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**FIXATION OF CARBON DIOXIDE BY PRODUCING
CARBONATES FROM MINERALS AND STEELMAKING
SLAGS**

Doctoral Dissertation

Sebastian Teir



**Helsinki University of Technology
Faculty of Engineering and Architecture
Department of Energy Technology**

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Sebastian Teir

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Engineering and Architecture for public examination and debate in Auditorium K216 at Helsinki University of Technology (Espoo, Finland) on the 2nd of June, 2008, at 12 noon.

**Helsinki University of Technology
Faculty of Engineering and Architecture
Department of Energy Technology**

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Supervisor	Carl-Johan Fogelholm, Prof.		
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Abstract			
<p>Capture and storage of carbon dioxide (CO₂) is internationally considered to be one of the main options for reducing atmospheric emissions of CO₂. In Finland, no suitable geological formations are known to exist for storing captured CO₂. However, fixing CO₂ as solid carbonates using silicate-based materials is an interesting alternative. The magnesium silicate deposits in Eastern Finland alone could be sufficient for storing 10 Mt CO₂ each year during a period of 200-300 years. Finnish steelmaking slags could also be carbonated, but the amounts produced provide a much smaller potential for CO₂ storage (0.5 Mt CO₂ per year) than magnesium silicates provide.</p> <p>The aim of this thesis was to study the possibility of reducing CO₂ emissions by producing calcium and magnesium carbonates from silicate materials for the long-term storage of CO₂ using multi-step processes. The production of carbonates from steelmaking slags and serpentinite, a magnesium silicate ore available from a metal-mining site, was studied both experimentally and theoretically. On the basis of the results, process concepts were developed and evaluated. Finally, the stability of synthetic calcium and magnesium carbonates as a medium for CO₂ storage was assessed.</p> <p>Experiments with aqueous extraction and precipitation processes showed that magnesium and calcium can easily be extracted from steelmaking slags and natural silicate minerals using acids. Natural minerals seem to demand stronger acids for extraction than slags. Relatively pure calcium carbonate (80-90% calcite) was produced at room temperature and a CO₂ pressure of 1 bar by adding sodium hydroxide to acetate solutions made from slag. Similarly, serpentinite was successfully converted into 93-100% pure hydromagnesite (a magnesium carbonate), using nitric acid or hydrochloric acid for the dissolution of serpentinite and sodium hydroxide for precipitation. The conversion of raw material to carbonate ranged from 60-90%. Although the results show that pure carbonates can be produced from industrial by-products and mining residues, the process concept suggested requires the recycling of large amounts of sodium hydroxide and acid, as well as low-grade heat for solvent evaporation. The methods suggested for recovering the spent chemicals were found to be expensive and cause more CO₂ emissions than the amount of CO₂ stored.</p>			
Keywords mineral carbonation, slag, carbon dioxide, dissolution, precipitation, carbonate			
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<p>Infångning och lagring av koldioxid (CO₂) anses på internationell nivå som en av de huvudsakliga alternativen för att minska på utsläppen av koldioxid till atmosfären. I Finland finns det inga kända geologiska formationer lämpliga för lagring av infångad koldioxid. Bindning av koldioxid som fasta karbonater genom användning av silikatbaserade material är emellertid ett intressant alternativ. Magnesiumsilikatfyndigheterna i enbart Östra Finland kunde räcka till för att årligen lagra 10 Mt CO₂ under en period på 200 – 300 år. Finsk stålslagg kunde också karboneras, men produktionsmängden kunde stå för en mycket mindre koldioxidlagringspotential (0.5 Mt CO₂ per år) än vad magnesiumsilikaterna kunde stå för.</p> <p>Målsättningen för avhandlingen var att studera möjligheten att minska på koldioxidutsläppen genom att tillverka kalcium- och magnesiumkarbonater från silikatmaterial med flerstegsprocesser för långtidslagring av koldioxid. Tillverkningen av karbonater från stålslagg och serpentinit, en magnesiumsilikatmalm som är tillgänglig från en metallgruva, studerades experimentellt och teoretiskt. På basen av resultaten utvecklades och evaluerades ett processkoncept. Slutligen fastställdes stabiliteten av syntetiska kalcium- och magnesiumkarbonater som koldioxidlagringsmedia.</p> <p>Experiment med vätskeutvinnings- och utfällningsprocesser visade att kalcium och magnesium kan lätt utvinnas från stålslagg och naturliga silikatmineraler genom att använda syror. Naturliga mineraler verkar kräva starkare syror för utvinning än vad slagg kräver. En rätt så ren kalciumkarbonat (80 – 90 % calcit) fälldes ut vid rumstemperatur och 1 bar CO₂ tryck genom att tillsätta natriumhydroxid till acetatlösningar tillverkade från slagg. På liknande vis konverterades serpentinit till 93 – 100 % ren hydromagnesit (en form av magnesiumkarbonat) genom att använda salpetersyra eller saltsyra för att lösa serpentiniten och natriumhydroxid för utfällningen. Konversionen från råmaterial till karbonat uppgick till 60 – 90 %. Fastän resultaten visar att ren karbonat kan produceras från industriella sidoprodukter och gruvdriftsresidual kräver processkonceptet återvinning av stora mängder av natriumhydroxid och syra samt lågkvalitetsvärme för förångning av lösningsmedel. Föreslagna metoder för återvinning av använda kemikalier konstaterades kostsamma och skulle ge upphov till mera koldioxidutsläpp än den lagrade mängden.</p>			
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Preface

Before you continue to read this thesis, I would ask you to take time and reflect upon one of the most serious threats that mankind has ever created for itself. Human activities have released so much CO₂ into the atmosphere that the current level has not been reached in the last 650,000 years, and still the emissions keep increasing. The latest reports from international experts stress the importance of stabilising our CO₂ emissions within the next 20-30 years. The urgency of reducing our CO₂ emissions has been my main motivation for carrying out this work. Considerable advances in technology for mitigating climate change are needed that will limit our CO₂ emissions considerably. Recent research has also shown that reducing our carbon footprint now will cost us much less than trying to reduce it in 20-30 years' time. Although global climate change is a serious threat, its mitigation is an important opportunity for global co-operation on a scale that has never been carried out before. We would save not only our environment but also our economy and our future.

The work presented in this thesis was carried out in the framework of three projects: "Nordic CO₂ sequestration" (NoCO₂, 2003-2007), funded by Nordic Energy Research, as well as "CO₂ Nordic Plus" (2003-2005) and "Slag2PCC" (2005-2007), funded by the Finnish Funding Agency for Technology and Innovation (TEKES), the Finnish Recovery Boiler Committee, Ruukki, UPM, and Wärtsilä. The projects were also supported by the Geological Survey of Finland, Outokumpu, Aker Kvaerner, Enprima, Foster-Wheeler Energy, Fortum, and Nordkalk. The Academy of Finland's "ProDOE"-project (2007-2010) is also acknowledged for support during the final stages of writing this thesis. I also thank the Graduate School in Energy Technology for a scholarship during 2007, as well as the Walter Ahlström foundation, Vasa Nation, and the Foundation for Promotion of Technology (TES) for research grants.

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providing part of the equipment needed for the experiments and Rita Kallio for analysis services. I thank Soile Aatos, Peter Sorjonen-Ward and Olli-Pekka Isomäki for discussion and information about serpentinites. I also thank the people at Ruukki, Ovako, Outokumpu, Nordkalk, and Dead Sea Periclase for providing us with slag and mineral samples for our experiments. Special thanks also go to all my colleagues and friends in the projects. I thank my parents Mona-Lisa and Henrik, as well as my sister Sabina, for their love and the support they continue to give me, and my friends for giving me something else to think about. Finally, I want to thank Heidi for giving me her love, support, strength, uncompromised opinions, and inspiration.

A handwritten signature in black ink, appearing to read 'Sebastian Teir', with a stylized flourish at the end.

Sebastian Teir

Espoo, 21st April 2008

List of publications

- I. TEIR, S., ELONEVA, S., ZEVENHOVEN, R., 2005. Production of precipitated calcium carbonate from calcium silicates and carbon dioxide. *Energy Conversion and Management*, 46, 2954-2979.
- II. TEIR, S., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Dissolution of Steelmaking Slags in Acetic Acid for Precipitated Calcium Carbonate Production. *Energy*, 32(4), 528-539.
- III. ELONEVA, S., TEIR, S., SAVOLAHTI, J., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Co-utilisation of CO₂ and Calcium Silicate-rich Slags for Precipitated Calcium Carbonate Production (Part II). In: *Proceedings of ECOS 2007, Padua, Italy, 25-28 June 2007, Volume II, 1389-1396* (submitted in a reworked form to *Energy*, March 2007).
- IV. TEIR, S., REVITZER, H., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Dissolution of natural serpentinite in mineral and organic acids. *International Journal of Mineral Processing*, 83(1-2), 36-46.
- V. TEIR, S., KUUSIK, R., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Production of magnesium carbonates from serpentinite for long-term storage of CO₂. *International Journal of Mineral Processing*, 85(1-3), 1-15.
- VI. TEIR, S., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2007. Carbonation of minerals and industrial by-products for CO₂ sequestration. In: *Proceedings of IGEC-III, 2007. The Third International Green Energy Conference. June 17-21, 2007, Västerås, Sweden. ISBN: 978-91-85485-53-6 (CD-ROM)* (a reworked version of this paper has been accepted for publication in *Applied Energy*, March 2008)
- VII. TEIR, S., ELONEVA, S., FOGELHOLM, C.-J., ZEVENHOVEN, R., 2006. Stability of Calcium Carbonate and Magnesium Carbonate in Rainwater and Nitric Acid Solutions. *Energy Conversion and Management*, 47, 3059-3068.

The author's contribution to the appended publications

- I. Sebastian Teir was responsible for planning and performing the process modelling and calculation work. The author also carried out half of the literature review, while the other half was carried out by Sanni Eloneva. The author was also responsible for the interpretation of the results and writing the paper.
- II. Sebastian Teir planned and carried out the experiments, as well as the interpretation of the results, in collaboration with Sanni Eloneva. Sebastian Teir carried out the thermodynamic calculations and wrote most of the article.
- III. Sebastian Teir planned and carried out the experiments in collaboration with Sanni Eloneva and assisted her with the interpretation of the results.
- IV. Sebastian Teir was responsible for all the experimental work except for the solvent selection experiment series, which was carried out by Hannu Revitzer. Sebastian Teir was responsible for planning the research, the experimental design, the interpretation of the results, performing the kinetic analysis, and writing the paper.
- V. Sebastian Teir was responsible for planning the research, the experimental design, performing the experiments, the interpretation of the results, and writing the paper.
- VI. Sebastian Teir was responsible for the process evaluation, the interpretation of the TGA analysis results, and writing the paper.
- VII. Sebastian Teir planned and carried out the experiments, as well as the interpretation of the results, in collaboration with Sanni Eloneva. Sebastian Teir wrote most of the article and carried out all the thermodynamic calculations.

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Nomenclature

Abbreviations

AAS	Atomic absorption spectrophotometry
AOD	Argon-oxygen decarburisation
BOF	Basic oxygen furnace
CCS	Carbon dioxide capture and storage
EAF	Electric arc furnace
ECBM	Enhanced coal bed methane recovery
EOR	Enhanced oil recovery
FT-IR	Fourier transform – infrared spectroscopy
ICP-AES	Inductively coupled plasma – atomic emission spectrometry
PCC	Precipitated calcium carbonate
SEM	Scanning electron microscope
TC	Total carbon content
TGA	Thermogravimetric analysis
TOC	Total organic carbon content
XRD	X-Ray diffraction
XRF	X-Ray fluorescence

Chemical compounds, minerals and rocks

Al_2O_3	Aluminum oxide
$\text{Ca}(\text{CH}_3\text{COO})_2$	Calcium acetate
CaCl_2	Calcium chloride
CaCO_3	Calcium carbonate (calcite, aragonite, vaterite); limestone
CaO	Calcium oxide; lime
$\text{Ca}(\text{OH})_2$	Calcium hydroxide; hydrated lime
CaSiO_3	Calcium metasilicate; wollastonite
CH_3COOH	Acetic acid
CH_3COONa	Sodium acetate
CO_2	Carbon dioxide
EDTA	Ethylenediaminetetraacetic acid
FeCO_3	Iron (II) carbonate; siderite
Fe_2O_3	Iron (III) oxide; hematite

Fe_3O_4	Iron (III) oxide; magnetite
Fe_2SiO_4	Iron (II) orthosilicate; fayalite
HCl	Hydrochloric acid
H_2CO_3	Carbonic acid
HCOOH	Formic acid
HF	Hydrofluoric acid
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
KOH	Potassium hydroxide
$\text{Mg}(\text{CH}_3\text{COO})_2$	Magnesium acetate
MgCl_2	Magnesium chloride
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Magnesium chloride hexahydrate
MgCO_3	Magnesium carbonate; magnesite
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	Magnesium carbonate trihydrate; nesquehonite
$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	Magnesium carbonate pentahydrate; lansfordite
$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	Magnesium carbonate; hydromagnesite
$\text{Mg}(\text{NO}_3)_2$	Magnesium nitrate
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Magnesium nitrate hexahydrate
MgO	Magnesium oxide; periclase
$\text{Mg}(\text{OH})_2$	Magnesium hydroxide; brucite
$\text{Mg}(\text{OH})\text{Cl}$	Magnesium hydroxide chloride
MgSO_4	Magnesium sulphate
MgSiO_3	Magnesium metasilicate; enstatite
Mg_2SiO_4	Magnesium orthosilicate; olivine (fosterite)
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Serpentine (chrysotile, lizardite, antigorite)
NH_3	Ammonia
NH_4Cl	Ammonium chloride
NH_4NO_3	Ammonium nitrate
NH_4OH	Ammonium hydroxide
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulphate
$(\text{NH}_4)_2\text{CO}_3$	Ammonium carbonate
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
NaHCO_3	Sodium bicarbonate
NaNO_3	Sodium nitrate
NaOH	Sodium hydroxide; caustic soda
SiO_2	Silicon dioxide; silica

Symbols

b	Stoichiometric coefficient	[-]
C_i	Molar concentration of i	[mol cm ⁻³]
D_e	Effective diffusion coef. in a porous structure	[cm ² s ⁻¹]
E	Activation energy	[kJ mol ⁻¹]
ΔG	Gibbs energy change	[kJ mol ⁻¹]
ΔH	Reaction enthalpy	[kJ mol ⁻¹]
k	Reaction rate constant	[s ⁻¹]
k_0	Frequency factor	[s ⁻¹]
K	Thermodynamic equilibrium constant	[-]
Q	Heat demand	[J]
P	Power demand	[J]
n	Amount of species	[mol]
ρ	Molar density	[mol cm ⁻³]
r	Radius of particle	[cm]
R	Ideal gas constant: 8.3145	[J K ⁻¹ mol ⁻¹]
R^2	Multiple regression correlation coefficient	[-]
t	Reaction time	[s]
T	Temperature	[K]
V	Volume	[l]
X_i	Conversion of i	[-]

1 Introduction

Since the mid-19th century, the global average surface temperature has increased by almost one degree Celsius, which is likely to be the largest increase in temperature during the past 1300 years (IPCC, 2007). Eleven of the last twelve years (1995-2006) were among the 12 warmest years since 1850. A few of the visible impacts of climate change are the widespread retreat of mountain glaciers, the rise in the global average sea level, and the increasing frequency and intensity of droughts in recent decades. While natural changes in the climate are common, it is now very likely that human activities have attributed significantly to the warming of the climate since the year 1750.

Certain gases in the atmosphere, mainly carbon dioxide (CO₂) and water vapour, trap infrared (heat) radiation from the Earth's surface, while letting solar radiation pass through. This heat-trapping mechanism, called the natural greenhouse effect, helps to keep the Earth's surface temperature, which otherwise would be around -19 °C, at an average of 14 °C. However, during the last two centuries the concentration of greenhouse gases (most importantly CO₂, but also methane, nitrous oxide, and fluorinated gases) and aerosols in the atmosphere has increased drastically as a result of human activities. According to data collected from ice cores, the current atmospheric concentration of CO₂ (380 ppm) exceeds by far the natural range over the last 650,000 years (180 to 300 ppm) (IPCC, 2007). Emissions of greenhouse gases are expected to continue to rise and strengthen the greenhouse effect, which is projected to lead to a rise in the average temperature of 1-6 °C during the next century (IPCC, 2001b).

The main source of anthropogenic CO₂ emissions (about three-quarters) is the combustion of fossil fuel. The rest is mainly due to land use changes, especially deforestation. Several industrial processes (such as oil refining and the manufacturing of cement, lime, and steel) are also significant sources of CO₂. The annual anthropogenic CO₂ emissions are currently about 26 Gt¹ CO₂ (IPCC, 2007).

Significant technological developments in reducing greenhouse gas emissions have been achieved during recent decades. Technological options for the reduction of emissions include more effective energy use, improved energy conversion technologies, a shift to low-carbon or renewable biomass fuels, a shift to nuclear power, zero-emissions technologies, improved energy management, the reduction of industrial by-product and process gas emissions, and carbon capture and storage (IPCC, 2001a). However, according to IPCC, none of these options alone can achieve the required reductions in greenhouse gas emissions. Instead, a

¹ 1 Gt = 1,000 Mt = 1,000,000 kt = 1,000,000,000 tonne

combination of these mitigation measures will be needed to achieve a stabilisation of the greenhouse gas concentration in the atmosphere.

According to the commitments under the 1997 Kyoto Protocol, industrial countries should reduce their greenhouse gas emissions by an average of 5% from their 1990 levels during 2008-2012 (Ministry of the Environment, 2001). The Kyoto protocol binds Finland to reduce its greenhouse emissions to their 1990 level (77.1 Mt CO₂ equivalent, excluding land use changes and forestry). According to the Ministry of Trade and Industry (2005), the permitted emission limit is likely to be exceeded by 15%, approximately 11 Mt per year, during the Kyoto protocol period 2008-2012.

1.1 Capture and storage of CO₂

Carbon dioxide capture and storage (CCS; CO₂ sequestration) is considered to be one of the main options for reducing CO₂ emissions caused by human activities. The concept of CCS includes the collection and concentration of CO₂ produced by an industrial or energy-related source (referred to as CO₂ capture), the transportation of CO₂ to a suitable storage location, and the storage of CO₂ in isolation from the atmosphere. CCS would significantly reduce current CO₂ emissions, allowing fossil fuels to continue to be used in the future.

The purpose of CO₂ capture is to produce a concentrated stream of CO₂ at high pressure that can be transported to a storage site (IPCC, 2005). For the energy sector, there are three main approaches to capturing the CO₂ generated from fossil fuels, biomass, or mixtures of these fuels, depending on the process or power plant application to which CO₂ capture is applied: post-combustion, pre-combustion, and oxy-fuel combustion systems (Figure 1.1). *Post-combustion* systems separate CO₂ from a flue gas stream², typically using a liquid solvent such as monoethanolamine. It is used for absorbing CO₂ from part of the flue gases from a number of existing power plants. It is also in commercial use in the natural gas processing industry. *Pre-combustion* systems remove CO₂ before combustion by employing gasification, water-shifting, and CO₂ separation. This technology is widely applied in fertiliser manufacturing and in hydrogen production. *Oxy-fuel combustion* systems use oxygen, instead of air, for the combustion of the primary fuel to produce a flue gas that consists mainly of water vapour and CO₂. This relatively new technology requires the production of pure oxygen from air and results in a flue gas with high CO₂ concentrations from which the water vapour is removed by condensation.

The main challenge for the development of CO₂ capture technology is to reduce the energy requirements of the capture processes. The energy needed for capturing 90% of the CO₂ from a power plant increases the fuel consumption per unit of electricity produced by

² Flue gases from power plants burning fossil fuel typically contain 3-15 vol-% CO₂.

11-40% (using the best current technology compared to power plants without capture; IPCC, 2005). Therefore, CO₂ capture also increases the cost of electricity production by 35-85% (Table 1.1).

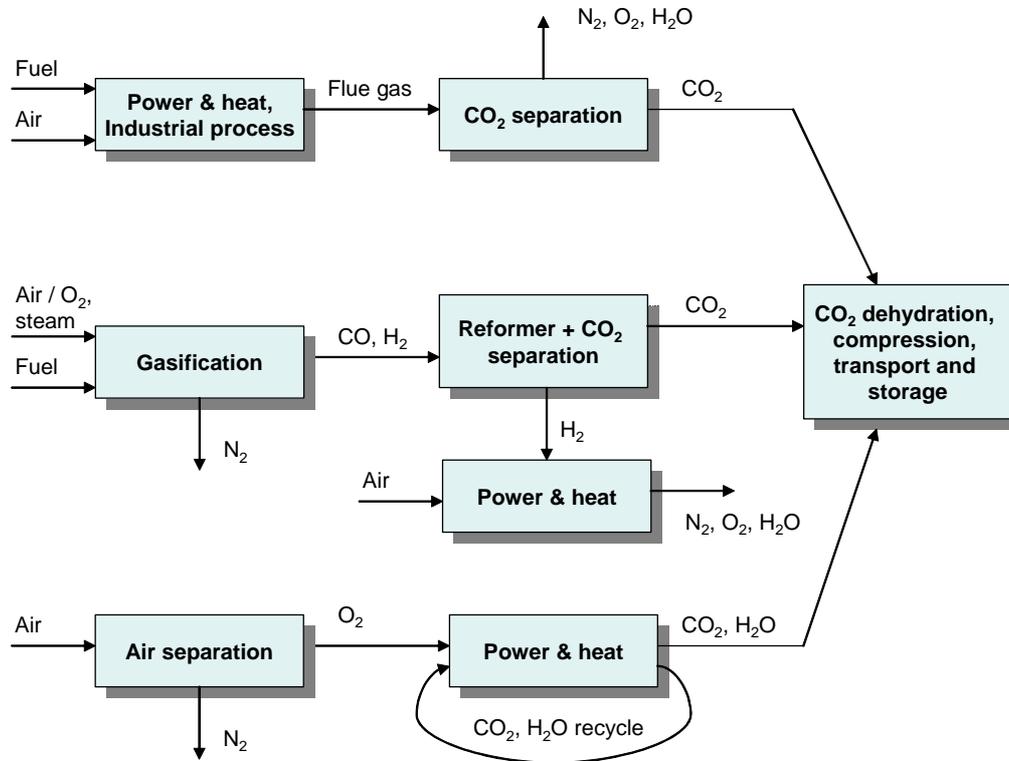


Figure 1.1. Options for capturing CO₂ from power plants.

The separated CO₂ must, in most cases, be transported to the storage site, since suitable storage sites are seldom located near the CO₂ source (IPCC, 2005). Transportation by pipelines is a mature technology, which has been in use for enhanced oil recovery since the 1970s. To avoid pipe corrosion the gas cannot contain any free water and must therefore be dehydrated before transportation. Transportation by ship or road and rail tankers is also possible. Gaseous CO₂ is typically compressed for transportation to a pressure above 80 bar in order to avoid two-phase flow regimes and increase the density of the CO₂, thereby making it easier and less costly to transport. The cost of pipeline transport is dependent on the flow rate, terrain, offshore/onshore transportation, and distance. For a nominal distance of 250 km the cost is typically 1-8 US\$/tCO₂.

In order for CCS to be a useful option for reducing CO₂ emissions, the captured CO₂ has to be stored for a long period of time, for at least thousands of years, in isolation from the atmosphere (IPCC, 2005). Currently, the only technology that has reached demonstration level for accomplishing this on a sufficiently large scale is the use of underground geological formations for the storage of CO₂. Nearly depleted or depleted oil and gas reservoirs, deep

saline formations, and unminable coal beds are the most promising options for the geological storage of CO₂. Suitable storage formations can occur in both onshore and offshore sedimentary basins (natural large-scale depressions in the Earth's crust that are filled with sediments). In each case, CO₂ is injected in compressed form into a rock formation at depths greater than 800 m, where the CO₂ is in a liquid or supercritical state because of the ambient pressures. To ensure that the CO₂ remains trapped underground, a well-sealed cap rock is needed over the selected storage reservoir. The geochemical trapping of CO₂ (i.e. fixation as carbonates) will eventually occur as CO₂ reacts with the fluids and host rock in the reservoir, but this happens on a time scale of hundreds to millions of years. In order to minimise the risk of CO₂ leakage, the storage sites must be monitored for a very long time. Currently, there are several projects running that demonstrate this technology. The injection of CO₂ into geological formations involves many of the same technologies that have been developed in the oil and gas exploration and production industry. 30 Mt of CO₂ is injected annually for enhanced oil recovery (EOR), mostly in Texas, USA, where EOR has been used since the early 1970s. However, most of this CO₂ is obtained from natural CO₂ reservoirs. At the moment three industrial-scale projects are storing 3-4 Mt of CO₂ annually in saline aquifers. The estimated total CO₂ storage capacity for geological formations worldwide is 2,000-10,000 Gt of CO₂, while the costs of storage in saline formations and depleted oil and gas fields have been estimated to be 0.5-8 US\$/tCO₂ injected, with an additional cost for monitoring³ of 0.1-0.3 US\$/tCO₂ (Table 1.1).

Another option for storing CO₂ is to inject CO₂ directly into the deep ocean at depths greater than 1000 m. This option is not a mature technology but has been under research for several decades. CO₂ can be transported via pipelines or ships to an ocean storage site, where it is either injected directly into the ocean or deposited into a CO₂ lake on the sea floor⁴. The analysis of ocean observations and models both indicate that injected CO₂ will be isolated from the atmosphere for at least several hundred years, and that the fraction retained tends to be higher with deeper injection. The cost of injecting CO₂ into the ocean at 3000 m has been estimated at 5-30 US\$/tCO₂ (Table 1.1). However, actively injecting CO₂ may have harmful effects on the ocean environment, about which little is known. Experiments show that adding CO₂ can harm marine organisms, but it is still unclear what effects the injection of several million tonnes of CO₂ would have on ocean ecosystems.

³ A scenario analysed in IEA (2007) for cost estimations, however, considers only 20 years of monitoring after 30 years of injection in a saline aquifer.

⁴ Such CO₂ lakes must be situated deeper than 3 km below the ocean surface where CO₂ is denser than sea water.

From Finland's perspective CCS does not provide an easy answer to reducing CO₂ emissions, since the Finnish bedrock is not suitable for the basin sequestration of CO₂. The offshore oil and gas fields and saline aquifers located in the North Sea and Barents Sea appear to be the closest suitable CO₂ sequestration sites. The distances to these sites are approximately 500-1000 km (Koljonen et al., 2004). Currently, the only known domestic large-scale CO₂ storage alternative for Finland is mineral carbonation, because of the availability of widespread deposits of the mineral needed for the carbonation process.

Table 1.1. Cost ranges for the components of large-scale CCS systems (IPCC, 2005).

CCS system components	Cost range	Remarks
Capture from a coal- or gas-fired power plant	15-75 US\$/tCO ₂ net captured	Net costs of captured CO ₂ , compared to the same plant without capture.
Capture from hydrogen and ammonia production or gas processing	5-55 US\$/tCO ₂ net captured	Applies to high-purity sources requiring simple drying and compression.
Capture from other industrial sources	25-115 US\$/tCO ₂ net captured	Range reflects use of a number of different technologies and fuels.
Transportation	1-8 US\$/tCO ₂ transported	Per 250 km pipeline or shipping for mass flow rates of 5 (high end) to 40 (low end) MtCO ₂ /a.
Geological storage ^a	0.5-8 US\$/tCO ₂ net injected	Excluding potential revenues from EOR or ECBM.
Geological storage: monitoring and verification	0.1-0.3 US\$/tCO ₂ injected	This covers pre-injection, injection, and post-injection monitoring, and depends on the regulatory requirements.
Ocean storage	5-30 US\$/tCO ₂ net injected	Including offshore transportation of 100-500 km, excluding monitoring and verification.
Mineral carbonation	50-100 US\$/tCO ₂ net mineralised	Range for the best case studied. Includes additional energy use for carbonation.

^aIn the long term, there may be additional costs for remediation and liabilities.

1.2 Mineral carbonation

CO₂ could be stored in the form of solid inorganic carbonates by means of chemical reactions. Calcium and magnesium carbonates are formed in nature by a process known as the weathering of rocks. In this natural process calcium and magnesium ions are leached out of silicate rocks by rivers and rainfall and react with CO₂, forming solid calcium and magnesium carbonates. The concept of an accelerated carbonation process for the storage of CO₂ is commonly referred to as *mineral carbonation*. The metal oxides in silicate rocks that can be found in the Earth's crust could in theory bind all the CO₂ that could be produced by the combustion of all available fossil fuel reserves (Figure 1.2). Alkaline industrial wastes and by-products, such as steelmaking slags and process ashes, also have high contents of magnesium and calcium, but their CO₂ storage capacity is much more limited. Mineral carbonation produces silica (SiO₂) and carbonates that are environmentally stable and can therefore be disposed of as mine filler materials or used for construction purposes. Magnesium carbonates (MgCO₃) and calcium carbonates (CaCO₃, limestone) are already plentiful in nature and are known to be sparingly soluble salts (Lackner, 2002). Since carbonation securely traps CO₂, there would be little or no need to monitor the disposal sites

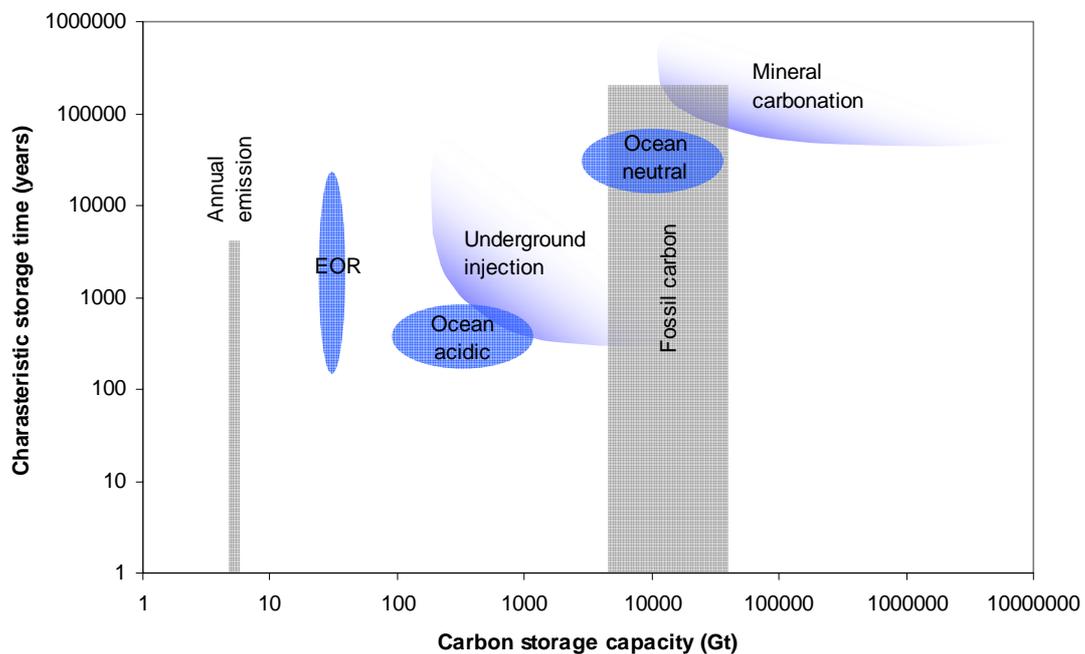
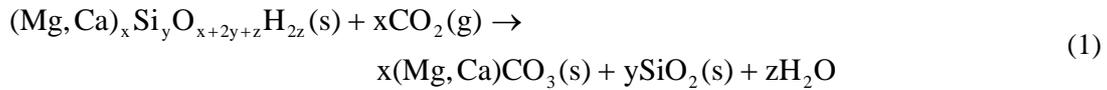


Figure 1.2. Estimated storage times and capacities for various CO₂ storage methods (after Lackner, 2003).

and the environmental risks would be very low (IPCC, 2005). The overall carbonation chemistry using calcium or magnesium silicates is presented in Equation 1:



Apart from the large and safe storage capacity, the exothermic nature of the overall carbonation reaction is another benefit of mineral carbonation which motivates further research. The natural carbonation of silicate materials is very slow, which means that the carbonation must be accelerated considerably to be a viable large-scale storage method for captured CO₂. Therefore, research in the field of mineral carbonation is focused on developing accelerated carbonation processes that are also energy-efficient. Additional requirements for a commercial CO₂ storage process by mineral carbonation are the mining, crushing, and milling of the mineral-bearing ores and their transportation to a processing plant that has access to a concentrated CO₂ stream from a capture plant. Accelerated carbonation technology for natural minerals is still in the development stage and is not yet ready for implementation. The best case studied so far is the wet carbonation of natural silicate olivine (Chapter 3.2.2.2), for which the estimated process costs are 50-100 US\$ per tonne of net CO₂ carbonation, excluding CO₂ capture and transport costs (Gerdemann et al., 2007). The energy requirements of this carbonation process are typically 30-50% of the output of the power plant from which CO₂ is captured. In combination with the power requirements of the capture facility, up to 60-180% more energy input is required per kilowatt-hour produced than for a power plant without CCS. The carbonation process would require 2-4 tonnes of silicates per tonne of CO₂ to be mined and produce 3-5 tonnes of material to be disposed of per tonne of CO₂ stored as carbonates, which will have a similar environmental impact to current large-scale surface mining operations (IPCC, 2005).

