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Carbon Dioxide Capture and Storage by Mineralisation

Using Recyclable Ammonium Salts

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the degree of Doctor of Philosophy

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Abstract

Carbon dioxide capture and storage by mineralisation (CCSM) is considered to be an alternative solution for reducing anthropogenic CO₂ in some regions, where geological storage is not possible or considered uneconomically viable. However, low efficiency of mineral dissolution and use of unrecyclable additives are two key barriers for the development of CCSM.

A novel CCSM process with recyclable ammonium salts is proposed to overcome these barriers in this study. This process integrates mineral carbonation with CO₂ capture by employing NH₃, NH₄HSO₄ and CO₂ containing ammonium salts in the capture step, mineral dissolution and carbonation steps, respectively. The NH₄HSO₄ and NH₃ can then be regenerated by thermal decomposition of (NH₄)₂SO₄, which is the by-product from the process. The use of CO₂ containing ammonium salts as the source of CO₂ can avoid desorption and compression of CO₂, which account for 70 % of the total energy consumption in the whole CCS chain.

In this work, a CCSM process route at low solid to liquid ratio (50 g/l) was experimentally investigated to validate the process concept. It was found that the dissolution efficiency of magnesium (Mg) can achieve 100 % by using NH₄HSO₄ and the carbonation efficiency can
reach 96.5 % by using CO₂ containing ammonium salts from the capture step and addition of aqueous NH₃. Three products, including Si rich residue, Fe rich residue and pure hydromagnesite were obtained from the process. The TGA studies reported that the regeneration efficiency of NH₄HSO₄ and NH₃ in this process was 95 %. Both dissolution and carbonation efficiencies achieved in this work are higher than the values reported in previous work.

In order to reduce the water usage, a CCSM process at high solid to liquid ratio (200-300 g/l) was developed. It was found that the dissolution efficiency of Mg was 64 and 72 % at 200 and 300 g/l, respectively. The increase of dissolution efficiency with a solid to liquid ratio could be explained by the removal of passive product layer caused by particle-particle interaction. At a solid to liquid ratio of 300 g/l, the highest carbonation efficiency achieved was 65.4 %. Magnesite instead of hydromagnesite was found after carbonation due to the CO₂ pressure caused by the decomposition of ammonium salts above 70 °C. Additionally, the carbonation efficiency was doubled by using (NH₄)₂CO₃ compared to that using NH₄HCO₃.

A preliminary evaluation was conducted to estimate the OPEX, including energy consumption, chemical costs and feedstock cost, based on the experimental results from the two process routes developed. In order to get low OPEX, the optimization process conditions, such as solid to liquid ratio and reaction time, were
determined. Then, experiments at these optimized conditions were conducted. The dissolution efficiency of Mg from serpentine with particle size 75-150 μm using 2.8 M NH₄HSO₄ at 100 g/l solid to liquid ratio for 1 h was around 80%. The carbonation efficiency was 96% when the molar ratio of Mg: CO₂ containing NH⁴⁺ salts: NH₃ was 1:1.5:2. Thus, the mass balance of the process showed that 3.0 t\(^1\) of serpentine, 0.2 t of NH₄HSO₄ and 0.1 t of NH₃ were required to sequester 1 t of CO₂ and produce 1.9 t of magnesite. Moreover, 1.7 t of high Si content (46.9 wt. %) and 0.3 t of high Fe content (60 wt. %) were produced.

Finally, a cost evaluation study including CAPEX and OPEX was made using Aspen plus software to simulate the optimized CCSM process with recyclable ammonium salts for a 100 MW coal-fired power plant. For the input of 60 t/h CO₂, 93% of them can be sequestered by the process with 29.5% energy consumption and the total carbon capture and storage costs was 71.8 US$/t CO₂ sequestered, excluding the product sale.

\(^1\) Metric tonne throughout thesis
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Chapter 1. Introduction

1.1 Climate change mitigation and CO₂ abatement

Concerns about climate change and its possible effects have risen during the past decade. It has been widely accepted that carbon dioxide (CO₂) emissions reduction is necessary for climate change mitigation (IPCC, 2007), with most of the CO₂ emissions coming from the combustion of fossil fuels. CO₂ abatement solutions include improvement of energy efficiency, alternative energy resources (such as renewables and nuclear energy) and carbon dioxide capture and storage (CCS). The replacement of fossil fuels by renewable energy or nuclear power is not an easy task, since fossil fuels dominate in the current energy supply (e.g., 70% in China and 50% in U.S.; IPCC, 2005). Moreover, renewable energy, such as wind, solar and tidal, is still less economical than fossil fuels and thus the replacement of fossil fuel energy has a high cost attached (IEA, 2008). Nuclear power suffers limitations due to potential safety risks and the problem of waste disposal (IPCC, 2005). The contribution from improvement of energy efficiency could be slowed down due to the "ceiling effect". For example, recent new technologies, such as integrated gasification combined cycle (IGCC)
and natural gas combined cycle (NGCC), are already getting close to the maximum efficiency boundary (40-50%). For these reasons, fossil fuels will still provide the majority of energy for the foreseeable future; CCS is then the only solution to allow for this continued use of fossil fuels while reducing CO₂ emissions. Therefore, CCS will play an important role in the portfolio of CO₂ emission reduction. It is predicted that CCS CO₂ abatement contribution can reach 19% by 2050 (IEA, 2008).

1.2 Carbon dioxide capture and storage and mineralisation

CCS consists of three main steps: capture and separation of CO₂ from industrial and energy-related sources, compressing of CO₂ and transportation to a storage location, and long-term isolation from the atmosphere. The most promising CCS approach is carbon capture and geological storage (CCGS) (IPCC, 2005). However, the development of CO₂ geological storage has been slow in respect of potential environmental impacts and regulation for CO₂ injection and monitoring (Class et al., 2009). Moreover, some countries, such as Finland and India, do not have sufficient storage capacity or lack suitable storage formations (Teir et al., 2007c). Besides, sometimes the construction of pipeline is very expensive due to the long distance between CO₂ emission sources and storage sites. For example, some small and medium emitters in southwest England
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are far from the suitable storage site in the North Sea. Therefore, there has been an increasing interest in alternatives to CCGS, including mineral carbonation.

Mineral carbonation or mineralisation is a promising strategy to permanently and safely store anthropogenic CO$_2$ in solid magnesium (Mg) and calcium (Ca) carbonates. The advantages of mineral carbonation include large storage capacity, worldwide availability feedstock, permanent and inherently safe sequestration of CO$_2$ and theoretical exothermic process (Lackner et al., 1995). However, mineral sequestration also faces barriers such as low efficiency of mineral dissolution, slow kinetics, and energy intensive pre-treatment processes (Lackner et al., 1995). Even though, some barriers such as low efficiency and slow kinetics have been solved by swinging the pH (Teir et al., 2007c; Park and Fan, 2004), the addition of large amounts of acid and base required for the dissolution and subsequent carbonation limit the development of mineral sequestration.

