an interesting alternative to conventional oxyfuel combustion and more research on the topic is warranted.[14]

3.1.5. In situ carbonation studies

Thus far, all the studies considered here have been related to *ex situ* mineral carbonation, which should be distinguished from *in situ* mineral carbonation. Basically, the difference between the two concepts is in the fact that *in situ* mineral carbonation only considers reactions taking place within a geological formation, while *ex situ*

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[14] *Carbonation of $Mg(OH)_2$ can be considered with the CO/water shift in a gasification or IGCC process: the carbonation generates the water for the CO oxidation (Zevenhoven, personal communication, Said et al., 2010).*

mineralisation is concerned with some form of reactor for the carbonation to take place.

In a previous literature review, Torróntegui (2010) concluded that there has been a notable increase in *in situ* carbonation studies in recent years. This is also evident from the literature published during the last one and a half years (Daval *et al.*, 2011; Domenik, 2011; Garcia *et al.*, 2010; Hövelmann *et al.*, In Press 2011; Kwak *et al.*, 2011; Liu and Maroto-Valer, 2010; Loring *et al.*, 2011; Matter *et al.*, 2011; Ragnheidardottir *et al.*, 2011; Schaef *et al.*, 2010). Although most of the studies clearly focus only on explaining reactions taking place at geological conditions, some studies also point out the value of their studies for improving the general understanding of mineralisation reactions that could be utilised for *ex situ* carbonation processes as well (*e.g.* Haug *et al.*, 2011; King *et al.*, 2010).

One of the main topics of *in situ* mineralisation studies at present is predicting the reaction rates. That water plays a key role in reactivity has been confirmed by several studies (Kwak *et al.*, 2011; Loring *et al.*, 2011; Schaef *et al.*, In Press 2011). Earlier, it was often predicted that the conversion of CO_2 into precipitated carbonates is very slow, thousands of years for the conversion of any significant fraction of CO_2 injected into sedimentary formations (White *et al.*, 2005). Recently however, White *et al.* (2011) came to the conclusion that the rate of mineralisation in basaltic saline formations might be much more significant or even the dominant form of CO_2 trapping within a century. This is noteworthy, although more evidence is still required, and could help to address the problem of long-term monitoring of injected CO_2 (although a century is still a very long time in human scale).

A small-scale demonstration project of *in situ* mineralisation (CarbFix, see e.g. Matter *et al.*, 2011) is ongoing in Iceland, where CO_2 is being injected into a basaltic underground formation. A recent cost assessment (Ragnheidardottir *et al.*, 2011) of different injection scenarios concluded that large-scale CO_2 injection at Hellisheidi could be between 12.5 and 30 €/t CO_2 injected, which is in the range of CO_2 emission taxes and the emissions trading scheme in Europe (although no uniform CO_2 taxation policy yet exits).

Another interesting *in situ* approach was reported by Keleman and Matter (2008), where it was suggested that the injection of pure 300 bar CO_2 into a pre-heated mass of peridotite could result in a carbonation rate that would maintain the required elevated temperature (185 °C) conditions. This idea was further considered in a review-type article by Keleman *et al.* (2011) and two different approaches for *in situ* carbonation were suggested, one of which was similar to that given above. The other idea was based on the use of seawater to enhance the rate of natural carbonation in hydraulically fractionated peridotite drill holes. This method would only require atmospheric CO_2, and the largest cost, depending on the possibility to utilise thermal convection, would arise from the pumping of vast amounts of seawater required for significant CO_2 sequestration. However, if the concept can be shown to work, scale-up is simple: drill more holes[15].

3.1.6. Additional CSM studies

Not all studies related to mineral carbonation are easily categorised into direct or indirect mineral carbonation routes, which is why a short summary of such recently published fundamental studies is given in Table 4. The studies are fundamental in the sense that they do not directly limit their scope to any particular CSM route, but instead investigate for instance dissolution or precipitation in general.

Table 4. Different studies conducted related to mineral carbonation in general during 2010–2011.

Main topic	**Ref.**	**Comments**
Olivine dissolution	(Prigiobbe and Mazzotti, In Press 2011)	Effects of two organic acid ligands (oxalate, citrate) at conditions relevant for aqueous mineral carbonation.
Olivine dissolution	(Haug *et al.*, 2010; Sandvik *et al.*, 2011)	Effects of mechanical activation. However, the use of additives and high energy demand are industrial unfeasible.
CO_2 sequestration capacity	(Vogeli *et al.*, 2011)	Platinum group mineral (PGM) tailings in South Africa were investigated for their theoretical CO_2 binding capacity and suitability/ranking. As an example two mining operations, Northam and BRPM, were evaluated for CO_2 binding potential: 388 and 270 kt CO_2/yr. Total capacity: potential of binding 43.6% of CO_2 emitted (95% pure) by synthetic fuel industry
Natural weathering	(Clow and Mast, 2010)	CO_2 uptake modelling based on field observations at Andrews Creek. CO_2 uptake increased as a function ($R^2 = 0.71$) of runoff water and temperature, effectively working against increasing atmospheric CO_2 levels
$CaCO_3$ precipitation	(Bang *et al.*, 2011)	Using microbubbles of CO_2. The precipitation-rate was found 50% faster compared to conventional bubbling.
CaO, MgO aqueous reactivity	(Back *et al.*, 2011)	Dissolution/carbonation reactions of CaO and MgO, mechanisms involved in aqueous CO_2 sequestration.
Nesquehonite stability	(Ballirano *et al.*, 2010)	Nesquehonite, stable under the temperature conditions that prevail at the Earth's surface. ($MgO \cdot 2MgCO_3$ is obtained as a reaction product of nesquehonite thermal treatment.
CO_2 sequestration capacity	(Renforth *et al.*, 2011)	Estimation of the global amounts of silicate waste resources (*e.g.* mine tailings), global annual carbon sequestration potential: 190 to 332 Mt of C per year (translating into between 0.7 and 1.2 Gt CO_2/yr).
Passive CO_2 uptake	(Wilson *et al.*, 2011)	Passive uptake of CO_2 by mine tailings, significant conversion to nesquehonite at cold and dry conditions.

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[15] *The sequestration of 1 Gt CO_2 per year would require one million drill holes, which is no more than the amount of oil and gas wells in the US alone (Kelemen et al., 2011).*

Passive CO_2 uptake	(Pronost *et al.*, In Press 2011)	Reactivity of ultramafic mining waste at ambient conditions, predicting CO_2 emissions that could be offset by mining companies.
Dry $Ca(OH)_2$ carbonation	(Liu *et al.*, 2010)	The influence of SO_2 on $Ca(OH)_2$ carbonation at low temperatures, even small amounts (> 100 ppm) of SO_2 were found to reduce the carbonation degree.
LCA[a]	(Khoo *et al.*, 2011b)	A preliminary LCA of CSM in Singapore. Unless flue gas can be used directly for carbonation the CSM routes were found unfeasible.

[a] *Life cycle assessment.*

Enhancing the dissolution rate and extent of different Mg- and Ca-rich raw-materials has been studied for a (comparatively) long time already and is evidently still (see Table 4) of great interest. Also natural weathering and passive CO_2 uptake studies have been made (Pronost *et al.*, In Press 2011; Wilson *et al.*, 2011), which in the case of some mining companies could be of great economic interest. In addition, Renforth *et al.* (2011) noted that there is a major gap in our knowledge of actual or existing silicate resources and estimated that a significant amount (0.7 to 1.2 Gt CO_2/yr) of potentially good (fines or industrial waste) raw material for *ex situ* mineralisation is produced globally every year. The silicate mineral sources considered (some of which have already been accounted for) were: fines from aggregate production, mine waste, cement kiln dust, construction waste, demolition waste, blast furnace slag, steel making slag, lignite ash, anthracite ash and bituminous ash. Another estimate of the global potential of these waste materials was considerably more cautious, assessing the global CO_2 uptake potential at around 0.32 Gt/yr (Zimmerman *et al.*, 2011).

3.1.7. Reviews addressing mineral carbonation

In addition to the CSM review by Torróntegui (2010), a number of CCS reviews (or review-like articles) were published recently addressing also, if only very briefly, mineral carbonation. Similarly to above, a list of these is given in Table 5.

Table 5. Different studies conducted related to mineral carbonation in general during 2010–2011.

Title	Ref.	Comments
A review of research progress on CO_2 capture, storage, and utilization in Chinese Academy of Sciences	(Li *et al.*, In Press 2011)	Overview of CCS technologies at CAS. Mineral carbonation, although interesting, will never be cheaper than most CCGS options. Best option indirect carbonation of industrial solid residues.
Carbon capture and utilization: preliminary life cycle CO_2, energy, and cost results of potential mineral carbonation	(Khoo *et al.*, 2011a)	Four different CSM scenarios of the ÅA-route were evaluated using LCA. The costs were found to be in the range of ~70 to 160 $US/t CO_2 avoided.
Recent developments on carbon capture and storage: An overview	(Pires *et al.*, 2011)	CCS an overview. Little was concluded about mineral carbonation, except that it is costly.
Understanding the chemistry of direct aqueous carbonation with additives through geochemical modelling	(Bonfils *et al.*, 2011)	Direct aqueous carbonation using organic salts is perhaps the most promising mineral carbonation route to date.

Carbon capture and storage by mineralisation	(Zimmerman *et al.*, 2011)	CSM is currently the only CCS option for small- and medium-scale (< 1 Mt/yr) CO_2 emitters. CSM cost: 100–300 €/t CO_2 (lower if direct flue gas capture can be used)

Besides the publications given in Table 5 and Paper III in this thesis, two additional recently published works should be mentioned here. One is a book chapter addressing mineral carbonation development (Zevenhoven and Fagerlund, 2010) and current situation in general (based largely on Sipilä *et al.*, 2008) and the other a review article (Zevenhoven *et al.*, 2011) focusing on the possibility of scaling up some of the most promising processes (see also chapter 2.1.2, p. 7).

Currently, the general consensus of mineral carbonation as a CCS option remains what it has been since it was first recognised: an expensive approach, with potential only for niche applications. However, based on the number of recently published patents (reviewed by Zimmerman *et al.*, 2011), it seems more people are willing to believe in CSM's commercial potential. Note that a lot is reported outside the CCS-realm of IEA-GHG, the bi-annual GHGT conferences and the IJ of GGC.