2 Objective of this thesis

The main challenge for using mineral carbonation for CO₂ sequestration is to develop an economically feasible process. To achieve this, economic and rapid methods for extracting reactive magnesium or calcium compounds (such as oxides, hydroxides, or base ions) from the rock and for carbonating these must be developed. An implemented carbonation process for CO₂ sequestration would be on the scale of an average-sized open mining facility, because of the large amounts of minerals required. Therefore, besides providing rapid conversion, the carbonation process must also convert as much as possible of the minerals to carbonates, in order for the environmental impact to be minimal.

An important aspect of mineral carbonation is the end-use or disposal of the carbonate product. Using mineral carbonation for sequestering CO₂, the material amounts of carbonates, silica, and other compounds (depending on the raw material used) from such a process would be huge: sequestering 1 Mt of CO₂ produces 2.3 Mt of CaCO₃ or 1.9 Mt of MgCO₃ (assuming a conversion efficiency of 100%) with various amounts of silica and other by-products, depending on the raw material used. Therefore, it is very important to be able to utilise these products as much as possible. Although the end-products of a carbonation process for CO₂ storage would eventually exceed the market demand, the possibility of selling them could help to introduce a technology infrastructure for mineral carbonation and develop it into a feasible CO₂ storage technology.

The technology for producing synthetic calcium carbonate from limestone is known and used on an industrial scale, but the carbonation of silicate minerals requires other processes than those used for limestone carbonation. While the direct carbonation of magnesium silicates and calcium silicates has been comprehensively studied, most of these processes produce an aqueous slurry of carbonates, unreacted silicates, silica, and other by-products, from which it is difficult to separate the individual components (O'Connor et al., 2005; Huijgen et al., 2006). Indirect (or multi-step) processes, such as those suggested by Lackner et al. (1995) and Kakizawa et al. (2001), allow for the separation of silica and other by-products, such as metals and minerals, before the carbonation step. An indirect process is therefore a better alternative for producing separate streams of carbonates and other materials for further recovery. The present work shows that industrial wastes and by-products can be converted into more valuable products using indirect carbonation processes. However, very little in the way of experimental data on these processes can be found in the literature. The relatively high price of precipitated calcium carbonate (over ten times that of raw limestone or steelmaking slag products) could justify the development of a carbonation process with high running costs.

However, the purity and crystal structure of the synthetic carbonate and other products of such a process determine their value.

The objective of this thesis was to study the possibility and potential of producing relatively pure calcium and magnesium carbonates from silicate materials for the long-term storage of CO₂ using indirect processes. The research tasks for achieving this were:

- i. Evaluate the CO₂ emission reduction potential by producing precipitated calcium carbonate from calcium silicates instead of limestone (Paper I).
- ii. Study the possibility of producing calcium carbonates from steelmaking slags for the reduction of CO₂ emissions by experimental and theoretical research (Papers II-III).
- iii. Study the possibility of producing magnesium carbonates from serpentinite for the sequestration of CO₂ by experimental and theoretical research (Papers IV-VI).
- iv. Evaluate the stability of synthetic magnesium and calcium carbonates as a medium for CO₂ storage (Papers VI-VII).

Processes for calcium silicate carbonation suggested in the literature were studied by process modelling and their energy use and net potential for CO₂ fixation were evaluated. An acetic acid process appeared to be the most promising of the systems studied for the carbonation of calcium silicates. Since natural calcium silicate mineral resources were found to be scarce, the use of steelmaking slags for carbonate production was investigated by means of experiments and theoretical calculations. The large resources of magnesium silicates justified the systematic development of an indirect process for converting magnesium silicates into magnesium carbonates. Finally, the stability of magnesium carbonate and calcium carbonate as a medium for CO₂ storage was evaluated.

3 Literature review

The purpose of this literature review was:

- To select raw materials potentially suitable for carbonation and readily available in Finland.
- To review the most comprehensively studied carbonation routes proposed in the literature, as well as the processes that are relevant for this work.
- To discuss potential markets and uses for the carbonates produced.

3.1 Suitable raw materials

In order to provide for significant storage of CO₂, large amounts of raw materials are required as feedstock for carbonation. Therefore, the raw materials used for carbonation must be abundant and cheap.

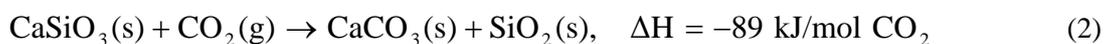
From a chemical elements perspective, both alkali (e.g. Na, K, etc.) and alkaline earth (e.g. Ca, Mg) metals can be carbonated (Huijgen and Comans, 2003; 2005). However, alkali metals are unsuitable for the long-term storage of CO₂, since alkali (bi)carbonates are soluble in water, which could release CO₂ back into the atmosphere. Additionally, a number of other metals (e.g., Mn, Fe, Co, Ni, Cu, and Zn) could potentially be carbonated, but most of these elements are either too rare or too valuable to be used for the sequestration of CO₂. Of the alkaline earth metals, magnesium and calcium are by far the most common in nature. The Earth's crust consists of roughly 2 mol-% magnesium and 2 mol-% calcium, primarily bound as carbonates and silicate minerals (Goff and Lackner, 1998; Brownlow, 1996).

In order to minimise the amount of raw material needed, materials with high concentrations of calcium and magnesium should be favoured, while materials already containing significant concentrations of carbonates should be avoided. From this perspective, magnesium and calcium oxides or hydroxides would be ideal materials, but these are rare in nature. Calcium silicates and magnesium silicates are particularly suitable for carbonation, since these materials are abundant in the Earth's crust. The storage capacity of silicate minerals has been estimated at 10,000-10,000,000 Gt of carbon (Figure 1.2), which exceeds the amount of carbon in known fossil fuel resources. Although calcium silicates tend to be more reactive for carbonation than magnesium silicates, calcium silicates with high concentrations of calcium are relatively rare (Lackner, 2002). The Finnish bedrock consists locally of rock types that contain an abundance of Mg and Ca silicates, such as serpentine, pyroxenes, amphiboles, and talc, which could be suitable for carbonation (Teir et al., 2006a). Several industrial residues and by-products, such as iron and steel slags, various process

ashes, and cement-based materials can have high concentrations of calcium and magnesium. Although the amounts of by-products and residues are much smaller than natural resources, by-products and residues are readily available, continuously produced, and tend to be more reactive than natural minerals.

3.1.1 Natural calcium silicates

A suitable source of natural calcium silicate is wollastonite, CaSiO_3 , which has a relatively high calcium content (48 wt-% CaO). Wollastonite is mainly found with crystalline limestone occurrences, since it has been formed in nature from the interaction of calcite (CaCO_3) with silica (SiO_2) under high temperatures and pressures. Wollastonite is used in the plastic, ceramic, and metallurgical industries as a filler and additive for various applications. For wollastonite, the carbonation reaction⁵ can be written as



Wollastonite deposits of economic value are rare. Although wollastonite is common, especially in limestone in the southern part of Finland, the mineral does not form economically interesting deposits in most of its occurrences (Eskola et al., 1929; Dahlberg, 2004). The worldwide production of wollastonite was estimated to be between 550 and 600 kt in 2003, of which Finland, as a major wollastonite supplier, produced slightly less than 20 kt (USGS, 2003). The price of wollastonite on the international market in 2002 ranged from 50 US\$/t for lump wollastonite to 1700 US\$/t for ultra-fine surface-treated wollastonite. Finnish fine-grain wollastonite can be obtained for 200 €/t. As a comparison, the average price for lime (CaO) was 63 US\$/t (USGS, 2003). The average composition of Finnish wollastonite can be found in Table 3.1.

Basalt rocks are also rich in calcium oxides and could therefore provide a feedstock for mineral carbonation. Basalt is the most common igneous rock and is found widely distributed throughout the world. Basalt has an average CaO content of 10 wt-%, but also contains iron (8 wt-% Fe) and magnesium (7 wt-% MgO) that could be carbonated (Table 3.1). In a recent study by McGrail et al. (2006), the potential for in situ carbonation (see Chapter 3.2) of flood basalts was estimated at 100 Gt of CO_2 in the eastern part of the U.S. alone. In Finland, all igneous rocks are metamorphosed and basalt does not exist as such. In northern Finland and Karelia, igneous rocks are metamorphosed from basalt, with the main

⁵ All enthalpy differences are calculated at 25 °C using Outokumpu HSC 5.1 with additional thermodynamic data for MgO, $\text{Mg}(\text{OH})_2$, and MgCO_3 from Robie *et al.* (1978) unless supplementary text specifies otherwise.

minerals being amphibole, plagioclase, and sometimes chlorite, with a CaO content of 7-9 wt-% (GSF, 2004).

Table 3.1. Examples of the composition of wollastonite and basalt (units: wt-%).

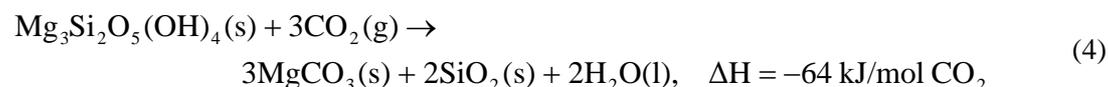
	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe	Ti	Mn
Wollastonite ^a	44	no data	no data	no data	0.1	no data	no data
Basalt ^b	9.5	49	6.7	16	8.2	1.1	0.2

^aData from Dahlberg (2004).

^bData from Cox et al. (1979).

3.1.2 Natural magnesium silicates

Since magnesium silicate rocks are usually richer in base ions than calcium silicate rocks (Lackner, 2002), most of the research into mineral carbonation has focused on the carbonation of olivine (Mg₂SiO₄; Equation 3) and serpentine (Mg₃Si₂O₅(OH)₄; Equation 4).



Suitable magnesium-rich, ultramafic rocks are distributed throughout the world. The amount of Mg in the Earth's crust (2.0 mol-%) is almost 60 times larger than the amount of C (0.035 mol-%). For instance, the large dunite body at Twin Sisters, Washington, U.S., could store almost 100 Gt of CO₂, which amounts to about 19 years' worth of U.S. CO₂ emissions (Goff and Lackner, 1998). The most common Finnish Mg rich rocks are ultramafic intrusive or extrusive rocks, i.e. peridotites, dunites, hornblendites, pyroxenites, and komatiites, and their metamorphic varieties, i.e. serpentinites, talc, and asbestos rocks. Of these ultramafic rocks, the most interesting for CCS purposes are the serpentinites, because they consist mainly of serpentine (Table 3.2). A detailed survey of Finnish ultramafic rocks suitable for carbonation has recently been made by Aatos et al. (2006). Millions of tons of poorly documented in situ or hoisted serpentinite or tailed serpentine deposits are situated mainly in central Finland. It has been estimated that in Eastern Finland alone there are about 121 km² of serpentinites. The effective sequestering capacity of these serpentinites is not known because of the considerable variation in the amount of pure serpentine in different serpentinite formations. To achieve the reduction in greenhouse gas emissions in Finland required by the Kyoto protocol (about 10 Mt/a), the carbonation of about 25 Mt/a of minerals would be required. Using these numbers,

the serpentinites of the Outokumpu-Kainuu ultramafic rock belt could theoretically be sufficient for 200-300 years of CCS processing (Teir et al., 2006a; Aatos et al., 2006).

Table 3.2. Composition of serpentinite from the Hitura mine (Teir et al., 2006a).

Source	MgO (wt-%)	SiO ₂ (wt-%)	CaO (wt-%)	S (wt-%)	Amounts (Mm ³)
Ore	35	32	0.2	3.1	No data
Processed tailings	33	40	1.1	1.9	8.3
Waste tailings	40	38	0.2	0.5	2.1

Rocks potentially suitable for carbonation are already mined, processed, piled, and stored at mines producing industrial minerals and metals, such as talc, soapstone, chromium, and nickel. The total amount of hoisted rock in Finnish mines was about 31 Mt in 2004, of which about 11 Mt was from ultramafic deposits in general (Söderholm, 2005; Figure 2.1). These resources of hoisted serpentine and serpentinite (33-39% MgO) at contemporary Finnish nickel, chromium, and talc mines are at least 29 Mt (Aatos et al., 2006).

One example is the Hitura nickel mine, where the main minerals are serpentine (antigorite), 80-90%, chlorite, calcite, and magnetite, 7-9% (Isohanni et al., 1985). A large part of the mineral deposit is barren in nickel. Low nickel-grade ore is stored as waste rock at the mining site for future use, while the processed ore is stored in tailing ponds (Table 3.2). The total nickel ore hoist has been about 14 Mt, which had an average Ni content of 0.60%

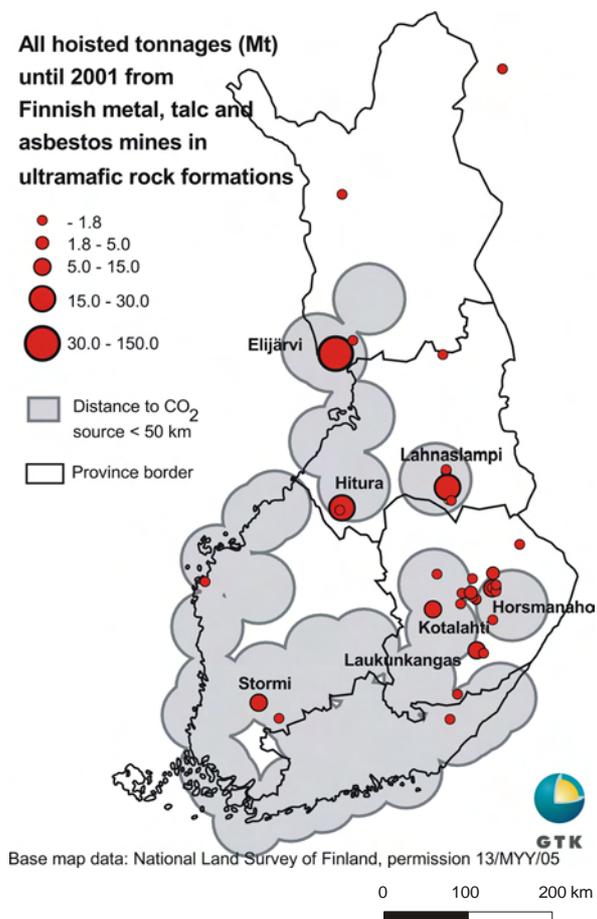


Figure 3.1. Possible sources of serpentine in Finland. Circles mark areas where the distance to a major stationary CO₂ emitter is < 50 km (Teir et al., 2006a).

(Teir et al., 2006b). If the hoisted ore has an average MgO content of 34 wt-%, 5.3 Mt of CO₂ could be stored using the presently hoisted ore alone.

3.1.3 Alkaline solid waste materials

While most research into mineral CO₂ sequestration focuses on the carbonation of natural silicate minerals, there have also been considerable and successful efforts to carbonate solid alkaline waste materials. Many various types of solid alkaline waste materials are available in large amounts and are generally rich in calcium. Wastes that have been considered for carbonation include ash from coal-fired power plants (CaO content up to 65 wt-%), bottom ash (~20 wt-% CaO) and fly ash (~35 wt-% CaO) from municipal solid waste incinerators, de-inking ash from paper recycling (~35 wt-% CaO), steelmaking slag (~30-60 wt-% CaO and MgO), and waste cement (Fernández Bertos et al., 2004; Johnson, 2000; Huijgen et al., 2005; Iizuka et al., 2004; Yogo et al., 2004; Uibu et al., 2005). Most research seems to have concentrated on carbonation as a means for immobilising toxic elements and heavy metals, as well as improving the structural durability of wastes and by-products to render them better suited for landfill or construction purposes. However, carbonation has also been found to increase the leaching of certain elements, such as vanadium in steel slag (Huijgen and Comans, 2006).

Finland has a large steel industry, which is very energy-intensive and has high CO₂ emissions. The largest single source of anthropogenic CO₂ emissions in Finland, accounting for 4.7 Mt of CO₂/a (Ruukki, 2005), is the steel plant at Raahe. Carbonating the steelmaking slags, which are by-products of the steelmaking processes, could be an interesting option for reducing the CO₂ emissions from the steel plant.

3.1.3.1 Iron and steel slag

Iron and steel slags (in short: steelmaking slags) are non-metallic by-products of many steelmaking operations and consist principally of calcium, magnesium, and aluminium silicates, as well as iron and manganese. The proportions vary with the conditions and the feedstock for the particular iron or steel production process where the slag is generated. Calcium compounds account for the largest constituents, with a CaO content of 40-52% (Stolaroff et al., 2005).

Crude or pig iron is produced in a blast furnace, where lime or limestone is used to remove oxygen and other impurities from iron and adjust the viscosity of the smelts. Limestone decomposes at high temperatures (see Chapter 3.2.5, Equation 36) and combines with impurities, such as silicon dioxide (SiO₂), to form a liquid calcium silicate melt called iron or blast furnace slag, which can be removed from the blast furnace separately from iron.



After the blast furnace, the crude iron produced is transported to a steel converter, usually a basic oxygen furnace (BOF), where the residual carbon content of the iron is reduced from 4 wt-% to 0.5 wt-%. Steel furnaces, particularly electric arc furnaces (EAF), may also use scrap metals as feedstock instead of pig iron. Impurities and carbon are also removed in the steel furnace by slag formation similarly to that in a blast furnace. Stainless steel grades (> 10 wt-% Cr) are usually produced in an induction or electric arc furnace, sometimes under vacuum. To refine stainless steel, a so-called argon-oxygen decarburisation (AOD) process is used.

The physical attributes of the solidified slags depend mainly on the cooling technique used: air-cooled, granulated (water-cooled), and pelletised (or expanded) slags are the three main types. The cooling method also largely determines the uses for the slag. After cooling, the slag may be further processed (mainly by crushing) prior to being sold (USGS, 2003). Steel slags are highly variable with respect to their composition, even those from the same plant and furnace. Apart from the feedstock impurities, slags (especially steel converter slags) may also contain significant amounts of entrained free metal. The amount of slag produced is largely related to the overall chemistry of the raw materials (Ahmed, 1993). The chemical composition of the slag is also variable and depends on both the chemical composition of the feed and the type of furnace used. Slags are widely used for road construction purposes, as asphalt and cement aggregate. Slags have very low prices (e.g. blast furnace slag from Ruukki can be bought for 10 €/t, excluding shipping costs) in comparison to steel products and are usually considered to be unwanted by-products of the steel production process.

Table 3.3. Production of steel mills in Finland in 2004 (units: kt/a).

Steel mill	Company	Steel production	CO ₂ ^e emissions	Iron slag	Steel slag	Ferrochrome slag
Raahe ^a	Ruukki	2719	4740	571	302	-
Koverhar ^b	Ovako	618	890	96	62	-
Tornio ^c	Outokumpu	1200	670	-	47	309
Imatra ^d	Ovako	243	58	36 ^f	-	-

^aData from Ruukki (2005).

^bData supplied by Magnus Gottberg, Ovako.

^cData from Outokumpu (2005).

^dData supplied by Helena Kumpulainen, Ovako.

^eFinland's total anthropogenic CO₂ emissions in 2004 were 69 Mt (excluding land use, land use change, and forestry: STAT, 2007).

^fNumber represents the total steelmaking slag production of the mill.

Table 3.4. Examples of average compositions of various slag products from steel producers in Finland (units: wt-%).

	CaO	SiO ₂	MgO	Al ₂ O ₃	Cr	Fe	Ti	Mn
Blast furnace slag ^a	41	35	10	9.2	0.0	0.6	1.0	0.4
Steel converter slag ^a	46	13	2.1	1.7	0.2	18	0.5	2.5
EAF slag ^b	40	26	11	5.8	5.2	1.1	2.3	1.8
AOD process slag ^b	56	30	8.3	1.2	0.3	0.6	0.4	0.3
Chrome converter slag ^b	39	36	17	3.5	1.0	0.3	1.1	0.2
Ferrochrome slag ^b	1.4	28	23	28	8.5	4.6	no data	no data

^aData from Rautaruukki steel plant at Raahе.

^bData from Outokumpu steel plant at Tornio.

As mentioned above, the steel industry is very energy-intensive and has high CO₂ emissions. It has been estimated that the world output in 2003 was 160-200 Mt of iron slag and 96-145 Mt of steel slag (USGS, 2003). In Finland, there are four steel plants in operation that produce a total of 1.4 Mt of slag per year (Table 3.3). Examples of the composition of the slag these plants produced in 2004 are listed in Table 3.4.

The high carbonation conversion achieved with steel slag with relatively mild process conditions (see Chapter 3.2.4) shows that steelmaking slags are suitable materials for carbonation.

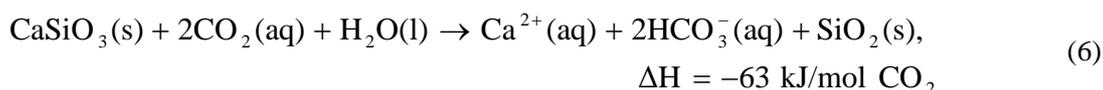
3.2 Carbonation processes

The major challenge hindering the large-scale use of silicate minerals for CO₂ sequestration is their slow conversion to carbonates. Therefore, most research in this field has focused on identifying faster reaction pathways, by characterisation of the mineral reactants and reaction products, as well as bench-scale experiments for determining reaction rates. Although the raw materials required are relatively cheap and the net carbonation reaction is exothermic, the process conditions (high pressures and temperatures) and additional chemicals for speeding up the carbonation reaction contribute to excessive process costs. However, several carbonation process routes that appear promising have been suggested. In the case of mineral-containing rocks, carbonation can be carried out either *in situ*, by injecting CO₂ into silicate-rich geological formations or alkaline aquifers, or *ex situ* in a chemical processing plant after mining the silicates (IPCC, 2005). Since this thesis considers the use of both steelmaking slags and of minerals, as well as the end products, only *ex situ* processes are relevant for this research. These processes can be divided into two main routes: *direct processes*, where the carbonation of the mineral takes place in a single process step, and

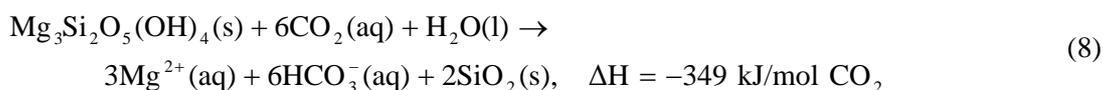
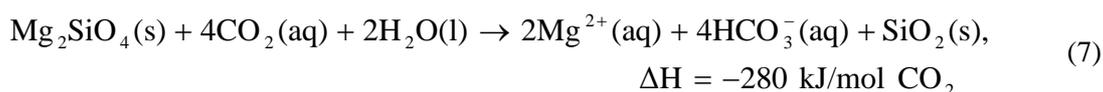
indirect processes, where calcium or magnesium is first extracted from the mineral and subsequently carbonated.

3.2.1 Weathering of rocks

The idea of CO₂ disposal by carbonate formation comes from the natural silicate weathering process, which binds about 100 Mt of carbon per year (Seifritz, 1990)⁶:



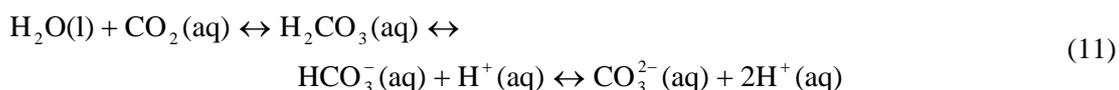
Rainfall is slightly acidic by nature, because atmospheric carbon dioxide dissolves in rainwater, producing weak carbonic acid. Calcium is therefore leached from calcium silicate-containing rocks by rainwater containing dissolved CO₂ (Brownlow, 1996). Magnesium silicates (olivine and serpentine) are similarly dissolved by rainwater:



Rainwater carries the leached calcium and magnesium to rivers and subsequently to the ocean, where calcium and magnesium precipitates and forms solid calcium and magnesium carbonates (M²⁺ represents either Ca²⁺ or Mg²⁺):



The precipitation and dissolution of carbonates controls the pH in the oceans naturally, according to the equilibrium involving CO₂ and calcium carbonate (Brownlow, 1996):



⁶ All enthalpy differences are calculated at 25 °C using Outokumpu HSC 5.1 with additional thermodynamic data for MgCO₃ from Robie *et al.* (1978) unless supplementary text specifies otherwise.



Increasing the CO₂ abundance will increase the amount of H₂CO₃, which in turn results in more dissolved carbonate minerals. Reducing the CO₂ abundance will result in the precipitation of solid carbonates. Using solubility constants and Henry's law, the distribution of carbonate species can be presented as functions of pH (Figure 3.2).

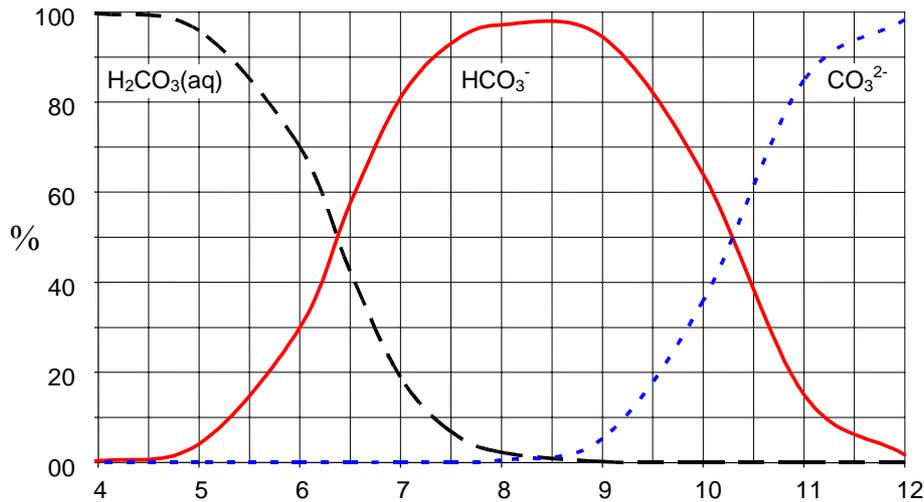


Figure 3.2 Distribution of carbonate species at equilibrium as functions of pH (calculated using Henry's law) (Paper V).

The application of the weathering of rocks for CO₂ sequestration was studied experimentally by Kojima et al. (1997). The aqueous carbonation of finely ground wollastonite (a representative diameter of 80 μm was reported) was tested in a continuously stirred tank reactor exposed to CO₂ at 25 °C and atmospheric pressure for 0-600 h. It took 400 hours before the concentration equilibrium of the calcium in the solution was reached, which is far too slow for an industrial application.

3.2.2 Direct carbonation

The routes via which the carbonation of the mineral takes place in a single process step are usually referred to as direct carbonation. These processes can further be divided into gas-solid processes and aqueous (three-phase) processes.

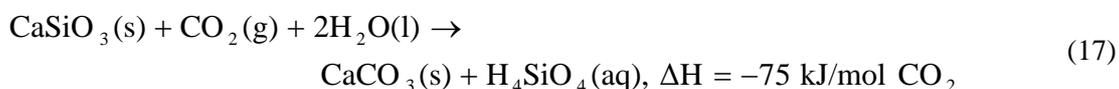
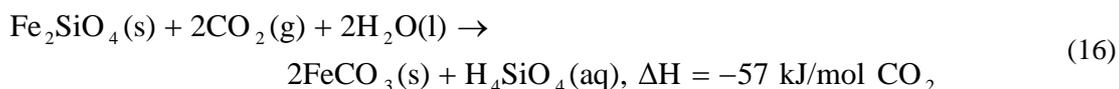
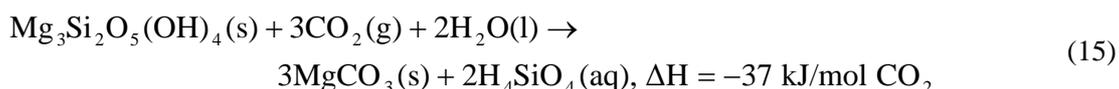
3.2.2.1 Direct gas-solid carbonation

In a direct gas-solid (dry) carbonation process, the only reactants are CO₂ and a mineral. This approach, first presented and studied by Lackner et al. (1995), is to convert

silicate minerals directly to carbonates (according to the reactions presented in Equations 2-4) using gaseous or supercritical CO₂. The advantages of the direct carbonate approach are its simplicity and the possibility of recovering heat at high temperatures. The high temperature heat that is generated could possibly be used for process requirements or even electricity generation (Zevenhoven and Kavaliauskaite, 2004). The reaction proceeds very slowly at room temperature, but the rate can be accelerated by increasing the temperature. However, above a certain temperature the reaction equilibrium shifts and favours free CO₂ instead of carbonates. This temperature limit can be raised by increasing the CO₂ pressure. The highest reported conversion by direct carbonation appears to be 25% of the stoichiometric maximum, which was achieved by exposing serpentine particles of 100 µm to a CO₂ pressure of 340 bars and a temperature of 500 °C for 2 h (Lackner et al., 1997a).

3.2.2.2 Direct aqueous carbonation

The most comprehensively studied carbonation process is the direct aqueous carbonation of magnesium silicates (O'Connor et al., 2000; Gerdemann et al., 2007). In this process a slurry of water and pre-treated olivine (Equations 13 and 14) or serpentine (Equation 15) is reacted with pressurised carbon dioxide to produce magnesium carbonate. Although the conversion chemistry involves three steps, it takes place in a single reactor. Carbon dioxide is dissolved in water to form carbonic acid (H₂CO₃), which dissociates to hydrogen cations (H⁺) and bicarbonate anions (HCO₃⁻) (Equations 10 and 11). The hydrogen cations reacts with the mineral, liberating magnesium cations (Mg²⁺), which react with the bicarbonate to form solid carbonate and silicic acid (which in turn becomes silica and water). According to O'Connor et al. (2005), the same process could be used for carbonating Ca- and Fe(II)-rich silicates as well (Equations 16 and 17).