O'Connor et al. (2002) have reported that mineral dissolution is the rate-limiting step in direct aqueous mineral carbonation, since the acidity produced by pressurised CO$_2$ in aqueous solution was not sufficient for mineral dissolution. In a second step, the carbonation of the leached solution was promoted by using a basic medium. This
indirect process is called pH-swing\textsuperscript{2}. Park et al. (2004) proposed a pH-swing process using mixed weak acid solvents with 1 vol% $\text{H}_3\text{PO}_4$, 0.9 wt% of oxalic acid and 0.1 wt% EDTA to promote mineral leaching. Nesquehonite ($\text{MgCO}_3\cdot3\text{H}_2\text{O}$) was obtained from the carbonation of a Mg-rich solution by raising the pH of the solution to 9.5 with $\text{NH}_4\text{OH}$. The overall conversion to MgCO$_3$ was $\sim$65%. However, the additives used in Park's process were not recycled and the dissolution efficiency was still low. Teir et al. (2007a) dissolved serpentine in HCl or HNO$_3$, and then hydromagnesite ($4\text{MgCO}_3\cdot\text{Mg(OH)}_2\cdot4\text{H}_2\text{O}$) was obtained by controlling the Mg-rich solution pH to 9 with addition of NaOH (Teir et al., 2007b). Although high carbonation conversion efficiency of Mg (80 - 90%) was obtained, the chemicals involved, such as HCl and NaOH, could not be reused. For Teir's process, 2.4 t NaOH and 2.1 t HCl acid (or 3.6 t HNO$_3$) were consumed per tonne of CO$_2$. The cost for make-up chemicals alone (600 - 1600 US$/t CO$_2$) is much larger than the budget for CO$_2$ emission allowances (30-40 US$/t CO$_2$) (IPCC, 2005). Thus, recycling of all chemicals involved is crucial to make CO$_2$ mineral carbonation viable.

Kodama et al. (2008) reported a pH swing CO$_2$ mineralisation process with recyclable additives. In their study, steel slags were reacted with ($\text{NH}_4$)$_2\text{SO}_4$ to extract Ca and produce NH$_3$. CO$_2$ was

\textsuperscript{2} Change the pH of the solution from acid to base condition
then purged to the Ca-rich solution to precipitate CaCO₃ and recycle (NH₄)₂SO₄. Kodama et al. (2008) reported a 62% dissolution efficiency but the effect of important parameters such as temperature, pressure and reaction time was not reported. Moreover, the value of 80% for the carbonation conversion efficiency was only derived from theoretical calculations and not from experimental work. Furthermore, the CO₂ storage capacity of steel slags is only 60-80 MtCO₂/year (Weber, 2000), which is very small compared with the vast capacity of mineral silicates, like serpentine and olivine that is estimated to be 100,000 GtCO₂ (Lackner, 2002).

Pundsack et al. (1967) used 1.4 M NH₄HSO₄ to dissolve serpentine at 95°C for 5 hours and obtained 92.8% Mg extraction efficiency, but the carbonation efficiency was only 35%. Pundsack's process aimed to produce pure magnesium carbonate and more work is needed to understand the dissolution kinetics, optimize reaction conditions of this process, improve the carbonation efficiency and investigate its potential application for mineral carbonation to store CO₂.

Krevor et al. (2009) tested NH₄Cl, NaCl, sodium citrate, sodium EDTA, sodium oxalate, and sodium acetate to dissolve serpentine. All experiments were carried out at 120 °C and 20 bars of CO₂ in a batch autoclave. When using 0.1 M citrate, EDTA and oxalate
solutions, 60 % dissolution efficiency of Mg from serpentine was achieved within 2 hours, rising to 80 % after 7 hours and reaching nearly 100 % between 10 and 20 hours. Therefore, the mineral dissolution with organic solvents is promising in terms of dissolution efficiency, but the dissolution rate is relatively slow and needs a long reaction time of up to 20 hours.

Fagerlund et al. (2009) proposed a process for production of Mg(OH)$_2$ from serpentine using (NH$_4$)$_2$SO$_4$. Solid-solid reaction of serpentine with (NH$_4$)$_2$SO$_4$ was carried out at above 440 °C to generate MgSO$_4$, that was then put into ammonia water to precipitate Mg(OH)$_2$ and regenerate (NH$_4$)$_2$SO$_4$. The Mg(OH)$_2$ was then carbonated with CO$_2$ directly in a pressurized fluidized bed (PFB) reactor at 470-550 °C and 20 bar. However, only 20-60 % extraction efficiency of Mg from serpentine was reported (Nduagu, 2010), and the carbonation efficiency of Mg(OH)$_2$ only achieved a maximum value of 45 %. This was due to the conversion of Mg(OH)$_2$ to MgO at the temperature range used, where the produced MgO cannot react with CO$_2$ to produce carbonates at the above temperature range (Zevenhoven, 2010). Therefore, work is needed to improve both dissolution and carbonation efficiencies of this indirect gas solid mineralisation process.
1.3 Aim and objectives

The aim of this research is to develop a pH swing mineral carbonation process using recyclable salts. It is hypothesised that ammonium salts would provide high efficiency of mineral dissolution and carbonation and can be recovered at the end of process. The research objectives are:

- To investigate the mineral dissolution of selected feedstock (serpentine) with ammonium salts, such as ammonium bisulphate, and to maximize the magnesium dissolution efficiency by changing temperature, reaction time, solid/liquid ratio, particle size and additive concentration.
- To investigate the precipitation of magnesium carbonates by reacting ammonium bicarbonate/carbonate with Mg$^{2+}$ rich solution, and to maximize the carbonation efficiency by changing temperature, reaction time and mass ratio between Mg:NH$_4$HCO$_3$:NH$_3$.
- In order to reduce the water usage so that lower the energy cost, a process route at high solid/liquid ratio is proposed to understand the effects of solid to liquid ratio in the dissolution and carbonation efficiencies.
- To study the thermal decomposition of ammonium sulphate and maximize the regenerative rate of ammonia and ammonia bisulphate.
• To estimate the OPEX of the two process routes by using an excel spreadsheet tool, and to optimize process conditions (solid to liquid ratio, reaction time, Mg:CO₂ containing NH₄⁺ salts:NH₃) according to the triggers from cost estimation.

• To study the dissolution and carbonation efficiency at these optimized process conditions, and maximize the efficiencies by changing the ratio of Mg:CO₂ containing NH₄⁺ salts:NH₃.

• To evaluate the CAPEX and OPEX of the optimized process using the chemical process simulation software (Aspen plus), including sensitivity analysis to understand the relationship between process conditions and cost.

This thesis presents the following structure. The literature review is presented in Chapter 2, followed by the introduction of two process routes for CCSM process with recyclable ammonium salts in Chapter 3. Chapters 4 and 5 describe the experimental work on dissolution and carbonation at low and high solid to liquid ratio, respectively. The process evaluation of the two process routes is discussed in Chapter 6 and then optimization experiments are presented in Chapter 7. Finally, Chapter 8 focuses on the cost evaluation and sensitivity analysis of the CCSM process with ammonium salts.
Chapter 2. Literature review

2.1 Climate change mitigation and CO₂ emissions

Climate change mitigation and global climate change negotiation

Fossil fuels combustion dominates energy production, and is likely to remain the key energy source for the foreseeable future (IPCC, 2005). However, large amounts of greenhouse gases (GHG) emissions, mainly CO₂, are associated with fossil fuel combustion and cause increasing CO₂ atmospheric concentrations from approximately 280 ppmv in the pre-industrial times to the current levels of 389.6 ppmv (Fig 2-1).