4. Gas-solid mineral carbonation - a stepwise approach

The key observation made by Seifritz in 1990 was that it might be possible to bind CO_2 via an exothermic process into a “stable, permanent substance”. However, he envisioned an aqueous process, which is unattractive from an energy point of view. It would be beneficial if the heat released from an exothermic carbonation reaction would not be diluted into water, but instead would be made available as a hot concentrated gas (Lackner *et al.*, 1997b). This has been the foundation of the work done in Finland and the process route described in this thesis.

The overall reaction of the mineral carbonation process described here can in principle be summarised by a single chemical equation:

$$\begin{gathered} xMO \cdot ySiO_2 \cdot zH_2O\ (s) + xCO_2\ (g) \\ \leftrightarrow xMCO_3\ (s) + ySiO_2\ (s) + zH_2O\ (l) \end{gathered} \tag{1}$$

where M stands for a divalent metal[16] such as Mg, Ca or Fe. If the mineral to be carbonated is serpentine (*i.e.* the main mineral of the rock type serpentinite), $3MgO \cdot 2SiO_2 \cdot 2H_2O$ (usually given as: $Mg_3Si_2O_5(OH)_4$), the reaction would proceed to the right at atmospheric conditions (0.0004 bar CO_2 and 25 °C) accompanied by a heat release of 62.4 kJ/mol CO_2[17]. This is a significant heat release, equivalent to roughly 15% of the heat released when producing the CO_2 by burning coal. However, there is one significant difference between the burning of coal and the carbonation of serpentine and that is the rate of reaction.

Carbonation of serpentine in nature is an exceedingly slow process and the heat released is diluted over a long time. Thus, in order to utilise the exothermicity of CO_2 mineralisation, the carbonation reactions have to be accelerated significantly. The obvious way to accelerate any chemical reaction is to increase the temperature, but thermodynamics put a constraint on how much the temperature can be increased. This can be exemplified by considering a simple carbonation reaction between magnesium oxide and CO_2:

$$MgO\ (s) + CO_2\ (g) \leftrightarrow MgCO_3\ (s)\ (+\ 118\ \text{kJ heat}) \tag{2}$$

From Reaction (2) it can be seen that the reaction will proceed to the right with the addition of CO_2 to the system in accordance to Le Chatelier’s principle. Similarly, it can be stated that the removal of heat shifts the equilibrium further to the right, again favouring carbonation. In other words, adding heat (increasing the temperature and reaction rate) to the system favours the reverse reaction, *i.e.* calcination. This, thermal decomposition of $MgCO_3$, is the reason why carbonation reactions cannot be accelerated by simple heating. Instead, an increase in temperature needs to be

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[16] *For reasons explained earlier Mg is the element of choice for large-scale mineral carbonation.*

[17] *Based on HSC Chemistry 5.11 software calculations and corrected thermodynamic values for $MgCO_3$ (Robie et al., 1979).*

accompanied by a simultaneous increase in the amount (*i.e.* pressure) of CO_2. For a given temperature and pressure the direction of the MgO carbonation reaction (2) can be determined by thermodynamics[18]. Figure 6 shows the decomposition temperature of magnesium carbonate as a function of temperature and CO_2 pressure.

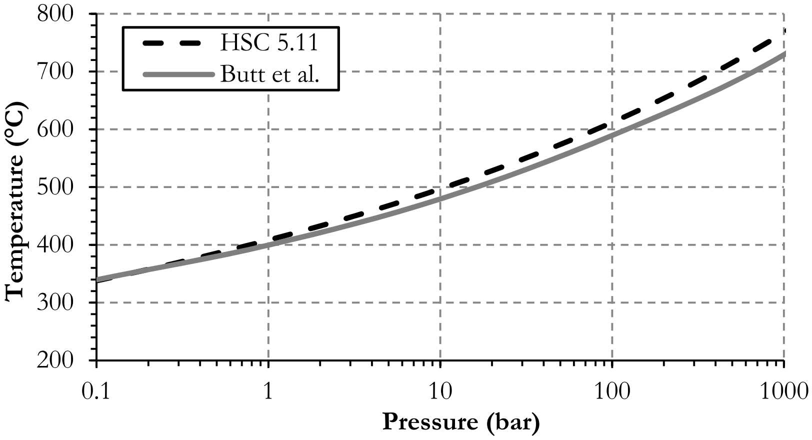

Figure 6. The stability of $MgCO_3$ as a function of CO_2 pressure and temperature based on two different sources. The solid line represents $MgCO_3$ stability as given by Butt et al. (1998), while the dotted line has been calculated using HSC Chemistry 5.11 software. Above the two lines $MgCO_3$ decomposes into MgO.

All in all, the basics of mineral carbonation are relatively simple, but due to the facts that:

- direct carbonation of for instance serpentinite does not yield sufficient reactivity even at relatively severe conditions (340 bar, 500 °C) (Lackner *et al.*, 1995) and
- pure sources of reactive MgO and $Mg(OH)_2$ are extremely rare in nature,

other indirect carbonation routes have to be employed, especially when considering gas-solid carbonation.

The indirect mineral carbonation route considered here can be divided into three steps: 1) extraction of Mg from magnesium silicates, 2) production of $Mg(OH)_2$ from extracted Mg and 3) carbonation of $Mg(OH)_2$ in a pressurised fluidised bed (PFB). Steps one and two have been investigated separately and in parallel to the carbonation (third) step. The following sections will deal with each step in order, presenting the principles and experimental procedures in some detail. It should be noted that the primary focus of this thesis is on the third step, while another thesis (by Nduagu, ÅA) is being produced that focuses on the first two steps.

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[18] *For a more detailed account see Appendix in Paper VII.*

4.1. Extraction of Mg from Mg-silicates

Because the reactivity of natural magnesium containing minerals towards CO_2 is low, a method of extracting magnesium from magnesium silicate rock (primarily serpentinite) was developed by Nduagu *et al.* (2008; In Press 2012a; In Press 2012b) at ÅA. A picture of the reactor/oven used for the Mg extraction experiments can be seen in Figure 7 together with an image of a typical small (~5 cm) Al-foil crucible used to contain the sample. The quartz tube inside the oven ensures that the developing gases can effectively be collected downstream.

Figure 7. Reactor/oven used for heating the AS + Mg-silicate samples in small (~5 cm) hand wrapped Al-foil crucibles (Pictures by E. Nduagu).

Similarly to work by Nduagu (2008), Figure 8 shows the results of HSC Chemistry software (Roine, 2002) equilibrium calculations suggesting that (at least) thermodynamically it should be possible to produce (water-soluble) $MgSO_4$ from serpentinite at temperatures above 200 °C. The four different graphs show the amount of different species at a given temperature, assuming equilibrium has been reached (and that all relevant species have been incorporated into the model). As input data to the model, one mole serpentine together with three moles of ammonium sulphate (AS) has been used (balancing reaction stoichiometry).

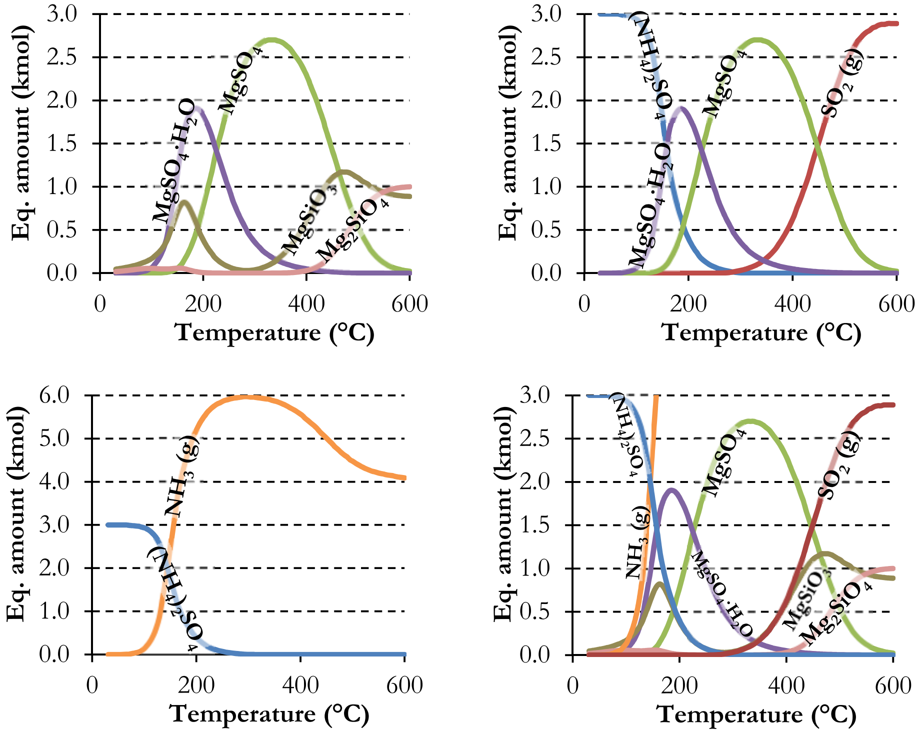

Figure 8. Equilibrium composition for a solid-solid reaction between serpentine (1 mol) and ammonium sulphate (3 mol). Graphs have been divided according to the three main elements Mg, S and N (notice y-axis scale). Bottom-right: composite graph, all (major) species.