Preliminary tests conducted at ambient temperature and sub-critical CO₂ pressures (below 74 bar) resulted in very slow carbonate formation. In later tests, using an aqueous solution of sodium bicarbonate (NaHCO₃) and sodium chloride (NaCl) at elevated temperatures and pressures, several silicate minerals were successfully carbonated to a large extent in one hour (Table 3.5). The lowest costs reported from a case-specific feasibility study regarding storing CO₂ using this method were 54 US\$/tCO₂ with olivine as feedstock, 64 US\$/tCO₂ with wollastonite as feedstock, and 78 US\$/tCO₂ using serpentine as feedstock (O'Connor et al., 2005; Gerdemann et al., 2007). The study included pre-treatment costs, but excluded CO₂ separation and transport costs (see Table 1.1 for these).

Huijgen et al. (2006) managed to carbonate wollastonite to a conversion of 70% in 15 min at 200 °C, 20 bar CO₂, using a particle size of <38 µm, which represents significantly milder process conditions than those required for the carbonation of magnesium silicates (Table 3.5).

In order to speed up the kinetics of the direct aqueous carbonation processes, various physical and chemical pre-treatment methods (e.g. Maroto-Valer et al., 2005a), mechanical activation methods (e.g. Park and Fan, 2004), and heat activation procedures of the minerals (e.g. McKelvy et al., 2004) to enlarge the particle reaction surface have been studied. It is possible to enhance the reactivity of the minerals considerably using these methods. But this requires chemical additives or energy, which for serpentine would indirectly cause more CO₂ emissions than are sequestered by the process (O'Connor et al., 2005). Chemical pre-treatment methods may also contribute to a reduction in the useful MgO content, which reduces the carbonation potential of the mineral.

Table 3.5. Best carbonate conversion achieved with aqueous carbonation with the following test conditions (batch autoclave with continuous stirring): 80% <37 µm feed; 1 hour residence time; T = 185 °C; P_{CO2} = 150 atm; 15% solids; 0.64 M NaHCO₃, 1 M NaCl (O'Connor et al., 2005).

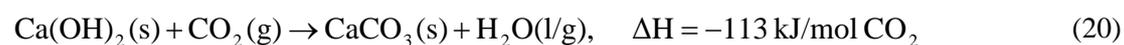
Rock / Mineral group	Mineral	Formula	Conversion to carbonate (%)
Feldspar	Anorthite	CaAl ₂ Si ₂ O ₈	9
Serpentine	Antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄	92
Pyroxene	Augite	CaMgSi ₂ O ₆ +(Fe,Al)	33
Basalt			15
Olivine	Fayalite	FeSiO ₄	66
Olivine	Fosterite	Mg ₂ SiO ₄	81
Serpentine	Lizardite	Mg ₃ Si ₂ O ₅ (OH) ₄	40
Oxide	Magnetite	Fe ₃ O ₄	08
Ultramafic	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	15
Ultramafic	Wollastonite	CaSiO ₃	82

3.2.3 Indirect carbonation

In indirect carbonation processes a reactive magnesium or calcium compound is first extracted from the mineral, after which the intermediate magnesium/calcium products are carbonated. Most of these processes usually provide a faster carbonation route than direct processes, but demand additional energy or chemicals.

3.2.3.1 Indirect gas-solid carbonation

In order to improve the conversion rate, the mineral could first be converted into an oxide or hydroxide (see Chapter 3.2.3.2) and subsequently carbonated:



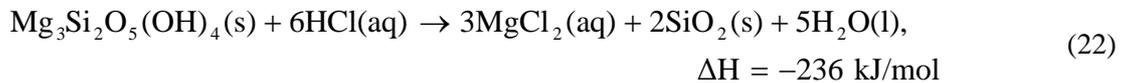
The direct gas-solid carbonation of calcium/magnesium oxides/hydroxides proceeds much faster than the gas-solid carbonation of calcium/magnesium silicates, although a high temperature and CO₂ pressure are required: 100% conversion of magnesium hydroxide, Mg(OH)₂, was achieved in less than 2 h using a CO₂ pressure of 340 bar and a temperature of 500 °C (Lackner et al., 1997b). It has been found that magnesium carbonate builds up on the particle surface and forms a kinetic barrier (Butt et al., 1996). Experiments with the gas-solid carbonation of Mg(OH)₂ in a fluidised bed reactor indicated that the carbonate build-up on the particle could be removed by promoting attrition and abrasion (Teir et al., 2004). Using a pressurised thermogravimetric analyser as a reactor, Mg(OH)₂ (75-125 μm) has been carbonated to conversion levels of the order 40-60% in 6 h at 540 °C and 45 bar total pressure (99% CO₂/1% H₂O) (Zevenhoven et al., 2006a). In these experiments, Mg(OH)₂ also seemed to carbonate faster than MgO (Zevenhoven and Teir, 2004). By grinding Mg(OH)₂ to a particle size of 0.1 μm, 90% conversion has been achieved at 565 °C and 53 bar in 30 minutes (Butt et al., 1998), which is fast enough for a feasible process.

However, magnesium/calcium oxides/hydroxides are rare in nature, and would have to be produced from calcium/magnesium silicates. Zevenhoven et al. (2006c) suggested a staged gas-solid process for the carbonation of serpentine. The process involves the extraction of reactive magnesium as magnesium oxide or hydroxide in an atmospheric pressure step, followed by carbonation at a higher temperature (>500 °C) and at elevated pressures (>20

bar) that allow for reasonable carbonation reaction kinetics under conditions where magnesium carbonate is thermodynamically stable. Thermodynamic calculations indicated that the process could be operated at close to zero energy input. The process is currently being further investigated.

3.2.3.2 Production of hydroxides for carbonation using HCl

Lackner et al. (1995; 1997b) and Butt et al. (1998) studied a carbonation process consisting of several steps, where magnesium hydroxide is first produced from minerals using an acidic solution, and carbonated as a gas-solid reaction (Figure 3.3). The carbonation could alternatively also be performed at low pressures in an aqueous environment. First, the mineral containing rock is decomposed in hydrochloric acid (HCl) at ~100 °C, forming magnesium chloride in the solution. The process steps using serpentine are given as examples:



The silica forms a gel that can be recovered by filtration. Any excess acid and water is boiled off at 150 °C, where the formed solid magnesium chloride (MgCl_2) decomposes and hydrochloric acid is regenerated:

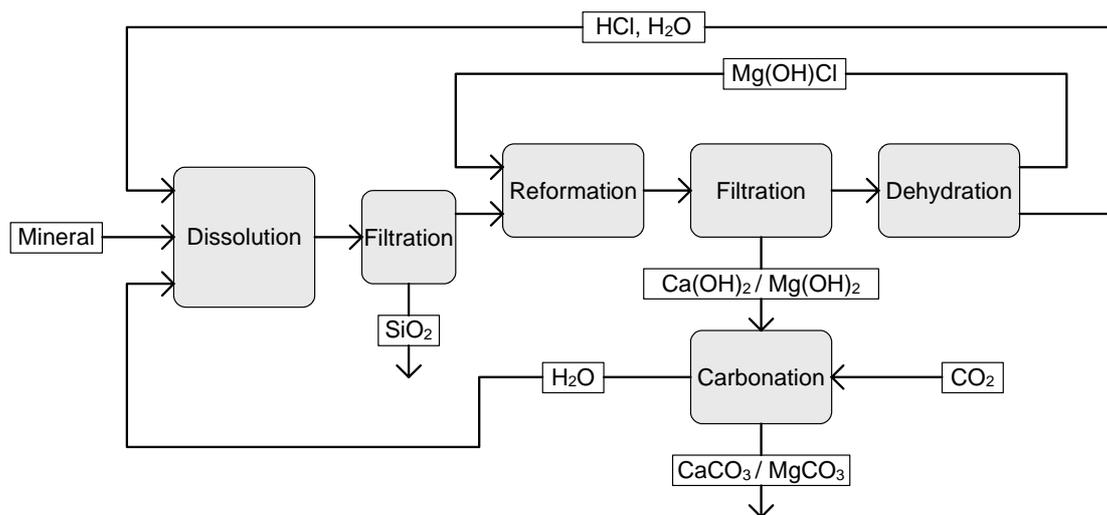
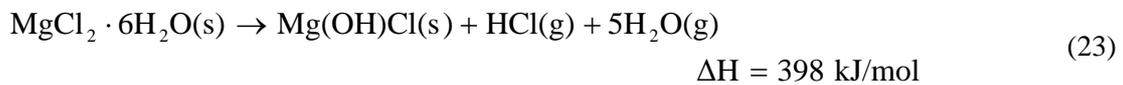


Figure 3.3. Indirect process for carbonating minerals using HCl.

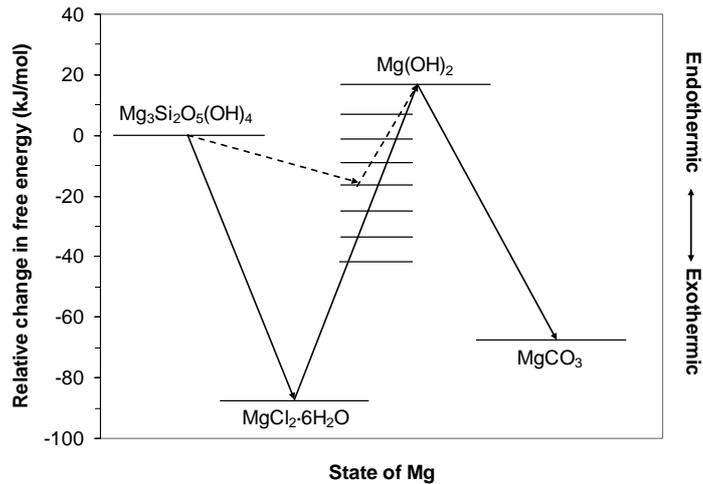
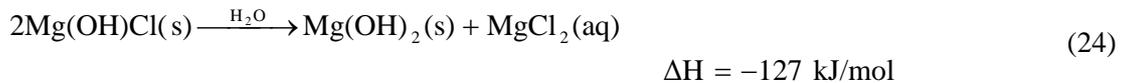


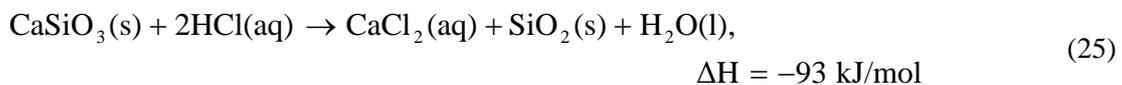
Figure 3.4. Relative free energy changes at the main process stages of the indirect carbonation process using HCl (after Butt et al., 1998).

After solution in water, magnesium hydroxide chloride forms magnesium hydroxide and magnesium chloride:

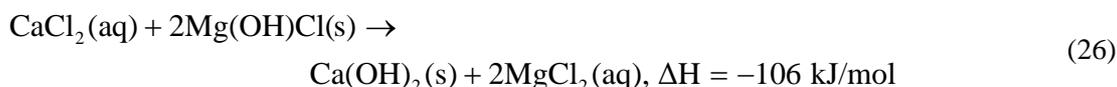


The magnesium hydroxide is separated, while the magnesium chloride is recycled through the acid recovery step. The solid magnesium hydroxide is carbonated at high temperatures and pressures (Equation 18, Chapter 3.2.3.1). The drawback of the process is its high energy demand for the evaporation of the aqueous solution and the large variations in free energy resulting from the necessary formation of intermediate products (Figure 3.4). Newall et al. (2000) calculated the process costs to be 233 US\$/t CO₂ sequestered. Additionally, to provide for the energy requirements of the process four times more CO₂ would be produced (because of fossil fuel combustion at the power plant) than is sequestered by the process (Newall et al., 2000).

The same process route could also be used for carbonating calcium silicates (Lackner et al., 1995; Newall et al., 2000). In this route (Figure 3.3), calcium silicate is dissolved in hydrochloric acid at 80 °C and calcium chloride (CaCl₂) is produced:



Silica is filtered out, and calcium chloride reacts with magnesium hydroxide chloride, Mg(OH)Cl, to produce calcium hydroxide, Ca(OH)₂:

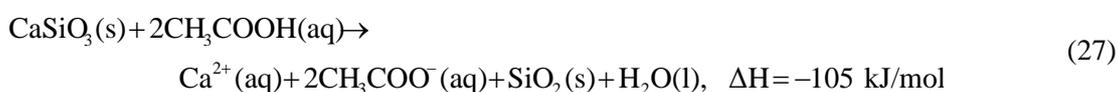


The calcium hydroxide produced is separated, dissolved in water, and then reacted with CO₂ to produce calcium carbonate. The Mg(OH)Cl is regenerated by dehydrating saturated MgCl₂ at 150 °C. Major drawbacks reported were the energy demand for the acid recycling stage and a very large water demand to hydrate the Ca(OH)₂ for the carbonation stage: 840 t H₂O/t Ca(OH)₂

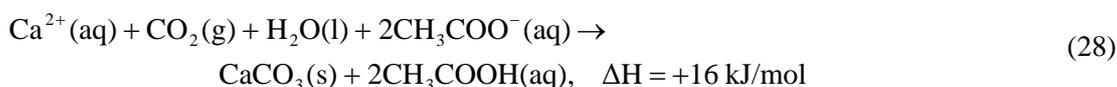
In order to lower the energy requirements for dehydration, several possibilities for dissolving minerals using molten salt (MgCl₂·nH₂O) instead of HCl were investigated by Wendt et al. (1998a; 1998b) using thermodynamic calculations. The direct carbonation of serpentinite in a molten salt melt at 300 °C using 30 bar CO₂ was considered to be the most suitable alternative. The process was calculated to have a CO₂ sequestration cost of ~80 US\$/tCO₂, but because of unavoidable losses of MgCl₂ in the process during the separation of the carbonates produced from the melt, there would be a significant demand for make-up MgCl₂ (or HCl for MgCl₂ production), which would probably render the process economically unviable (Newall et al., 2000).

3.2.3.3 Indirect carbonation of calcium silicate using acetic acid

A similar process for the carbonation of calcium silicate was studied by Kakizawa et al. (2001). The chemical reactions in the process occur in two steps (Figure 3.5). The first step is the extraction of calcium ions from calcium silicate (e.g. wollastonite) using acetic acid (CH₃COOH):



The solid SiO₂ precipitates and is separated using a thickener. Gaseous CO₂ is injected into the solution, which causes calcium carbonate to crystallise and deposit:



According to Kakizawa et al., the Gibbs free energy change of each step is negative, which indicates that the reactions would proceed spontaneously. At 25 °C, the theoretical conversion that can be achieved is 40% at 1 bar and 75% at 30 bar. The acetic acid is recovered in this step and recycled for use in the extraction step.

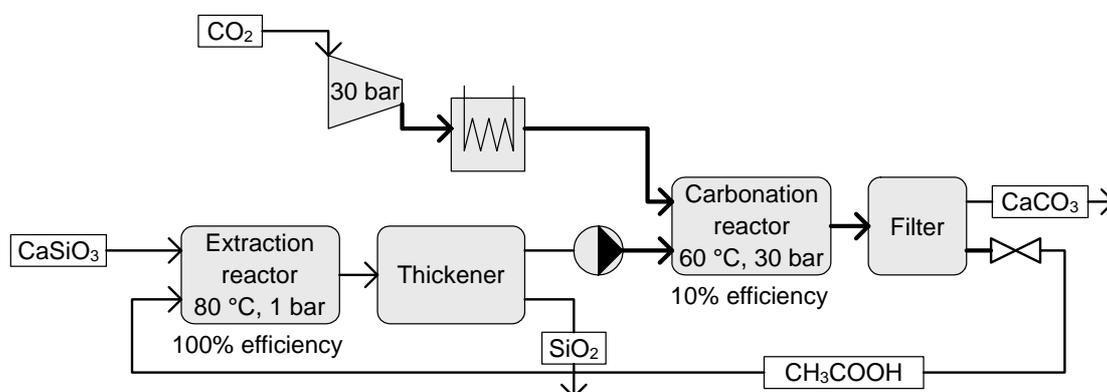


Figure 3.5. Indirect carbonation of calcium silicate using acetic acid.

Kakizawa et al. conducted extraction experiments with wollastonite (particle size $<37 \mu\text{m}$) at 60 °C and atmospheric pressure in a batch reactor. The extraction of calcium reached 48% in 250 minutes using 13.3 g of wollastonite in an aqueous solution of acetic acid (acetic acid/water = 13.7 g/50 g). The further pulverisation of the feed of wollastonite particles was suggested in order to attain a higher extraction. Crystallisation experiments were conducted at 5-50 bar in a batch reactor of 200 ml. The best carbonation conversion achieved was about 20% in 60 min under a total pressure of 30 bar using CO_2 . However, the conversion was calculated from the total amount of precipitate produced, and the chemical composition of the precipitate was not reported.

Kakizawa et al. also modelled the process as a carbon dioxide capture and storage process operating at 60 °C using an extraction pressure of 1 bar (100% calcium conversion assumed) and a carbonation pressure of 30 bar (10% calcium conversion assumed). Using these values and a calculated approximation for the required energy for pulverisation, the total energy requirement for separating CO_2 from a 100 MW thermal plant and using it to produce 142 t/h CaCO_3 from 165 t/h of wollastonite was 20.4 MW. This included the power demand of the capture of CO_2 from flue gases (27%), the compression of CO_2 for transportation (23%), and the pulverisation of the wollastonite particles (26%). The total cost (including the separation, compression, and pulverisation costs) of using this method to capture and store CO_2 was estimated at 55 US\$/t CO_2 .

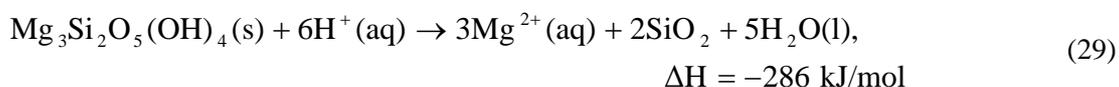
3.2.3.4 *Multi-step carbonation process using caustic soda*

Blencoe et al. (2003) developed a carbonation process that uses caustic soda (NaOH) to dissolve silicate minerals. First, serpentine reacts with a concentrated solution of caustic soda, which forms crystalline brucite and an aqueous solution rich in dissolved silica. Injecting CO₂ into the solution causes magnesite and a silica gel to form. According to Blencoe et al., both olivine and (hydroxylated) serpentine are rapidly decomposed by an aqueous solution of caustic soda (30-80 wt-% NaOH) at relatively low temperatures (at 200 °C and below), and the pressure required to achieve rapid and efficient carbonation is about 15 bar. The process was also used for carbonating calcium silicates (Blencoe et al., 2004). According to Blencoe et al. (2004), 90% pure carbonate can be produced in 72 h under these process conditions. However, the reaction times reported seem too long for industrial applications, and large amounts of NaOH are consumed in the process.

3.2.3.5 *Two-step process for carbonation of serpentine*

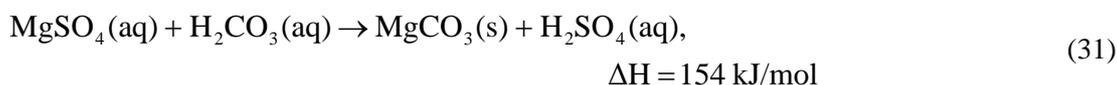
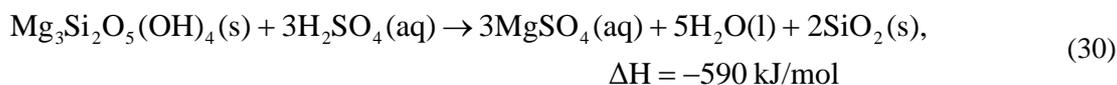
Park et al. (2003) studied the dissolution of serpentine in aqueous solutions of HCl, acetic acid, ethylenediaminetetraacetic acid (EDTA), orthophosphoric acid, and oxalic acid for subsequent carbonation. Park found that a mixture of orthophosphoric acid, oxalic acid, and EDTA gave the best extraction of magnesium from serpentine. However, when an acidic solvent was used for aqueous mineral carbonation, the overall carbonation rate was limited by the dissolution of CO₂ and dissociation of carbonic acid, rather than the dissolution rate of the mineral.

Park and Fan (2004) proposed a two-step process for the carbonation of serpentine. First, ground serpentine is dissolved at 70 °C and under ambient pressure using either (a) an aqueous solution of 1 vol-% orthophosphoric acid, 0.9 wt-% oxalic acid, and 0.1 wt-% EDTA or (b) 1.4 M ammonium bisulphate:

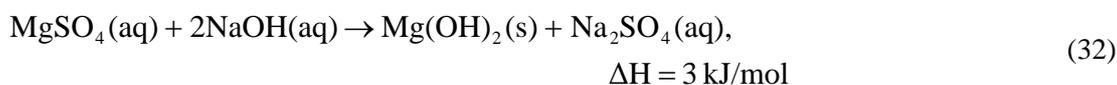


Experiments showed that after 1 h 65% of the magnesium in the serpentine had been extracted using solvent a), while 42% had been extracted using solvent b). After this stage, solid SiO₂ was separated by filtration. By raising the pH of the filtrate to pH ~ 8.6 using NH₄OH, iron, dissolved from the serpentine ore, precipitated as amorphous iron oxide. After the precipitated iron oxide had been removed by filtration, CO₂ was bubbled through the solution at 1 atm. The pH of the solution was further increased to pH ~ 9.5 using NH₄OH, which caused relatively pure MgCO₃·3H₂O to precipitate.

Maroto-Valer et al. (2005b) proposed a similar process for leaching calcium and magnesium from silicate minerals using sulphuric acid (Equation 30) for subsequent carbonation (Equation 31). The process steps using serpentine are given as examples:



Alternatively, magnesium hydroxide could be produced for subsequent carbonation:



Additionally, the addition of calcium nitrate or calcium hydroxide for the carbonation of the extracted magnesium sulphate has been proposed. However, this would consume large amounts of sodium hydroxide, calcium nitrate, or calcium hydroxide. According to Maroto-Valer et al., the maximum magnesium extraction achieved from serpentine was 71% using sulphuric acid, 21% using hydrochloric acid, and 25% using phosphoric acid (25 °C, 12 h). Using 41 bar CO₂ at 20 °C, a conversion of about 54% (based on CO₂ consumption) of the magnesium sulphate was achieved. However, it is not likely that the use of sulphuric acid instead of hydrochloric acid would reduce the drawbacks related to the recycling of the acid, as mentioned above (see Chapter 3.2.3.2).

3.2.4 Carbonation of industrial residues and by-products

The process routes described above could also be used for carbonating industrial residues and by-products. These seem to carbonate more easily and therefore do not require process conditions as demanding as those needed for natural minerals. For instance, Huijgen et al. (2005) achieved a maximum carbonation degree of 74% in 30 min at 19 bar CO₂ and 100 °C, using steel slag with a particle size of <38 μm. To reach a similar conversion of wollastonite, a temperature of 200 °C was required (Huijgen et al., 2006). Similarly, Uibu et al. (2005) were able to carbonate oil shale ash in 20-40 minutes to the extent of 89-100% by introducing CO₂ into an aqueous solution at atmospheric pressure and room temperature. A carbonation degree of only 47% was achieved using CaSiO₃ under the same process conditions. Although most research in this field has focused on the direct aqueous carbonation of industrial residues and by-products (Fernández Bertos et al., 2004; Johnson, 2000; Huijgen

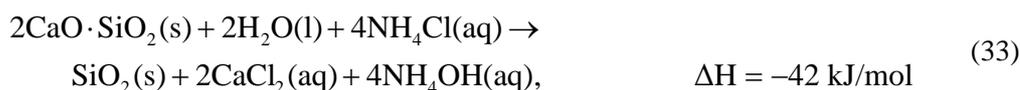
et al., 2005; Uibu et al., 2005), there are a few studies focusing specifically on the indirect carbonation of these materials.

Fujii et al. (2001) studied the possibility of applying the indirect carbonation process using acetic acid (presented in Chapter 3.2.3.3) to carbonate waste concrete. Waste concrete was found to dissolve much faster than wollastonite: 43% of the calcium contained in waste concrete was extracted in 15 min at 60 °C with a mixture of 13 g of waste concrete, 15 g of acetic acid, and 50 g of water at ambient pressure. Varying the temperature of the solution between 60-100 °C or the stirring speed had little effect upon the dissolution rate.

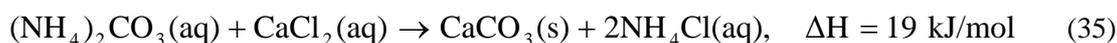
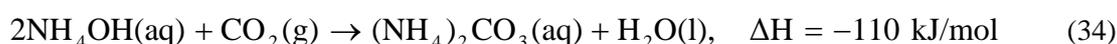
Iizuka et al. (2004) proposed using pressurised CO₂ for carbonating waste cement. First, calcium is extracted from waste cement in an aqueous solution using pressurised CO₂. After extraction, the pressure is reduced. This causes the extracted calcium to precipitate as calcium carbonate. Experiments showed that up to 50% of the calcium in waste cement was extracted using CO₂ pressures of 9-30 bar. The solution was saturated after 5-60 min. The precipitate formed was identified as calcite, CaCO₃. The power consumption for this route, mostly caused by the separation and compression of CO₂ from a flue gas stream, was calculated to be 420 kWh/t CO₂, which corresponds to sequestration costs of 23 US\$/t CO₂. Katsuyama et al. (2005) calculated that the production of CaCO₃ using this process would cost 136 US\$/t CaCO₃ for desulphurisation purposes and 323 US\$/t for high-purity CaCO₃.

Stolaroff et al. (2005) studied an indirect route where Ca(OH)₂ and CaO from steel slag or concrete waste was dissolved in water and carbonated with CO₂ in ambient air. Experimental results showed that a major part of the available calcium dissolved in a time scale of hours, which was taken to be sufficiently fast for use in an industrial process. No carbonation experiments were performed. Stolaroff et al. nonetheless proposed a carbonation process in which an aqueous solution is sprayed over a bed of slag or concrete waste. The solution dissolves CaO and Ca(OH)₂ from the alkaline solids and drops into a pool underneath the bed, from which the solution is recycled through the sprayers. The saturated solution absorbs CO₂ from the air, producing CaCO₃ that precipitates and allows more CaO and Ca(OH)₂ to dissolve. The operating cost of this scheme was estimated to be 8 US\$/tCO₂ sequestered (excluding the transportation costs of the slag). However, using steelmaking slag as raw material would increase the total costs by 25 US\$/tCO₂ (calculated using a market price of 8 US\$/t steelmaking slag).

Yogo et al. (2004) proposed and tested the carbonation of waste concrete and steelmaking slag by an indirect process using ammonium chloride (NH₄Cl) or ammonium nitrate (NH₄NO₃). First, calcium and/or magnesium ions are extracted in a solution of NH₄Cl from calcium silicate-rich materials, such as waste concrete or steelmaking slags:



While HCl and 2-ethylbutyric acid were more effective for dissolving the materials, NH_4Cl and NH_4NO_3 were found to be suitable for the selective extraction of calcium. In 30 minutes 44 wt-% of the calcium in the steel slag had dissolved in 1 N NH_4Cl , while 46 wt-% dissolved in 30 minutes in 1 N NH_4NO_3 . The solution was also found to be effective for absorbing CO_2 (Equation 34) and precipitating CaCO_3 (Equation 35). At an NH_3 concentration of 4% and 7% CaCO_3 precipitated as vaterite (a polymorph of aragonite and calcite), while calcite was the favoured form at a 10% NH_3 concentration.



Kodama et al. (2006) studied this concept further. Their theoretical calculations showed that the pH for the extraction of calcium needs to be lower than 9, while the pH for the precipitation reaction needs to be higher than 5. The pH variations of the solvent used during the process were in this range. The maximum calcium extraction from steelmaking slag achieved with experiments was 70% for particles smaller than 106 μm in 1 h at 60 °C. The selectivity for calcium and magnesium extraction was ~99%. The energy consumption of the process was calculated to be 300 kWh/t CO_2 (which corresponds to 15 €/t CO_2 ⁷) captured and stored. However, it was pointed out that large amounts of alkaline vapours (62 kg/t CO_2 captured) may leak from the absorption tower in the process. Although the process is suggested to be suitable for the simultaneous capture of CO_2 from flue gases and storage to carbonates, the conversion or rate of precipitation of carbonates was not reported.

3.2.5 Production of precipitated calcium carbonate

Today, synthetic calcium carbonate is already produced on an industrial scale. Synthetic calcium carbonate, commonly known as precipitated calcium carbonate (PCC), is produced by three different processes: a lime-soda process, a calcium chloride process, and a calcination/carbonation process. In the lime-soda process, calcium hydroxide is reacted with sodium carbonate to produce a sodium hydroxide solution, from which the calcium carbonate is precipitated. This process is widely used by alkali manufacturers, for whom sodium

⁷ Calculated for an electricity price of 0.05 €/kWh (STAT, 2003).

hydroxide recovery is the main objective and the coarse PCC produced is only a by-product. In the calcium chloride process calcium hydroxide is reacted with ammonium chloride, forming ammonia gas and a calcium chloride solution. After purification this solution is reacted with sodium carbonate to form a calcium carbonate precipitate and a sodium chloride solution. This process is the simplest of the three, but requires a low-cost source of calcium chloride if it is to be economical (Casey, 1983). Therefore, it is usually carried out in a satellite facility adjacent to a Solvay process soda ash plant.

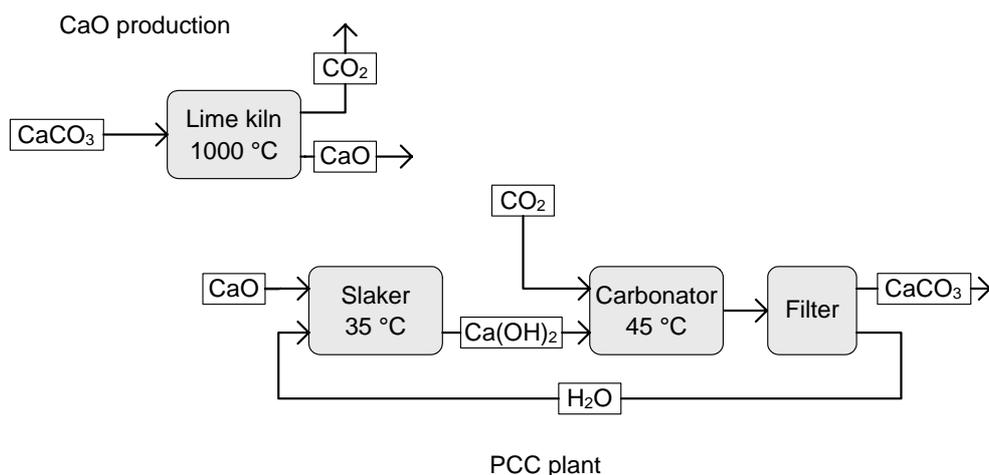
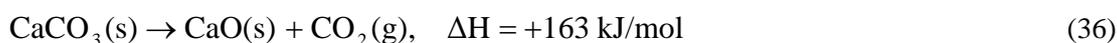


Figure 3.6. PCC production by carbonation.