![Atmospheric CO₂ at Mauna Loa Observatory](figure2_1.png)

Figure 2-1: Average annual atmospheric CO₂ concentration based on direct measurements at Mauna Loa Observatory from 1960-2010 (Dr Pieter Tans, NOAA/ESRL, [www.esrl.noaa.gov/gmd/ccgg/trends](http://www.esrl.noaa.gov/gmd/ccgg/trends), accessed on 15th March, 2011)
Records of temperature and atmospheric CO₂ concentration have been reconstructed from ice-cores drilled in Antarctica for the last 400,000 years (ADIAC, 2004). Atmospheric CO₂ concentrations never exceeded 300 ppmv before 1950, and temperature increase presents the same trend as seen with the change of atmospheric CO₂ concentration. To date, the most credible estimation of future climate from mathematical models based on physical approximations predicts that climate change with greenhouse gas increases (IPCC, 2007). Although uncertainties remain, there is no doubt that without drastic reductions in GHG emissions climate change will occur, leading to severe consequences. According to the United Nations Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 2007), “climate change has been proven to be unequivocally linked to human activity from observation of increases in global air and ocean temperatures, rising global average sea levels and widespread melting of sea-ice in the Arctic”. Irreversible impacts are likely to occur in the near future as follows (IPCC, 2007):

- Approximately 20-30 % of species assessed so far are likely to be at increased risk of extinction.
- Between 75 and 250 million people projected to be exposed to increased water stress in Africa by 2020.
- Many of the world’s major cities (22 of the top 50) are at risk of flooding from coastal surges, including Tokyo, Shanghai,
Hong Kong, Mumbai, Calcutta, Karachi, Buenos Aires, St Petersburg, New York, Miami and London. Numerous international efforts are being made to control climate change, including the United Nations Framework Convention on Climate Change (UNFCCC) in 1994 and the Kyoto Protocol in 1997 that entered into force in 2005 to reduce GHG emissions by 5.2 % of 1990 levels by the year 2010. In 2006, the Stern review (2006) showed the need to stabilize greenhouse gas concentrations between 450 and 500 ppm CO2-eq\(^3\) in order to substantially reduce the worst impacts of climate change. In November 2008, the UK Climate Change Act set a target of 80% reduction of CO\(_2\) emission with respect to 1990 levels by 2050 (DECC, 2009).

**CO\(_2\) emissions**

The major emissions of GHGs worldwide in 2004 were 56.6 % CO\(_2\) from fossil fuel use, 17.3 % CO\(_2\) from deforestation and decay of biomass, 14.3 % methane (CH\(_4\)) and 7.9 % nitrous oxide (N\(_2\)O) (IPCC, 2007). Therefore, CO\(_2\) is the most important anthropogenic greenhouse gas.

Global CO\(_2\) emissions were 28.4 Gt in 2008 (IEA, 2010a). In terms of worldwide CO\(_2\) emissions by fuel, 43 % were produced from coal, 37 % from oil and 20% from gas. In terms of CO\(_2\) emission by 3 \(^3\) CO\(_2\)-equivalent emissions are the amount of CO\(_2\) emissions that would cause the same time-integrated radioactive forcing, over a given time horizon.
region, two-thirds of world emissions for 2008 originated from just ten countries, where China and U.S. produced 6.5 GtCO$_2$ and 5.6 GtCO$_2$, respectively (Fig. 2-2). In terms of CO$_2$ emission by sectors, two sectors, electricity and heat generation (41 %) and transport (22 %), produced two-thirds of global CO$_2$ in 2008 (Fig. 2-3).

![Figure 2-2: The top 10 CO$_2$ emitting countries (IEA, 2010a).](image)

The World Energy Outlook 2009 predicts that demand for electricity will be almost twice as high as current demand by 2030 and global demand for transport appears unlikely to decrease in the foreseeable future (IEA, 2009). The urgent need to reduce CO$_2$ emissions and increasing energy demand drive the development of CO$_2$ abatement technologies in a low carbon society.
Figure 2-3: World CO₂ emissions by sector in 2008 (IEA, 2010a).

2.2 Carbon dioxide abatement and carbon dioxide capture and storage

2.2.1 CO₂ abatement

Efficiency improvement, alternative energy resources (such as renewable and nuclear energy) and carbon dioxide capture and storage (CCS) are considered to be the three most important CO₂ emissions abatement strategies (IPCC, 2005). According to the International Energy Agency's (IEA) Energy Technology Perspectives in 2008, in the 450 ppm scenario, efficiency enhancement technology will constitute 65 %, 57 % and 54 % in the global emissions abatement portfolio by 2020, 2030 and 2050, respectively (Fig. 2-4). However, with the ceiling effect of efficiency enhancement (large increase of cost only resulting in small increase
of efficiency) and the difficulties in replacing fossil fuels with alternative energy resources, CCS abatement contribution has to grow from 3% of the global abatement portfolio in 2020 to 10% in 2030 and finally reach 19% in 2050 to stabilize the CO₂ atmospheric concentration at 450 ppm (Fig. 2-4) (IEA, 2008).

![Figure 2-4: Shares of contributions to CO₂ emission reductions by technologies from 2005-2050 (IEA, 2008)](image)

Furthermore, according to an IEA study (2008) on the costs of various emissions abatement technologies, implementing CCS will contribute to the least-cost route of emissions abatement. To reach the 450 ppm scenario⁴ without utilizing CCS would lead to a 70%

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⁴ 450 ppm scenario is to control the atmosphere CO₂ concentration under below 450 ppm so that limit the global temperature rising below 2 °C (Stern, 2006). In Copenhagen conference, all countries reached a consensus on the 2 °C target.
increase in the total cost of emissions abatement by 2050 compared with that of utilizing CCS (IEA, 2008).

In addition, CCS can reduce anthropogenic CO₂ emissions from large point sources, and particularly fossil fuel fired power plants, by up to 90% (IPCC, 2005). The most important key feature of CCS is that it allows for the continued use of fossil fuels. On a global scale, CCS could potentially reduce between 1.4 GtCO₂ (Stern, 2006) and 4 GtCO₂ (IEA, 2007) by 2030.

2.2.2 Carbon dioxide capture and storage

CCS is defined as a process consisting of three main steps: capture and separation of CO₂ from industrial and energy-related sources, compression of CO₂ and transportation to a storage location, and long-term isolation from the atmosphere by a variety of methods (Fig. 2-5). The main storage formations include oceans, depleted gas, oil and coal reservoirs, and saline aquifers. In addition, mineral carbonation, which was first described by Seifritz (1990), refers to the fixation of the CO₂ using binary oxides such as magnesium oxide (MgO) and calcium oxide (CaO) into carbonate for long term CO₂ storage. Mineral carbonation also has the potential to convert CO₂ into beneficial products, for example, carbonates used as construction materials.
Figure 2-5: Overview of carbon capture and storage technologies (IPCC, 2005)

CCS combines three separate technologies: capture, transportation and storage, where each technology seems relatively mature (IPCC, 2005). For example, CO\textsubscript{2} storage is not new, and uses similar technologies applied in enhanced oil recovery (EOR), which is a mature technology in the oil industry. However, the integration of individual technologies in CCS attracts public concerns on the maturity of the technology and potential health and safety impacts. Moreover, the development of individual technologies in the CCS chain are at different stages of technology readiness level (TRL), as shown in Table 2-1. It can be seen that mineral carbonation is currently in the research stage and demands more research work.
Table 2-1: The current development stages of individual CCS technologies (IPCC, 2005)

In order to prove the feasibility of CCS and accumulate experience in operation and management, there are 77 pilot-scale CCS projects around the world (GCCSI, 2010). Governments and energy corporations are developing and implementing incentives to facilitate widespread deployment of CCS technologies in the near future. The UK government has planned to build one of the first commercial-scale CCS projects by 2014 (BERR, 2008; BERR, 2009; APGTF, 2009). The EU has implemented a programmed of 10-12 demonstration CCS projects to be in operation by 2015 (APGTF, 2009). China is also making significant progress in CCS. For example, the GreenGen project led by eight Chinese energy companies and Peabody Energy plan to develop a 400 MW
Integrated gas cycle combustion (IGCC) power plant with CCS by 2020; Shenhua Group, the largest coal production company in China, has implemented a 1 Mt CO₂ project in Ordos, Inner Mongolia, and has started to inject CO₂ into a saline aquifer from January, 2011. In April 2009, the Australian government launched the Global Carbon Capture and Storage Institute (GCCSI), which aims at accelerating the worldwide commercial development of CCS technologies. The Department of Energy (DOE) in the U.S. has formed a national network of Regional Carbon Sequestration Partnership (RCSP) to help determine the best approach for CCS. In May 2011, Canadian authorities approved a fund of US$ 1.3 billion for a CCS demonstration plant in Saskatchewan, which aims to reduce annual greenhouse gas emissions by around 1 Mt CO₂.