Although Figure 8 predicts the formation of $MgSO_4$, it is unwise[19] to rely on such data alone and experiments have shown that higher temperatures than predicted give the best result (depending on solids mixing). The method consists of heating (400–500 °C) fine grinded (75–125 µm) magnesium containing rock (such as serpentinite) together with ammonium sulphate (AS). The temperature and reaction time are important and very recently, work using a rotating reactor has commenced. Up until now, the solids have been pre-mixed and heated in a simple unstirred vessel. The improved contact in a rotating reactor between AS and the Mg-silicate rock should enhance the following solid-solid reaction:

$$\begin{array}{c} Mg_3Si_2O_5(OH)_4\ (s) + 3(NH_4)_2SO_4\ (s) \rightarrow \\ 3MgSO_4\ (s) + 2SiO_2\ (s) + 5H_2O\ (g) + 6NH_3\ (g) \end{array} \qquad (3)$$

In addition, continues mixing might allow for lower reaction temperatures as predicted by equilibrium calculations (Nduagu *et al.*, In Press 2012b). In the above reaction equation, serpentine is used as Mg source. Serpentine is a pure mineral and the principal, but not the only, component of serpentinite rock. Therefore, Reaction (3)

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[19] *Thermodynamic data does not consider any restrictions to reactivity. In other words, all reactions are assumed to go to completion and kinetic constraints are not accounted for. Also, there are uncertainties in thermodynamic data over wide temperature ranges and it may be that not all reaction products are being considered.*

represents the ideal case, unaffected by impurities such as iron and calcium. Still, the fact that typical Finnish serpentinite[20] contains a significant fraction of iron (13%-wt assuming FeO) could be beneficial (Paper VI). Similarly to Reaction (3), also iron can react to form iron sulphate following the overall reaction below:

$$\begin{gathered} FeO\ (s) + (NH_4)_2SO_4\ (s) \rightarrow \\ FeSO_4\ (s) + H_2O\ (g) + 2NH_3\ (g) \end{gathered} \tag{4}$$

As a result of the solid-solid reactions, ammonia is released as a gas. This ammonia needs to be recovered and as will be discussed below, it can be used to increase the pH in the following $Mg(OH)_2$ production step. The solid material that is recovered from the solid-solid rector is dissolved in water and the residue (SiO_2 and any unreacted serpentinite) is separated by filtration. In an ideal case, the residue would consist of only SiO_2, but unfortunately, this is not the case. However, the best result to date (not accounting for results from the new rotating reactor that is now available at ÅA) has shown a 78% extent of extraction (Paper V).

4.2. Production of $Mg(OH)_2$

From the extraction step (Reactions 3 and 4, plus dissolution), the aqueous solution containing dissolved $MgSO_4$ and $FeSO_4$ (and $CaSO_4$) is subjected to a gradual increase in pH. This can be achieved by adding NH_4OH to the solution. The ammonia solution is the result of recycling the ammonia gas together with water.

In principle, all of the ammonium sulphate can be recycled as shown in the schematic overview in Figure 9, but in practice, the situation is somewhat different. It may be that not all of the reactions taking place (or species involved) during the first extraction step have been considered. If, for instance, some of the ammonia or sulphur is bound in the solid residue that is removed prior to precipitation, it will have to be compensated for downstream in the process. The minimisation of chemical losses is crucial from both a cost and environmental point of view. In a recently published paper (VI), make-up streams of both AS and ammonia solution were calculated to be necessary.

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[20] *As a byproduct of nickel mining at Hitura (Finland) a large amount of serpentinite is being processed and piled as mining tailings.*

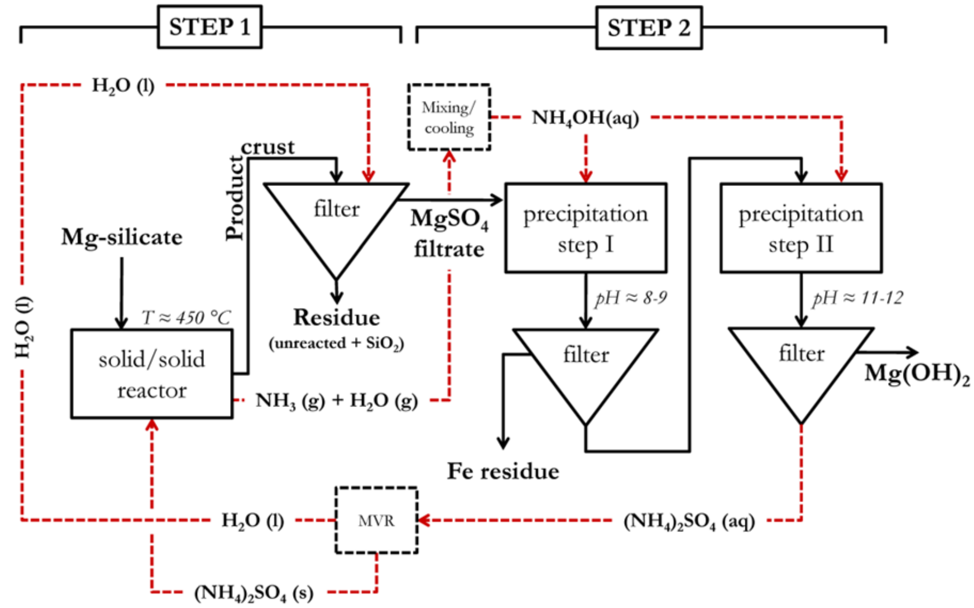

Figure 9. Schematic overview of magnesium extraction (step 1) and $Mg(OH)_2$ production (step 2) according to the ÅA CSM route. The dotted (red) lines represent material streams that can (and should) be recycled. MVR = mechanical vapour recompression.

As the pH of the filtrate from the Mg-extraction step is increased, different precipitates are formed as given by the reaction equations below:

$$\begin{gathered} FeSO_4\ (aq) + 2NH_4OH\ (aq) \\ \rightarrow Fe(OH)_2\ (s) + (NH_4)_2SO_4\ (aq) \end{gathered} \tag{5}$$

$$\begin{gathered} Fe_2(SO_4)_3\ (aq) + 6NH_4OH\ (aq) \\ \rightarrow 2Fe(OH)_3\ (s) + 3(NH_4)_2SO_4\ (aq) \end{gathered} \tag{6}$$

$$\begin{gathered} MgSO_4\ (aq) + 2NH_4OH\ (aq) \\ \rightarrow Mg(OH)_2\ (s) + (NH_4)_2SO_4\ (aq) \end{gathered} \tag{7}$$

Between pH 8 and pH 9, iron hydroxide from both Fe^{2+} and Fe^{3+} is formed (precipitation step I) and can be extracted from the solution by filtration, while an additional increase in pH to around 11 (precipitation step II) leads to the formation of $Mg(OH)_2$. In theory, after both precipitation steps, complete recovery of the now pure ammonium sulphate solution is possible by removing the excess water. This, however, can be a very energy-intensive step, but by employing mechanical vapour recompression (MVR) the only energy penalty comes from driving the compressor, which is considerably less than the energy required to evaporate the liquid (Björklöf, 2010). Naturally, there are a number of other places, especially the Mg extraction step, were energy requirements have to be considered, but AS recovery has been shown to be one of the most significant (Paper VI).

4.3. Carbonation of $Mg(OH)_2$

While developing a cost- and energy-efficient way of producing $Mg(OH)_2$ is extremely important, so is its subsequent carbonation to $MgCO_3$ for the successful employment of the ÅA CSM route. Based on previous studies of various carbonation reactions, it became evident that gas-solid carbonation quickly becomes rate-limited by the formation of a carbonate layer (Béarat *et al.*, 2006; Zevenhoven *et al.*, 2008). It was then suggested that a fluidised bed (FB) might be a suitable reactor for subsequent carbonation studies (Lackner *et al.*, 1995; Zevenhoven *et al.*, 2006b; 2008), based mainly on three properties associated with a FB reactor (Kunii and Levenspiel, 1991):

- good mixing of the solid phase, *i.e.* homogeneous bed composition,
- frequent collisions between particles,
- and uniform heat distribution.

At ÅA, a small (bed-height ~0.5 m) laboratory-scale pressurised fluidised bed (PFB) has been built to evaluate carbonation of $Mg(OH)_2$ at various pressure and temperature conditions. From Figures 10 and 11 the basic layout of the PFB setup can be seen, but it should be noted that in Figure 11, some of the heating elements have been removed to show what the actual preheater and PFB look like. The principal components of the setup are better shown in a schematic drawing, such as that in Figure 10. The temperatures of the preheater and fluidised bed are controlled individually and monitored at different locations as shown in Figure 10. In addition, the pressure and pressure difference over the bed are monitored and tracked via a computer logger.

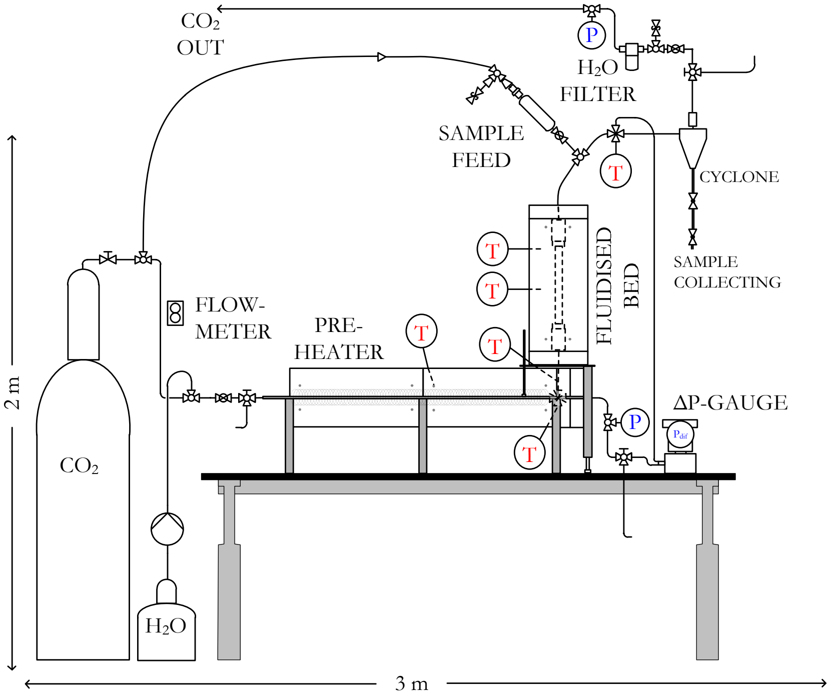

Figure 10. Overview of the lab-scale PFB setup at ÅA. Height of PFB ~0.5 m, inner diameter 1.4 cm.