The third and most commonly used PCC production process is the carbonation process (Figure 3.6), because it can use cheap raw material (limestone). In this process, crushed limestone is burned at about 1000 °C in a lime kiln, where it decomposes into lime (calcium oxide, CaO) and carbon dioxide⁸:



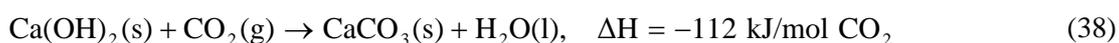
The dry CaO is transported to a PCC plant (located next to a paper mill), where it is slaked (hydrated) with water at temperatures of 30-50 °C, producing a calcium hydroxide slurry (Koppinen et al., 2003). The slurry production starts with stored lime being sent to a slaker tank, which is stirred by a high shear mixing agitator, after which water at the desired temperature is added and the slurry is formed⁹:

⁸ reaction enthalpy calculated for 1000 °C

⁹ reaction enthalpy calculated for 35 °C and assuming all minerals appear as solids



The slurry contains undissolved calcium hydroxide, calcium ions (Ca^{2+}), and hydroxide ions (OH^-). The calcium ion concentration in the slurry depends on the solvent solubility limit, which decreases as the temperature increases. Before carbonation, the process slurry is screened to remove impurities originating from the limestone. The slurry is then fed to a three-phase stirred tank reactor, either at atmospheric pressure or under pressure, where it reacts with CO_2 in stack gas, supplied from the lime kiln of a nearby paper mill¹⁰:



Adjusting the reactor temperature, carbon dioxide partial pressure, flow rate of the carbon dioxide, lime slurry concentration, and agitator speed controls the particle size, size distribution, shape, and surface properties of the calcium carbonate particles. The carbonation reaction is regulated by solution equilibrium; as the calcium ions are converted to calcium carbonate and precipitated out, more calcium hydroxide dissolves to equalise the concentration of calcium ions (Ca^{2+}). The rate of dissolution of Ca(OH)_2 into Ca^{2+} depends on pressure and temperature, while the reaction rate of calcium ions combining with carbonate ions is very fast. Therefore, the rates of formation of calcium and carbonate ions are the primary limitations for the overall reaction rate. With a pressurized reactor (1-10 bar pressure) the overall reaction rate is higher than with an atmospheric reactor, since the solubility of carbon dioxide is higher at elevated pressure (Mathur, 2001).

3.3 Utilisation of carbonate products

In order to provide for significant storage of CO_2 , large amounts of raw materials are required as feedstock for carbonation. Therefore, the raw materials used for carbonation must be abundant, but also cheap. However, it is possible that a relatively pure carbonate product could be valuable.

Currently, calcium carbonates find much wider uses than magnesium carbonates (Zevenhoven et al., 2006b). In the U.S. alone, 1 Gt of limestone was mined in the year 2003 for constructional, chemical, metallurgical, and agricultural use (USGS, 2003). Calcium carbonate is used in growing amounts in the pulp and paper industry as a paper filler (instead of clay) and in coatings to provide opacity, high brightness, and improved printability because of its good ink receptivity (Hase et al., 1998).

¹⁰ reaction enthalpy calculated for 45 °C and assuming all minerals appear as solids

Limestone is also used for producing precipitated calcium carbonate, of which the worldwide production was almost 8 Mt in 2004 (Roskill, 2007). By synthesising calcium carbonate from limestone (calcium carbonate rock), a purer calcium carbonate than natural or ground calcium carbonate can be produced (see Chapter 3.2.5). The most important crystalline forms of PCC are the rhombohedral calcite type, the orthorhombic acicular aragonite type, and scalenohedral calcite, of which the scalenohedral calcite is the favoured form in most applications (Imppola, 2000). Important qualities of the limestone used for providing raw material for the PCC process are a low manganese and iron content, since these elements have a strongly negative influence on the brightness of the PCC product (Ciullo, 1996). The iron content of PCC should be less than approximately 0.1% for a commercial product (Dahlberg, 2004).

Magnesium carbonate is primarily produced from mined rock, especially dolomites, and is used for producing magnesium metal and basic refractory bricks. It is also used in rubber processing, cosmetics, and pharmaceuticals. Magnesite (MgCO_3) can be used as a slag former in steelmaking furnaces, in conjunction with lime (CaO). The world-wide production of magnesite was 12 Mt during 2003 (USGS, 2003).

4 Production of PCC from calcium silicates – concept and potential

To determine the feasibility of a possible process to produce calcium carbonate from calcium silicate, three processes were chosen for modelling and a comparison of their power and heat requirements¹¹ (Paper I): indirect carbonation using hydrochloric acid (Chapter 3.2.3.2: Lackner et al., 1995; Newall et al., 2000); indirect carbonation using acetic acid (Chapter 3.2.3.3: Kakizawa et al., 2001), and the conventional PCC production method by carbonation for comparison (Chapter 3.2.5). Unfortunately, the articles by Yogo et al. (2004), Stolaroff et al. (2005), and Kodama et al. (2006) had not yet been published when we selected the processes for the comparison (see Chapter 3.2.4). The process with the highest CO₂ reduction potential was selected for further experimental and theoretical studies. Using the results from the process comparison, the potential for CO₂ emission reduction and PCC production using domestic calcium silicate-containing resources was assessed.

4.1 Process comparison and evaluation

The processes were modelled using Aspen Plus 12.1 and Outokumpu HSC 4.0 software (Paper I). HSC is a computer program based on the minimisation of Gibbs free energy for determining the chemical composition of reaction systems at thermodynamic equilibrium. Although complex chemical process can be modelled using Aspen Plus, only simple steady-state models were constructed because of the scarcity of experimental data from the calcium silicate carbonation processes. All the processes were modelled on the assumption that sources of pure CO₂ and CaSiO₃ are readily available for the process at room temperature and atmospheric pressure. Chemical kinetics was not taken into account. The CO₂ emissions from external heat demand were calculated assuming the combustion of heavy fuel oil that has a heat content of 41.1 MJ/kg and CO₂ emissions of 77.4 kg CO₂/GJ (STAT, 2003). The CO₂ emissions from electrical power demand were calculated assuming power is supplied from a coal-fired subcritical power plant, producing 830 kg CO₂/MWh (IEA, 1993). The temperature and pressure of the environment were set to be 25 °C and 1 bar, respectively.

4.1.1 PCC production from limestone

A basic model of the PCC production process was constructed (Figure 3.6). Since the process was modelled as an atmospheric carbonation process, there were no power requirements for compression and pumping in the model. The only heat-requiring step was

¹¹ In order to simplify the comparison of existing and potential PCC processes, all heat and power units have been written as kilojoules per kilogram of PCC produced (kJ / kg CaCO₃).

found to be the limestone calcination, since both the hydration (slaking) step and carbonation step are exothermic. Since limestone calcination takes place in a separate facility, only the calcination step was modelled.

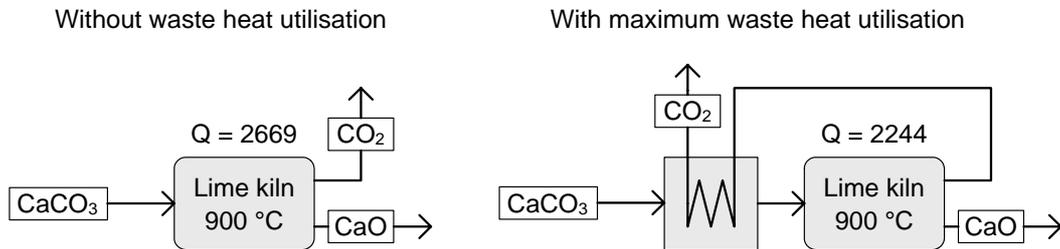


Figure 4.1. Model of a lime kiln with and without waste heat utilisation (unit for results Q: kJ/kg CaCO₃ produced).

The lowest possible temperature at which the calcination reaction (Equation 36) can occur was found to be 894 °C at atmospheric pressure by calculating the Gibbs free energy change for the components involved in the reaction. Therefore, the lime kiln temperature in the model was set to 900 °C. The calcination process was modelled using a multiphase reactor module that calculates the product composition by Gibbs free energy minimisation. The lime kiln was found to be very energy-intensive: 2669 kJ/kg CaCO₃ is needed for calcining calcium carbonate at 900 °C (Figure 4.1, left-hand model). The released carbon dioxide can be used for preheating the limestone feed, lowering the external heat requirements to 2244 kJ/kg CaCO₃ (Figure 4.1, right-hand model), assuming that the flue gases are cooled down to 35 °C. Although this figure might be too low in practice, it shows the maximum waste heat utilisation possible (assuming a minimum temperature difference of 10 °C). The process produces 0.44 kg CO₂/kg CaCO₃, which is later bound in the PCC production process. If heavy fuel oil were used to provide the heat required, an additional 0.21 kg CO₂/kg CaCO₃ would be emitted, making the total emissions from the calcination process 0.65 kg CO₂/kg CaCO₃. If the waste heat could be fully used, the emissions from the additional combustion would be reduced to 0.17 kg CO₂/kg CaCO₃, resulting in total emissions of 0.61 kg CO₂/kg CaCO₃ from the calcination step. However, in a real lime kiln excess heat is needed to compensate for heat transfer losses. According to Nordkalk (2007), the production of CaO releases 1.2 t CO₂/t CaO (or 0.67 kg CO₂/kg CaCO₃), which verifies the process calculations and assumptions presented here.

4.1.2 Calcium carbonate production by indirect carbonation of calcium silicate using hydrochloric acid

The process suggested for the carbonation of calcium silicates by Lackner et al. (1995) and further evaluated by Newall et al. (2000) (Chapter 3.2.3.2) was modelled both without a carbonation reactor (Figure 4.2) and with a carbonation reactor (Figure 4.3). All the chosen reactor models use Gibbs free energy minimisation for determining the product compositions and minimum heating/cooling requirements. The only significant difference between the results from these process models and process values calculated by Newall et al. was the temperature requirement for the dehydration unit, which separates HCl and H₂O from Mg(OH)Cl by evaporation. According to our Aspen Plus model, a temperature of 227 °C was required for the evaporation of HCl and H₂O, while Newall et al. used 150 °C in their calculations. The dehydration unit was, as expected, the most energy-demanding step, requiring 11830 kJ/kg Ca(OH)₂ (or 8760 kJ/kg CaCO₃). This requirement alone is over three times the heat needed for calcining limestone. The only additional energy requirement for the process was for the separation of calcium hydroxide, requiring 240 kJ/kg Ca(OH)₂ (or 178 kJ/kg CaCO₃). If heavy fuel oil was used to provide the heat for the process, 0.69 kg CO₂/kg CaCO₃ would be emitted in the Ca(OH)₂ production process, which is more than the calcination step for conventional PCC production emits (Chapter 4.1.1).

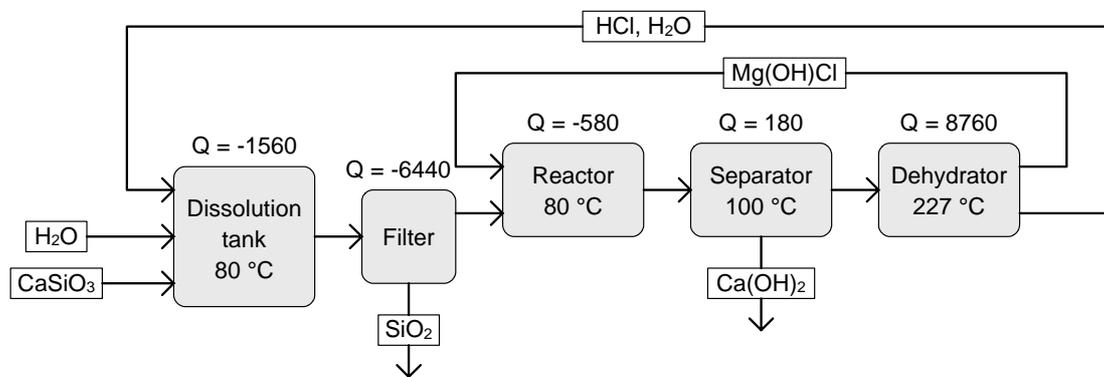


Figure 4.2. Model of Newall's process without a carbonation reactor (unit for results Q: kJ/kg CaCO₃ produced).

In an attempt to reduce the heat demands, a dry carbonation reactor was integrated with the hydroxide production process model. The carbonation reactor uses the heat released in the carbonation process to preheat the Ca(OH)₂ and CO₂ prior to carbonation, while the hot products from carbonation can be used to preheat the Mg(OH)Cl stream before it enters the dehydration unit (Figure 4.3). Making use of the exothermic nature of the carbonation process, the reaction temperature was raised to 560 °C, which is the point at which all the heat

released in carbonation can be used to preheat the reactants. The results from the integration showed that the heat from the carbonation process can only supply 7.6% of the total heat demand for the dehydration unit. Since the carbonation process binds CO₂, the net emissions of this process would be 0.20 kg CO₂/kg CaCO₃ (using heavy fuel oil to supply heat), which is almost as much as the net emission of the current PCC production chain. Therefore, the process was considered unsuitable for reducing overall CO₂ emissions in PCC production.

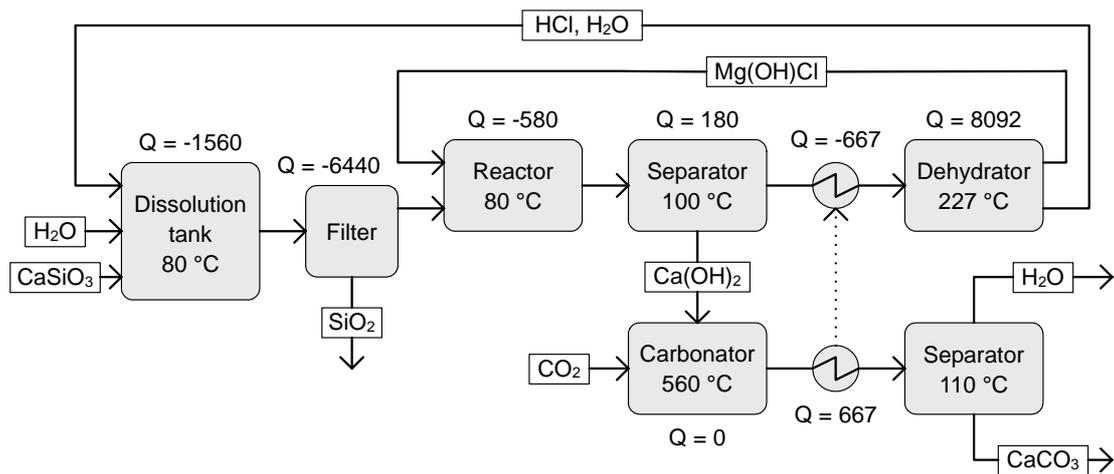


Figure 4.3. Model of Newall's process with carbonation reactor integrated (unit for results Q: kJ/kg CaCO₃ produced).

4.1.3 Calcium carbonate production by indirect carbonation of calcium silicate using acetic acid

The carbonation process studied by Kakizawa et al. (2001) (Chapter 3.2.3.3) was also modelled using Aspen Plus (Figure 4.4). To be able to compare our model with the process model results presented by Kakizawa et al. we chose similar conversion parameters for the process steps: a calcium extraction efficiency of 100% and a carbonate conversion of 10% were used. Therefore, stoichiometric reactor models that calculate the yield on the basis of user-specified conversion efficiencies were used in our process model. The partially regenerated solution was assumed to be returned to the extraction reactor. The carbonation reactor was chosen to run at 30 bar, which is the optimum pressure for the precipitation of calcium carbonate from calcium ions in acetic acid, according to Kakizawa et al. (2001). In order to achieve the high pressure of the carbonation reactor, a compressor and pump were included in the model. The isentropic efficiency of the compressor that was modelled was set to 0.8, and the total efficiency for the pump was set to 0.8. A cooler was also included to lower the temperature of the compressed CO₂ stream before it entered the reactor, which, in practice, may be unnecessary if the hot stream can be fed directly into the crystallisation

reactor to cover for the heat demand. In order to further compensate for the heat demand in the carbonation reactor, the heat released in the extraction reactor can be used. Therefore, the temperature of the extraction reactor was set to 80 °C, while the temperature of the carbonation reactor was set to 60 °C.

The total power demand of the process that was modelled was 223 kJ per kg of CaCO₃ produced. As the process is based on a carbonate-free raw material, the process binds 0.44 kg CO₂/kg CaCO₃ produced. However, the power needed to drive the compressor and the pump accounts for 0.10 kg CO₂/kg CaCO₃, reducing the net CO₂ emissions avoided to 0.34 kg CO₂/kg CaCO₃. If this process was used for replacing current PCC facilities, an additional 0.21 kg of CO₂ emissions per kg of CaCO₃ produced could be prevented due to the reduced demand for calcined limestone. On the basis of these calculations, the acetic acid process seems to have a high potential for simultaneously reducing CO₂ emissions and producing PCC.

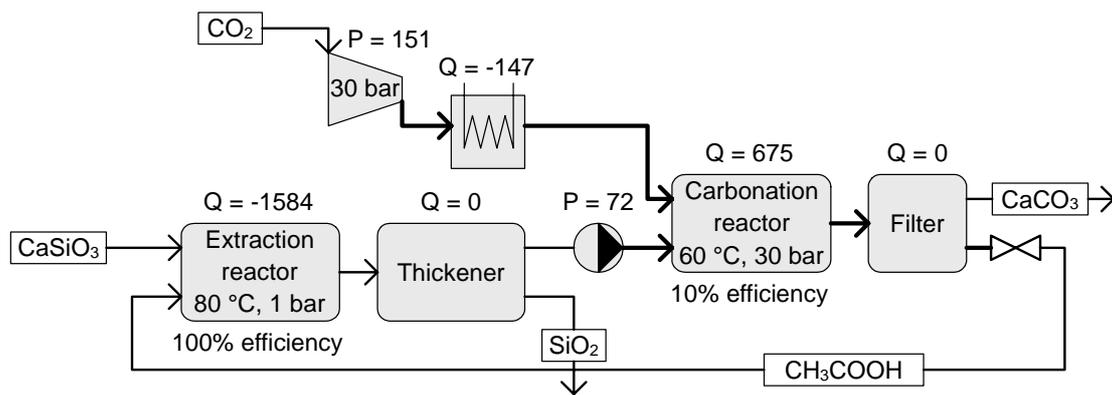


Figure 4.4. Model of Kakizawa's process (unit for results Q: kJ/kg CaCO₃ produced).

4.2 Potential

To estimate the amount of CO₂ reduction that is possible by the carbonation of natural calcium silicate minerals, rocks and steelmaking slags, their carbonation potential has been evaluated in this chapter. According to the numbers presented by various sources, the known world-wide wollastonite resources can be estimated at a few hundred megatonnes, of which the Finnish resources are less than thirty megatonnes (Paper I). On the other hand, basalt is the most common igneous rock, and is found widely distributed throughout the world. While the availability of basalt seems sufficient, the mining of very large amounts of rock would be needed for producing calcium carbonates. However, using steelmaking slag for carbonation, no mining operations would be needed, but the carbonation capacity is limited.

Table 4.1. Relative CO₂ storage capacity by carbonation of the CaO and MgO components of Finnish steelmaking slags in comparison to wollastonite and basalt.

Slag type	CaO content (%)	MgO content (%)	CO ₂ storage capacity (tCO ₂ /t)	CaCO ₃ production potential (tCaCO ₃ /t)
Blast furnace slag ^a	40.5	10.3	0.43	0.72
Steel converter slag ^a	46.2	2.1	0.39	0.82
EAF slag 1 ^b	39.6	11.0	0.43	0.71
EAF slag 2 ^b	43.3	5.6	0.40	0.77
AOD process slag 1 ^b	55.6	8.3	0.53	0.99
AOD process slag 2 ^b	57.1	7.5	0.53	1.02
Chrome converter slag ^b	38.5	16.6	0.48	0.69
Ferrochrome slag ^b	1.4	22.6	0.26	0.024
Slag mixture ^c	37.1	4.5	0.34	0.66
Blast furnace slag ^d	33.6	17.1	0.45	0.60
Steel converter slag ^d	54.3	1.5	0.44	0.97
Slag average	40.6	9.7	0.42	0.73
Basalt ^e	9.47	6.73	0.15	0.17
Wollastonite ^f	44.0	no data, 0 % assumed	0.35	0.79

^aSlag composition data supplied from Rautaruukki steel plant at Raahe.

^bSlag composition data supplied from Outokumpu steel plant at Tornio.

^cSlag composition data supplied from Ovako steel plant at Imatra.

^dSlag composition data supplied from Ovako steel plant at Koverhar.

^eBasalt composition data taken from Cox *et al.* (1979).

^fWollastonite composition data supplied from Nordkalk wollastonite production at Lappeenranta.

The relative CO₂ storage capacity of Finnish calcium silicate-based minerals and steelmaking slags has been summarised in Table 4.1. Assuming that all the MgO and CaO components of steelmaking slag can be carbonated, 260-530 kg of CO₂ would theoretically be stored per tonne of slag carbonated, depending on the type of slag used. Carbonating wollastonite would bind 350 kg of CO₂ per tonne of pure wollastonite (assuming a zero MgO content), and basalt carbonation would bind 150 kg of CO₂ per tonne of basalt rock. Thus, the current world production of wollastonite would only allow for an annual reduction of 190-210 kt of CO₂, which is an insignificant reduction compared to the annual global anthropogenic CO₂ emissions of (currently) 26 Gt. The CO₂ reduction capacity of carbonating steelmaking slags is much higher: using the world production estimates of steelmaking slag (256-345 Mt; USGS, 2003) with the average CO₂ storage capacities of slag in Table 4.1, the reduction potential can be estimated as 110-150 Mt CO₂/a. Although the potential for CO₂ sequestration in basalts is much higher, the large mining operation required (about 7 t basalt needed per t

CO₂ stored) makes it unattractive for ex situ carbonation. Therefore, the potential for basalt carbonation was not further assessed. The potential for reducing CO₂ emissions in Finland by carbonating domestically produced steelmaking slag (based on the production in 2004) was calculated as 550 kt of CO₂ per year (Table 4.2). This corresponds to a reduction of almost 9% of the CO₂ emissions from Finnish steel plants. If only the calcium compounds in the steelmaking slags were used, 840-860 kt of CaCO₃ could be produced from the slags. Producing CaCO₃ by the acetic acid process (presented in Chapter 3.2.3.3) would reduce the CO₂ emissions by 290 kt of CO₂ (according to the calculated process requirements presented in Chapter 4.1.3), which corresponds to almost 5% of the CO₂ emissions from Finnish steel plants.

Table 4.2. CO₂ reduction potential by carbonation of steelmaking slags.

	Slag production (kt)	Theoretical CO ₂ reduction potential by slag carbonation ^a		CaCO ₃ production potential of slags ^b (kt CaCO ₃)	CO ₂ reduction by CaCO ₃ production from slags ^c	
		(kt CO ₂)	(%)		(kt CO ₂)	(%)
Steel mill	(kt)	(kt CO ₂)	(%)	(kt CaCO ₃)	(kt CO ₂)	(%)
Raahe	873	362	7.6%	662	225	4.7%
Koverhar	158	71	7.9%	118	40	4.4%
Tornio	356	98-104	14.3-15.2%	40-55	14-19	2.1-2.8%
Imatra	36	12	21.1%	24	8	14%
Total	1423	543-549	8.5-8.6%	843-858	287-292	4.5-4.6%

^aCalculated using the CO₂ storage capacity numbers in Table 4.1, i.e. carbonating both the MgO and CaO components of the slags.

^bCalculated using the CaCO₃ production potential numbers in Table 4.1, i.e. CaCO₃ production from carbonating only the CaO components of the slags.

^cCalculated using the process modelling results for carbonation of calcium silicates by acetic acid: a net reduction of 0.34 t CO₂ per tonne of CaCO₃ produced, with CO₂ emissions from the power production for the process taken into account.

The production of CaCO₃ from the carbonation of iron and steel slag could also be a profitable refining method for the slag products, if the purity requirements for commercial PCC could be achieved. In Finland, granulated blast furnace slag can be purchased for 10 €/t, which is approximately the same price as for limestone lumps used for producing lime for PCC manufacturing (11 €/t), while the cheapest available PCC type has a price tag of 120 €/t. As a comparison, Finnish fine-grained wollastonite costs 200 €/t (Dahlberg, 2004). Although the world-wide demand for PCC is forecast to rise (Roskill, 2007), the market is very small in comparison with the need for global CO₂ emission reductions.

4.3 Discussion

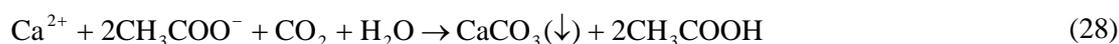
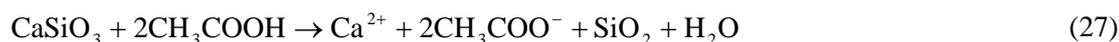
Two processes found in the literature (until the year 2004) for carbonating calcium silicates were compared to the current lime carbonation process used by the industry. A two-step carbonation method using acetic acid was found to be the most promising process for the PCC production of calcium silicates. Using this process, a net fixation of 0.34 t CO₂ could be achieved per ton of calcium carbonate produced. The process has no external heat input requirements, and the total energy requirements seem to be much lower than the current PCC production chain. However, the process produces calcium carbonate directly, and not calcium oxide, meaning that more mass must be transported to the PCC facilities, which would raise the cost of transportation. It would also require a relatively pure stream of CO₂. Only limited experimental data was available for this process (Kakizawa et al., 2001, Fujii et al., 2001), and the quality of the calcium carbonate produced from the process had not been reported.

Wollastonite seems to be too expensive and too rare to be used for the reduction of CO₂ emissions by carbonation. Although its chemical composition makes it an attractive material for carbonation, the limited availability of the mineral makes it too expensive. Even if the product could be sold as PCC, the economic value of the reduced CO₂ emissions would probably not compensate for the use of a raw material twenty times more expensive than limestone. While basalt is more common and cheaper than wollastonite, the former would require (because of its low calcium oxide content) a mining operation five times larger than that needed for quarrying limestone. The potential for reducing CO₂ emissions by the carbonation of steelmaking slags was found to be sufficient to motivate further study. While the CO₂ storage potential for using iron and steel slags is low in comparison with other CO₂ storage options found in the literature, the annual CO₂ reduction potential of 8-21% is a significant reduction for an individual steel mill in Finland. The cost per mass of steelmaking slags is similar to the cost per mass for limestone. However, steelmaking slags contain a multitude of other elements, which may require additional separation measures, depending on the carbonation process used.

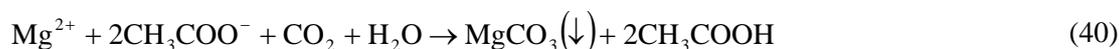
The potential for using the calcium carbonate produced relies on the purity and variety of the crystal structures achievable by the carbonation process. While commercial wollastonite is relatively pure, basalts and slag products would require unwanted elements to be separated in the carbonation process to achieve a pure enough product. The relatively high price of PCC might justify the development of a carbonation process that is more expensive than other CO₂ storage alternatives.

5 Production of calcium carbonate from steelmaking slag

The carbonation process using acetic acid, represented by Equations 27 and 28 (see also Chapter 3.2.3.3 and 4.1.3), could possibly also be used for carbonating steelmaking slags instead of natural calcium silicates, since several slag types contain calcium silicates or other forms of calcium oxides.



However, steelmaking slags also have high contents of other compounds, such as magnesium silicates, which may react with acetic acid:



In this chapter, the possibility of producing calcium carbonate from steelmaking slag using acetic acid was studied both theoretically and experimentally (Papers II-III). On the basis of the experimental findings, a process scheme was set up and its potential evaluated.

5.1 Thermodynamic calculations

No data on the compositions of the precipitated products were provided neither by Kakizawa et al. (2001) nor Fujii et al. (2001). Therefore, thermodynamic equilibrium calculations were carried out to see if calcium carbonate and magnesium carbonates are possible products of the process before the steps were studied experimentally (Paper II). The solution equilibrium was calculated using Outokumpu HSC 5.1. Although the program only calculates chemical equilibria between pure substances and ideal solutions, the calculations should give an indication about what products can be expected from the process steps.

5.1.1 Equilibrium of reaction equations

The Gibbs free energy calculations of the extraction reactions (Equations 27 and 39) showed that both the extraction of calcium ions from CaSiO_3 and magnesium ions from

MgSiO₃ are thermodynamically possible throughout the temperature range where water is in liquid form (Figure 5.1). The Gibbs free energy calculations of the carbonation reactions (Equations 28 and 40) showed that the carbonation of Ca ions is already proceeding at temperatures over 45 °C, while the carbonation of Mg ions should only be possible at temperatures over 144 °C. The calculations also show that the extraction reactions are exothermic ($\Delta H < 0$), while the carbonation reactions are endothermic ($\Delta H > 0$). However, the net reactions of both calcium silicate carbonation (Equations 27 and 28 together) and magnesium silicate carbonation (Equations 39 and 40 together) are exothermic.

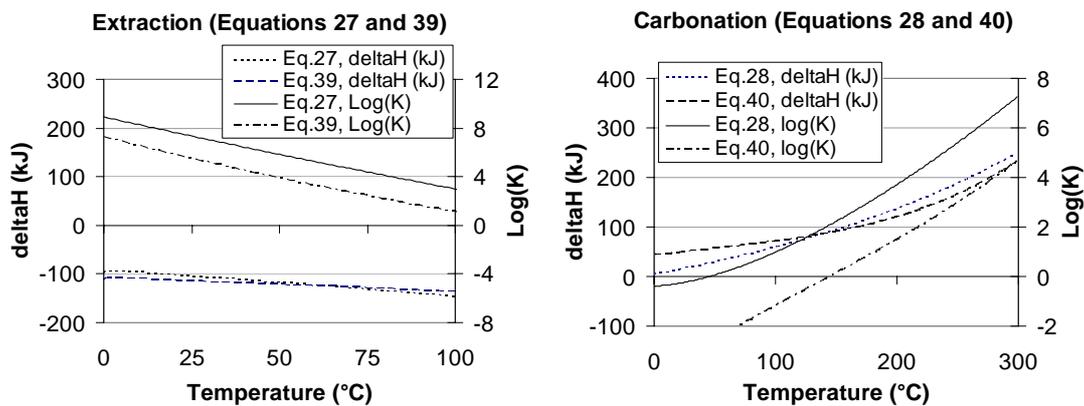


Figure 5.1. Equilibrium constant (K) and reaction heat (ΔH) calculated for extraction of CaSiO₃ (Equation 27) and MgSiO₃ (Equation 39) in acetic acid and carbonation of the solutions (Equations 28 and 40) (Paper II).

5.1.2 Dissolution of blast furnace slag

The dissolution of blast furnace slag in acetic acid was studied in more detail by calculating the chemical composition at thermodynamic equilibrium. The input parameters were set to simulate the extraction experiments carried out later on, using 4.2 g of blast furnace slag in a 250-ml aqueous solution of 33.3 wt-% acetic acid. Only the six largest species of blast furnace slag were used as input data, to simplify the results. All the compounds in the database of HSC 5.1 were used as potential products, except for C, C_xH_y, and all carbonates, which are unlikely products from an extraction process performed in the absence of CO₂. The results and input data are summarised in Table 5.1. The results show that all compounds (except for Ti) dissolve, forming magnesium acetate, calcium acetate, and iron(II) acetate ions. Although kinetics may affect which components actually dissolve in the time frame of hours, the modelling results show that the extraction of calcium from steelmaking slags should be theoretically possible, but may require the separation of unwanted elements from the resulting solution.

Table 5.1. Thermodynamic equilibrium composition of a solution of blast furnace slag (six main species) in acetic acid (33.3 wt-%) and water (66.7 wt-%). The results are presented as conversion ratios of various elements (Paper II).