However, some difficulties in developing CCS technologies include the absence of financial support, regulations and policy frameworks and potential lack of public support. The major barriers are probably the high energy penalties, costs and potential impacts due to CO₂ leakage (IPCC, 2005).

The IPCC’s CCS special report (IPCC, 2005) presents the costs of the different CCS technologies. It can be seen in Table 2-2 that capture technologies are very expensive and account for 75% of the total cost of CCS. The cost of geological storage is relatively low at 0.6-8.3 US$/tCO₂. The cost of mineral carbonation was based on
the direct aqueous process developed by O’Connor (2005), where 185 °C and 150 P_{CO_2}^5 pressure were used. It must be pointed out that estimating the cost of CCS technologies involves a high degree of uncertainty on how these costs may develop over time and in terms of potential variations in the technical requirement, scale and application of projects. McKinsey & Company (2008) released a report on CCS predicted costs based on a case-study approach. According to the findings of the report, early commercial CCS projects by 2020, are estimated to cost 45-65 US$/tCO_2 with CO_2 capture being the most expensive step and accounting for 33-42 US$/tCO_2.

Table 2-2: The costs of current CCS technologies (IPCC, 2005).

<table>
<thead>
<tr>
<th>CCS-system components</th>
<th>Cost range</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capture from a coal- or gas-fired power plant</td>
<td>15-75 US$/tCO_2 net captured</td>
<td>Net costs of captured CO_2, compared to the same plant without capture.</td>
</tr>
<tr>
<td>Capture from hydrogen and ammonia production or gas processing</td>
<td>5-55 US$/tCO_2 net captured</td>
<td>Applies to high-purity sources requiring simple drying and compression.</td>
</tr>
<tr>
<td>Capture from other industrial sources</td>
<td>25-115 US$/tCO_2 net captured</td>
<td>Range reflects use of a number of different technologies and fuels.</td>
</tr>
<tr>
<td>Transportation</td>
<td>1-8 US$/tCO_2 transported</td>
<td>Per 250 km pipeline or shipping for mass flow rates of 5 (high end) to 40 (low end) MtCO_2 yr^{-1}.</td>
</tr>
<tr>
<td>Geological storage^{a}</td>
<td>0.5-8 US$/tCO_2 net injected</td>
<td>Excluding potential revenues from EOR or ECBM.</td>
</tr>
<tr>
<td>Geological storage: monitoring and verification</td>
<td>0.1-0.3 US$/tCO_2 injected</td>
<td>This covers pre-injection, injection, and post-injection monitoring, and depends on the regulatory requirements.</td>
</tr>
<tr>
<td>Ocean storage</td>
<td>5-30 US$/tCO_2 net injected</td>
<td>Including offshore transportation of 100-500 km, excluding monitoring and verification.</td>
</tr>
<tr>
<td>Mineral carbonation</td>
<td>50-100 US$/tCO_2 net mineralized</td>
<td>Range for the best case studied. Includes additional energy use for carbonation.</td>
</tr>
</tbody>
</table>

^{a} CO_2 partial pressure in autoclave reactor
2.2.3 The shortages of carbon capture and geological storage (CCGS)

The most promising CCS approach is carbon capture and geological storage (CCGS) (IPCC, 2005). However, the development of CO₂ geological storage has been slow recently in respect of avoiding leaking risk and lacking of regulation for CO₂ injection and monitoring. Some countries, such as Finland and India, do not have sufficient geological storage capacity or lack suitable storage formations (Teir et al., 2009; Devleena Mani, 2008). Moreover, the distance from the emission point source to a suitable geological storage location sometimes may be thousands of kilometres away, e.g., the main power plants in China located in Huabei area, the suitable geological sites are more than 1000 km away in Bohai (NZEC, 2009). Therefore, the construction and maintenance of a high pressure CO₂ pipeline may be relatively costly up to 1.6 million US$/mile (ZEP, 2011). Furthermore, Oman wants to use their abundant natural resources of ophiolite to mineralize CO₂, since Oman has mineral capacity large enough to store the world CO₂ emissions from fossil fuels for 200 years (Matter et. al., 2009). Another example is Singapore, where they want to use the carbonate products from CO₂ mineralisation for land reclamation (AStar/ICES, 2009). Geological storage might not be able to offer the necessary capacity soon enough to match the urgent emission reduction targets. In a recent international conference, it was
reported that the total worldwide capacity of geological storage (identified and surveyed) increased ~7 Mt CO$_2$/y in 2008 and is expected to increase to 24 Mt CO$_2$/y in 2012 (Thambimuthu, 2009). It may be hard to match the sequestration rate of many Gt CO$_2$/y within near future, putting pressure on the development of alternatives, such as mineralisation.

2.3 Mineral carbonation

Mineral carbonation or mineralisation is a promising strategy to permanently and safely store anthropogenic generated CO$_2$ in solid magnesium (Mg) and calcium (Ca) carbonates. The reaction of mineral carbonation can be expressed by the following equation:

\[ MO + CO_2 \rightarrow MCO_3 + \text{heat} \]

Equation 2-1

Where M refers to a metallic element such as calcium, magnesium or iron.

Mineral carbonation can be classified into in-situ mineral carbonation and accelerated mineral carbonation. In-situ mineral carbonation is closely related to geological storage as it involves the injection of CO$_2$ underground, but it differs from geological storage, in that it explicitly aims at enhancing the formation of carbonates with alkaline-minerals present in the geological formation. The mineral trapping in geological storage is same to mineral carbonation, but it
requires very long times (Fig. 2-6). The first in-situ mineral carbonation project, called Carbfix, started at Hellisheidi (Iceland) in 2008 (Oelkers et al., 2008). In order to speed up the reaction rate, the Carbfix project firstly dissolves the CO₂ from a geothermal power plant in water at elevated pressure and then injects it through wells down to a basalt formation below 400-800 m (Matter et al., 2009). Recently, Kelemen et al. (2010) finished the geological survey work on an ophiolite complex in Oman and plan to launch an in-situ mineral carbonation project in future. Although the timescale of in-situ mineral carbonation is shorter than that for solubility trapping and mineral trapping in CO₂ geological storage (Fig. 2-6), it still takes hundreds of years to permanently store CO₂ into carbonates (Matter et al., 2009). In contrast, the timescale of accelerated mineral carbonation is only in the order of hours, or even minutes. It must be pointed out that accelerated mineral carbonation may produce some beneficial by-products, and therefore it is also classified as a CO₂ utilization process. For the purpose of this thesis, mineral carbonation is the term used to refer to accelerated mineral carbonation.
The first advantage of mineral carbonation compared to geological storage is the environmentally benign and permanent trapping of CO₂. Unlike geological storage, there is no need for post-storage monitoring for potential environmental impacts. In a recent study, Teir et al. (2006) investigated the stability of Ca and Mg carbonate formed from mineralisation when subjected to an acidic aqueous environment (similar to acidic rain, pH 3-5) and concluded that Ca and Mg carbonates are resistant from corrosion from local environmental effects.