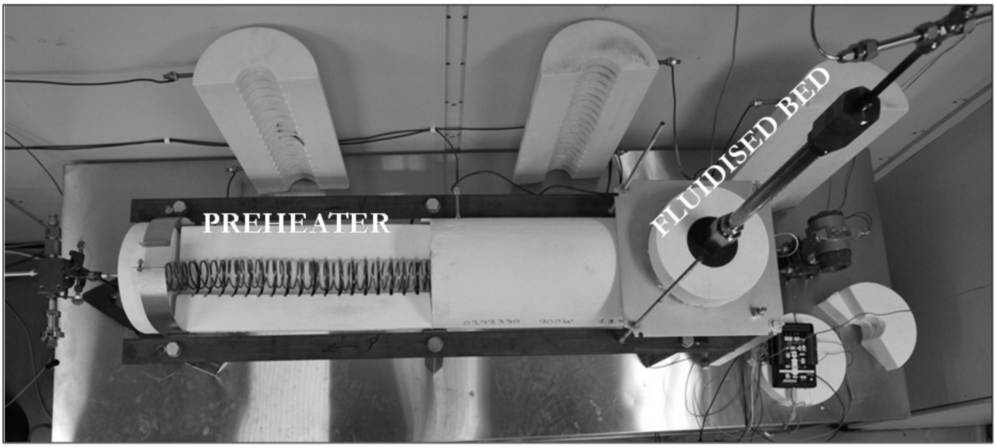

Figure 11. Photo of the PFB setup from above with some of the heating elements removed (Photo by J. Irjala)

Typically an experiment is performed by heating the system to the target temperature, inserting the sample material into the sample feeder (which is at room temperature), increasing the pressure to its target value, adjusting the gas flow to its target value (kept constant during the experiment), inserting the material from the sample feeder to the PFB, gradually increasing the flow to achieve fluidisation (monitored using the differential pressure gauge), maintain steady-state during the experiment and finally (after the experiment time is reached) blowing out the bed-material/sample for separation and removal from the cyclone. Thus, in the laboratory the PFB works on a batch principle, but on a larger scale it would be necessary to operate it in a continuous and possibly circulating fluidised bed mode, as shown in Figure 12.

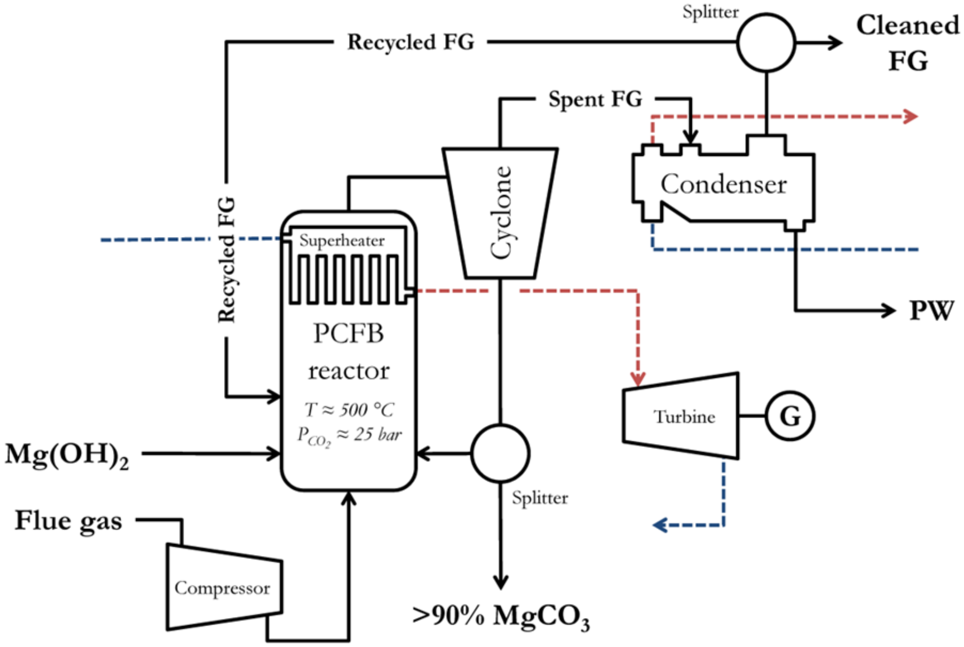

Figure 12. Schematic view of a carbonation reactor operating on CO_2 rich flue gas, the dotted lines indicating possible major heat recovery systems. PCFB = pressurised circulating fluidised bed, PW = process water.

In a preliminary (atmospheric pressure) fluidised bed experiment performed by Zevenhoven *et al.* (2005), it was noted that fluidisation does enhance carbonation. Although the overall carbonation extent of the experiment performed at atmospheric pressure was small (~5%), the extent of carbonation of the particles removed from the cyclone was almost twice as high as for the bed fraction. This result allows one to picture a process where a continuously operated FB reactor would produce a steady stream of fine $MgCO_3$ particles that could be removed by a cyclone located directly after the FB. To keep the process going, a continuous stream of $Mg(OH)_2$ would be fed into the FB, where the particles would react and the $MgCO_3$ formed would be chipped of and carried away by the passing CO_2, to be collected by the cyclone. Unfortunately however, the result achieved by Zevenhoven *et al.* (2005) could not be directly translated into production of pure $MgCO_3$ from $Mg(OH)_2$ as discussed in Paper I. The force of particle-particle interactions appears too weak to break the particles at the reaction conditions studied, together with the fact that $Mg(OH)_2$ carbonation is more complex than initially assumed (Papers I; IV; VII).

4.4. Analytical methods

For the purpose of this work, the most important parameter to consider/analyse is the carbonation degree. Fortunately, this can be achieved in a relatively simple (and cost effective) manner by measuring the gas released during the reaction between a carbonate containing sample and an acid (*e.g.* HCl). However, it should be noted that the method does not allow for distinguishing between different forms of carbonates and the CO_2 released is always compared to that of pure $MgCO_3$. Thus, a sample consisting of, for instance, pure hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) could not have a higher conversion degree than 72.1%. Nevertheless, the formation of hydrated carbonate species is unlikely due to the elevated temperature conditions employed in the PFB.

The gasometric carbonation analysis method has been presented in detail in Paper II, but the principal idea can be understood from Figure 13. Knowing the carbonate content of a sample enables the determination of its H_2O content as well by simple heating and measuring of the weight loss. The overall composition can then be given as MgO-$Mg(OH)_2$-$MgCO_3$, although X-ray diffraction (XRD) analysis has revealed the presence of other crystal structures as well (Paper VII).

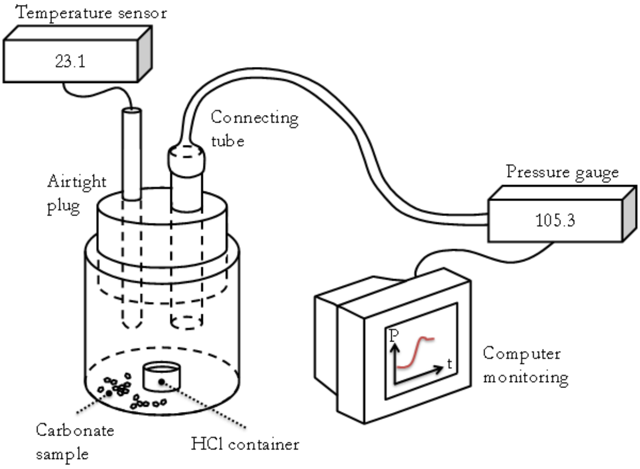

Figure 13. Gasometric determination of the carbonate content in a solid sample (Paper II).

In addition to the composition, also the particle properties have been analysed, using both scanning electron microscopy (SEM) and surface area measurements. While SEM imaging can be a very useful method for determining how the particles have been affected when subjected to carbonation in a PFB, the results achieved have not proven conclusively to determine whether carbonate layering or unreacted shrinking core behaviour occurs (Papers I, IV).

5. Key findings and discussion

As mentioned earlier, the focus of this thesis is on the carbonation of $Mg(OH)_2$ in a pressurised fluidised bed, but for the purpose of giving a better overall picture, some of the key findings (by E. Nduagu, I. Romão and R. Zevenhoven) regarding the ÅA CSM process route at large are also presented.

5.1. Mg extraction and $Mg(OH)_2$ production

Although thermodynamic equilibrium calculations (Figure 8 and *e.g.* Nduagu, 2008) predict that $MgSO_4$ would start to form below 200 °C, experiments have shown that much higher temperatures (~400 °C) give both better (i.e. a higher extraction yield) and faster results (Nduagu *et al.*, In Press 2012b). In a way, this is unfortunate, since in contrast to $Mg(OH)_2$ carbonation, the Mg extraction step is endothermic, meaning that heat has to be added to keep the process going. Therefore, it would be beneficial if the temperature of the reaction between ammonium sulphate and magnesium silicate could be kept as low as possible.

To date, an Mg extraction efficiency of around 65%[21] has been achieved (for Finnish Hitura serpentinite) using temperatures between 400 and 440 °C and reaction times between 30 and 60 minutes. However, the results are also very much dependent of other factors than temperature and time, such as Mg-silicate type, particle size fraction and ammonium sulphate (AS) to Mg-silicate ratio. Still other factors that have been considered are reactor vessel type and mixing. Below, a short list summarising the discussion and experimental results around the various factors is given (Nduagu *et al.*, In Press 2012a; In Press 2012b):

- **Temperature** - High temperatures result in faster chemical kinetics, but are restricted by the thermodynamic stability of the reactants and products involved. Thermodynamics predict that much lower temperatures than experimentally observed could be used to completely extract Mg from serpentinite, demonstrating the influence of temperature dependent chemical kinetics.
- **Time** - 30–60 minutes. Reaction times over 60 minutes seem excessive and do not favour the extraction of Mg from serpentinite, especially for temperatures around 400–500 °C, while reactions under 30 minutes are generally too short.
- **Mg-silicate type** - Serpentinite is more reactive than olivine (at least in the absence of water).
- **Particle size fraction** - Specifically, surface area and porosity have been shown important, while a suitable particle size fraction is between 75 and 125 μm.

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[21] *Recently an Mg extraction yield of 78% was reported (Paper VI) for Portuguese serpentinite.*

- **AS to Mg-silicate ratio** - Increasing the amount of AS improves Mg (and Fe) extraction, but over-stoichiometric amounts (more than three moles of AS per mole of serpentine) are detrimental to chemical recycling, as excess SO_2 would reduce the basicity of the simultaneously released ammonia that is collected and used for $Mg(OH)_2$ precipitation later on.
- **Reactor vessel type** - A critical aspect of reactivity and an important factor in scaling up. To ensure good contact between AS and the Mg-silicate, a rotary kiln is now used for additional experiments.
- **Mixing** - Effects still to be tested, but at least reproducibility should improve with homogenous mixing every time.
- **Dry vs. wet** - The benefit of using wet AS comes from reduced energy requirements of chemical recovery. In addition it appears to allow for increased reactivity at lower temperatures (Romão *et al.*, 2011), especially for Mg-silicates, such as olivine, that do not contain crystal water (as serpentine does).