Input	Composition (g)	Output	Element	Extraction of element (%)		
				at 30 °C	at 50 °C	at 70 °C
H ₂ O(aq)	166.7	CaCH ₃ COO ⁺	Ca	62	65	70
CH ₃ COOH(aq)	83.3	Ca ²⁺	Ca	38	35	30
CaO	1.70	Si(OH) ₃ ⁻	Si	100	100	100
SiO ₂	1.46	Mg(CH ₃ COO) ₂ (aq)	Mg	76	70	69
MgO	0.43	Mg ²⁺	Mg	24	30	31
Al ₂ O ₃	0.39	Al ₃ (OH) ₄ ⁵⁺	Al	100	100	100
Ti	0.042	Ti ²⁺	Ti	0	0	0
Fe	0.026	Fe(CH ₃ COO) ₂ (aq)	Fe	91	89	89
S	0.008	Fe ²⁺	Fe	9	11	11
		S ₄ O ₃ ⁻²	S	99	99	98
		S ₅ O ₃ ⁻²	S	1	1	2

5.1.3 Carbonation of calcium-rich solution of acetic acid

To predict the precipitation of CaCO₃ from a calcium-rich acetic acid solution, the thermodynamic equilibrium of the species and products participating in the reaction in Equation 28 was calculated. According to the results, higher temperatures and pressures favour the precipitation of calcium carbonate. At a CO₂ pressure of 1 bar and a solution temperature of 25 °C, only 46% of the calcium ions were predicted to form CaCO₃. Calculating the equilibrium composition for the same system at a pressure of 30 bar raises the conversion to 74% at 25 °C. These results agree with the theoretical carbonation conversions reported by Kakizawa et al.: 40% at 1 bar and 75% at 30 bar. However, adding a surplus of acetic acid to the system seems to inhibit the formation of calcium carbonates. For instance, 2 additional moles of CH₃COOH(aq) caused no CaCO₃ formation at temperatures below 40 °C, while 4 additional moles of CH₃COOH(aq) prevented CaCO₃ formation below 88 °C at atmospheric pressure. Raising the CO₂ pressure compensated slightly for the presence of acetic acid. However, raising the conversion back to 40% when 4 additional moles of CH₃COOH(aq) are present would require a CO₂ pressure of 95 bar. The addition of NaOH to a system with a 10 mol surplus of acetic acid predicted no formation of CaCO₃ until the molar amount of NaOH exceeded half that of the acetic acid (Figure 5.2). According to these results, a 100% conversion to CaCO₃ would require practically all the surplus acetic acid to be neutralised with NaOH.

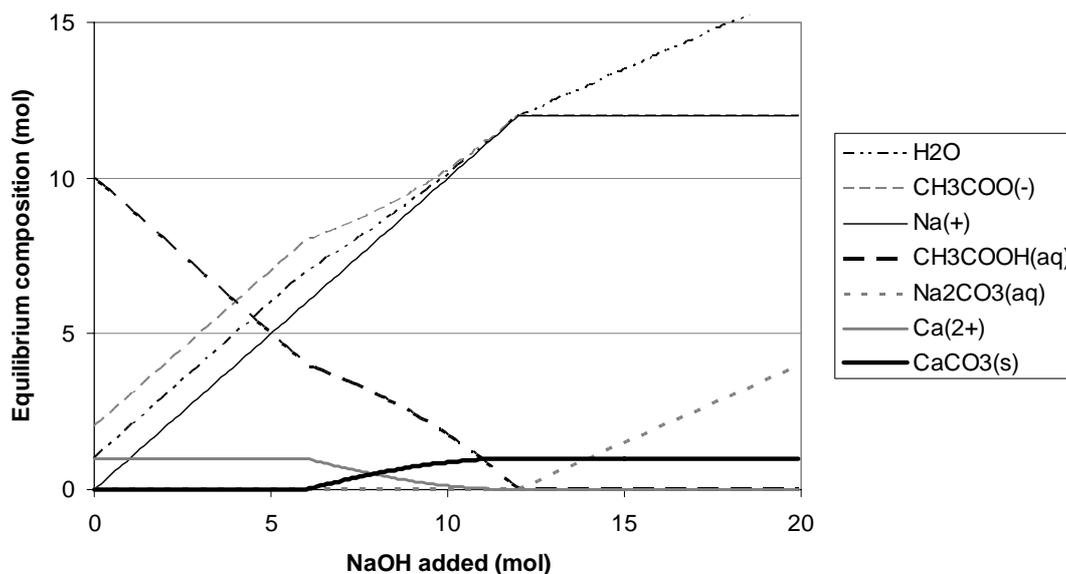


Figure 5.2. Effect of the presence of NaOH in a system at thermodynamic equilibrium at 25 °C consisting of 1 mol Ca²⁺, 2 mol CH₃COO⁻, 1 mol H₂O, 100 mol CO₂ (at 1 bar), and 10 mol CH₃COOH.

5.2 Characterisation of materials

The steelmaking slag types studied in our experiments were provided by the Raahe steel works (Ruukki) and Tornio steel works (Outokumpu). Wollastonite from Lappeenranta (Nordkalk) was also used for comparison. Particles were sieved to 125-500 µm and only the sieved fractions were studied, while materials in powder form were used as such. The compositions of the calcium silicate-based materials used in the experiments were analysed using X-ray fluorescence spectroscopy (XRF). The crystal orientations of the samples were determined by X-ray diffraction (XRD). On the basis of the XRF analyses, the five most common main elements in the materials, Ca, Mg, Al, Fe, and Si, were measured by total acid digestion and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) of the resulting solution.

A summary of the elemental composition of the materials used is shown in Table 5.2 (Paper II). All the slags tested contained similar amounts of calcium to that found in wollastonite (39-41 wt-%), except for AOD slag, which contained almost 70 wt-% CaO. The results of the XRD analyses are summarised in Table 5.3. Crystalline phases could be identified in all materials except for the blast furnace slag sample, since its crystal structure is mostly amorphous. Calcium silicate in the form of Ca₂SiO₄ was identified both in AOD process slag and steel converter slag. Apart from high amounts of calcium silicates, the slags

also contained considerable amounts of other compounds, such as magnesium, iron, and aluminium oxides.

Table 5.2. Elemental composition of calcium silicate-based materials used in the experiments as determined by XRF analysis and ICP-AES analysis after total digestion (units: wt-%^a).

Element	Blast furnace slag (350-500 µm)	Steel converter slag (350-500 µm)	Electric arc furnace slag (125-350 µm)	AOD process slag (< 125 µm)	Wollastonite (< 250 µm)	Analysis method
CaO	39.0	41.4	38.9	69.4	38.8	ICP-AES
SiO ₂	25.7	11.0	21.2	22.0	32.2	ICP-AES
Fe ₂ O ₃	0.404	26.0	3.82	0.252	0.201	ICP-AES
MgO	11.9	1.42	6.05	6.51	0.506	ICP-AES
Al ₂ O ₃	8.64	1.88	6.34	1.22	1.17	ICP-AES
F	0.07	0	0.11	5.5	0.02	XRF
Cr	0.003	0.232	5.07	0.228	0.001	XRF
Ti	1.03	0.512	2.64	0.356	0.012	XRF
Mn	0.376	2.39	2.29	0.076	0.005	XRF
S	1.73	0.086	0.092	0.273	0.008	XRF

^aOnly elements present at > 1 wt-% are shown.

Table 5.3. Minerals in calcium silicate-based materials identified by XRD analyses (Paper II).

Material analysed	Highest peak (counts)	Phases identified
Wollastonite	2500	wollastonite CaSiO ₃ , quartz SiO ₂
AOD process slag	1000	fluorite CaF ₂ , periclase MgO, calcium silicate Ca ₂ (SiO ₄)
Electric arc furnace slag	350	gehlenite Ca ₂ Al(AlSiO ₇), merwinite Ca ₃ Mg(SiO ₄) ₂ , magnesiochromite (Mg, Fe)(Cr,Al) ₂ O ₄
Steel converter slag	300	srebrodolskite Ca ₂ Fe ₂ O ₅ , lime CaO, iron Fe, calcium silicate Ca ₂ SiO ₄ , calcium iron oxide Ca ₂ Fe _{15.6} O ₂₅
Blast furnace slag		Mostly amorphous phases

5.3 Dissolution of steelmaking slags

The extraction of calcium from various iron and steel slags in solutions of acetic acid was studied using batch experiments (Paper II). The experiment setup is displayed in Figure 5.3. Acetic acid solutions of various concentrations were heated to 30, 50, and 70 °C in a glass reactor of 250 ml, which was put in a temperature-controlled water bath. The reactor was equipped with a tap-water condenser so as to prevent losses from evaporation of the solvent. Nitrogen was continuously fed to the reactor (above the surface of the solution) at 1 l/min to prevent the CO₂ in the air from interfering with the experiments. The solution was stirred using a magnetic stirrer at approximately 600-700 rpm. When the temperature of the

solution had stabilised after heating up to the desired temperature, 4.2 g of a calcium silicate-based material was added to the solution. The solution was stirred for 2 h and samples were extracted during the experiment. The samples were immediately filtered through syringe membrane filters with a pore size of 0.45 μm and analysed for Ca, Mg, Si, Al, and Fe using ICP-AES and Atomic Absorption Spectrophotometry (AAS). The accuracy of the ICP-AES and AAS analyses were estimated to be $\pm 2\%$.

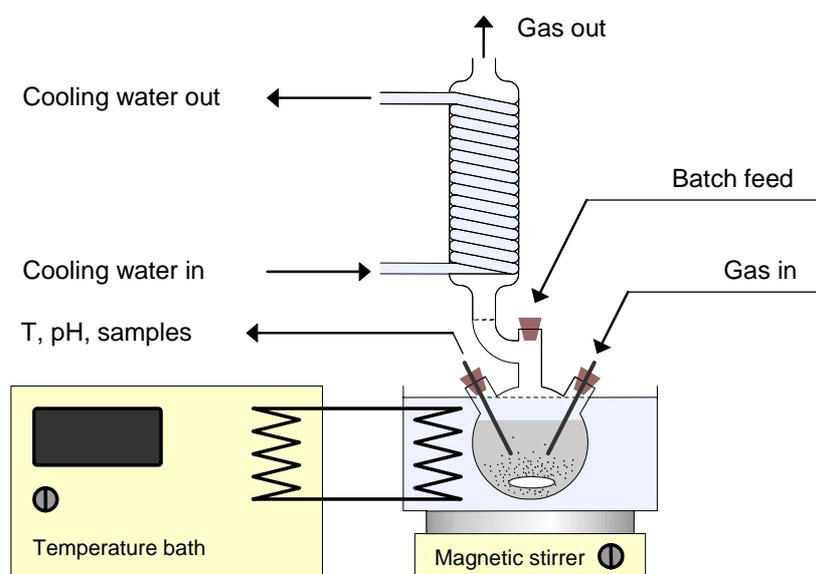


Figure 5.3. Experimental setup (Paper II).

To compare the potential for leaching calcium out from iron and steel slags, various slags were dissolved in aqueous solutions of acetic acid (33 vol-%¹² acetic acid and 67 vol-% distilled water, initial pH of 1.5) at 50 °C. The results from the AAS and ICP-AES analyses (Figure 5.4) show that only 51% of the calcium fixed in wollastonite could be extracted during 2 h, which is similar to the results reported by Kakizawa et al. (2001) (48% extracted during 250 min: see Chapter 3.2.3.3.). We found that the extraction of calcium from steelmaking slags was much faster; almost all the calcium from steelmaking slags dissolved in 15 minutes. The extraction efficiencies were calculated by comparing the concentration of selected elements in the filtered solution samples with the concentrations of the elements in the raw materials (Table 5.2) and accounting for the loss of solution volume resulting from sample extraction. However, other elements dissolve as well (see Figure 5.5), as predicted by the thermodynamic equilibrium calculations. The calculated extraction efficiency of blast furnace slag (Figure 5.4-Figure 5.5) was found to exceed 100%. This indicates that the

¹² 1 litre acetic acid = 1.05 kg

concentration of calcium in the blast furnace slag sample analysed (Table 5.2) was slightly lower than in the samples used in the experiments, although they were taken from the same batch.

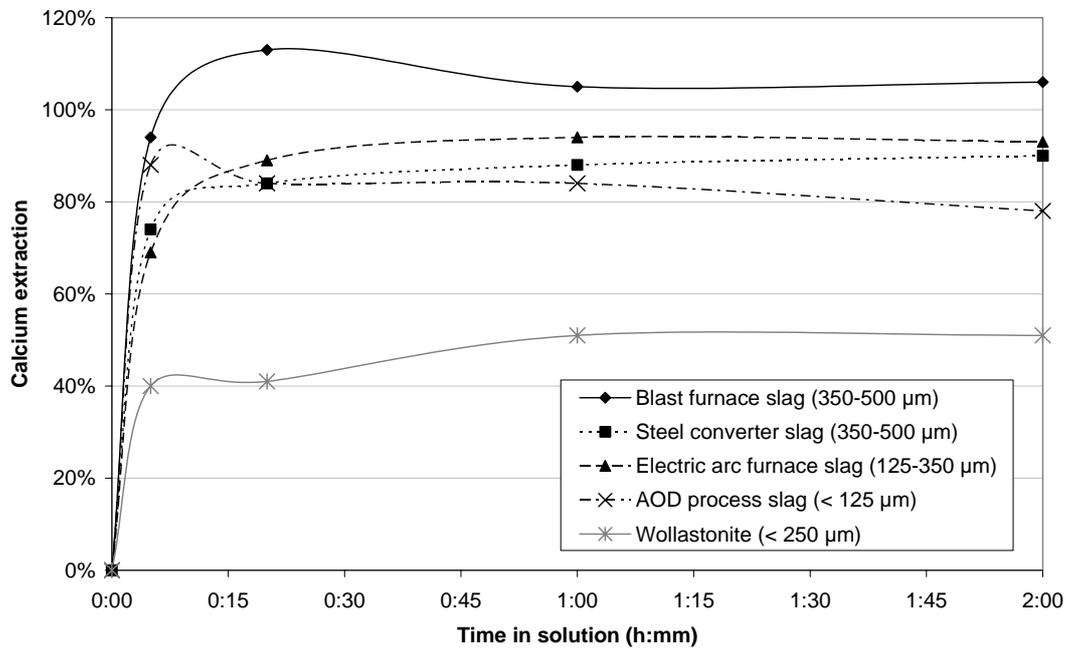


Figure 5.4. Extraction of calcium from various steelmaking slags and wollastonite (batch of 4.2 g added at 0:00) in 250 ml aqueous solutions of acetic acid (33 vol-% CH_3COOH).

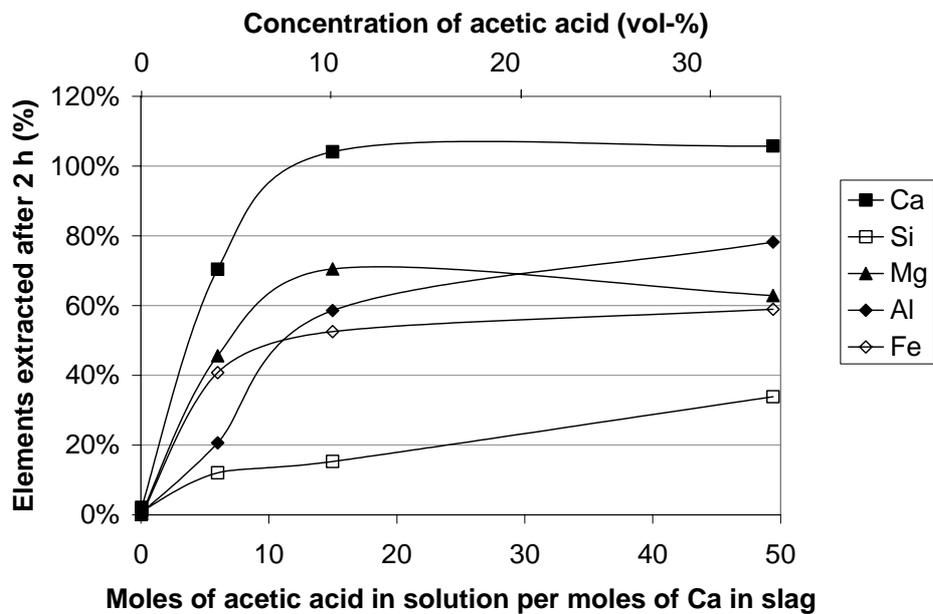


Figure 5.5. Effect of concentration of acetic acid (0 – 33 vol-%) upon dissolution of blast furnace slag (batch of 4.2 g added at 0:00, 250 ml solution kept at 50 °C).

Experiments were carried out with dissolving blast furnace slag at 50 °C in aqueous acetic acid solutions of varying concentrations. The results of the AAS and ICP-AES analyses show that the acetic acid concentration of the solution (i.e. the initial pH) has a dramatic effect upon the extraction of calcium in the range 0-10 vol-% acetic acid (Figure 5.5). Almost all of the calcium in the batch of slag was extracted in a solution of 10 vol-% acetic acid, which corresponds to 15 mol CH₃COOH per mol Ca (Figure 5.5).

The effect of temperature upon the extraction efficiency was also investigated for blast furnace slag at 30 and 70 °C. The results of the AAS and ICP-AES analyses (Figure 5.6) showed that temperature has a significant effect upon the solubility of calcium (and other elements as well) from blast furnace slag. At 30 °C the extraction is significantly slower than at 50 °C, but on the other hand more calcium can be extracted than at 50 or 70 °C. This is probably due to the solubility of calcium, which decreases with increasing temperature. However, this can be compensated for by increasing the acetic acid concentration in the aqueous solution: almost identical extraction efficiencies for all temperatures were achieved using a solution concentration of 33 vol-% (Teir et al., 2005).

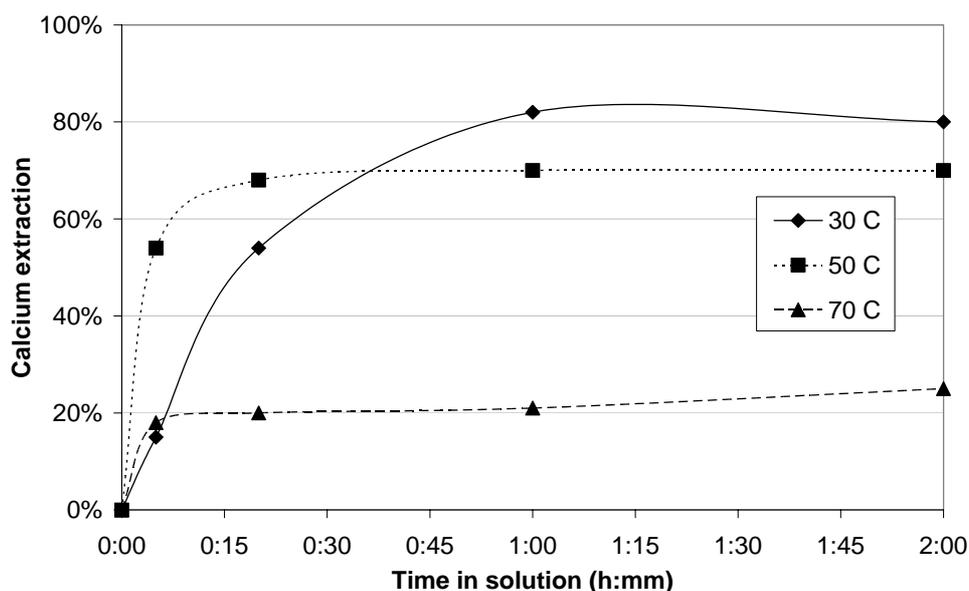


Figure 5.6. Extraction of calcium from blast furnace slag in aqueous solutions (250 ml) of acetic acid (4 vol-%) at 30 °C, 50 °C, and 70 °C (batch of 4.2 g added at 0:00).

To produce a solution suitable for the precipitation of CaCO₃, i.e. with a high concentration of calcium but a low concentration of silica, 50 g of blast furnace slag was dissolved in a 300-ml aqueous solution of 33 vol-% CH₃COOH at 70 °C for 2 hours, after which the solution was filtered using membranes with a pore size of 0.45 μm. The filtrate contained 17 g Ca/l (37% dissolved), and only 0.13 g Si/l (0.3% dissolved), showing that it is

possible to minimise the dissolved silica content by leaching slag at 70 °C and removing the silicon-rich gel that is formed by mechanical filtration. However, other separation measures are needed to remove aluminium, iron, magnesium, and other elements released from the solution of the dissolved slag.

5.4 Precipitation of carbonates

Since blast furnace slag was found to be easy to dissolve and contain low amounts of iron (an unwanted element in PCC), blast furnace slag was selected for carbonation experiments. The experiments were performed using a similar reaction setup as in Figure 5.3. The possibility of producing precipitated carbonates from blast furnace slag was tested using two different approaches: 1) by injecting CO₂ into filtered acidic solutions containing dissolved blast furnace slag, and 2) by first precipitating acetates by evaporation and then injecting CO₂ into aqueous solutions of the slag-derived acetates.

5.4.1 Carbonation of dissolved blast furnace slag

Solutions suitable for carbonation, i.e. with high concentrations of calcium and low concentrations of silica, were prepared similarly to those in the extraction experiments: 25-50 g of blast furnace slag (0.5-1 mm) was dissolved in a glass reactor (250 or 500 ml) filled with an aqueous solution of acetic acid (20-33 vol-% acetic acid) at 70 °C for 2 h under constant N₂ gas flow (1 l/min) and stirring (600-1000 rpm), after which the solution was vacuum filtered using Supor membranes (0.45 µm). This produced solutions containing 11-19 g Ca/l, 2-4 g Mg/l, and 1 g Al/l. The solutions also contained small amounts of Fe and Si (0.1-0.3 g/l).

The carbonation of 225 ml aqueous solutions of acetic acid and dissolved blast furnace slag was tested at 30, 50, and 70 °C. After heating up to the desired temperature under nitrogen flow (1 l/min), the nitrogen flow was switched to carbon dioxide gas flow (1 l/min). After four hours of continuous exposure to the carbon dioxide flow, the reactor was removed from the bath and the solution was filtered. The filtered solids were dried and analysed using XRD. Only 0.3-0.7 g of precipitate per litre of solution was formed in the experiments. No carbonate had been formed; the dried precipitates contained magnesium acetate hydrate and calcium acetate hydrate. Because of the low initial pH of the solution (pH 3), the precipitation of carbonates was apparently impossible (see Figure 3.2 and Chapter 5.1.3). In a conventional PCC production process (Chapter 3.2.5) the precipitation of calcium carbonate occurs in an alkaline environment. Additionally, Kodama et al. (2006) calculated that in order to precipitate calcium carbonate out of an aqueous solution a pH >5 is required.

In order to raise the alkalinity of the solution, the precipitation experiments at 30, 50, and 70 °C were repeated with the addition of sodium hydroxide (aqueous solution of 50 wt-% NaOH) during carbonation. After the temperature of the prepared solution (100 ml) had

stabilised under nitrogen flow and the gas flow had been switched to carbon dioxide (1 l/min), the sodium hydroxide solution was added stepwise until the acidic solution became alkaline (pH 11.0-11.6). The change was also visibly noticeable, since the solution turned from clear to white. One hour after the final addition of sodium hydroxide, when the pH level had settled at pH 7, the resulting slurry was cooled to room temperature, rinsed with nitrogen gas, and filtered using syringe membrane filters with a pore size 0.45 μm . At all three temperatures, 16 ml 50 wt-% NaOH was required to make the solution alkaline, which corresponds to 10-11 g of NaOH per gram of calcium in solution. The XRD analyses of the filtered and dried precipitates showed that the precipitates contained calcium carbonate in the form of aragonite and calcite, as well as sodium acetate, calcium aluminium oxide, and carbonates containing both magnesium and calcium (Table 5.4). While calcite magnesium was the dominant form of carbonate at 30 °C, raising the temperature to 70 °C seemed to favour the formation of aragonite and calcite.

Table 5.4. Phases identified by XRD in filtered precipitates from carbonation experiments with dissolved blast furnace slag where sodium hydroxide was added.

Temperature (°C)	Phases identified (in descending apparent order of magnitude)
30	Calcite magnesium ((0.06Mg, 0.94Ca)(CO ₃)), Calcium aluminium oxide (Ca ₃ (AlO ₃) ₂), Calcite (CaCO ₃), Sodium acetate (CH ₃ COONa), Aragonite (CaCO ₃)
50	Calcite magnesium ((0.06Mg, 0.94Ca)(CO ₃)), Calcite (CaCO ₃), Sodium acetate (CH ₃ COONa), Aragonite (CaCO ₃), Calcium aluminum oxide (Ca ₃ (AlO ₃) ₂)
70	Sodium acetate (CH ₃ COONa), Calcite (CaCO ₃), Aragonite (CaCO ₃), Calcite magnesium ((0.06Mg, 0.94Ca)(CO ₃)), Calcium aluminium oxide (Ca ₃ (AlO ₃) ₂)

5.4.2 Carbonation of acetates derived from blast furnace slag

Since large amounts of NaOH were required for precipitating calcium carbonate from the solutions containing dissolved blast furnace slag, the possibility of raising the alkalinity (and recovering more acetic acid) by evaporation of the excess acetic acid was tested. Solutions were prepared similarly to those in the extraction experiments: 50 g of blast furnace slag (<1.0 mm) was dissolved in a glass reactor (1000 ml) filled with an aqueous solution of 20 vol-% acetic acid at 70 °C for 2 h under constant N₂ gas flow (1 l/min) and stirring (1000 rpm), after which the solution was vacuum filtered using 5- μm filter paper (Whatman 3). The filtrates were evaporated overnight, producing a solid acetate salt precipitate for use in the precipitation experiments. XRD analyses showed that the precipitated solids contained calcium acetate hydrates and magnesium acetate. XRF analyses showed that the precipitates

contained mostly calcium (20 wt-%) and magnesium (4 wt-%), but also small amounts of Al, Si, Fe, and Mn (0.2-1 wt-%). The precipitation experiments were carried out under both atmospheric and pressurised conditions, with and without additional sodium hydroxide for pH adjustment.

5.4.2.1 Carbonation at atmospheric pressure

The precipitation experiments at atmospheric pressure were performed using 10 g of acetate (derived from blast furnace slag) dissolved in water to form a solution of 200 ml. The reactor setup was similar to that in the previous carbonation experiments: a glass reactor of 250 ml was set up in the temperature-controlled water bath and heated to a specific temperature and stirred with a magnetic stirrer at 600-700 rpm. Nitrogen (1 l/min) was bubbled through the solution until the solution temperature had stabilised at the desired level (30, 50, or 70 °C). When the nitrogen flow was switched off, a carbon dioxide gas flow (1 l/min) was switched on. After 20 minutes, when the pH and temperature of the solution had stabilised, a specific amount (0, 2, 5 or 20 ml) of a sodium hydroxide solution (50 wt-%) was introduced into the solution. The pH of the solution was allowed to stabilise during 2¼ h, after which the carbon dioxide flow was switched off and the solution was filtered (Whatman 50, 3-µm filter paper). The filtered precipitate was washed and dried, after which it was analysed using XRD and XRF. The carbonate content was calculated from the carbon content, measured using Total Carbon (TC) analysis.

The experiments performed at 30, 50, and 70 °C produced only 18-24 g of precipitate per kg of acetate in solution. Of these, only the precipitate produced at 70 °C contained traces of calcite. The solutions carbonated with the addition of NaOH produced 150-380 g of precipitate per kg of acetate used (Figure 5.7). The temperature had a very small effect upon the amount of precipitate formed in comparison to the addition of sodium hydroxide, which clearly increased precipitation. However, adding more than 2 mol NaOH per mol Ca in solution did not have any significant effect on the precipitate yield. Apparently, 2 mol NaOH per mol calcium in solution (about 2 g of NaOH per g of Ca) is required for maximal yield. However, this is significantly less than in the previous experiments, in which at least 11 g of NaOH per g of Ca was required (see Chapter 5.4.1). All the precipitates formed using NaOH addition contained high amounts of calcium carbonates in the form of calcite, aragonite, and calcite magnesium (0.1 mol Mg and 0.9 mol Ca per mol CO₃). However, other elements too, such as Al, Si, Na, Mn, and Fe were found in the precipitates (Figure 5.8). Assuming that all the carbon was bound as calcium carbonates, the precipitates produced when using 2.0 and 7.7 mol NaOH per mol calcium contained roughly 80-90 wt-% calcium carbonate (Figure 5.8). This corresponds to a calcium carbonate conversion of 60-70% of the calcium in the solutions. Very little magnesium precipitated in comparison to calcium, and it appeared only

as calcite magnesium. The magnesium content in the precipitate was found to depend linearly on the amount of sodium hydroxide added, with the precipitate produced using 7.7 mol NaOH/mol Ca containing 3 wt-% Mg.

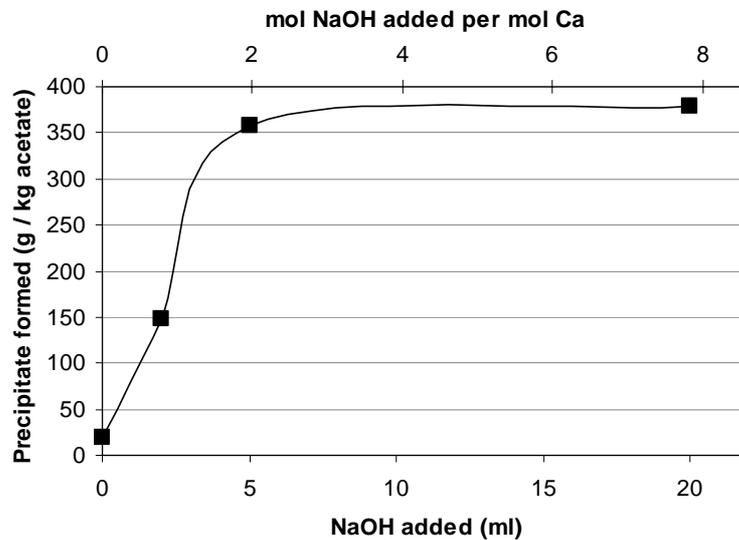


Figure 5.7. Effect of addition of NaOH on precipitate formation when carbonating aqueous solutions containing 10 g acetate (20 wt-% Ca), derived from blast furnace slag, at 30 °C.

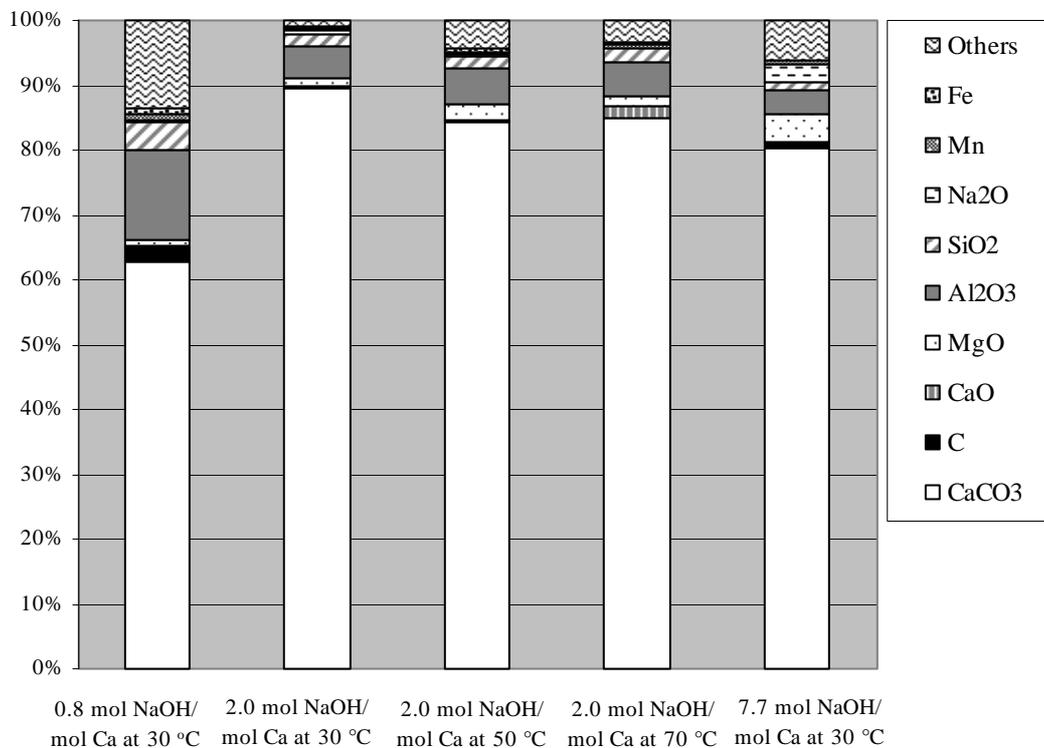


Figure 5.8. Elemental compositions of the dried and washed precipitates from the experiments with carbonating slag-derived acetate solutions as determined by XRF and total carbon content analyses (units wt-%).