The second advantage of mineral carbonation is the significant large capacity and worldwide availability of the minerals required. The
estimated capacity of various CO₂ storage options are summarized in Table 2-3, which states that mineral carbonation is capable of fixing all the CO₂ worldwide output from combustion of fossil fuels. The most abundant feedstocks are magnesium silicate minerals such as serpentine and olivine, while there are some other interesting feedstocks such as calcium-rich silicate minerals (wollastonite), waste materials from steel, cement and water sewage industries and brine water (see Section 2.3.1.). CO₂ mineralisation for storing several Mt of CO₂ per year will involve solids handling of a scale similar to a typical metal ore or mineral mining and processing activity (IPCC, 2005). An example of a large-scale processing of solids is the mining and processing of oil sands in Alberta, Canada, where 1 Mt oil sands are moved each day (Kunzig, 2009).

Table 2-3: Estimated Capacity of CO₂ storage and utilization options

<table>
<thead>
<tr>
<th>Options</th>
<th>Estimated global capacity [GtC]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal reserves worldwide</td>
<td>&gt;10,000</td>
<td>Lackner, 2002</td>
</tr>
<tr>
<td>Total CO₂ output during the 21st century</td>
<td>2,300</td>
<td>Lackner, 2002</td>
</tr>
<tr>
<td>CO₂ Mineral sequestration</td>
<td>Very large (more than the total output of carbon from fossil fuel); Mg/Ca silicates &gt; 30,000</td>
<td>Kohlmann, 2001; Lackner, 2002</td>
</tr>
<tr>
<td>Ocean disposal</td>
<td>&gt;1,000; 300-600</td>
<td>Kohlmann, 2001;</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Cost Source</th>
<th>Cost Range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline aquifers</td>
<td>1,000-20,000</td>
<td>IPCC, 2005; IEA, 2008</td>
</tr>
<tr>
<td>Depleted gas reservoirs</td>
<td>&gt;140</td>
<td>Kohlmann, 2001</td>
</tr>
<tr>
<td>Depleted oil reservoirs</td>
<td>&gt;40</td>
<td>Kohlmann, 2001</td>
</tr>
<tr>
<td>Improved forestry and reforestation</td>
<td>50-100</td>
<td>Kohlmann, 2001</td>
</tr>
<tr>
<td>Enhanced oil recovery</td>
<td>65</td>
<td>Kohlmann, 2001</td>
</tr>
<tr>
<td>Bio fixation</td>
<td>1.35</td>
<td>Kohlmann, 2001</td>
</tr>
<tr>
<td>Chemicals</td>
<td>0.09</td>
<td>Kohlmann, 2001</td>
</tr>
</tbody>
</table>

The third advantage of mineral carbonation is that theoretically the carbonation reaction could proceed without energy input, since carbonates have a lower thermodynamic energy state than CO₂ (Fig. 2-7), but this has not been accomplished. However, the carbonation process takes a geological time (thousands of years) to complete, the reaction rate must be improved to industry time (hours). A high energy penalty is caused from the pre-treatment of minerals and the high temperature and pressure conditions applied to accelerate the kinetics of carbonation process. It is expected that optimisation and process integration should allow reducing the net energy input.
The fourth advantage of mineral carbonation is that it can provide a CO₂ sequestration solution to some countries, where large geological reservoirs do not exist and ocean storage is not feasible. Finland, Korea and India have started studies on mineral sequestration of CO₂ due to the lack of suitable geological formations (Kohlmann, 2001; Devleena Mani, 2008; Lee et al., 2005). In Lithuania and the Baltic region, mineral sequestration of CO₂ is also being studied, as the saline aquifers in Lithuania have been found unsuitable for CO₂ storage (Stasiulaitiene et al., 2007; Shogenova et al., 2009). Moreover, the distance from the emission source to a suitable storage location sometimes may be hundreds or thousands of kilometres away, such as hundreds of coal fired power plants in South China, central of India, southwest of U.S., east of Russia and south of Europe (Fig. 2-8).
Figure 2-8: Geographical relationship between CO$_2$ emission sources and prospective geological storage sites (Bradshaw, 2004)

The last advantage of mineral carbonation is the potential use of products from the process. Recent papers have investigated the use of Mg carbonates in building materials or flame retardants (Teir et al., 2007b; Laoutid et al., 2006), applications of Ca carbonates in paper production (Eloneva et al., 2009) and the use of by-products, such as high purity silica from mineral dissolution as aggregates and high Fe contain products from pH-swing as feedstock for the steel industry (Teir et al., 2007b; Xiaolong Wang, 2010a). In addition, mineralisation is receiving increased attention from mineral, cement, metal, paper and power plant industries, where the waste materials produced could be a good feedstock for mineralisation to avoid the transportation of minerals. In addition, the high reactivity of many calcium-containing industrial wastes could avoid the high energy penalty from mineral pre-treatment.

Although the advantages of mineral carbonation include vast
storage capacity, permanent storage and the fact that mineralisation is exothermic, mineral sequestration also faces many problems such as low efficiency of mineral dissolution, slow kinetics, and energy intensive pre-treatment processes (Lackner et al., 1995). Even though, some barriers such as low efficiency and slow kinetics have been solved by swinging the pH (Teir et al., 2007c; Park and Fan, 2004), the addition of large amounts of acid and base required for the dissolution and subsequent carbonation limit the development of mineral sequestration.

2.3.1 Raw materials and capacity

Table 2-4, lists various materials investigated for mineral carbonation. Alkaline earth metals, Ca, Mg and Fe, can be used for mineral carbonation. Fe has been suggested for carbonation, but as it is a valuable mineral resource it is sought after for other purposes. Mg and Ca metals comprise 2.0% and 2.1% of the Earth’s crust, respectively (Goff et al., 1998), and therefore they are generally selected as feedstock for mineral CO2 sequestration. Carbonation of Ca is easier, but Mg minerals are favoured, because Mg silicates are widely available worldwide. Furthermore, the ratio of magnesium oxide required to bind CO2 is 3.3:1, compared with calcium oxide’s 4.7:1. Therefore, magnesium-containing minerals are the most promising feedstock for mineral carbonation. In addition, there are
also industrial solid wastes that contain large amounts of Mg, Ca and even Fe, such as steel slags, fly ash and waste cement.

Table 2-4: Raw materials studied in literature and associated references.

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula/Composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt</td>
<td></td>
<td>Oelkers et al., 2008; Matter et al., 2009; Gislason et al., 2010</td>
</tr>
<tr>
<td>Forsterite</td>
<td>Mg$_2$SiO$_4$</td>
<td>Giammar et al., 2005</td>
</tr>
<tr>
<td>Olivine</td>
<td>(Mg$<em>x$Fe$</em>{1-x}$)SiO$_4$</td>
<td>Hänchen et al., 2006; Hänchen et al., 2007; Prigiobbe et al., 2009b; Gerdemann et al., 2007; Krevor and Lackner, 2009; Jarvis et al., 2009; Dufaud et al., 2009; O'Connor, 2005; Prigiobbe et al., 2009a; Munz et al., 2009; Haug et al., 2010</td>
</tr>
<tr>
<td>Serpentine</td>
<td>Mg$_3$Si$_2$O$_5$(OH)$_4$</td>
<td>Blencoe et al., 2003; Ron Zevenhoven, 2002; Zevenhoven et al., 2006; Zevenhoven et al., 2008; Teir et al., 2009; Teir et al., 2007b; Teir et al., 2007c; Mercedes Maroto-Valer et al., 2005; Alexander et al., 2007; Xiaolong Wang, 2011a; Xiaolong Wang, 2011b; Park and Fan, 2004; Van Essendelft and Schobert, 2009a; Van Essendelft and Schobert, 2009b; Van Essendelft and Schobert, 2010; McKelvy et al., 2004; Fouda et al.</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feldspar</strong></td>
<td>CaAl$_2$Si$_2$O$_8$</td>
<td>O'Connor, 2005</td>
</tr>
<tr>
<td><strong>Pyroxene</strong></td>
<td>CaMgSi$_2$O$_6$+(Fe, Al)</td>
<td>O'Connor, 2005</td>
</tr>
<tr>
<td><strong>Talc</strong></td>
<td>Mg$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>O'Connor, 2005</td>
</tr>
<tr>
<td><strong>Wollastonite</strong></td>
<td>CaSiO$_3$</td>
<td>Teir et al., 2005; Huijgen et al., 2006; Daval et al., 2009; Kakizawa et al., 2001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brucite</strong></td>
<td>Mg(OH)$_2$</td>
<td>Blencoe et al., 2003; Ron Zevenhoven, 2010</td>
</tr>
</tbody>
</table>

a Basalt (%): SiO$_2$: 49.2, TiO$_2$: 1.84, Al$_2$O$_3$: 15.74, Fe$_2$O$_3$: 3.79, FeO: 7.13, MnO: 0.2, MgO: 6.73, CaO: 9.47, Na$_2$O: 2.91

b Further categorized into different mineral types: chrysotile, lizardite and antigorite