In order to find the optimal conditions for Mg extraction, all of the above listed factors have to be balanced against process cost and energy requirements. While long reaction times can give higher extraction yields, it also translates into larger reactor units and higher energy demands. Similarly, small particles are known to react faster, but at some point the energy required to achieve a certain small size is outweighed by the benefits it brings. Exactly where the line in each case should be drawn is still being investigated and could vary depending on the Mg-silicate type, but recent (and earlier) results suggest that this method has significant potential for scale-up[22].

5.2. $Mg(OH)_2$ carbonation

At the outset of this study, a number of $Mg(OH)_2$ carbonation experiments were performed using a pressurised thermogravimetric analyser (PTGA) (Zevenhoven *et al.*, 2006c; 2008). The results showed that $Mg(OH)_2$ carbonation is much faster than MgO carbonation, but complete carbonation was not achieved. The experiments were performed using 75–125 μm $Mg(OH)_2$ particles from Dead Sea Periclase Ltd. (DSP), the same material that has been used for most of the PFB experiments discussed in this thesis.

The results[23] given in Figure 14 show that $Mg(OH)_2$ carbonation does improve with increasing temperature and pressure, but not in a straightforward way. The reason why the carbonation degree of the 35 bar experiments decrease with increasing temperature is not easily explained when the "approach temperature" is still positive.

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[22] *This is especially the case at locations where comparatively high value (250–400 °C) waste heat is available, such as cement plants (Paper VI).*

[23] *Two points have been removed: one performed at 370 °C and 1 bar and another that was recently (Paper VII) observed to be very likely erroneous.*

The approach temperature is defined as the difference between the equilibrium temperature and the experiment temperature (T_{eq} - T) for stable $MgCO_3$. A negative approach temperature indicates that $MgCO_3$ is not thermodynamically stable at the investigated experimental conditions. Based on previous observations (Butt *et al.*, 1996; 1998; Béarat *et al.*, 2002), carbonation increases exponentially when approaching the equilibrium temperature of stable $MgCO_3$, but from Figure 14, this effect cannot be readily observed.

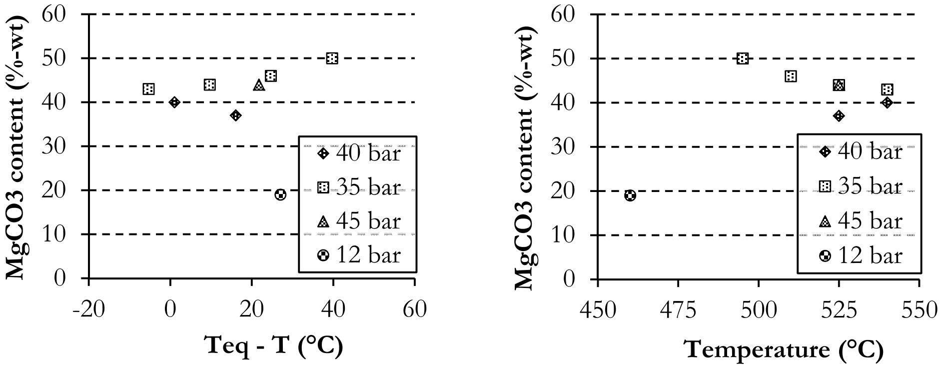

Figure 14. Carbonation extent as a function of temperature (left) and "approach temperature" for eight, six hour PTGA experiments performed using 75–125 µm DSP-$Mg(OH)_2$ at different pressures (mod. from Zevenhoven *et al.* 2008). The gas consisted of 99%-vol CO_2 and 1%-vol H_2O.

One aspect regarding the results in Figure 14 is that DSP-$Mg(OH)_2$ has a relatively low pore volume. Actually (as discussed in Paper VII), it appears that the carbonation content of this material is limited by the available pore space. This is likely due to the fact that carbonation of $Mg(OH)_2$ results in an increase in solid material volume 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. Fortunately, this is only a problem in the rare case of very low porosity material such as DSP-$Mg(OH)_2$ and experiments using $Mg(OH)_2$ from different sources have shown that pore volume limitation can be ignored (Paper VII). However, due to the fact that other sources of $Mg(OH)_2$ have been less readily available and that this phenomena was only recently identified, most of the PFB experiments to date have been performed using DSP-$Mg(OH)_2$.

Already after the first few experiments using the laboratory scale PFB (at ÅA), it became evident that experiment times of several hours are not necessary to achieve complete carbonation (Paper I) and it was realised that most of the carbonation takes place after only minutes in the PFB (Papers I; IV; VII). This is of course good news, but at the same time it became evident that (for reasons discussed below) carbonation equally quickly levelled off prior to complete carbonation and would not go to completion even after long reaction times. This suggests that the fluidising motion experienced by the particles is not able to remove the assumed[24] carbonate layer (Paper I). This is further supported by the fact that particle sizes stay largely unchanged, and significant amounts of fines are not produced. One possible solution could be to increase the fluidisation velocity considerably, but this would most likely require the use of a circulating fluidised bed. However, this is not a straightforward option either, as discussed below.

Similarly to the previous section (section 5.1), a list of factors affecting the outcome of the PFB experiments gives a convenient overview of the research in question:

- **Temperature** - The obvious way to enhance chemical reactions is to increase the temperature, as faster molecular motion also means more frequent collisions and a greater chance for chemical reactions. However, due to thermodynamic constraints, increasing the temperature too much results in solid decomposition, "calcination" (see Reaction (2), p. 22), unless the pressure of the gaseous species is also increased.
- **Pressure** - Particularly the CO_2 partial pressure is of importance and determines the maximum allowable temperature, which in turn largely governs the reaction rates. However, in the case of $Mg(OH)_2$, increasing the pressure too much reduces the reactivity as H_2O diffusion from the particle becomes hindered by a high H_2O pressure.
- **Time** - The reactivity of $Mg(OH)_2$ is high and long (> 1 h) reaction times do not favour the formation of $MgCO_3$ at elevated temperatures, where $Mg(OH)_2$ is thermodynamically unstable.
- **$Mg(OH)_2$-type** - The "type", or more specifically the properties of the $Mg(OH)_2$ particles play a critical role in determining the required reaction conditions. The "type" of $Mg(OH)_2$ depends on and can be determined by the conditions at which it is formed.
- **Particle size fraction** - In the case of a batch of $Mg(OH)_2$ from the same source, particle size fraction (ignoring the very large > 500 μm and very small < 38 μm sizes) represents a bulk-property and does not influence the reactivity significantly. However, fluidisation properties are affected by this and very fine powders represent a problem for fluidised beds. Circulating fluidised beds might allow for finer particles.
    - ***Porosity*** - If below a certain threshold value, may limit the final conversion degree. However, this is not a problem for serpentinite-derived $Mg(OH)_2$.
    - ***Surface area*** - Similarly to temperature, a key factor in determining the reactivity. A high surface area increases the

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[24] *Carbonate layer formation has not been (convincingly) detected using SEM, which is similar to what Butt et al. (1996) noted in a study on $Mg(OH)_2$ carbonation.*

initially available carbonation sites and reduces the effect of layering.

- **Bed composition** - Inserting an inert material such as SiO_2 into the FB can improve fluidisation and adds thermal inertia to the system. In addition, attrition between particles is increased, but separation of product and inert bed material can pose a problem together with the increased energy requirements of fluidisation.
- **Fluidisation velocity** - A high fluidisation velocity (but still under the terminal velocity) increases the beds motion and enhances carbonation. Compared to no fluidisation, velocities just above the minimum fluidisation velocity appear to improve reactivity the most, with little benefit achieved from additional velocity increase.
- **Dry vs. wet** - H_2O plays an important role in carbonation, even in gas-solid carbonation (Highfield *et al.*, 2011). When $Mg(OH)_2$ decomposes, which by default is necessary prior to carbonation, H_2O is released and it has been shown that H_2O catalyses carbonation (Highfield *et al.*, 2011, see also Paper VII). Thus, compared to MgO, $Mg(OH)_2$ appears much more reactive, but in the presence of some steam, even MgO starts to form carbonates at a comparatively rapid rate.

The list above is comprehensive, yet incomplete when it comes to distinguishing between different chemical reactions taking place inside the PFB reactor. For instance, increasing the temperature increases carbonation, but at the same time it also increases dehydroxylation. Similar conclusions can be drawn for the other factors as well and based on our results (and others, see Paper VII), the chemistry taking place inside the fluidised bed appears much more complex than initially assumed from the overall magnesium hydroxide carbonation equation:

$$Mg(OH)_2\ (s) + CO_2\ (g) \leftrightarrow MgCO_3\ (s) + H_2O\ (g) \qquad (8)$$

Looking at the thermodynamics for the reaction above, magnesium carbonate stability is a function of both CO_2 and H_2O pressures and the minimum partial pressure ratio for carbonate formation can be given in the form of the following equation (Zevenhoven *et al.*, 2008):

$$\ln K_p = \ln\left(\frac{p^{eq}_{H_2O}}{p^{eq}_{CO_2}}\right) = -3.535 + \frac{4794.5}{T} \qquad (9)$$

where $p^{eq}_{H_2O} / p^{eq}_{CO_2}$ is the equilibrium partial pressure ratio at a specific temperature, T. In other words, for instance at 500 °C, Reaction (8) is at equilibrium if the H_2O/CO_2 pressure ratio is close to 14.4, increasing this ratio slightly shifts the reaction to the left, while decreasing it shifts it to the right. Thus carbonation is favoured, at 500 °C, if the CO_2 pressure is more than 7% (= 1/14.4) of the H_2O pressure.

Unfortunately however, Reaction (8) is not an elementary reaction and (at least) two additional reactions need to be considered, one of which is the carbonation/calcination reaction given by Reaction (2, p. 22) and the other one is $Mg(OH)_2$ dehydroxylation according to:

$$Mg(OH)_2\ (s) \leftrightarrow MgO\ (s) + H_2O\ (g) \tag{10}$$

If thermodynamic equilibrium is reached, it is possible to predict the outcome of any chemical reaction based on thermodynamic data alone. For instance, if the CO_2 pressure is greater than $p_{CO_2}^{eq}$ at a given temperature, according to Equations (9) and (11), both MgO and $Mg(OH)_2$ should convert to $MgCO_3$.

$$\ln K_p = \ln\left(p_{H_2O}^{eq}\right) = 20.624 - \frac{13789}{T} \tag{11}$$

However, in our experiments MgO has systematically been observed in the reaction product (at conditions favouring $MgCO_3$ formation), indicating that thermodynamic equilibrium is hindered by kinetic and phase equilibrium (mixing) factors. Also it should be noted, that although bubbling fluidised beds are usually considered to provide fairly homogenous reaction conditions, the behaviour of the bed is very complex (Kunii and Levenspiel, 1991) and is likely to be a source of some discrepancy in the experimental results presented here[25]. A circulating FB reactor may perform better operating with smaller particles.