5.4.2.2 Carbonation at elevated pressures

Kakizawa et al. (2001) achieved the best precipitation efficiency at a carbon dioxide pressure of 30 bar using aqueous solutions of pure calcium acetate. Therefore, we performed two additional precipitation experiments at 30 bar. 10 g of acetate produced from blast furnace slag was dissolved in water producing an aqueous solution of 100 ml. A volume of 5 ml of aqueous sodium hydroxide solution (50 wt-%) was added to one of the acetate solutions prepared, while the other was used without additives. The solution was put in a closed reactor vessel, which was heated to 50 °C using a water-heated copper coil (see Figure 5.9), and stirred using a magnetic stirrer at 1000 rpm. When the temperature of the solution had stabilised at 50 °C, the reactor was pressurised to 30 bar using pure carbon dioxide. After 2 hours, the pressure was lowered to 1 bar and the solution was filtered through a pressurised filtration unit (utilising membrane filters with a pore size of 0.45 µm). The filtered precipitate was washed and dried, after which it was analysed using XRD, XRF, and total carbon analysis.

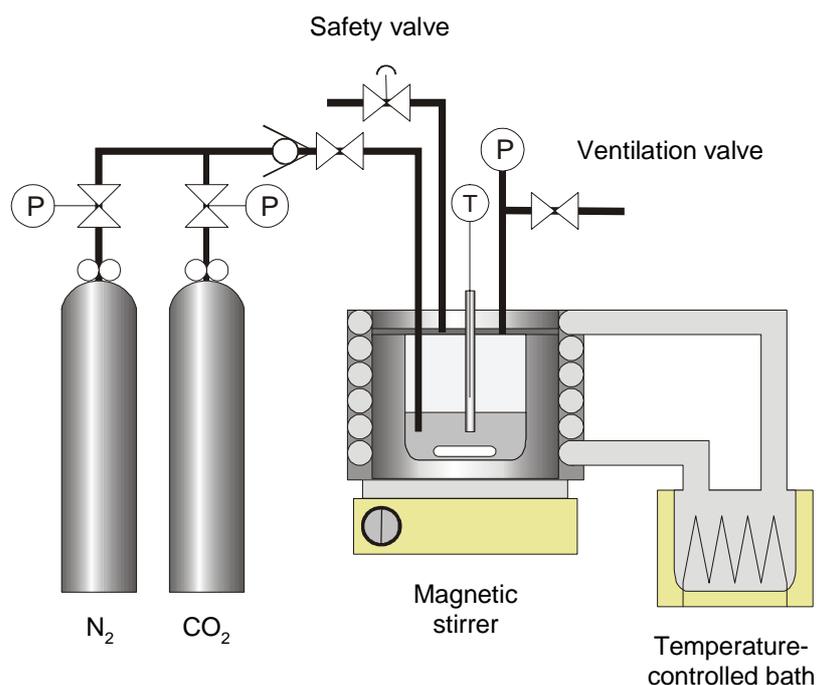


Figure 5.9. Experimental setup used for acetate solution carbonation experiments performed at 30 bar total pressure and 50 °C.

In the experiment performed without the addition of NaOH only 30 g of precipitate was formed per kg of acetate used, which was slightly more than in the atmospheric experiments (18-24 g). The precipitate consisted only of amorphous phases but the amount was not enough for performing XRF analysis. In the experiment performed with the addition of NaOH, 380 g

of precipitate was formed per kilogram of acetate used. The precipitate consisted mostly of calcium carbonate as calcite magnesium. The yield and the composition of the precipitate produced at a total pressure of 30 bar were similar to the yield and composition of the precipitate produced at atmospheric pressure.

5.5 Process evaluation

According to the experimental results, the excess of acetic acid required for completely dissolving blast furnace slag seems to prevent the precipitation of calcium carbonate. While this obstacle can be overcome by increasing the alkalinity of the solution by the addition of sodium hydroxide, the amount of sodium hydroxide required was found to be large. The evaporation and condensation of the acidic solution allows for a relatively easy recycling of a large part of the acid. However, evaporation requires energy, and its production causes CO₂ emissions in most cases. Additionally, the production of sodium hydroxide is known to be energy-intensive. An advantage of the process is that the pressurisation of the CO₂ is not necessary. Therefore, a process concept was set up (Figure 5.10), based on the experimental procedures and results, and its energy requirements were evaluated (Paper III).

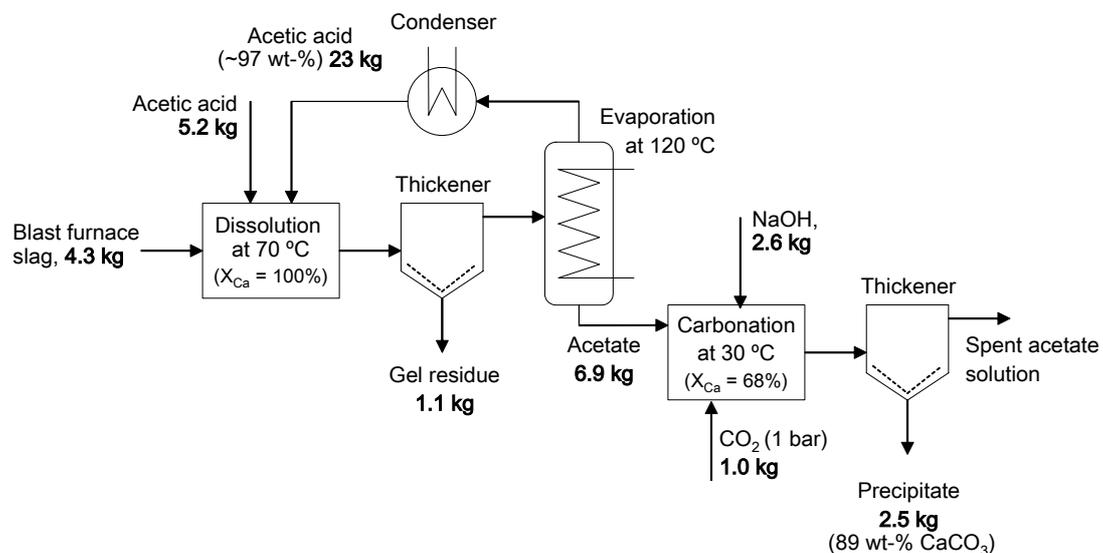
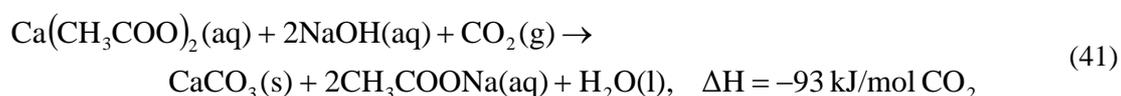


Figure 5.10. Process scheme for producing calcium carbonate from blast furnace slag. Numbers based on experimentally verified results.

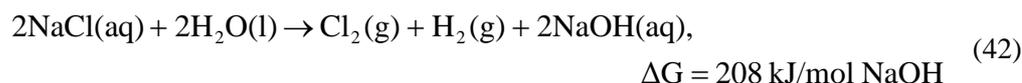
The best conditions for precipitating calcium carbonate from the acetate solutions was found to be at 30 °C and 1 bar CO₂, using 2 mol NaOH per mol Ca in the acetate solution (or 0.38 kg of NaOH per kg of acetate produced). These conditions produced 0.36 kg of precipitate per kg of acetate used. The precipitate contained 89 wt-% CaCO₃ (as calcite), and the conversion of calcium acetate to calcium carbonate was 68%. Our dissolution experiments

showed that using 6 l of acetic acid per kg of blast furnace slag a complete dissolution of the slag was possible. Using these compositions, 4.3 kg of blast furnace slag would be required per kg of CO₂ stored as calcium carbonate. This would produce 2.5 kg of precipitated carbonates (89 wt-% CaCO₃) and 1.1 kg of SiO₂, but also require 2.6 kg of NaOH for the carbonation step. While the excess acid could be recycled by evaporation and condensation, 5.2 kg of acetic acid is spent on producing the acetates.

The heat requirements¹³ of the main process steps were calculated from reaction enthalpies using Outokumpu's HSC 5.1 software. The reaction heat for the dissolution of blast furnace slag in acetic acid at 70 °C was simplified using wollastonite data instead of the actual blast furnace slag composition (Equation 27). The reaction is exothermic, producing about 985 kJ of heat per kilogram of wollastonite dissolved. As only part of the acetic acid reacts with blast furnace slag to produce acetate and water, the excess acetic acid would have to be evaporated. Raising the temperature to 120 °C and evaporating the solution would require 930 kJ of heat per kg of solution evaporated. The produced acetate would be dissolved in water, after which carbon dioxide and sodium hydroxide would be introduced. Since neither temperature nor pressure was found to have a significant effect on the carbonation process, the acetate would be carbonated at 30 °C and a carbon dioxide pressure of 1 bar (i.e. there would be no need for reactor pressurisation). The heat requirement of this process step can be calculated from Equation 41:

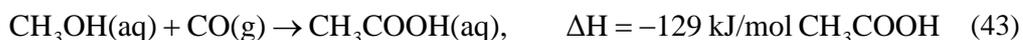


According to the calculations, the carbonation step is also exothermic, producing about 2.1 MJ of low-temperature (30°C) heat per kilogram of carbon dioxide stored. The acetic acid and sodium hydroxide spent in this step would have to be purchased or regenerated. Sodium hydroxide can be produced through the electrolysis of an aqueous solution of sodium chloride. The amount of electricity needed for the electrolysis can be calculated as the change in Gibbs free energy for the reaction (Equation 42):



¹³ All reaction enthalpies are calculated at 25 °C (using Outokumpu HSC 5.1) unless stated otherwise.

This shows that approximately 5.2 MJ of electricity would be required to produce 1 kilogram of sodium hydroxide. The most common acetic acid manufacturing process is methanol carbonylation, in which methanol reacts with carbon monoxide, but requires methanol and carbon monoxide as raw materials:



Heat calculations showed that most process steps do not require external energy input. However, evaporation requires 20 MJ of heat (at ≥ 120 °C) for separating the solution from the acetate required to bind 1 kilogram of carbon dioxide. Since the carbon dioxide emission factor for hard coal combustion is 94.6 g CO₂/MJ (STAT, 2003), producing the heat required for this process step would emit twice the amount of carbon dioxide stored by the process. Since the temperature required for the evaporation step is quite low, it is very likely that the required heat could be acquired by process integration using waste heat from the steelmaking plant itself. However, this requires the carbonation plant to be situated near the steel mill.

Since the carbon dioxide emissions from a coal-fired power plant are roughly 800 kg/MWh (IEA, 1993), generating the electricity required for producing sodium hydroxide would produce three times the amount of carbon dioxide bound in the carbonation step. Although hydrogen and chlorine gas are both by-products of sodium hydroxide production, the electricity requirements of electrolysis make the process described above unsuitable for carbon dioxide storage, unless the sodium hydroxide can either be replaced by a cheaper alkaline (waste) stream or recycled.

If waste heat and alkaline waste solutions from other processes could be supplied to the carbonation process, no carbon dioxide emissions would be generated. Instead, 0.25 kg of carbon dioxide would be stored per kilogram of blast furnace slag used in the process. The conventional PCC production chain produces approximately 0.2 kilogram of carbon dioxide per kilogram of calcium carbonate produced (Chapter 4.1.1). If PCC production facilities using blast furnace slag replaced conventional PCC production facilities, it would prevent the CO₂ emissions caused by calcination. However, these savings are small in comparison with the carbon dioxide generated from sodium hydroxide production. An additional benefit would be achieved if the carbonation step could directly use the carbon dioxide in flue gases without separation, as conventional PCC production processes do. However, the purity requirements of carbon dioxide, the suitability of the produced precipitate for use as PCC, and process integration, as well as the recycling of sodium hydroxide, must be further investigated.

5.6 Discussion

The possibility of producing calcium carbonate from steelmaking slags using acetic acid was studied. According to the calculations, the dissolution of calcium silicate and blast furnace slag was thermodynamically favourable in the studied temperature range (30-70 °C). Experiments showed that the total dissolution of the steelmaking slags tested was faster and that a higher conversion was achieved than with the dissolution of wollastonite. While only 50% of the calcium in wollastonite dissolved in an aqueous solution of acetic acid at 50 °C, 80-100% of the calcium in steelmaking slag was extracted under similar conditions. Other elements, such as silicon, iron, aluminium, and magnesium, dissolved as well. Because of the high acid concentrations used in the experiment (33 vol-% acetic acid), no connection between the dissolution rates of the calcium silicates and the crystallinity of the material was observed. Using solutions with leaner concentrations of acid would probably have shown more differences between the leaching behaviour of the materials.

The effect of various process parameters upon the dissolution step was tested using blast furnace slag. Experiments showed that for the complete dissolution of blast furnace slag 15 mol acetic acid was required per mol calcium in slag (at 50 °C), which is 7-8 times the theoretical requirements for extracting calcium (Equation 27). One reason for the large acid requirement is that other elements in slag react with the acid as well. However, when the dissolution was complete, the pH of the solutions was still about 3-4, which indicates that not all the acid had been neutralised. When the temperature of the solution was raised, less calcium dissolved, but this can be compensated for by using higher concentrations of acid. At 70 °C and 80 °C (and large concentrations of dissolved slag), almost all the dissolved silicon precipitated as gel and was successfully removed by filtration. However, other separation measures will be needed to remove aluminium, iron, magnesium, and other elements released from the slag or to prevent these elements from ending up in the carbonate product.

Thermodynamic calculations predicted that the precipitation of carbonates from acetate solutions would be favourable at temperatures over 45 °C. However, experiments with carbonating solutions of dissolved blast furnace slag and acetic acid produced no carbonate precipitate during 4 h at 30-70 °C. Thermodynamic calculations verified that the solution was too acidic to allow for carbonate precipitation. While the addition of sodium hydroxide raised the pH of the solution, resulting in the formation of a precipitate containing carbonates, a considerable amount of sodium hydroxide was required, which also reduces the amount of acetic acid that can be recovered for re-use. By evaporating the solution containing dissolved slag and mixing the precipitated acetate with water prior to carbonation, the sodium hydroxide requirements were reduced to the stoichiometric requirements (of Equation 41). Bubbling CO₂ gas through the acetate solution precipitated relatively pure (80-90%) calcium carbonate.

Based on the results it seems that the process concept suggested by Kakizawa et al. (2001) cannot work as such. The extraction of calcium from the calcium silicate-containing material seems to demand a surplus of acetic acid for achieving a significant extraction. Since only part of the acid is consumed the resulting solution is acidic, which in turns prevents precipitation of calcium carbonate. Also, the acetic acid that is formed simultaneously with calcium carbonate in the carbonation step (Equation 28) lowers the solution pH and makes the precipitation of calcium carbonate unfavourable. In order to favour precipitation of calcium carbonate, the acid needs to be neutralised.

Our experimental results showed that improving the process concept by recycling the surplus of acid by evaporation and adding sodium hydroxide to the carbonation step allows for calcium carbonate to be produced. Preliminary calculations showed that the heat requirements for the evaporation of the acetic acid are large, but could be covered by using low-grade waste heat (120 °C) from other industrial processes. The requirements for sodium hydroxide and make-up acetic acid were also relatively large, requiring the recovery and processing of the produced sodium acetate solution. However, the large amount of dissolved impurities would probably make recovery of the solution difficult. Since the precipitate produced contained a high amount of impurities (10-20%), the product would probably not have a high value. Therefore, the use of acetic acid does not seem to be a feasible option for producing carbonates from blast furnace slag.

Although the results demonstrate that it is possible to produce relatively pure calcite (80-90%) from blast furnace slag and CO₂, the acetic acid carbonation process does not seem feasible for reducing CO₂ emissions. While acetic acid dissolves steelmaking slag easily, it is quite expensive and also dissolves many unwanted elements from slags. A solvent that extracts calcium selectively from slags (e.g. Yogo et al., 2004) would significantly reduce the requirements for additional separation measures.

6 Production of magnesium carbonate from serpentinite

Although steelmaking slags can be used for the fixation of CO₂, the world-wide CO₂ storage potential using these (110-150 Mt CO₂/a) is small compared to the anthropogenic CO₂ emissions (24 Gt CO₂/a). This also applies to Finland's slag resources in comparison to national CO₂ emissions. For large-scale CO₂ storage purposes, magnesium silicates, such as serpentinite, are more interesting because of their large CO₂ storage potential and availability (see Chapter 3.1.2). However, they are known to be more difficult to carbonate than steelmaking slags. In order to test whether pure magnesium carbonate could be produced from serpentinite, while simultaneously storing CO₂, a series of experiments were performed using similar experimental procedures to those described in Chapter 5 (Papers IV and V). Since magnesium silicates are harder to dissolve than steelmaking slags, an extensive solvent selection study was carried out, followed by experiments with selected solvents for constructing a kinetic model of the dissolution process. Carbonation experiments were subsequently carried out with the most promising solvents. On the basis of the outcome of the experiments, the feasibility of the CO₂ storage method was evaluated (Paper VI).

6.1 Characterisation of serpentinite

A batch of 7 kg of serpentinite rock was selected from the stockpile of the Hitura nickel mine (located in central Finland and currently owned by Belvedere Resources Ltd), ground to a median diameter of 0.1 mm (<0.5 mm), and sieved to various fractions. The serpentinite was analysed using XRD, XRF, total acid digestion with ICP-AES, and Total Organic Carbon (TOC) analyses. A summary of the results from the analysis of the serpentinite is shown in Table 6.1. The ICP-AES values were used in calculations instead of the XRF values where available. On the basis of the Mg content and Fe content of the sample and XRD data (Figure 6.1), the serpentinite consisted of 83 wt-% serpentine, (Mg₃Si₂O₅(OH)₄; chrysotile, lizardite and antigorite), and 14 wt-% magnetite (Fe₃O₄).

Table 6.1. Composition of serpentinite used in experiments (74-125 µm; units: wt-%).

MgO ^a	SiO ₂ ^b	Fe ^a	Al ₂ O ₃ ^a	CaO ^a	S ^b	Cr ^a	Ni ^a	Cl ^b	CO ₃ ^c
36.2	40.3	10.1	0.08	0.48	0.52	0.007	0.02	0.21	< 0.1

^aAs determined by ICP-AES.

^bAs determined by XRF.

^cAs determined by TOC.

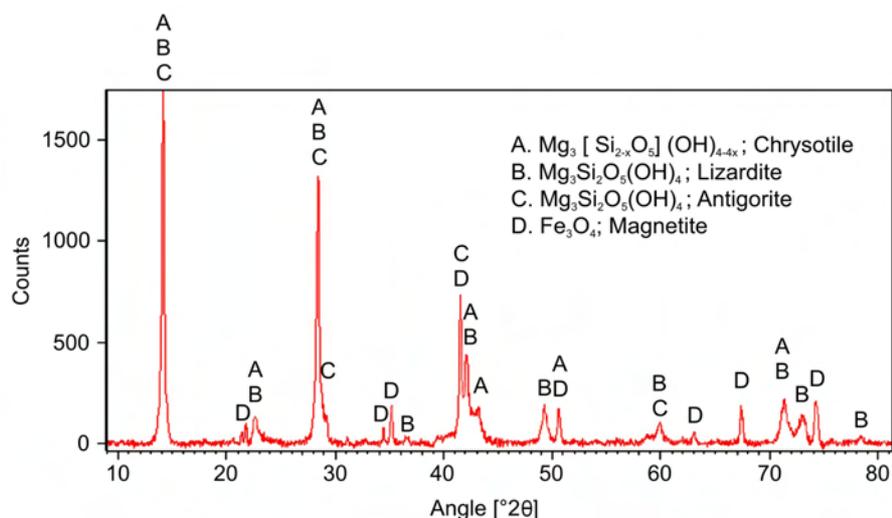


Figure 6.1. X-Ray diffractogram of the sieved (74-125 μm) serpentinite fraction.

6.2 Selection of solvent

Instead of all the experiments being performed with one selected solvent (as in the study of steelmaking slags in Chapter 5), a series of tests were performed to select a solvent suitable for extracting magnesium from serpentinite (Paper IV). Common mineral acids (HCl, H₂SO₄, HNO₃) and weak organic acids (HCOOH and CH₃COOH) were tested for dissolving serpentinite. Both acids and bases are known to extract magnesium from its silicates. The high alkalinity of bases favours the formation of carbonates. Therefore, the dissolution of serpentinite was also tested using three common bases: NaOH, KOH, and NH₃. Since ammonium salts have been found to dissolve calcium and magnesium selectively from steelmaking slags (Yogo et al., 2004), NH₄Cl, NH₄NO₃, and (NH₄)₂SO₄ were also tested.

A batch of 1 g of serpentinite (74-125 μm) was dissolved in 50 ml aqueous solutions of 1, 2, and 4 M concentrations of the respective solvent. One test was also performed with distilled water. The solutions were continuously stirred for 1 h at 100 rpm, 20 °C, and 1 atm, after which the solutions were immediately filtered with 0.45 μm membrane filters. Since the serpentinite contained very low concentrations of other metals, only the concentrations of Mg, Fe, and Si in the filtrates were measured with ICP-AES.

All the acids tested were able to extract 3-26% of the magnesium from serpentinite in 1 h, while water extracted only 0.2% (Figure 6.2). However, none of the acids tested extracted Mg selectively from serpentinite: Fe (2-16%) and some Si (0-3%) were also extracted. H₂SO₄ was most efficient at extracting magnesium from serpentinite, followed by HCl, HNO₃, HCOOH, and CH₃COOH (listed in descending order of magnesium extraction efficiency). Higher acid concentrations resulted in slightly more magnesium and iron ions being

dissolved, except for the solutions of CH_3COOH , which behaved more irregularly. The ammonium salt solutions tested extracted only 0.3-0.5% of the magnesium from serpentine in 1 h. However, the ammonium salt solutions were the only solvents tested that seemed to extract magnesium selectively: no iron or silicon concentration was found in the salt solutions after filtration. No measurable amount of magnesium or iron, and no more than 0.3% of the silicon, had dissolved in any of the alkaline solutions tested. Therefore, H_2SO_4 , HCl , and HNO_3 were selected for further studies, which are reported below.

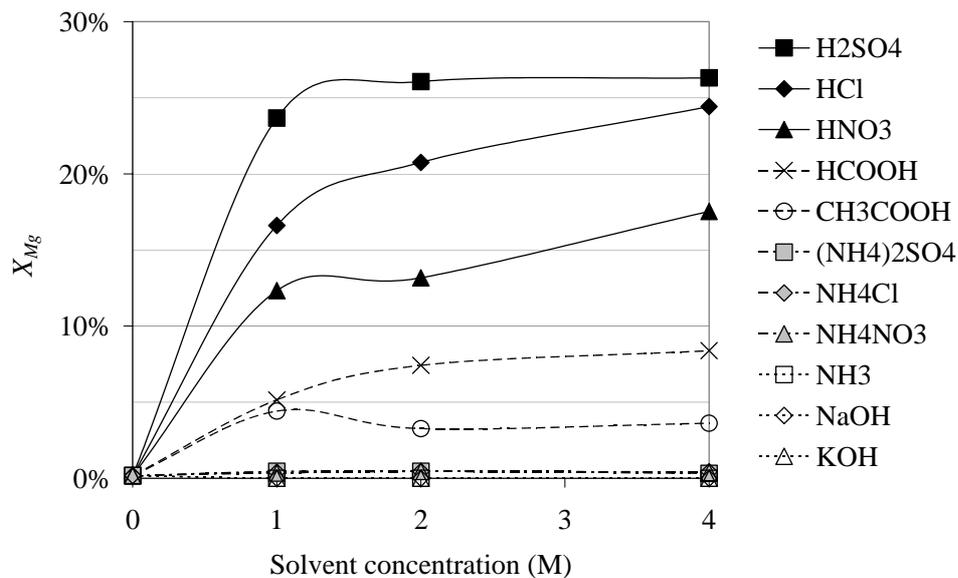


Figure 6.2. Extraction of magnesium from serpentine (74-125 μm) in 1, 2, and 4 M concentrations of solvent (1 h, 20 $^\circ\text{C}$).

6.3 Effect of concentration, temperature, and particle size on dissolution of serpentine

The effect of acid concentration was studied by extending the solvent experiments presented in the previous chapter with 0.1, 0.2, and 0.5 M concentrations of HCl or HNO_3 . The results of the ICP-AES analyses (Figure 6.3) showed that even dilute acid concentrations (0.1 M) significantly increased the extraction of Mg and Fe in comparison to that of pure water. The extraction of silica did not occur in 0-0.5 M solutions of acid.

Experiments for determining the dissolution rate of serpentine in H_2SO_4 , HCl , and HNO_3 were carried out in an open spherical glass batch reactor (1 atm) heated by a temperature-controlled water bath and equipped with a water-cooled condenser to minimise evaporation losses (setup similar to that presented in Figure 5.3). 500 ml of the desired solvent (as a 2 M solution) was added to the reaction vessel. The solutions were well mixed

using a magnetic stirrer set to 600-700 rpm. After the temperature had stabilised (at 30, 50, or 70 °C), 10 g of serpentinite (74-125 µm) was added to the solution. Solution samples (5 ml per sample) were extracted while the experiment progressed and immediately filtered with 0.45 µm membrane filters. The Mg, Fe, and Si concentrations of the samples were measured using ICP-AES.

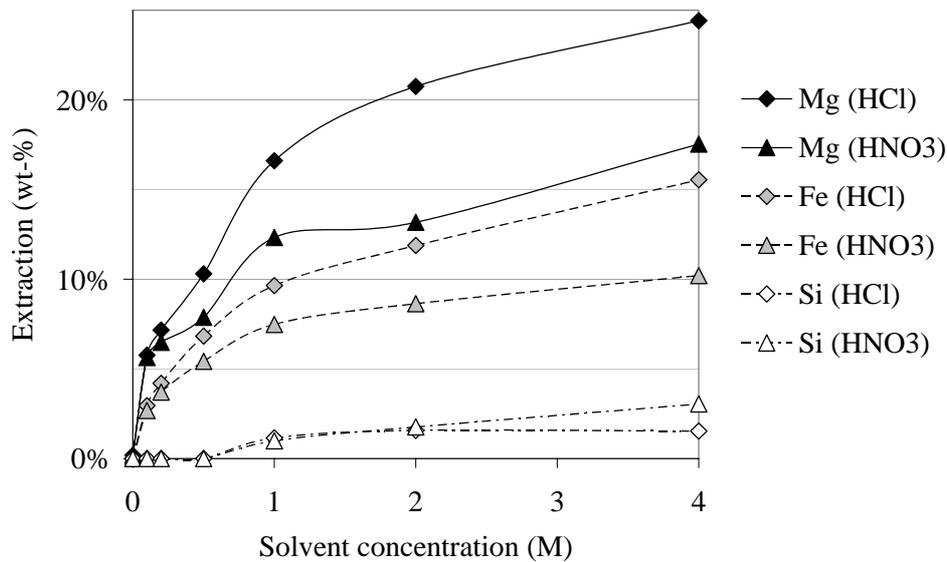


Figure 6.3. Extraction of Mg, Fe, and Si from serpentinite (74-125 µm) in various concentrations of HNO₃ or HCl (1 h, 20 °C).

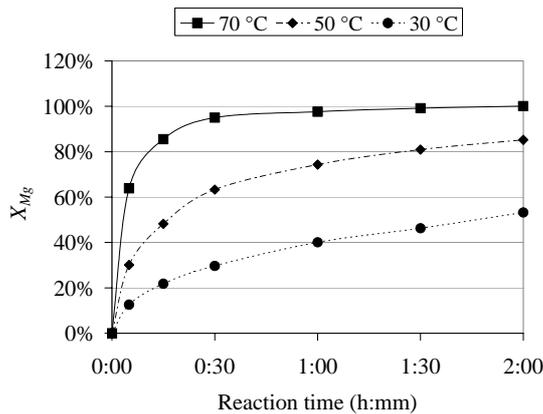


Figure 6.4. Effect of temperature on extraction of Mg from 74-125 µm serpentinite using 2 M H₂SO₄.

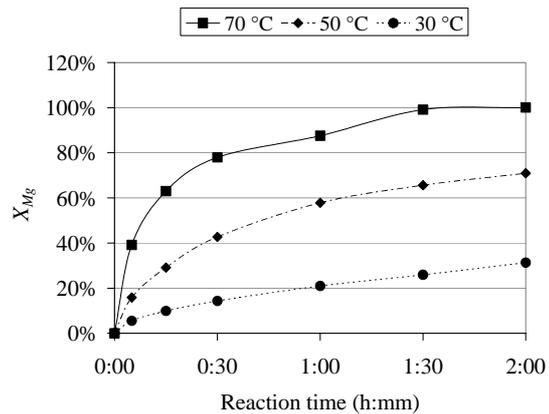


Figure 6.5. Effect of temperature on extraction of Mg from 74-125 µm serpentinite using 2 M HNO₃.

Figures 6.4-6.6 show that higher temperatures yield higher reaction rates for each acid tested. At 70 °C, the acids tested were able to leach all of the magnesium in serpentinite

within 1-2 h. However, 38-67% of the iron, as well as 3% of the silicon in serpentinite, was also dissolved. Apparently, magnesium and iron are extracted, leaving behind mostly silica and small quantities of magnetite. While nitric acid was slower at dissolving serpentinite than the other acids, it was more selective in extracting magnesium at 70 °C.

The effect of the particle size was analysed similarly in 2 M HCl at 70 °C, using sieved serpentinite fractions of 74-125, 125-250, 250-350, and 350-500 µm. The extraction of magnesium (Figure 6.7) was most effective for the smallest particle sizes (74-125 µm). However, particle size did not seem to have a significant effect on magnesium extraction from the other fractions tested, which gave almost equal magnesium extraction rates, settling at 78-81% extraction after 1-2 h.

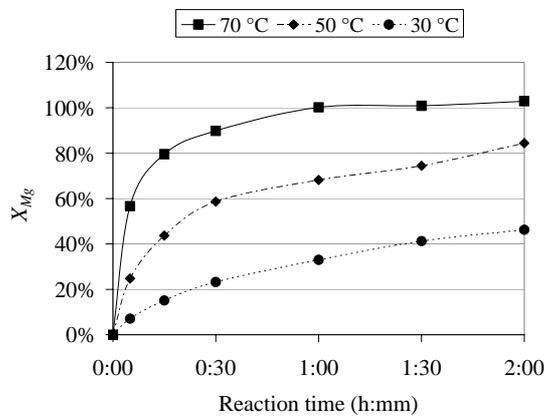


Figure 6.6. Effect of temperature on extraction of Mg from 74-125 µm serpentinite using 2 M HCl.