From the Table 2-4 above it can be concluded that the most investigated minerals are olivine, serpentine and wollastonite. Magnesium-rich silicate minerals, especially serpentine, are found in large deposits worldwide (see Fig. 2-9), with large reservoirs being known, for example, on both the East and West coast of North America and in Scandinavia. Previous studies of mineral reserves in the U.S. have concluded that there is enough mineral volume to sequester the total US (2006 level) CO$_2$ emissions of 7 Gt/year for more than 500 years (Krevor, 2009). Lackner (2000) reported a deposit in Oman of 30,000 km$^3$ (350×40×5 km, 30 % pure, i.e. 25000-30000 km$^3$ of olivine) magnesium silicates which alone would be able to store most of the CO$_2$ generated by the combustion of the
world's coal reserves. Serpentinites in eastern Finland (Outokumpu-Kainuu ultramafic rock belt) alone could provide 2.5-3.5 GtCO₂ storage capacity (Teir et al., 2009). Kelemen et al. (2008) also found large mineral deposits in Oceania and around the Adriatic Sea. Therefore, serpentine and olivine occur in sufficient magnitude to be considered viable candidates for mineral carbonation; however the abundant and wide availability of serpentine makes it particularly attractive.

Figure 2-9: Distribution of magnesium silicate mineral deposits worldwide (Ron Zevenhoven, 2001)

\( R_{\text{CO}_2} \) gives the theoretical mass amount of a given material necessary to convert a unit mass of CO₂ into mineral carbonate. The typical composition of various minerals, their specific \( R_{\text{CO}_2} \) and the capacities of feedstock are given in Table 2-5. The main Mg ultramafic rocks, such as olivine and serpentine have much higher MgO wt. % values than waste materials. The main Ca ultramafic
rocks, such as wollastonite have similar CaO wt. % values to waste materials.

Table 2-5: Composition of various materials and carbon dioxide sequestration characteristics $R_{CO_2}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>MgO [wt%]</th>
<th>CaO [wt%]</th>
<th>FeO [wt%]</th>
<th>$R_{CO_2}$ [kg/kg]</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine$^a$</td>
<td>45-50</td>
<td>0.1-0.5</td>
<td>6-10</td>
<td>1.8</td>
<td>10000 Gt c</td>
</tr>
<tr>
<td>Serpentine$^a$</td>
<td>38-45</td>
<td>0</td>
<td>5-8</td>
<td>2.3</td>
<td>10000 Gt c</td>
</tr>
<tr>
<td>Wollastonite$^b$</td>
<td>-</td>
<td>35-48</td>
<td>-</td>
<td>3.6</td>
<td>Small c</td>
</tr>
</tbody>
</table>

$^a$ O'Connor, 2001; $^b$ Daval et al., 2009; $^c$ Lackner, 2002.

Magnesium and calcium rarely occur as binary oxides in nature, and they are typically found as silicate minerals. These minerals are capable of being carbonated because carbonic acid is stronger than silicic acid ($H_4SiO_4$). The reactions of Mg and Ca silicates (olivine, serpentine and wollastonite) with CO$_2$ and the thermodynamic data are described in Table 2-6. The carbonation reactions of olivine, serpentine and wollastonite can generate 89, 64 and 90 kJ/mol CO$_2$.

Table 2-6: Thermodynamic data of reaction for various carbonation reactions of typical minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction</th>
<th>$\Delta H$(kJ/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$</td>
<td>-89</td>
</tr>
<tr>
<td>Serpentine</td>
<td>$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$</td>
<td>-64</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$</td>
<td>-90</td>
</tr>
</tbody>
</table>

$^a$ IPCC, 2005.
2.3.2 Historical development

The concept of mineral carbonation was first mentioned by Seifritz (1990). A few years later, CO₂ storage by conversion of Ca-rich brine into carbonates was conducted by Dunsmore (1992). Detailed investigations of abundant and cheap natural silicate minerals such as olivine, serpentine and wollastonite, and also basalt rock were then conducted by Lackner and co-workers at Los Alamos National Laboratory (LANL) and the National Energy Technology Laboratory (NETL) (Lackner et al., 1995). From then, mineral carbonation research developed quickly and can be divided into two different approaches: direct carbonation, where the carbonation of the mineral takes place in a single process step; and indirect carbonation, where calcium or magnesium is first dissolved from the mineral and subsequently carbonated (Fig 2-10).

![Diagram of direct and indirect carbonation]

Figure 2-10: Schematic representation of the principles of direct and indirect carbonation.
Direct gas-solid carbonation using pressurised CO₂ at high temperature (25 % carbonation conversion at 340 bars, 500 °C after 2 h with 50-100 μm serpentine) was studied by Lackner et al. (1998). In addition, Butt and Lackner et al. (2002) reported an indirect gas-solid process, which produced Mg(OH)₂ from Mg silicates by using hydrochloric acid (HCl), followed by gas-solid carbonation of Mg(OH)₂ and then regeneration of HCl from MgCl₂•nH₂O or Mg(OH)Cl. The carbonation of Mg(OH)₂ was found to be significantly faster than carbonation of MgO, where 90% conversion from Mg(OH)₂ to carbonates was obtained after 30 mins at 565 °C and 52 bar. Due to the complexity and energy penalty of this process, work started on a direct aqueous route.

O’Connor et al. (2001) at Albany Research Center (ARC) in the U.S. studied a direct aqueous process with optimisation of solution chemistry, heat treatment and grinding. They reported 84 % carbonation conversion within 6 h at 185 °C and 150 bar for ground olivine with particle size less than 38 μm; for heat treated serpentine the carbonation conversion was 60 % within 6 h at 155 °C and 115 bar using 0.64 M NaHCO₃ and 1 M NaCl solution; and for wollastonite the carbonation conversion reached 80 % within 30 mins at 100 °C and 40 bar in distilled water (O’Connor, 2005; Gerdemann et al., 2007). This process was considered to be the most successful route for mineral carbonation and the cost of CO₂ sequestration by mineral carbonation based on this process was
estimated to be 54, 78 and 64 US$/t CO\textsubscript{2} sequestered (excluding CO\textsubscript{2} capture and transportation) for olivine, serpentine and wollastonite, respectively. Herzog (2002) gave a critical assessment of this method and concluded that this process would cause a 20 % energy penalty for a coal-fired power plant. The IPCC’s special report on CCS used the highest cost of the ARC’s process to compare mineralisation to other CCS approaches that presented a much lower cost. Nonetheless, mineralisation still received attention and improvements were made by using high-alkali bicarbonate concentrated (5.5 M KHCO\textsubscript{3}) solutions, fluid-flow conditions and sonication (McKelvy et al., 2006; Jarvis et al., 2009). Zevenhoven (2008) reported that the costs of the ARC process were overestimated partly due to unrealistic calculation of energy efficiency and costs, where the costs of process heat input were significantly over-estimated when charged the same way as power input, giving a false impression of overall process economics. However, it remains unclear whether the CO\textsubscript{2} carbonated comes from the target CO\textsubscript{2} injected or from the NaHCO\textsubscript{3} added to the solution (see Section 2.3.4).