In a recently submitted paper (VII), an attempt to describe the factors affecting carbonation was made in order to explain and prevent the excessive dehydroxylation of $Mg(OH)_2$ during PFB experiments. Similarly to other heterogeneous reaction systems, gas-solid carbonation of $Mg(OH)_2$ is also highly dependent on reactive surface area (SA). The higher the area, the faster the reactions, as can be seen from the difference in carbonation degree for experiments performed using serpentinite-derived $Mg(OH)_2$ compared to DSP-$Mg(OH)_2$ in Figure 15.

The encircled experiments in Figure 15 have been performed using serpentinite-derived $Mg(OH)_2$, which has a much higher surface area and porosity than DSP-$Mg(OH)_2$. Thus, it can be seen that the reactivity of these two materials is very different at similar experimental conditions. The high level of scattering of the data shows the sensitivity of experiments to other parameters than temperature (as discussed above, p. 35–36).

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[25] *Based on the experimental results obtained so far, a more detailed investigation of the fluidisation behaviour is warranted, and the subject of ongoing $Mg(OH)_2$ carbonation optimisation studies.*

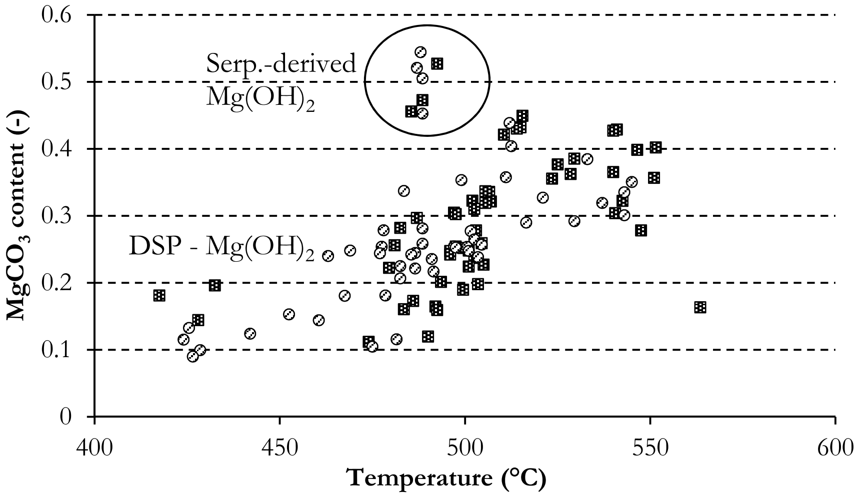

Figure 15. Results, i.e. carbonation degree, from various PFB mineral carbonation experiments as a function of temperature using mainly DSP-$Mg(OH)_2$, but also serpentinite-derived $Mg(OH)_2$, as indicated by the circle. (Squares also analysed for MgO content, and used in Figure 16)

Despite the strong scattering of the results in Figure 15, an underlying trend becomes evident when the same results (squares = analysed for MgO content as well) are plotted in a ternary diagram. This diagram shows the average composition (MgO-$Mg(OH)_2$-$MgCO_3$) of the extracted samples and interestingly enough most of the results end up on the same apparent line, in spite of the fact that the experimental conditions have been very different. The variations in experimental conditions for the "Main data" in Figure 16 have been summarised in Table 6.

Table 6. Summary of experimental conditions used to obtain the "Main data" results in Figure 16.

	PSD (μm)	**Mass (g)**	**Time (min)**	**P_{FB} (bar)**	**T_{FB} (°C)**	**T_{appr} (K)**	**v_{FB} (cm/s)**	**v_{FB}/v_{MF}**	**V_{H2O}/V_{CO2}**
Min	169	4.0	1.0	20	418	-7	2.5	0.3	0.0%
Max	363	20.0	158.0	75	564	93	21.3	2.2	16.9%
Mean	212	5.7	18.4	32	503	25	9.1	1.2	0.6%
Median	231	4.0	14.8	25	501	22	8.9	1.0	0.0%

The "Main data" in Figure 16 consists of DSP-$Mg(OH)_2$, which has a very low porosity (~0.024 cm^3/g) and it is speculated that this is the major factor influencing the carbonation results. Magnesium carbonate formation from $Mg(OH)_2$ is followed by a volume increase and incidentally the maximum carbonation degree of around 45% for DSP-$Mg(OH)_2$ fits well with the predicted maximum conversion degree obtained for a particle with the porosity of this material (Paper VII). However, not all results fit the apparent trend given in Figure 16 and these have been given different names in the figure legend. Apparently, high pressure and high surface area particle experiments behave differently to the rest, while significant potential for increased reactivity may be found when alternating between dry and humid CO_2 carbonation conditions.

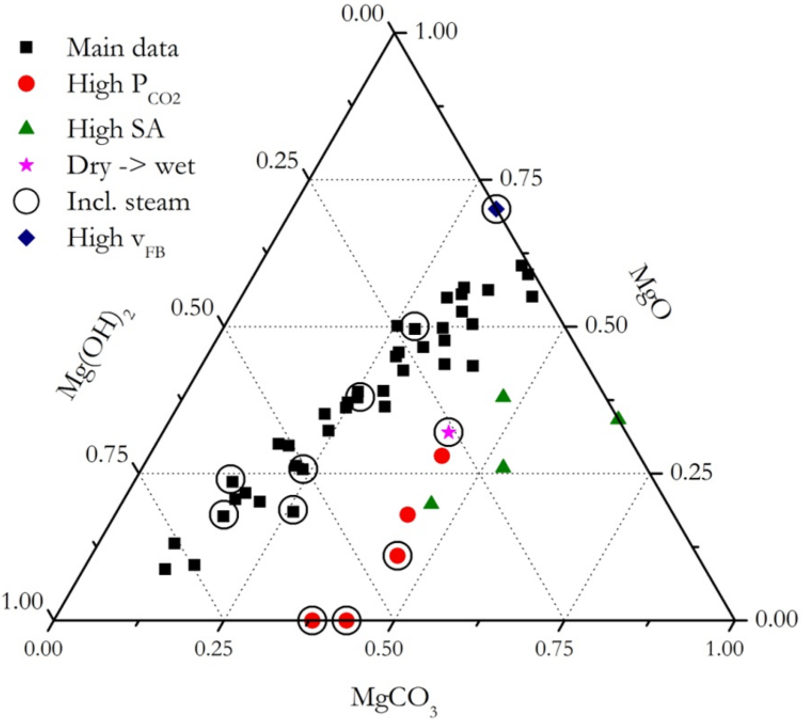

Figure 16. Ternary diagram of $Mg(OH)_2$ carbonation results obtained using a PFB at various conditions (Paper VII). Main data consists of experiment performed using DSP-$Mg(OH)_2$.

The influence of steam is one of the most interesting factors when it comes to mineral carbonation. In the case of MgO, steam has been shown to improve the carbonation significantly (Highfield *et al.*, 2011), but the same cannot be stated for $Mg(OH)_2$ carbonation. Based on previous results (Papers I; IV; VII) and the results given in Figure 16, little effect of H_2O addition can be seen, except for the single experiment performed using both dry and humid conditions (Dry → wet). The possibility to "reactivate" a completely dehydroxylated sample is intriguing, and provides an option to increase the carbonation degree of already (dry) treated samples. At the same time, it would also translate into increased complexity of the system and preferably an industrial-scale carbonation reactor would rather be operated at steady conditions.

The option of "reactivating" partially carbonated and dehydroxylated $Mg(OH)_2$, derives from the fact that MgO has been found to carbonate considerably faster in the presence of steam (Highfield *et al.*, 2011; Submitted Dec. 2011). This and research around similar materials such as calcium oxide (Lee, 2004; Manovic and Anthony, 2010), suggests that magnesium carbonation is highly dependent on the presence of H_2O, but not to its source. Whether H_2O is mixed with CO_2 in the gaseous phase or present intrinsically such as in the case of $Mg(OH)_2$ seems not very important.

In a recent paper (VII), it was suggested that the reaction between CO_2 and magnesium takes place inside a (surface formed) water layer from which $MgCO_3$

precipitates. Exactly how this reaction takes place is not clear, but has been modelled with relative accuracy for PTGA experiments using MgO and assuming the formation of an intermediate species, $MgO \cdot H_2O$. Similarly, it is assumed that the reaction between $Mg(OH)_2$ and CO_2 also goes via this intermediate species, but in the absence of steam in the gas phase, $MgO \cdot H_2O$ can either carbonate or decompose to MgO, depending on the experimental conditions.

Four different species ($MgCO_3$, MgO, $Mg(OH)_2$ and $MgO \cdot H_2O$) were used for modelling $Mg(OH)_2$ carbonation in a PFB together with a fifth parameter representing the diminishing available pore volume of the $Mg(OH)_2$ particles in accordance to the following equations:

$$\frac{\mathrm{d}c_{MgCO_3}}{\mathrm{d}t} = k_2 \cdot p_k \cdot c_{\mathrm{MH}} \cdot c_{pore}^{n_4} \tag{12}$$

$$\frac{\mathrm{d}c_{MgO}}{\mathrm{d}t} = k_3 \cdot c_{\mathrm{MH}} \tag{13}$$

$$\frac{\mathrm{d}c_{Mg(OH)_2}}{\mathrm{d}t} = -k_1 \cdot f\left(c_{Mg(OH)_2}\right) \tag{14}$$

$$\frac{\mathrm{d}c_{MH}}{\mathrm{d}t} = k_1 \cdot f\left(c_{Mg(OH)_2}\right) - k_2 \cdot p_k \cdot c_{\mathrm{MH}} \cdot c_{pore}^{n_4} - k_3 \cdot c_{MH} \tag{15}$$

$$\frac{\mathrm{d}c_{pore}}{\mathrm{d}t} = -\frac{\mathrm{d}c_{MgCO_3}}{\mathrm{d}t} \tag{16}$$

where k_1 is an Arrhenius function with a pre-exponential factor incorporating pressure, fluidization velocity and particle size, and MH stands for $MgO \cdot H_2O$. The other kinetic parameters k_2 and k_3 are described using Arrhenius kinetics coupled with individual diffusion terms $\left(1 - c_{MgCO_3}\right)^{n_i}$ that consider the effect of an growing $MgCO_3$ layer. The variable p_k is a pressure term that incorporates the effect of carbonation as an Arrhenius function, based on the fact that increasing the CO_2 pressure was found to reduce carbonation kinetics (Churakov *et al.*, 2004). Furthermore, it was found that the inverse of the temperature of the onset of dehydroxylation followed a linear trend when plotted against the natural logarithm of CO_2 pressure (Pfeiffer, In Press 2011). The term $f\left(c_{Mg(OH)_2}\right)$ stands for a dehydroxylation equation and is based on a separate analysis of the dehydroxylation behaviour. The rate of dehydroxylation and thus also the rate of conversion to reactive $MgO \cdot H_2O$ intermediate was found to obey the following diffusion equation:

$$\frac{\mathrm{d}c_{Mg(OH)_2}}{\mathrm{d}t} = -k_1 \cdot f\left(c_{Mg(OH)_2}\right) = -k_{Mg(OH)_2}\left[\left(c_{Mg(OH)_2}\right)^{-1/3} - 1\right]^{-1} \tag{17}$$

where k_1 (= $k_{Mg(OH)_2}$) is an Arrhenius-type parameter that also takes into account the particle size and fluidization velocity (determined for DSP-$Mg(OH)_2$). A summary of the results can be found below (but a more detailed description of the model is given in Paper VII).