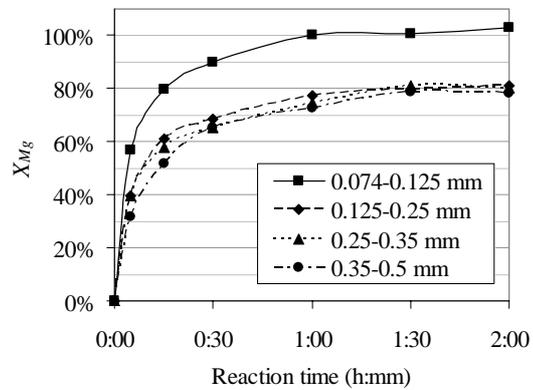
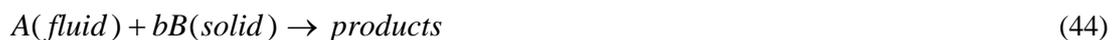


Figure 6.7. Effect of particle size on extraction of Mg from serpentinite using 2 M HCl.

6.4 Dissolution kinetics

The data from the experiments with HCl, HNO₃, and H₂SO₄ (Figures 6.4-6.6) were used for determining the kinetic parameters and rate-controlling step of the extraction process. Heterogeneous fluid-solid reactions may be represented by:



In these reactions, the rate is generally controlled by one of the following steps: diffusion through the fluid film (quantifying for external mass transfer), diffusion through the “ash” (or solid product) layer on the particle surface, or the chemical reaction at the reaction surface. The rate of the process is controlled by the slowest of these sequential steps. The experimental data were analysed according to the integral analysis method (Levenspiel, 1972). The integral

analysis method puts a selected model to test by integrating its rate equation and comparing the predicted concentration-versus-time curve with the experimental concentration-versus-time data. The experimental data were fitted to integral rate equations for five common unreacted-core models representing film diffusion control, product layer diffusion control, and chemical reaction control for both unchanging size and shrinking size (i.e. the product layer stays on the particle or is removed; see Figure 6.8).

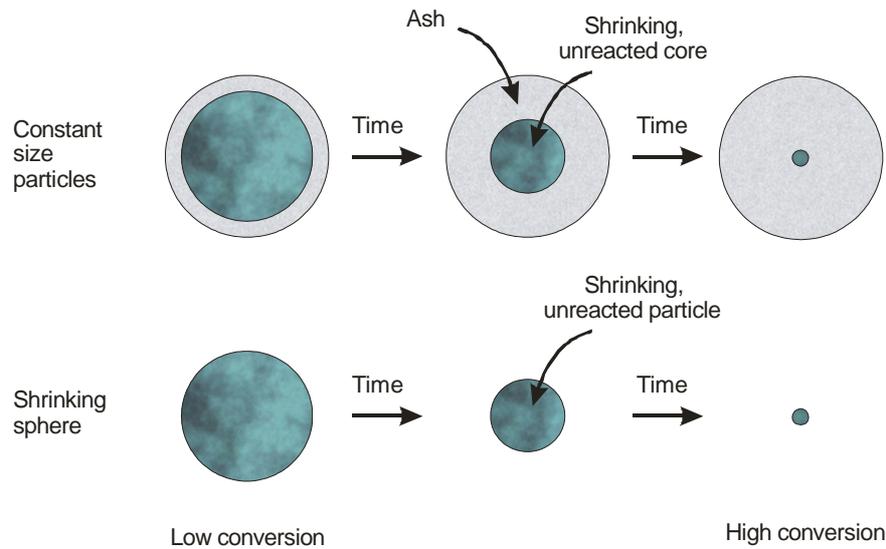
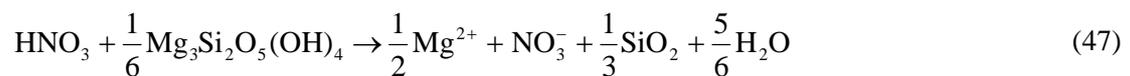
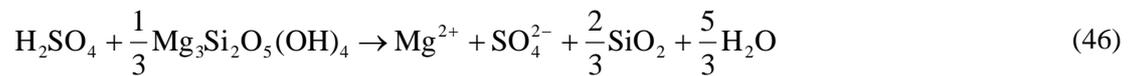
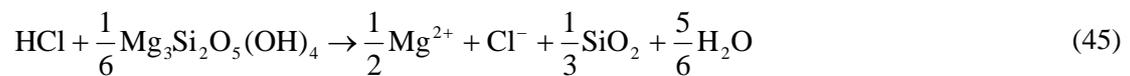


Figure 6.8. According to the unreacted-core models, the reaction proceeds at a narrow front that moves into the solid particle. The reactant is completely converted as the front passes by (after Levenspiel, 1972).

Since magnesium exists as serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) in serpentinite, the extraction of magnesium in the acids tested can be described in the form of Equation 44:



The experimental data (magnesium extracted vs. time) from all three solvents was plotted against the integral rate equations. According to the regression correlation coefficients (Table 6.2 and Table 6.3) the experimental data from all three solvents were best fitted towards the

integral rate equation for product layer diffusion (of constant size spherical particles) (Figures 6.9-6.11):

$$t = \frac{\rho_B r^2}{6bD_e C_A} \left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right] = \frac{1}{k} \left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right] \quad (48)$$

This unreacted-core model equation for product layer diffusion control follows from equating the rate of weight loss of a spherical particle to the rate of diffusion of reactant (in this case acid) through the product layer. Its derivation, as well as that for rate control by chemical kinetics or film diffusion (i.e. external mass transfer), and particles without a product layer (i.e. shrinking sphere) are given by Levenspiel (1972).

Table 6.2. Multiple regression coefficients for experimental kinetic data fitted to unreacted-core models of constant size spherical particles (Paper IV).

Model	Integral rate equation	$R_{\min}^2 - R_{\max}^2$
Product layer diffusion	$kt = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$	0.936 – 0.998
Chemical reaction controls	$kt = 1 - (1 - X_B)^{1/3}$	0.661 – 0.901
Film diffusion	$kt = X_B$	-0.760 – 0.863

Table 6.3. Multiple regression coefficients for experimental kinetic data fitted to unreacted-core models of small shrinking spherical particles (Paper IV).

Model	Integral rate equation	$R_{\min}^2 - R_{\max}^2$
Chemical reaction controls	$kt = 1 - (1 - X_B)^{1/3}$	0.661 – 0.901
Film diffusion	$kt = 1 - (1 - X_B)^{2/3}$	0.483 – 0.882

The apparent rate constants were determined from the slope of the lines in Figures 6.9-6.11. The apparent extraction rate constant can be used for determining the temperature dependency by Arrhenius' law:

$$k = k_0 e^{-E/RT} \quad (49)$$

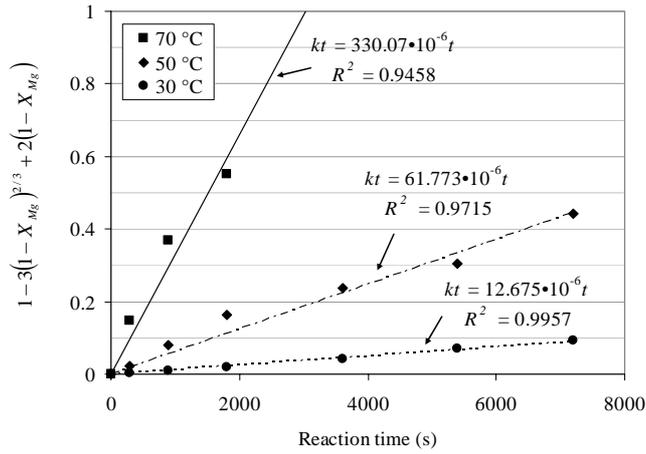


Figure 6.9. $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ vs. reaction temperature for extraction of Mg from 74-125 μm serpentinite in 2 M HCl (Paper IV).

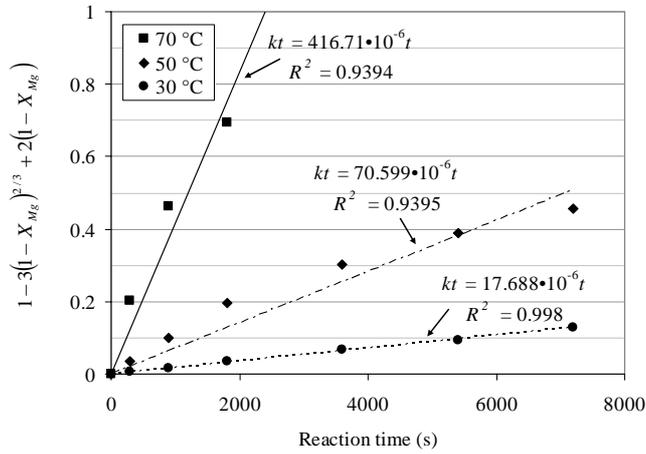


Figure 6.10. $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ vs. reaction temperature for extraction of Mg from 74-125 μm serpentinite in 2 M H_2SO_4 (Paper IV).

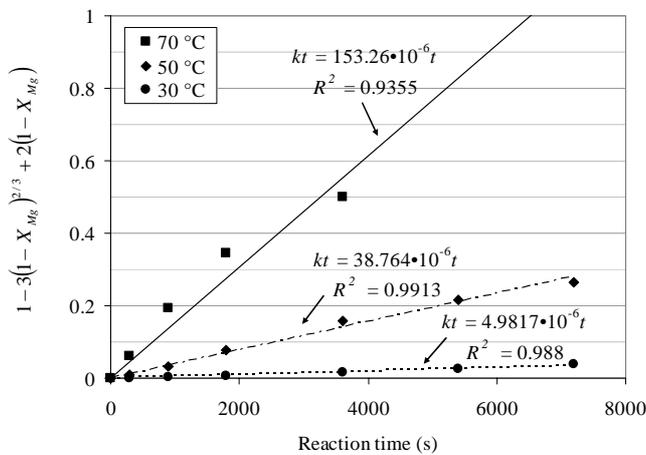


Figure 6.11. $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ vs. reaction temperature for extraction of Mg from 74-125 μm serpentinite in 2 M HNO_3 (Paper IV).

By plotting the apparent rate constants for each experiment in an Arrhenius plot (Figure 6.12), the activation energies (E) and the frequency factors (k_0) were determined; the results are shown in Table 6.4. The order of the activation energies found in the present study is similar to those found in similar studies with roasted serpentine ore and natural olivine (Fouda et al., 1996a-b; Apostolidis and Distin, 1978; Jonckbloedt, 1998; Chen and Brantley, 2000; Hänchen et al., 2006). No previous kinetic studies on untreated serpentine ore were found in the open literature for comparison to this work.

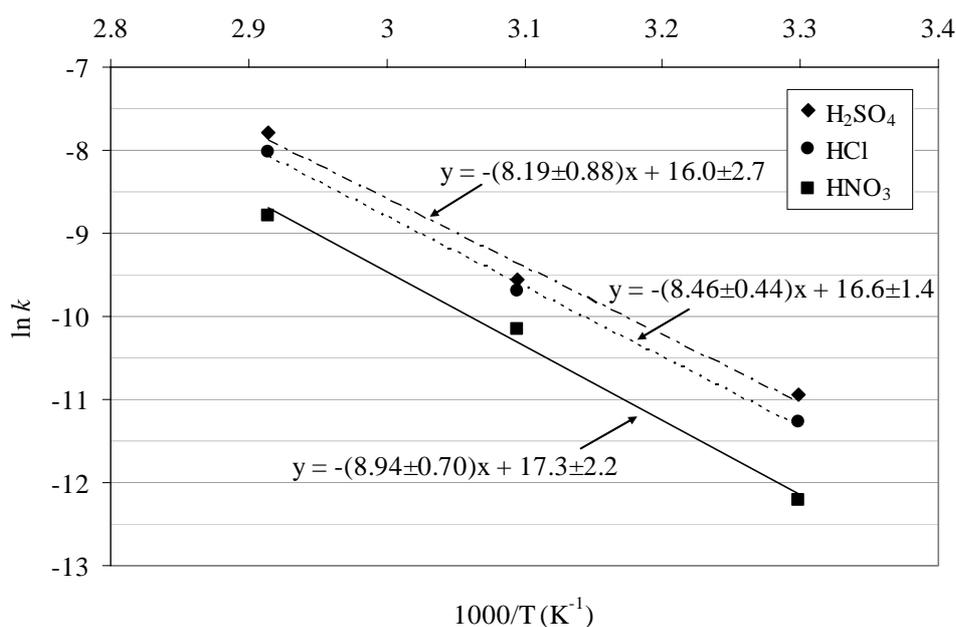


Figure 6.12. Arrhenius plot for extraction of Mg from 74-125 μm serpentinite in 2 M H_2SO_4 , 2 M HCl , or 2 M HNO_3 including standard errors for the coefficients of the trend lines (Paper IV).

Table 6.4. Activation energy and frequency factor calculated using the coefficients of the trend lines of the Arrhenius plots in Figure 6.12 (Paper IV).

Solvent	Activation energy E [$kJ mol^{-1}$]	Frequency factor k_0 [s^{-1}]
H_2SO_4	68.1 ± 7.3	$8.6 \cdot 10^6$
HCl	70.4 ± 3.7	$1.6 \cdot 10^7$
HNO_3	74.3 ± 5.8	$3.4 \cdot 10^7$

The results indicate that the rate-limiting step for the dissolution of serpentinite in HCl , H_2SO_4 , and HNO_3 is product (or “ash”) layer diffusion. This result is in agreement with Luce et al. (1972), who found that the diffusion of ions either in the mineral lattice itself or through a product layer is the rate-controlling mechanism for the dissolution of magnesium silicates.

For a pure diffusion-controlled process, the activation energy should be rather low, but the results show that the extraction is very temperature-sensitive with relatively high activation energies. It is possible that the chemical reaction is rate-limiting at the beginning of the reaction, with product layer diffusion gradually becoming rate-limiting as the product layer of silica builds up and the reaction surface area decreases.

6.5 Precipitation of carbonates

As discussed in Chapter 5, the evaporation of the excess solvent after magnesium extraction could allow for the partial recycling of the acid used. Because of their relatively low boiling point, HCl and HNO₃ were selected for preparing solutions for carbonation (Paper V). Two batches were prepared by dissolving 100 g of serpentinite in 1 l of 4 M HNO₃ and 4 M HCl, respectively, at 70 °C for 2 h, using a mechanical stirrer at 650 rpm. This resulted in the extraction of 88-93% of the magnesium in the serpentinite. The slurries were filtered with filter paper (5 µm), leaving highly porous solid residues consisting of more than 80 wt-% amorphous silica. The filtrates were evaporated at 105 °C, leaving concentrated slurries, which were dried in an oven for 1-2 days at 130-180 °C. After drying, the cooled residues were dissolved in 2 l H₂O, respectively. The resulting solutions contained no measurable concentrations (< 5 mg/l) of Si. During the dissolution of the residue prepared from HNO₃ in water, all of the dissolved iron precipitated spontaneously as hematite, Fe₂O₃. This produced a magnesium-rich solution (21 g Mg/l) of pH 7 that contained no measurable concentration (< 5 mg/l) of Fe. The residue prepared from HCl had formed a crust while drying, preventing a small part of the acid from evaporating. When this residue was dissolved in water, the acidity (pH 1) seemed to prevent the iron from spontaneous precipitation. A large part of the dissolved iron was precipitated as magnetite, Fe₃O₄, by raising the pH to 7 using NaOH. However, the resulting solution still contained 9 g Fe/l, in addition to 22 g Mg/l. Enrichments of nickel and copper were found in the iron oxides precipitated from both the solutions.

The magnesium-rich solutions prepared from serpentinite were used for investigating the possibility of precipitating magnesium carbonates from them. For each pH level, 150 or 300 ml of each solution was exposed to 1 litre CO₂/min in a glass reactor, after initial heating up of the solution to 30 °C in an N₂ atmosphere. The glass reactor was equipped with a condenser, heated with a temperature-controlled water bath and stirred at 600-700 rpm with a magnetic stirrer (setup similar to Figure 5.3). Ten minutes after switching to CO₂ gas, the pH was adjusted to a specific level by the drop-wise addition of an aqueous solution of 50 wt-% NaOH. After 30 min of pH regulation the gas flow was switched back to N₂ (2 l/min). After 15 minutes under N₂, the prepared solids were collected and washed by filtering them through 0.45 µm membrane filters and dried at 120-135 °C overnight. The composition of the precipitates formed was analysed using XRF and XRD and the carbonate content was

measured by TC and verified using TOC. A scanning electron microscope (SEM) was used for observing the morphologies of the samples. Experiments were carried out for solution pH 7, 8, 9, 10, 11, and 12 with both salt solutions prepared.

When CO₂ was introduced into the prepared solutions, the pH immediately dropped from 7 to 5. However, no precipitate was formed during experiments performed without pH regulation. Regulating pH by the addition of NaOH produced precipitates from both solutions.

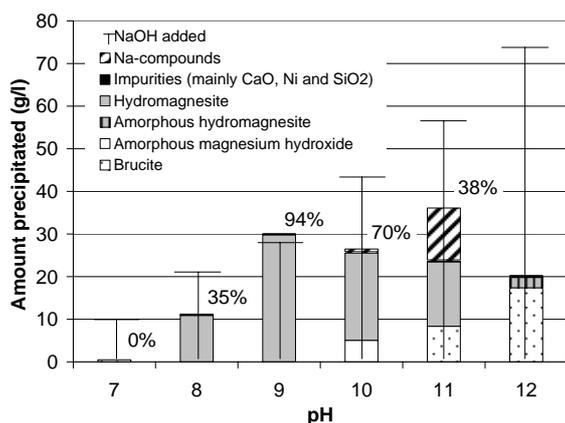


Figure 6.13. Precipitates formed by CO₂ injection and pH regulation in the solution prepared using HNO₃. The conversion to hydromagnesite is shown in percentages (Paper V).

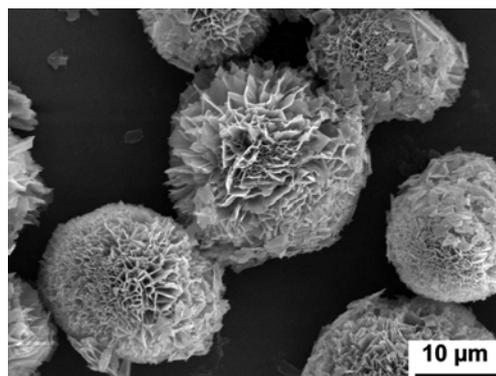


Figure 6.14. SEM image of hydromagnesite precipitated at pH 9 from the solution prepared using HNO₃ and serpentinite (Paper V).

For the solutions prepared using HNO₃, magnesium precipitated as hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) and brucite, as well as amorphous hydroxide and carbonate (Figure 6.13). The major part of the precipitated magnesium was bound as carbonates at pH 8-11, with the precipitate produced at pH 9 consisting of > 99% pure hydromagnesite. The solids precipitated at pH 9 were found by TOC analysis to have the highest carbonate content (50 wt-% CO₃²⁻) of the precipitates formed. At pH 9, the conversion of magnesium ions in solution to hydromagnesite was the highest (94%), while at the same time the NaOH requirements were the lowest (0.9 g NaOH/g precipitate). The precipitates formed at pH 9 were uniformly sized spherical crystals with a lamellar structure (Figure 6.14). The experiment performed at pH 9 was repeated by adding the total amount of NaOH required in the previous experiment as a single batch at the beginning of the experiment. After the addition of the batch, the pH was not regulated. This produced a similar amount of precipitate, again containing 99 wt-% hydromagnesite, but the crystals produced were more irregular.

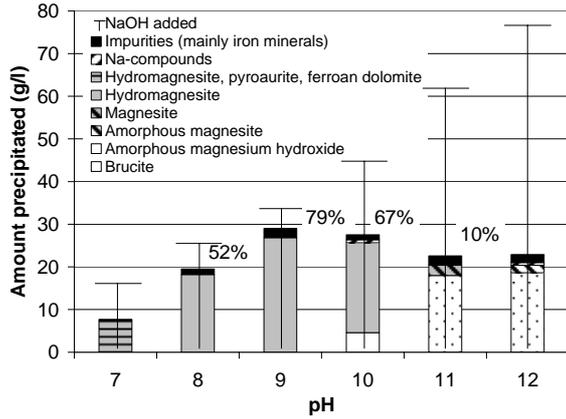


Figure 6.15. Precipitate formed by CO₂ injection and pH regulation in the solution prepared using HCl. The conversion to hydromagnesite is shown in percentages (Paper V).

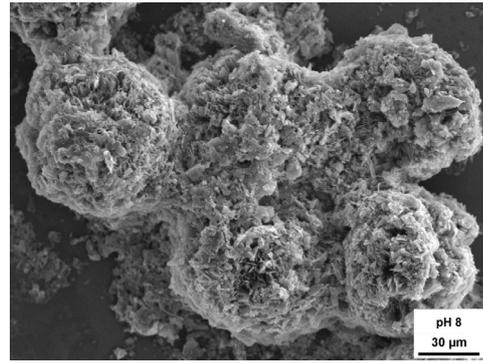


Figure 6.16. SEM image of precipitate formed at pH 8 from the solution prepared using HCl and serpentinite (Paper V).

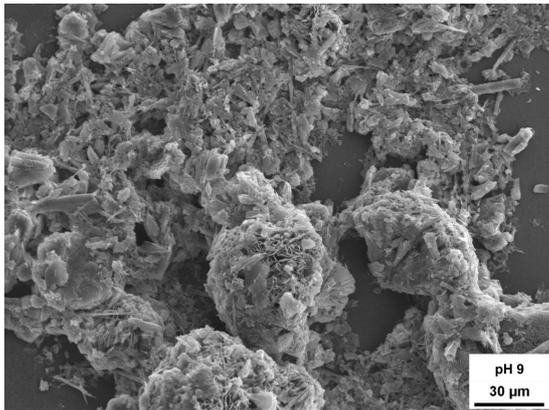


Figure 6.17. SEM image of precipitate formed at pH 9 from the solution prepared using HCl and serpentinite (Paper V).

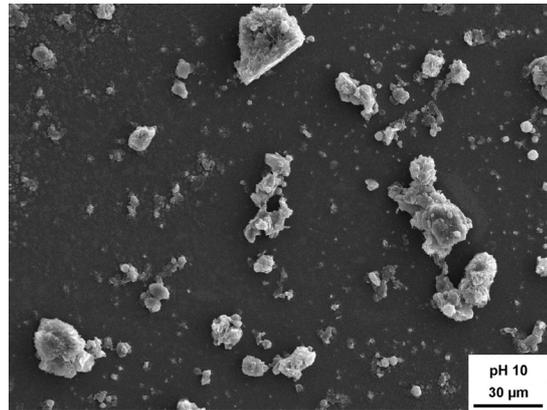


Figure 6.18. SEM image of precipitate formed at pH 10 from the solution prepared using HCl and serpentinite (Paper V).

For the solutions prepared using HCl, the magnesium precipitated as hydromagnesite, magnesite (MgCO₃), and brucite, as well as in amorphous forms (Figure 6.15). The major part of the precipitated magnesium was bound as carbonates at pH 7-10, with the precipitate produced at pH 9 consisting of 93% hydromagnesite. Since the solution was contaminated with some iron, the precipitates produced consisted of 3-9 wt-% Fe. The solids precipitated at pH 9 were found by analysis using TOC and TC to have the highest carbonate content of the precipitates formed: 48 wt-% CO₃²⁻. At pH 9 the conversion of magnesium ions in solution to hydromagnesite was the highest (79%), while at the same time the NaOH requirements were the lowest (1.1 g NaOH/g precipitate). As can be seen from the SEM images (Figure 6.15-6.17), the crystals that precipitated at higher pH levels were smaller and more compact than

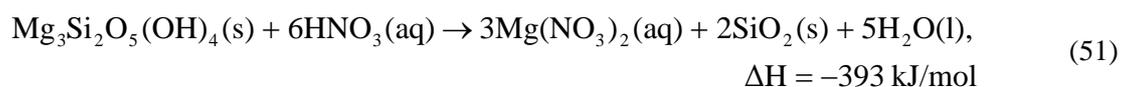
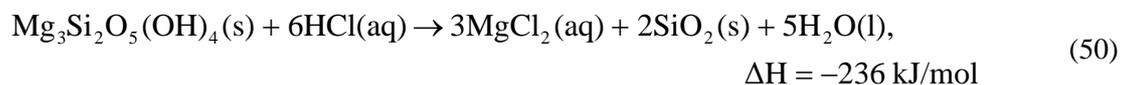
those precipitated at lower pH levels. The crystals precipitated at pH 8 were similarly-sized spherical particles with diameters of 40-60 μm , while those precipitated at pH 9 and pH 10 had more irregular shapes. Both irregularly shaped and needle-like particles were observed at pH 9, while the particles formed at pH 10 were more compact crystals with diameters ranging from 1-100 μm . It may be that the iron contamination affected the crystallisation of the particles, which might otherwise have borne a closer resemblance to those precipitated from the solution prepared using HNO_3 .

The experiment performed at pH 9 with the solution prepared from HCl was repeated using a gas mixture (at 1 l/min) of 10 vol-% CO_2 and 90 vol-% N_2 instead of pure CO_2 . This time only 6 g of precipitate was formed per litre of solution. Additionally, the iron contamination affected the precipitation more than in the previous experiments: the precipitate contained mostly pyroaurite, $\text{Mg}_6\text{Fe}_2\text{CO}_3(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$, with traces of hydromagnesite and brucite. Better dispersion and a higher rate of gas flow, as well as longer residence times of CO_2 , might be required for the formation of hydromagnesite.

6.6 Process evaluation

From the experimental procedures and results, a process scheme can be constructed, which shows the current development stage of the process studied (Paper VI). The carbonation of serpentinite using HCl or HNO_3 is described next as an example for visualising the process (Figure 6.19 and Figure 6.20).

First, magnesium and iron are extracted from serpentinite using HCl or HNO_3 at 70 $^\circ\text{C}$. As the experiments showed, magnesium can be extracted from relatively coarse serpentinite particles (80% conversion for 125-500 μm particles, 100% conversion for 74-125 μm). This produces aqueous magnesium chloride and iron chlorides or aqueous magnesium nitrate and iron nitrates. All of the silicon dioxide in serpentinite can be recovered at this stage as highly porous, amorphous silica (Paper V). Since serpentinite consists mostly of serpentine, the main reactions¹⁴ are:



¹⁴ All reaction enthalpies have been calculated for 25 $^\circ\text{C}$, except where explicitly mentioned. Reaction enthalpies and heat requirements were calculated using Outokumpu HSC 5.1 software.

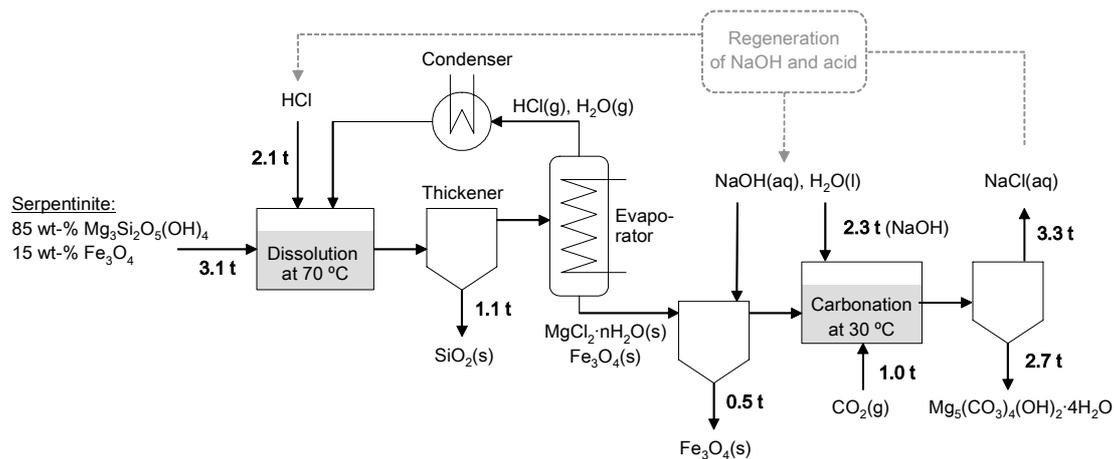


Figure 6.19. Process scheme for production of hydromagnesite from serpentinite using HCl (100% conversion of streams assumed). The solid black lines and boxes show process streams and stages that were experimentally verified, while dotted grey lines and boxes show additional streams and stages not tested.

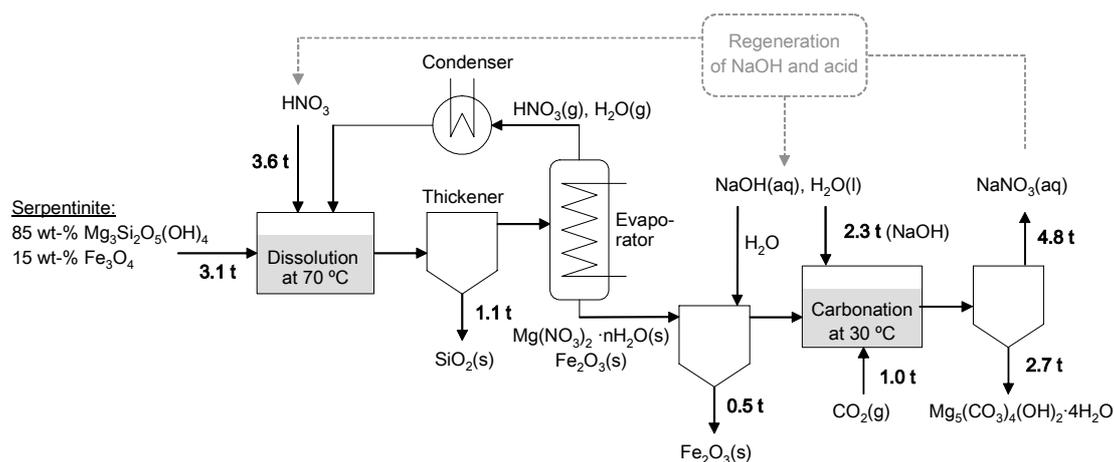
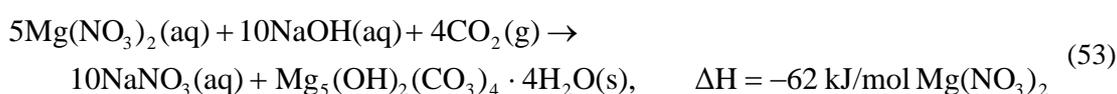
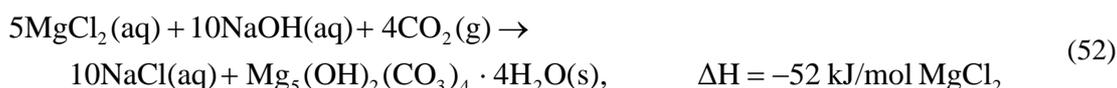


Figure 6.20. Process scheme for production of hydromagnesite from serpentinite using HNO₃ (100% conversion of streams assumed). The solid black lines and boxes show process streams and stages that were experimentally verified, while dotted grey lines and boxes show additional streams and stages not tested.

In our extraction studies (Chapter 6.3) an excess of acid was needed in order to maximise the extraction ratio. This makes the solution very acidic and prevents the formation of carbonates. The solution is therefore evaporated to attain solid magnesium salts, while the evaporated acid solution is condensed and recovered. When the solvent is evaporated, magnesium chloride or nitrate (including iron compounds) precipitates. Upon dissolving the magnesium chloride or nitrate in water (and possibly adding NaOH or another base so as to neutralise any remnants of the acid), iron oxides precipitate and can be removed prior to carbonation. If CO₂ gas is

injected and the pH of the solution regulated to a pH of 9 using NaOH, magnesium carbonate precipitates as hydromagnesite. This amount of NaOH required (0.9-1.2 g NaOH/g hydromagnesite) is very close to the stoichiometric requirements (0.86 g NaOH/g hydromagnesite) for cation exchange with the magnesium chloride or nitrate (Equations 52 and 53). The magnesium chloride required slightly more NaOH, which was probably due to the parallel reaction of NaOH with the iron-ion impurity in the solution used.