CO\textsubscript{2} mineral sequestration studies were initiated in Finland in 2000 and started with direct gas-solid route at elevated temperatures. The objective of this work was to make use of the possibility of covering process energy requirements with the heat from the carbonation reaction (Zevenhoven, 2002). Then, stepwise gas-solid
carbonation with Finnish serpentine and calcined Mg(OH)$_2$ powder was investigated in a pressurised thermogravimetric analyser (PTGA) (Zevenhoven et al., 2008). Still, the chemical kinetics of gas-solid carbonation are relatively slower than aqueous carbonation. In order to improve the carbonation kinetics by increasing the intra-particle mechanical effects, a fluidised bed (FB) reactor was designed working at 20-40 bar of CO$_2$ pressure and 400-600 °C of temperature conditions. With the CO$_2$ acting as a fluidising gas, the carbonate product that built up on the reacting particles (Mg(OH)$_2$ powder) was removed as fines from the reactor with the exit gas flow. However, the production of Mg(OH)$_2$ became the limiting step, since Mg(OH)$_2$ is not naturally available in large quantities. Recently, Experience et al. (2010) proposed a solid-solid reaction process for production of Mg(OH)$_2$ from serpentine using (NH$_4$)$_2$SO$_4$ at 440 °C to generate MgSO$_4$, following addition of ammonia water to precipitate Mg(OH)$_2$ (Fagerlund et al., 2009; Nduagu, 2010). Mg(OH)$_2$ was then carbonated with CO$_2$ directly in a pressurized fluidized bed (PFB) reactor at 470-550 °C and 20 bar. However, only 20-50 % dissolution efficiency of Mg from serpentine was reported (Nduagu, 2010). Moreover, the carbonation efficiency of Mg(OH)$_2$ only achieved a maximum value of 50 % due to the conversion from Mg(OH)$_2$ to MgO at the temperature range used, and the produced MgO could not be carbonated at the above
reaction temperature (Zevenhoven, 2010). Therefore, work is needed to improve both dissolution and carbonation efficiencies.

In order to avoid energy-intensive pre-treatment, research teams worldwide embarked on indirect aqueous routes, where Mg or Ca were dissolved from minerals or industrial wastes by using strong or weak acids, alkali or ligands solutions (Maroto-Valer et al., 2005; McKelvy et al., 2004; Park and Fan, 2004; Blencoe et al., 2003). However, a problem with these routes is that the chemicals used could not be recovered and re-used. For example, Teir and co-workers dissolved serpentinite with strong HNO₃ and HCl solution, and the prepared Mg-rich solutions were used to precipitate pure hydromagnesite (Mg₅(CO₃)₄(OH)₂•4H₂O), while regulating the pH by adding NaOH, which is needed for precipitation (Teir et al., 2007b and 2007c). However, the energy and costs of makeup acids and NaOH (using 2 t NaOH and 2-3 t acid per tonne CO₂ sequestered) made this process uneconomic with costs of 600-1600 US$/t CO₂ sequestered (Teir et al., 2009). Another example of such indirect aqueous process is the pH-swing process suggested by Kodama et al. (2008), where steel slags were dissolved with ammonium chloride (NH₄Cl), followed by carbonation with NH₃, which was produced from the dissolution, and recovery of NH₄Cl from the carbonation. The energy penalty of this process was reported to be 300 kWh/t CO₂ sequestered. Meanwhile, much work is currently carried out on enhancing carbonation chemistry of magnesium
silicates in aqueous systems using weak acids and additives such as citrates, oxalates and ethylenediamine tetraacetic acid (EDTA) (Park, 2008; Krevor and Lackner, 2009; Prigiobbe et al., 2010). The organic acid dissolution proceeds rapidly, achieving dissolution greater than 60% and 80% within 2 and 7 hours, respectively, and near 100% dissolution is achieved between 10 and 20 hours. Although the use of organic acids can minimise the use of chemicals, their complete recovery and reuse is not feasible (Krevor, 2011).

Various pre-treatment methods (chemical, mechanical and thermal) have been developed (McKelvy et al., 2004; Musvoto et al., 2000; Maroto-Valer et al., 2005). In the UK, Alexander et al. (2007) studied the effect of process parameters, such as solvent concentration, temperature, reaction time, \( \text{CO}_2 \) pressure and particle size on serpentine mineralisation. In Switzerland, Mazzotti, Hanchen and co-workers at Eidgenössische Technische Hochschule Zurich (ETH) investigated the reaction kinetics and modelling of dissolution and carbonation reactions (Hänchen et al., 2006 and 2008). In Netherlands, Huijgen and Comans (2006 and 2007) at the Energy Research Center of the Netherlands (ECN) conducted experimental work on direct aqueous carbonation of wollastonite and steel slags.

Many researchers (Teir et al., 2007c; Huijgen et al., 2006; Bearat et al., 2006; Xiaolong Wang, 2010a) have reported that the rate-
limiting step of mineral carbonation is mineral dissolution, when a passive silicate layer is formed and prevents further dissolution. Chemical reaction control dominates the fast initial dissolution, while product layer diffusion control dominates further dissolution and the produced passive layer becomes the barrier preventing further dissolution. Intensive particle-particle (mechanical) interactions inside a reactor or the presence of abrasion can enhance the kinetics of dissolution.

Recently, the Global Institute of Carbon Capture and Storage (GICCS) in Australia and CO₂ Technology Centre (TCM) in Norway have provided funding for mineralisation projects. Dlugogorski et al. (2010) at the University of Newcastle in Australia and Munz (2009) at the Institute for Energy Technology in Norway are further developing the ARC’s direct aqueous carbonation.

Despite these recent developments, little progress has been made when it comes to the recovery and recycling of additives, which is a key issue for the development of mineral carbonation. In general, the additive-free process is not able to match the additive-enhanced process in terms of dissolution and carbonation efficiencies. Moreover, there is a risk that the cost of additives may make the process uneconomic.
2.3.3 Process routes classification

The CO₂ mineral sequestration technology is likely to be conducted in a dedicated processing plant (Fig. 2-11). The CO₂ is captured at the power plant or other emission source. In order to minimize transportation costs, the location of a mineral carbonation plant can be sited either within the power plant or close to the mine or industry plant, where solid wastes are produced. The CO₂ can be transported by pipeline, minerals and wastes can be transported by shipping or railway. After carbonation, the Mg or Ca carbonates can either be reused in construction or other purposes, or landfilled at a storage site.

Figure 2-11: Material fluxes and process steps of mineral carbonation (IPCC, 2005)

The mineral carbonation technology applied in the plant will be one of the various process routes described in Fig. 2-12, ranging from the most basic accelerated weathering of minerals to advanced
multi-step processes. As described here, some of the process routes suggested earlier have been abandoned, such as molten salts and pressure swing, and are not included here. The definitions of direct and indirect processes have been explained in Figure 2-10. For the direct aqueous mineral carbonation, various pre-treatment methods are presented. For the indirect aqueous mineral carbonation, research mainly focuses on different additives.