Unfortunately, due to experimental design, no intermediate data from experiments using the PFB at ÅA can be obtained and the influence of time requires multiple experiments at similar conditions. Figure 17 shows two such sets of experiments, together with predicted composition based on a model described in Paper VII. Despite the apparent good fit of the model to the experimental data, predicting the outcome of every experiment is still highly uncertain, as can be seen from Figure 18.

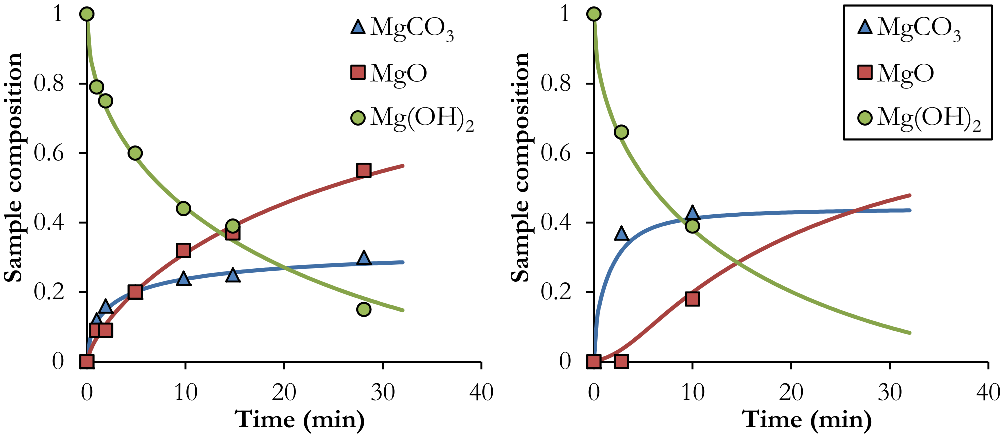

Figure 17. Two sets of PFB experiments using DSP-$Mg(OH)_2$ plotted as a function of time. Left: carbonation at 495 °C and 25 bar. Right: 540 °C and 59 bar (Paper VII).

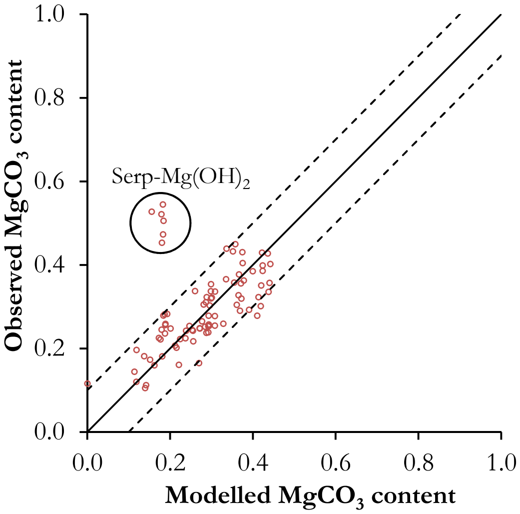

Figure 18. Observed vs. modelled $MgCO_3$ content of various PFB experiments (Paper VII).

One of the most obvious uncertainties comes from the small number[26] of experiments performed using material other than DSP-$Mg(OH)_2$, but interestingly enough, the advantage of using serpentinite-derived $Mg(OH)_2$ becomes very evident from Figure 18. Assuming that the material is DSP-$Mg(OH)_2$, the model predicts a conversion degree of around 20% compared to the actual conversion degree obtained of around 50%. Additional experiments using materials with various surface areas are still required, but although complete carbonation has not yet been achieved, it is fairly certain that given the right conditions, complete carbonation or close to complete (> 90%) carbonation can be achieved within minutes.

In the most recent experiment, the highest carbonation degree yet achieved (65% in ≤ 15 min) was obtained for a serpentinite-derived sample at the relatively severe conditions of 51 bar CO_2 and 545 °C. Interestingly enough, the results showed a composition matching $MgO{\cdot}2MgCO_3$, with a much lower theoretical CO_2 binding capacity than $MgCO_3$, or more precisely only 66.7% compared to $MgCO_3$. Even in the absence of an XRD analysis of this particular sample it appears that this so called oxymagnesite (Hladky, 1975) has formed, as it was found in most of the previously analysed samples subjected to a range of different experimental conditions.

The formation of oxymagnesite has not been discussed in the CCS literature, except for a recent mention (Ballirano *et al.*, 2010). Its thermodynamic properties are not recorded and thus its formation cannot be predicted for any specific conditions, but it is clear that the reduction in CO_2 binding capacity associated with its formation cannot be considered acceptable from a CO_2 sequestration point of view.

Similarly, the high pressure required to obtain 65% conversion is probably on the upper limit (if not already too high) of acceptable considering industrial feasibility. For instance, in view of a relatively CO_2 rich flue gas, such as that from a lime-kiln, achieving a 50 bar CO_2 partial pressure would require a total flue gas pressure of around 250 bar. Compressing flue gas to such a pressure is not only technically challenging, but highly energy demanding, requiring a very efficient energy recovery system. According to Chakravarti *et al.* (2001), compressing a typical flue gas (CO_2 content: 10%) to more than 80 bar generates more CO_2 than what can be sequestered. However, in theory (assuming an ideal gas), exergy losses (or energy that cannot be recovered by the process) due to compression are comparatively low; in the order of the energy required for grinding magnesium silicate (0.15 MJ/kg CO_2 sequestered). A more detailed analysis of energy requirements and the theoretical potential of the ÅA CSM route can be found in the following section (and more thoroughly in Paper VI). Also, it should be noted that despite the seemingly high energy requirements of

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[26] *This is largely due to the fact that producing significant quantities of serpentinite-derived $Mg(OH)_2$ has not been possible, while the Mg-extraction step is still being developed.*

mineral carbonation, process integration and optimisation reduces the overall energetic costs significantly.

5.3. Process scale-up

The usual approach to scaling up a process involves the principle of similarities, where different parameters are grouped together (into so called dimensionless groups) and their mutual relationships are held constant during scale-up. In the case of fluidised beds, it can only be noted that scale-up has been recognised as a particularly challenging task (Rüdisüli *et al.*, In Press 2011) and any future process involving gas-solid carbonation in a PFB will require a great deal of attention.

Based on preliminary attempts at scaling up the Mg-extraction step, it has also become evident that it needs to be modified. Simple batch-processing of for example serpentinite and AS in an unmixed reactor vessel is not sufficiently successful and another approach is required. For this, a rotating tube reactor has been purchased that allows for considerably larger (120 g vs. 5 g) batches of samples to be processed.

Following the Mg-extraction step is the $Mg(OH)_2$ production, which also requires some optimisation still. One important aspect, which to date has been overlooked, is the controlling of the properties (*e.g.* particle size, surface area) of the $Mg(OH)_2$ produced. As discussed in section 5.1, the properties of $Mg(OH)_2$ have a considerable impact on the reaction conditions required for the carbonation step and higher surface area particles could allow for less severe carbonation conditions.

5.3.1. Simulating a CSM plant

Assuming that the practical problems, such as increasing Mg extraction yield and conversion and determining large-scale equipment requirements, are solved and the processes optimised what might an actual mineral carbonation plant designed in accordance to the ÅA CSM route look like? How large would the material streams be, and how much CO_2 could be avoided? To answer these questions, findings, based largely on a Paper VI, are given here.

The ÅA CSM route has been modelled using Aspen Plus® software and a number of different scenarios have been considered. In the simplest case, not requiring Aspen simulations, it was calculated based on chemical conversions alone that ideally (assuming complete Mg extraction and carbonation), 2.5 kg of rock (Hitura-type serpentinite) together with 3.98 MJ of energy (as heat) is required to sequester 1 kg of CO_2. This is unacceptably high considering that it does not even include the energy requirements associated with CO_2 capture. Thus, it can be concluded that, as such, the process is too energy intensive and integration with other alternatives is required.

Considering that the Mg extraction step can result in a considerable (depending on the Mg-silicate) amount of iron by-product, one obvious option would be to link the process with iron- and steel industry, as also modelled by Romão *et al.* in Paper VI.

This would reduce the raw material requirements of the steel industry and result in an overall CO_2 reduction much higher than that of the simple stand-alone case. It was estimated that (assuming 80% Mg extraction and complete carbonation), 2.22 MJ as heat at 125–550 °C, 0.82 MJ as power and 3.1 kg of rock would be required to sequester 1 kg of CO_2. It was assumed that CO_2 would be supplied to the site via a pipeline at 140 bar, enabling a significant energy recovery due to expansion to the reaction pressure (50 bar). In addition, grinding of serpentinite was not included in the model, but its share of the overall power requirements should be modest in the order of 0.15 MJ/kg CO_2 sequestered (Gerdemann *et al.*, 2007).