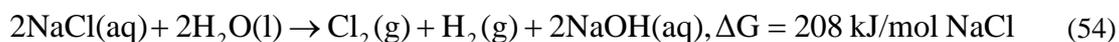
Assuming for the sake of simplicity that serpentinite consists of 85 wt-% serpentine and 15 wt-% magnetite, 3.1 t of serpentinite is required for storing 1 tonne of CO₂. This would produce 0.5 t of magnetite or hematite, 1.1 t of amorphous silica, and 2.7 t of hydromagnesite. In our experiments, we were able to produce carbonates using gas mixtures of 10 vol-% CO₂ and 90 vol-% CO₂. Therefore, it might be possible to absorb CO₂ from flue gas streams directly, by mixing NaOH with the magnesium salt solution and using the resulting solution in a flue gas scrubber. This would eliminate the need for a separate CO₂ separation process and be a significant benefit, unless the solids involved have to be transported long distances.

The evaporation of the solvent would require a lot of heat. To reduce the amount of solvent evaporated, the solid-to-liquid ratio should be significantly higher than in our experiments. Additionally, less acid could be used in relation to serpentinite, but then also less magnesium would be extracted from the raw materials. This is illustrated in Figure 6.3, where 0.36 M of acid is the theoretical amount required for dissolving serpentinite (according to Equations 50 and 51).

According to Outokumpu Mining (1998), the energy required for grinding the serpentinite to a fineness of 60% below 74 µm is about 14-17 kWh per tonne of ore. Since 3.1 t of serpentinite is required for storing 1 t of CO₂, the energy requirements for the grinding of serpentinite would amount to 160-190 MJ per tonne of CO₂ stored. Assuming that the CO₂ emissions from a coal-fired power plant are roughly 800 kg/MWh (IEA, 1993), the generation of the power required for grinding the ore would cause 40-50 kg of CO₂ per tonne of CO₂ stored as carbonates.

The precipitation of carbonates from magnesium or calcium salts seems to demand large amounts of NaOH or another alkaline compound (over 2 t of NaOH per tonne of CO₂

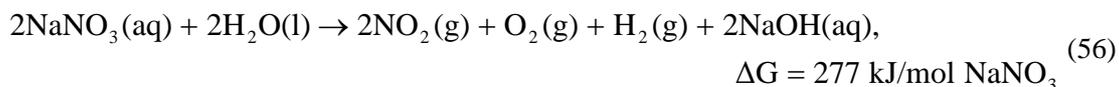
stored). The process would also demand large amounts of acid (over 2 t of HCl or 3 t of HNO₃ per tonne of CO₂ stored). Electrolysis could be one option for recycling the resulting aqueous sodium chloride solution. In the chloro-alkali industry, aqueous sodium chloride solutions are electrolysed, producing chlorine gas, sodium hydroxide, and hydrogen gas:



The chlorine gas can be re-combined with the hydrogen gas, forming chemically pure hydrogen chloride gas:



As this last reaction is exothermic, it is carried out in an installation called an HCl oven. The resulting hydrogen chloride gas is absorbed in water, resulting in hydrochloric acid. It is possible that sodium hydroxide could be regenerated in a similar way from sodium nitrate solutions by electrolysis:



Since product gases from the electrolysis of sodium chloride can be used for forming hydrogen chloride, a similar procedure might be possible for sodium nitrate. The exothermic HCl (and possibly HNO₃) production reaction could cover part of the heat needed for the evaporation of the solution. However, the electrolysis of sodium chloride or sodium nitrate would require 11.8 MJ or 15.7 MJ, respectively, of electrical power per kg of CO₂ stored. Since the CO₂ emissions from a coal-fired power plant are roughly 800 kg/MWh (IEA, 1993), the power consumed by the electrolysis of sodium chloride or sodium nitrate would release 2.6 or 3.5 times the amount of CO₂ bound in the carbonation process, respectively. Even if this power could be provided by renewable energy sources, it would cost 160 or 210 €/per ton of CO₂ stored, respectively¹⁵. Furthermore, the heat requirements for the evaporation of the water released would be large. Although this heat could be provided using low-grade waste heat (~130 °C or higher), the amounts of acid and base chemicals needed in the process are significant.

¹⁵ Calculated for an electricity price of 0.05 €/kWh (STAT, 2003).

6.7 Discussion

Mineral acids were found to be the most favourable of the solvents tested for dissolving magnesium from serpentinite rock. At 70 °C, all the magnesium in serpentinite was dissolved during 1-2 h in 2 M HCl, HNO₃, or H₂SO₄. The dissolution kinetics were found to follow rather well a shrinking-core model for constant particle size with product diffusion as the rate-controlling step for all three mineral acids tested. The low concentration of dissolved silicon and enrichment of silica in the serpentinite residue support the theory of the build-up of a product layer of silica on the particles.

To further enhance the dissolution rate a grinding medium (e.g. fluidisation using glass beads) could be used simultaneously to remove the silica layer from the particles (Park and Fan, 2004). Studies have also shown that after roasting at 700-800 °C serpentinite ore decomposes to olivine, which has a higher reactivity than serpentine. For roasted serpentinite and olivine, the dissolution kinetics have been found to follow a shrinking-core model, while surface chemical reaction is the rate-limiting step (Fouda et al., 1996a, 1996b; Apostolidis and Distin, 1978; Jonckbloedt, 1998; Hänchen et al., 2006). However, heat activation of the mineral considerably increases the energy demand of the process.

When dissolving a larger amount of serpentinite in 4 M HCl or 4 M HNO₃, mostly amorphous silica stayed in the serpentinite residue, while iron oxides were precipitated and separated by filtration. When the magnesium-rich solutions produced using HCl/HNO₃ were carbonated, 93%/99% pure magnesium carbonate was produced in the form of hydromagnesite, converting 79%/94% of the dissolved magnesium ions to magnesium carbonate. The optimum alkalinity for carbonate precipitation was found to be pH 9, which required 1.1 g/0.9 g of NaOH per gram of hydromagnesite produced. This amount is similar to the stoichiometric requirements for cation exchange with the magnesium chloride or nitrate (Equations 52 and 53). The magnesium chloride required slightly more NaOH, which may be due to the parallel reaction of NaOH with iron ions in the chloride solution.

Although the results demonstrate that very pure hydromagnesite can be produced from serpentinite and CO₂ at low temperatures and atmospheric pressures, quite large amounts of NaOH are required and only part of the acid used can be recovered by distillation. The production of NaOH and HCl from NaCl is a working industrial process. Therefore, the process scheme suggested for the production of pure hydromagnesite from serpentinite by using hydrochloric acid is largely based on proven technology. While it is possible that similar technology could be used for the recovery of NaOH and HNO₃ from NaNO₃, such a process is not as common.

Calculations showed that the evaporation of solvent and the regeneration of sodium hydroxide are the most energy-demanding steps of the process. Both the dissolution of

serpentinite and the precipitation of hydromagnesite (by reaction with NaOH) are exothermic. The grinding of the ore would only cause 40-50 kg of CO₂ emissions per tonne of CO₂ stored. Because of the large energy requirements for electrolysis and solvent evaporation, the process as such is not feasible for reducing CO₂ emissions. Although integration with existing processes would reduce the energy requirements, the amounts of chemicals needed are very large. The by-products of the process (hydromagnesite, silica, iron oxides) may have some commercial value, but the production of hydromagnesite and silica from a large-scale carbonation process would probably exceed the market demand. On the other hand, hematite and magnetite are common iron ore minerals, so these by-products may be suitable as raw material in steel production.

More research is required for reducing the amounts of sodium hydroxide required by the process. By carrying out the evaporation at a higher temperature, Mg(OH)Cl could possibly be separated and converted to Mg(OH)₂ for subsequent carbonation, while allowing the acid to be recycled without the need for electrolysis (Lackner et al., 1995; Chapter 3.2.3.2). However, iron oxide would probably also precipitate with magnesium hydroxide and their separation would require additional measures. Another option for eliminating the need for the regeneration of chemicals is to dissolve serpentinite in a melt of MgCl₂ and HCl, producing MgOHCl as an intermediate product for carbonation, or carbonated directly in a melt of MgCl₂ (Wendt et al., 1998a-b). However, these processes, which have not yet been experimentally tested, would require higher process temperatures and possibly high CO₂ pressures as well.

7 Stability of calcium carbonate and magnesium carbonate

In order to use CCS for reducing atmospheric CO₂ emissions, not even a small re-release or leakage rate from storage sites can be accepted, since it would reduce the effective amount of captured and stored CO₂¹⁶. Apart from atmospheric emissions, any CO₂ leaking from storage sites could also affect the local surroundings. A sudden release of CO₂ gas could be hazardous, since it is heavier than air and can cause death by asphyxiation. Even a small but steady leakage might be harmful through accumulation in soil or in populated areas.

Since carbonate minerals have a lower energy state than their reactants (silicates and CO₂) in ambient conditions, they are thermodynamically stable and could theoretically store CO₂ permanently. However, although carbonate minerals are only sparingly soluble in water, they dissolve readily in strong acids (Lackner, 2002). Therefore, there is a small risk that CO₂ gas could be released after contact between carbonate mineral and e.g. acid rain. Rain is normally slightly acidic (pH 5-7) through reactions with atmospheric CO₂, natural emissions of sulphur and nitrogen oxides, and certain organic acids. Human activities continuously produce these acidifying compounds, resulting in the formation of sulphuric and nitric acid in rainwater. Because of these strong acids, the pH of rain becomes less than 5. According to Brownlow (1996), the pH of acid rain can occasionally be below 2.4. In Finland, where emissions of sulphur and nitrogen oxides are strictly controlled, the lowest monthly mean value of rainwater was between pH 3.9 and pH 4.5 during years the 2000-2002, while the lowest daily mean value was pH 3.6 (EMEP, 2004).

Although carbonate minerals can be dissolved by acids, the amounts of sulphur and nitrogen oxides emitted are far lower than the scale of CO₂ emissions. Natural carbonate mineral reserves are estimated at 90 million gigatonnes (Lackner, 2002), which also confirms the stability of carbonates. However, natural carbonate minerals have been produced on a geological time scale, and most of this natural reserve is underground. Synthetic magnesium and calcium carbonates will be produced on a time scale of hours or less, presumably by precipitation, and would therefore be in the form of a powder which, because of its particle size, would be more easily soluble than large blocks of natural carbonate minerals.

¹⁶ “Even if only one per cent of the remaining carbon dioxide were to leak out every thousand years, it could still pose a threat. That would mean the loss of 87 per cent in 200,000 years, with the result that more carbon dioxide was released into the atmosphere and the seas than if CCS had not been implemented, since the energy consumed in capturing and storing carbon dioxide means that more coal has to be burned.” (Acid News, 2007).

To our knowledge, there is little literature available on magnesium and calcium carbonate stability from the perspective of the long-term storage of CO₂ as carbonates. Therefore, we made a short study of the stability of synthetic magnesium and calcium carbonates in nitric acid solutions and a rainwater sample from Finland (Paper VII).

Moreover, while magnesite and calcite are thermodynamically stable up to 400 °C and 900 °C respectively, the thermal stability of hydromagnesite (the product from the process studied in Chapter 6) is more complex. Therefore, the thermal stability of the hydromagnesite produced was also studied (Paper VI).

7.1 Stability of carbonates in rainwater and solutions of nitric acid

The stability of synthetic magnesium carbonate (MgCO₃·5H₂O, lansfordite, < 40 µm) and calcium carbonate (CaCO₃, calcite, < 10 µm) in acidic solutions was tested in sterilised water with various concentrations of nitric acid (HNO₃), which is present in acid rain in addition to sulphuric acid (Paper VII). Sulphuric acid was not used in the tests, to prevent sparingly soluble calcium or magnesium sulphate forming coatings on the particles. The carbonates were put into solutions of nitric acid (HNO₃), and sterile water with pH values of 1-7. One experiment for each carbonate was also performed using rainwater which had been recovered at Espoo, Finland during August-September 2004. The pH of the rainwater was in the range 4.9-5.8. The amount of carbonate mineral batch used was 1 mol/l of solution. Thus, 10.0 g of calcium carbonate or 8.4 g of magnesium carbonate was put into in a decanter glass containing 100 ml of the solution, which was stirred with a magnetic stirrer at 300-500 rpm. The temperature and pH were monitored and recorded. After stirring for 1-3 hours the stirrer was turned off, and the batch was left to stabilise in an open container for 3-11 days. By then the particles had formed a sediment layer, allowing the clear liquid to be separated and analysed using AAS. The filtration residue was also recovered, and a few selected samples of this were analysed using TOC and XRD. The theoretical concentrations of magnesium and calcium in aqueous HNO₃ solutions at thermodynamic equilibrium were calculated using Outokumpu HSC 4.0.

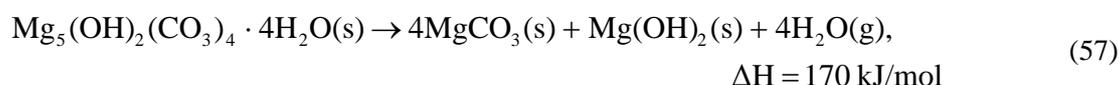
The results from the analyses of the experiments performed indicate that a relevant dissolution (over 1%) of magnesium carbonates and calcium carbonates occurred only for nitric acid solutions with an initial pH < 2. The concentration of dissolved magnesium and calcium ions in solution seemed to be linearly dependent on the H⁺ concentration (or acid concentration). The measured concentrations of dissolved magnesium and calcium ions were in agreement with the theoretically calculated values for concentrations at thermodynamic equilibrium at pH 1-7. TOC analyses of the carbonates leached at pH 1 and pH 2 showed, unexpectedly, that they all had slightly higher carbonate contents (2-3%-units) than the

untreated carbonates. It is possible that the leached carbonates were reactive and re-carbonated after the experiments.

In order to measure how much of the CO₂ stored in the carbonates escapes as gas upon dissolution, the experiments at pH 1 and pH 2 were repeated using a FT-IR gas analyser connected to the reactor outlet. Approximately 1.5 vol-% of the CO₂ stored in CaCO₃ was released during 3 h of mixing at pH = 1. At pH = 2, 0.1 vol-% of the CO₂ stored in CaCO₃ was released during the first 20 min, but after 3 h the net amount of gas released amounted to zero. The corresponding experiment with MgCO₃ registered only a brief emission of CO₂ gas directly after the addition of carbonate batch at pH = 1. The experiments indicate that magnesium carbonate is a more stable material than calcium carbonate for storing CO₂.

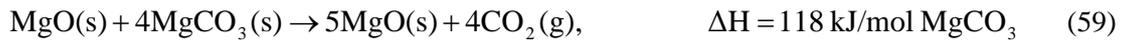
7.2 Stability of synthetic hydromagnesite

The thermal stability of the hydromagnesite produced at pH 9 with the solution prepared from HNO₃ and serpentinite (see Chapter 6.5) was tested using thermogravimetric analysis (TGA) (Paper VI). Thermodynamic equilibrium calculations, performed using Outokumpu HSC 5.1 software, predicted that magnesium hydroxide would decompose to magnesium oxide at temperatures > 265 °C, and that the decomposition of magnesium carbonate to CO₂ and MgO should take place at temperatures > 406 °C. Three runs from 25 to 900 °C were performed in an N₂ atmosphere, using heating rates of 2 °C/min, 5 °C/min (Figure 7.1), and 10 °C/min, respectively. After an initial mass loss of 2-6 %-units during heating up from 25 to 170 °C, the material decomposed mainly in two clearly endothermic steps: first, at 170-300 °C a mass loss of an additional 12-17%-units occurred, after which 35-38%-units were lost during heating up from 300 to 550 °C. The total mass loss that occurred during heating up from 25 to 300 °C (18-21 wt-%) is similar to the total molar weight of water that can be released by the dehydration and dehydroxylation of hydromagnesite (19 wt-%)¹⁷:



The net loss of mass during heating up from 300 to 550 °C (44-51 wt-%) corresponds to the expected loss of mass caused by the release of CO₂ (47 wt-%):

¹⁷ All reaction enthalpies have been calculated for 25 °C. Reaction enthalpies were calculated using Outokumpu HSC 5.1 software with additional data for MgCO₃, MgO, and Mg(OH)₂ from Robie et al. (1978).



The TGA analysis and thermodynamic calculations indicate that hydromagnesite should be a safe and stable CO₂ storage medium up to 300 °C. However, in order to verify these results, the experiments could be repeated using an FT-IR gas analyser to measure the CO₂ content in the gas at the outlet of the TGA reactor.

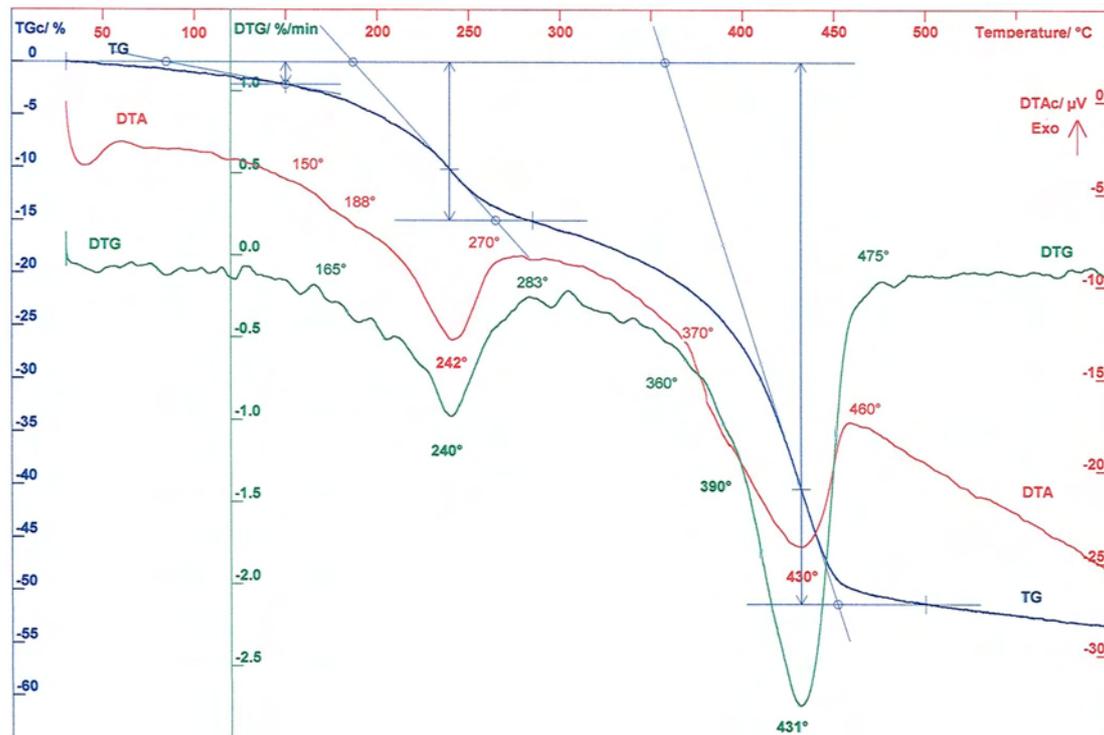


Figure 7.1. Thermogravimetric analysis of precipitated hydromagnesite in N₂ atmosphere (heating rate: 5 K/min). TG = mass change of the sample; DTG = rate of the mass change; DTA = local minima indicate endothermic reactions, while local maxima indicate exothermic reactions.

7.3 Discussion

The results from the various analyses of the experiments performed indicate that a relevant dissolution of magnesium carbonates and calcium carbonates occurs only for strong acidic solutions. Concluding from the experimental results and literature data, magnesium carbonate should be a more stable option than calcium carbonate for storing CO₂. At pH = 1, the release of gaseous CO₂ was very low for calcium carbonate and even lower for magnesium carbonate. The higher carbonate content of leached carbonate minerals and the measured CO₂ gas release imply that acid rain would not necessarily have a negative effect on

the amount of CO₂ stored. When taking into account the relatively low acidity of rain water and the very low rates and amounts of CO₂ gas emitted from nitric acid solution leaching of carbonates, the local environmental effects of CO₂ emissions from a carbonate mineral storage site would probably be insignificant, even if the storage site were not protected from rainwater. The small amount of magnesium carbonates dissolved by rainwater would eventually be transported to the seas and oceans, as in natural weathering (see Chapter 3.2.1). However, experiments in batch reactors eventually reach a solubility equilibrium, which prevents further leaching of the carbonate. If the carbonate were continuously rinsed with an acidic solution it would eventually dissolve completely. A flow-through reactor would be a better choice for simulating the leaching effect of rainfall or a continuous flow of large volumes of acidic water. More research on this issue should therefore be conducted when mineral carbonation technology matures.

The thermal stability study of hydromagnesite shows that it should be a safe and stable storage medium for CO₂ up to 300 °C. Since the solubility of hydromagnesite in water is lower than that of lansfordite (used in the tests presented in Chapter 7.1), hydromagnesite seems to be a suitable material for the long-term storage of CO₂.

8 Conclusions

The carbonation of magnesium and calcium silicates is an interesting alternative to geological storage methods, providing for permanent storage of carbon dioxide in the form of solid carbonates. Finland has large resources of potentially suitable magnesium silicates that could be used for several hundred years for the mitigation of CO₂ emissions from industrial sources. Industrial residues and by-products, especially steelmaking slags, also appear suitable for carbonation. While the available slag resources are significantly lower than those of natural minerals, these materials are produced steadily and could help introduce carbonation technology, since slags are more reactive than natural minerals.

The work reported in this thesis was concentrated on the design and evaluation of new multi-step, indirect carbonation processes for the fixation of CO₂ by the production of carbonates from natural minerals and steelmaking slags. Since only scant experimental data related to indirect carbonation processes were found in the literature, the main part of the work was on the experimental determination of process parameters. Additionally, the stability of carbonates as media for the storage of CO₂ was preliminarily assessed.

From the work presented in this thesis, the following issues can be concluded:

- The additional value from producing pure calcium carbonates from steelmaking slag would make for a far more expensive carbonation process than the current market value of CO₂ allows.
 - The high price and limited resources of wollastonite mineral make it an unattractive material for carbonation
 - Steelmaking slag, which is steadily produced and cheap, could provide for local CO₂ emission reductions by carbonation
- Acidic solutions extract calcium or magnesium from minerals and steelmaking slag efficiently, but the acidity of the solutions prevents the precipitation of carbonate.
 - Strong acids are required for extracting magnesium from serpentinite.
 - The dissolution (i.e. extraction of Mg) kinetics of serpentinite in HCl, HNO₃ or H₂SO₄ at 30-70 °C was found to be restricted by product layer diffusion.
 - Steelmaking slags dissolve more easily than wollastonite in aqueous solutions of acetic acid.
 - For maximum extraction or gel facilitation the solution temperature should be 70 °C or possibly higher.

- Evaporation recycles only part of the solvent, since part of the solvent is converted into a salt (e.g. magnesium and calcium acetate, nitrate, or chloride).
- While iron oxides and amorphous silica can each be separated easily from serpentinite upon dissolution in acids, steelmaking slags contain many other compounds as well, which may require additional separation measures (depending on the materials used).
- As CO₂ dissolves in a neutral, aqueous magnesium/calcium salt solution, the solution turns acidic and prevents the precipitation of carbonate. Therefore, a base must be added to raise the pH of the solution and precipitate dissolved magnesium, calcium, and CO₂ as carbonates.
 - The temperature of the solution affects the morphology of the precipitated carbonates, but not the yield.
 - The optimal amount of NaOH for the precipitation of hydromagnesite was similar to the stoichiometric requirements for cation exchange with magnesium-bearing salt.
- A new process concept, based on experimental results and procedures, was constructed and evaluated. The process concept allows for the production of relatively pure calcite (80-90%) from blast furnace slag and pure hydromagnesite (99%) from serpentinite.
 - Preliminary process calculations indicated that a similar process (Kakizawa et al., 2001) could store more CO₂ than is indirectly produced by the process. However, successful extraction of calcium ions was found to demand a surplus of acid, which effectively prevents the precipitation of carbonates from the solution. Therefore, a modification of the process approach is required.
 - Calculations concerning the suggested process concept showed that the process would produce 3-4 times more CO₂ than is stored in the process as a result of the electricity requirements for the regeneration of spent chemicals.
- Preliminary experiments with magnesium carbonate (as lansfordite) and calcium carbonate (as calcite) indicated that these should be safe alternatives for the storage of CO₂, as regards their low solubility, even in lean acidic solutions. Calculations and TGA experiments indicated that the hydromagnesite produced should likewise provide safe and permanent and practically leakage-free storage of CO₂

Experimental research has shown that CO₂ can be bound into pure and stable carbonate products using silicate-based materials. While relatively pure carbonate products and by-products, such as amorphous silica and iron oxides, can be produced using the processes presented here, the current obstacle to scaling up the suggested processes seems at this point

to be the regeneration of the additional chemicals spent in the process. The products and the by-products of the processes may have some commercial value, but the regeneration of NaOH and acid probably requires electrical power, which makes the process as such unfeasible as an overall storage method for CO₂. However, the potential to simultaneously produce pure synthetic minerals and the possibility that a costly CO₂ capture step could be omitted are significant benefits which warrant more research on the development of indirect, multi-step mineral CO₂ sequestration processes.

8.1 Significance of this work

In this work, the CO₂ storage potential in Finland of wollastonite and steelmaking slag has been assessed for the first time. The findings show that the carbonation of Finnish wollastonite for CO₂ storage would give very small emission reductions and that it is too expensive as a CO₂ storage process. However, it was also found that by carbonating Finnish steelmaking slags almost one per cent of Finland's annual anthropogenic CO₂ emissions could be disposed of. In comparison to these results, Finnish serpentinites seem to have by far the largest potential for CO₂ sequestration.

Reliable experimental data are valuable for the further development of a functional mineral carbonation process. This work presents new experimental data with respect to the dissolution of natural minerals and steelmaking slags in various acids and bases. The results give an overview of the suitability of common solvents for the extraction of magnesium from serpentinites or serpentine. Apart from their application in mineral carbonation processes for the storage of CO₂, the results can also be used in the mineral processing industry, where valuable metals are extracted from serpentinites.

The fixation of CO₂ by the precipitation of magnesium carbonates and calcium carbonates from solutions containing dissolved serpentinite or blast furnace slag has also been studied. Only very scant public research data were previously available on the precipitation of carbonates from magnesium and calcium actually extracted from silicate minerals or steelmaking slags. The results shed some more light on feasible precipitation parameters and process requirements.

A new concept for producing relatively pure precipitated calcium and magnesium carbonates from calcium silicates and magnesium silicates was suggested. Although the process concept does not in its current form bring about a net reduction in CO₂ emissions, it is one of the few indirect carbonation process concepts presented in the public literature that is primarily based on experimentally verified results. It also demonstrates that it is possible to produce a relatively pure calcite from blast furnace slag and a pure hydromagnesite from serpentinite.

Previous to this work, only scant experimental data had been presented on the stability of synthetic calcium carbonate and magnesium carbonate as media for storing CO₂. Although the studies presented here are preliminary, the results indicate that carbonates are safe and stable CO₂ storage materials, even when exposed to acid rain.

8.2 Recommendations for future work

The current obstacle to the process concept under study seems to be the major requirements for make-up solvent and chemicals that can raise the pH of the solution, such as sodium hydroxide. Additionally, the additional separation requirement for unwanted elements (mainly metals) after dissolution is another problem, making the concept more difficult to apply to steelmaking slags. While serpentinite seems to require strong acids for extracting magnesium, steelmaking slag could possibly be extracted in solvents milder than acetic acid. However, if the primary goal is to bind very large volumes of CO₂, then only natural magnesium silicate reserves provide sufficient storage capacity. The ideal solvent would be a solvent that extracts magnesium and/or calcium selectively from the silicate material and is alkaline after dissolution. The selectivity could nearly eliminate the need for additional separation methods and produce pure carbonate products. The alkalinity of a solution containing calcium and magnesium would favour the rapid precipitation of carbonates, and the solution could possibly be used as such for stripping flue gas of CO₂.

Future work should therefore aim in the first place to reduce the requirements for additional chemicals by focusing on solvent selection and the development of more reversible methods. Integration with other industrial processes could allow alkaline or acidic waste streams from these to be used in the carbonation process and should therefore also be investigated. These issues are currently being further studied at Helsinki University of Technology.

Alternatively, a simpler process that compromises carbonate product quality and therefore would not require the use of expensive chemical additives and solvents could be a better alternative for storing CO₂. An example could be the staged gas-solid serpentine carbonation processes that are being developed at Åbo Akademi University.

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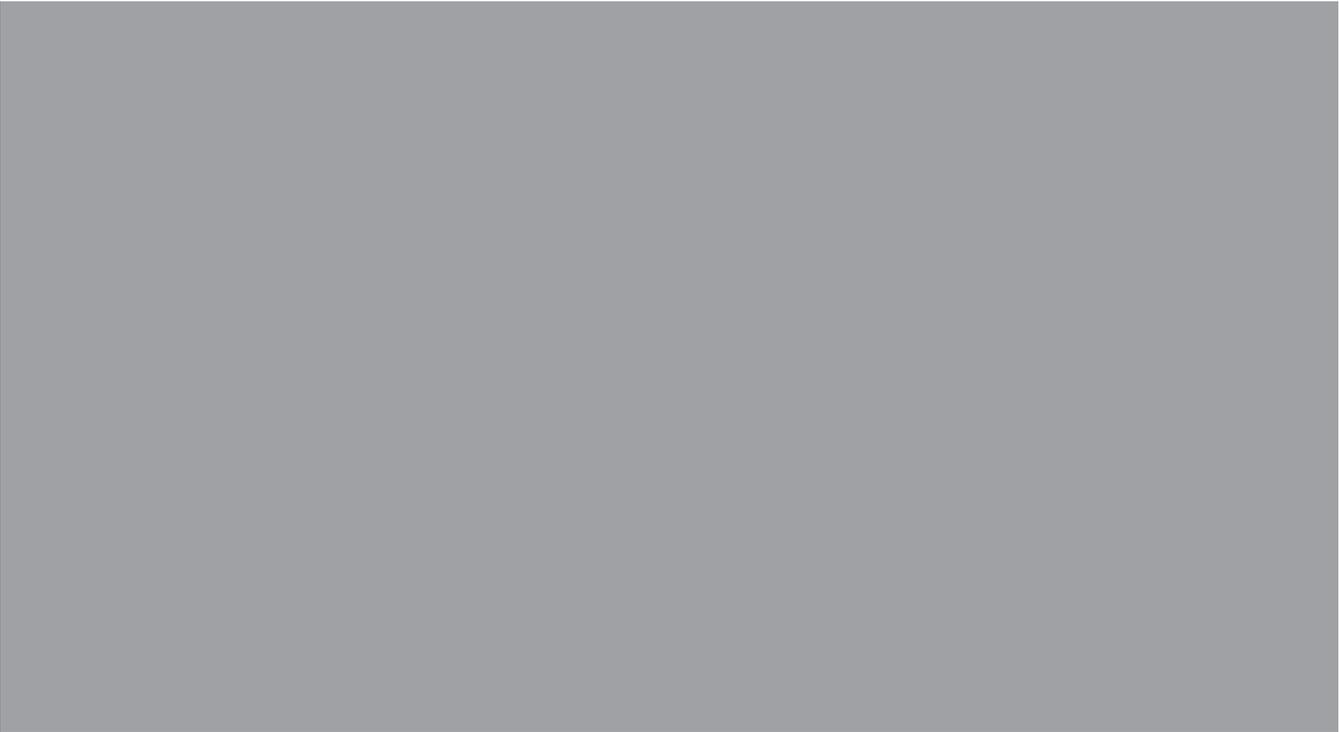
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