In accordance to a simple model presented by Huijgen *et al.* (2006)[27] for the efficiency of CO_2 sequestration:

$$\begin{aligned}\eta(CO_2) &= \frac{\mathrm{CO_2\ avoided}}{\mathrm{CO_2\ sequestered}} \times 100\ \% = \\ 100 &- \frac{\mathrm{E_{power}} \cdot \varepsilon_{\mathrm{power}} + \mathrm{E_{heat}} \cdot \varepsilon_{\mathrm{heat}}}{\mathrm{CO_2\ sequestered}} \times 100\ \%\end{aligned} \tag{18}$$

where E_{power} and E_{heat} are the amounts of power and heat required by the carbonation process (kWh) and ε_{power} and ε_{heat} represent the amounts of CO_2 emitted while doing so (kg CO_2/kWh), the efficiency of the process would be 74% (or 71.5% with grinding). This result is obtained using previously determined values for ε_{power} and ε_{heat}, *i.e.* 0.6 and 0.2 kg CO_2/kWh, respectively (Huijgen *et al.*, 2006). However, it should be noted that these values can be subject to significant changes depending on the source (and temperature) of heat and power (as discussed in the Appendix of Paper III).

Based on the values above, a large scale (0.1 Mt/CO_2 year) mineral carbonation plant would require some 35.4 t/h of rock processing, while simultaneously producing 2.6 t/h of iron by-product, 22.5 t/h mineral residue and 21.7 t/h of $MgCO_3$. Assuming that the CO_2 would derive from a coal fired (30 MJ/kg) combined heat and power (CHP) plant with typical thermal and power efficiencies of 62% and 28%, respectively, the overall power output of the plant would be reduced by 46%. This large reduction in power output comes from the fact that also CO_2 capture consumes a lot of power (for instance around 20% of total output for a coal-fired power plant (Feron, 2010)) and helps to point out the necessity of a combined capture and mineralisation unit, *i.e.* CSM.

Figure 19 shows the major mass and energy streams associated with a stand-alone mineralisation unit working with pure CO_2 transported via pipeline from a 10 MWe CHP power plant. The iron extraction efficiency is assumed to be 45% and the overall

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[27] *See also the appendix of Paper III, for a more detailed CO_2 sequestration efficiency estimation procedure based on exergy analysis.*

composition of the serpentinite rock to be 83% serpentine, 13% FeO and 4% other. Based on the assumptions given above the amount of rock material that requires processing is considerably larger than for example the amount of coal, 35.4 t/4.3 t = 8.3, suggesting that the optimal location for the mineral carbonation plant should be close to the Mg-silicate mine.

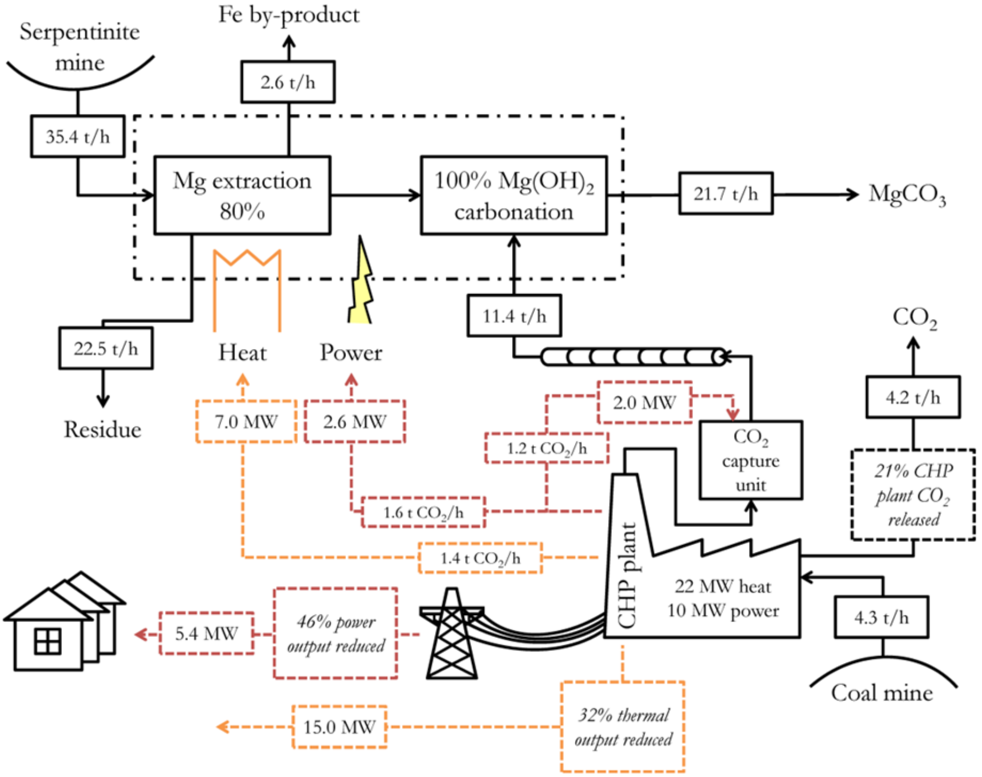

Figure 19. Stand-alone mineralisation of CO_2 derived from a CHP plant with CO_2 capture. Mineral carbonation plant values based on data from Paper VI.

The huge reductions in both thermal (32%) and power (46%) efficiencies due to CO_2 capture and mineralisation render the option depicted in Figure 19 unreasonable, but there are a number of alternatives to reduce the energetic and financial costs. The most significant coming from the possibility to:

- combine CO_2 capture and mineralisation (no need for a separate CO_2 capture unit),
- drive the Mg extraction step with industrial waste heat,
- reduce the heating requirements of the Mg extraction step,
- recover the AS salt,
- and utilise the solid products in a meaningful way.

All of the above listed improvement opportunities are very reasonable, but as of yet lack experimental verification. In addition, although CO_2 capture and storage could be achieved in a single step, it will require flue gas compression that could be both technically and energetically challenging. Reducing the Mg extraction heat requirements or increasing the yield seem theoretically possible and adding some water to the solid-solid Mg-extraction step has been shown to reduce the heating requirements by around 50 °C (Romão *et al.*, 2011). Also, the product streams are of importance in making the process route economically feasible, but to date little research has been directed towards this field.

6. Conclusions and suggestions for future work

Mineral carbonation, also known as carbon dioxide mineralisation, has been studied as a way to mitigate climate change for just over twenty years and despite being a potentially successful way to reduce point-source CO_2 emissions, it has not yet received large-scale global recognition. Since 2000, however, mineral carbonation has attracted more and more attention within the framework known as carbon dioxide capture and storage (CCS), mostly due to the fact that other CCS options are not progressing fast enough or are limited by some other means. For instance, Finland lacks suitable underground storage formations for CO_2, rendering the only options for large-scale CCS to be mineral carbonation (not accounting for CO_2 export).

Fortunately however, Finland is rich in suitable Mg-silicate minerals making it an ideal location for implementing CO_2 mineralisation. While no single best option for achieving mineral carbonation yet exists, *ex situ* mineral carbonation according to the ÅA CSM route presented here, is currently one of the only (for an *in situ* alternative, see also Kelemen *et al.* 2011) routes aiming at utilising the heat provided by the high temperature exothermic carbonation reaction. The heat of reaction is significant, and in the case of $Mg(OH)_2$ carbonation, results in high temperature steam which could be utilised to minimise the energy requirements of its production.

Producing $Mg(OH)_2$ from serpentinite or some other Mg-silicate rock is at present more energy intensive than what its subsequent carbonation can cover for. Thus, in order to make the ÅA CSM route economically interesting, integration with suitable industries such as cement- or steel- is required. Utilising waste heat for $Mg(OH)_2$ production together with the possibility to utilise flue gas instead of pure CO_2 for carbonation provides a very interesting alternative to paying CO_2 emission taxes. Additional benefits could come from creating markets for the processed (end) materials of the discussed mineral carbonation route, including SiO_2 rich residue, FeOOH and $MgCO_3$. Particularly in countries (such as Singapore) that are looking to further expand their land area, the possibility to produce large amounts of material suitable for land reclamation is a very powerful motivator for developing mineral carbonation.

Experiments have shown that both Mg extraction and $Mg(OH)_2$ carbonation are feasible, but the need for further improved extraction (> 90%) and carbonation yields (> 90%) are still evident. Currently, the best results showed extraction and (quite rapid) carbonation efficiencies of around 65% (rendering the overall Mg utilisation efficiency to just over 40%). Here the focus has been on the carbonation step and although it has been more challenging than initially assumed, significant understanding of the factors controlling the reaction kinetics have been obtained. It is evident that initial carbonation of $Mg(OH)_2$ is fast, but becomes limited by the lack of reactive surface sites even when using a fluidised bed. This limitation can be avoided by optimising the $Mg(OH)_2$ particle properties and carefully controlling the rate of dehydroxylation that is apparently closely connected to the rate of carbonation. In addition, changing from a bubbling fluidised bed to a circulating one is still to be tested (allowing for finer particles).

Water is a necessary element in magnesium carbonation, but it does not need to be present in the fluidising gas: it is enough (or even better) if it is provided intrinsically, *i.e.* as a result of $Mg(OH)_2$ dehydroxylation. Therefore, future carbonation experiments will focus on finding the conditions that prevent excessive dehydroxylation, thereby allowing for complete carbonation. To achieve this, a combination of $Mg(OH)_2$ properties, temperature, CO_2 and H_2O partial pressures, and fluidisation velocity needs to be carefully balanced. The addition of impurities, which are present in typical industrial flue gases, needs to be accounted for and at least SO_2 has been shown to have a significant affinity for $Mg(OH)_2$ at conditions favouring $MgCO_3$. These issues must be dealt with when operating CSM on a flue gas directly, without CO_2 pre-separation.

Besides improving the carbonation extent, extracting Mg from Mg-silicates needs even more attention as it stands for the largest energy penalties at present. In the process models given in Paper VI it was noted that the biggest energy penalty is associated with the solid-solid reaction, and research is currently ongoing to improve the extraction efficiency and reduce the required reaction temperature by means of a rotary kiln and H_2O addition (steam or moist AS). AS recovery is another major energy sink, which, however, could be diminished by employing mechanical vapour recompression (MVR).

In short, while the process considered here is still not ready for large-scale implementation, a number of important questions have been answered. It seems that the major obstacles have been identified allowing for future research efforts to be more accurately directed to where they are needed. This, together with the fact that the knowhow of mineral carbonation processes at large (both abroad and within ÅA) has increased considerably during the past few years gives reason to expect that lab-scale testing is about to give way for larger scale application and demonstration.

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