![Figure 2-12: Process routes of mineral carbonation.](image)
2.3.4 Direct and indirect gas-solid mineral carbonation

Gas-solid mineral carbonation is the most straightforward approach in mineral carbonation, where gaseous CO$_2$ reacts with solid Ca/Mg silicates at an elevated temperature and pressure (Lackner et al., 1997; Zevenhoven, 2002):

\[
\text{Ca/Mg - silicate(s) + CO}_2(g) \rightarrow (\text{Ca/Mg})\text{CO}_3(s) + \text{SiO}_2(s)
\]

Equation 2-2

2.3.4.1 Direct gas-solid carbonation

The dry process of direct gas-solid carbonation has the potential of producing high temperature steam or electricity, while converting CO$_2$ into carbonates and producing silica. However, the reaction rates of this process have been too slow (7 days) and the process suffers from thermodynamic limitations. Activation of minerals by heat treatment can improve the carbonation rate, but it is energy prohibitive. Therefore, most of the studies about this process have been abandoned. In a previous literature review conducted by Huijgen and Comans (2003), it was concluded that the direct gas-solid carbonation route does not have the potential to become an industrially viable process.

However, developments suggest that there are still significant improvements to be made in the process when using waste materials (Rendek et al., 2006; Baciocchi, 2006a and 2006b).
advantages of CO₂ storage and lowering the hazardous nature of waste make this carbonation route interesting. However, the potential CO₂ storage capacity of this waste is limited.

### 2.3.4.2 Indirect gas-solid carbonation

**i. Three steps pressurised thermogravimetric analyser (PTGA) process via Mg(OH)₂.**

Indirect gas-solid carbonation, involving dissolution of magnesium oxide or hydroxide and subsequent dry carbonation at elevated temperature and pressure, could be more attractive than direct gas-solid carbonation for reasons of better kinetics. Butt *et al.* (1998) found that the gas-solid carbonation of Mg(OH)₂ can be considered feasible and faster than the carbonation of MgO. But since hydroxides do not occur in a significant amount in nature, these have to be produced from Mg-silicates. Zevenhoven *et al.* (2008) firstly suggested a three steps process using serpentine as follows (Fig. 2-13): a) MgO production in a high temperature (>500 °C) reactor, b) MgO hydration and c) carbonation of Mg(OH)₂ at elevated pressure. The experimental results showed that 40~60% carbonation conversion was achieved at 495-540 °C and at 35-45 bar for 6 h in a PTGA. Although this process enhanced the reaction rates compared to the two step carbonation of MgO (Butt *et al.*, 1998), it is still too slow (6 hrs) to produce Mg(OH)₂ from serpentine.
ii. **Pressurised fluidised bed (PFB) with ammonium sulphate (AS) via Mg(OH)$_2$.**

Fagerlund *et al.* (2009) developed the use of gas/solid PFB reactors (see Fig. 2-14), where carbonate removal is possible due to particle collisions (attrition or abrasion) and the flue gas can carry the particles out of the reactor. Moreover, particle collisions can improve the overall carbonation reaction rate since product layer diffusion has been shown to be the rate limiting step and this can be partly overcome by particle collisions (Bearat *et al.*, 2006).
Recently, Nduagu et al. (2010) developed a new method to produce Mg(OH)$_2$ from serpentine. Firstly, solid-solid reaction of serpentine with ammonium sulphate (AS) (NH$_4$)$_2$SO$_4$) was carried out at above 440 °C for 20-60 mins to generate MgSO$_4$, that was then put into ammonia water to precipitate Mg(OH)$_2$ and regenerate (NH$_4$)$_2$SO$_4$, and finally Mg(OH)$_2$ was carbonated with CO$_2$ directly in a PFB reactor at 470-550 °C and 20 bar for 15-60 mins (shown in Fig. 2-15). Interestingly, most of the carbonation took place at only 30 minutes. However, only 20-60 % dissolution efficiency of Mg from serpentine was reported (Nduagu, 2010), and the carbonation efficiency of Mg(OH)$_2$ only achieved a maximum value of 50 % (see Fig. 2-16). The low carbonation efficiency was due to the conversion of Mg(OH)$_2$ to MgO at the temperature range used (470-550 °C), and the produced MgO could not react with CO$_2$ to produce
carbonates at the above temperature range (Zevenhoven, 2010). Therefore, work is needed to improve both dissolution and carbonation efficiencies.

Figure 2-15: Flow diagram of the Mg(OH)$_2$ production process from serpentine with ammonium salts (Fagerlund et al., 2009).

Figure 2-16: The composition of MgO, Mg(OH)$_2$ and MgCO$_3$ with temperature in FB reactor (Zevenhoven, 2010).
2.3.5 Direct aqueous mineral carbonation

The presence of water can significantly enhance the reaction rate of carbonation processes (O'Connor, 2001). The direct aqueous mineral carbonation process is performed in an aqueous solution and in single step, but there are three reactions taking place simultaneously. Firstly, CO₂ dissolves into water and dissociates to bicarbonate and H⁺ resulting in a pH of about 4.0-5.5 at high CO₂ pressure:

\[ \text{CO}_2(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq) \]

Equation 2-3

Secondly, Ca/Mg leached from the mineral matrix by H⁺:

\[ \text{Ca/Mg-silicates}(s) + 2\text{H}^+(aq) \rightarrow \]
\[ (\text{Ca/Mg})^{2+}(aq) + \text{SiO}_2(s) + \text{H}_2\text{O}(l) \]

Equation 2-4

Finally, the (Ca/Mg)²⁺ reacts with HCO₃⁻ and precipitates as Ca/Mg carbonates:

\[ (\text{Ca/Mg})^{2+}(aq) + \text{HCO}_3^-(aq) \rightarrow (\text{Ca/Mg})\text{CO}_3(s) + \text{H}^+(aq) \]

Equation 2-5
2.3.5.1 ARC process.

The Albany Research Centre's process was regarded as a state-of-the-art technology in direct aqueous mineral carbonation. Various pretreatment methods were developed for this process to improve the reaction rate of both dissolution and carbonation. Thermodynamic studies were also conducted to understand the controlling mechanism of reactions. Additionally, further additive-enhanced processes and organic acid processes were investigated as the continuous work of ARC's process.

In order to maximise the reaction rate, a careful selection of process conditions such as particle size, temperature and CO₂ pressure was made by O'Connor et al. at ARC (O'Connor, 2001). The process diagram of the direct aqueous mineral carbonation process is presented in Fig. 2-17 and the optimum conditions and the carbonation conversions are listed in Table 2-7.
Chapter 2 – Literature review

Figure 2-17: Process flow diagram for the direct carbonation process (O'Connor, 2001)

Table 2-7: Optimum carbonation conditions and carbonation conversion (Gerdemann et al., 2007)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$T$ (°C)</th>
<th>$P_{\text{CO}_2}$ (bar)</th>
<th>Carrier solution</th>
<th>Reactio n time (h)</th>
<th>Carbonation conversion (%)</th>
<th>Carbonation conversion, 1 h (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>185</td>
<td>150</td>
<td>0.64 M NaHCO$_3$, 1 M NaCl</td>
<td>6</td>
<td>91.0</td>
<td>49.5</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>100</td>
<td>40</td>
<td>distilled water</td>
<td>-</td>
<td>97.8</td>
<td>81.8</td>
</tr>
<tr>
<td>HT serpentine</td>
<td>155</td>
<td>115</td>
<td>0.64 M NaHCO$_3$, 1 M NaCl</td>
<td>-</td>
<td>80.0</td>
<td>73.5</td>
</tr>
</tbody>
</table>
In O'Connor's work, particle size reduction (<4 μm), by intensive grinding for olivine and heat treatment at high temperature (above 600 °C) for serpentine were studied to improve the reaction rate. However, the energy intensive pre-treatment became a barrier for large-scale application. Bicarbonate/salt (NaHCO₃/NaCl) mixture solution was found to accelerate the reaction (O'Connor, 2001). The NaHCO₃ increased the HCO₃⁻ concentration, which in turn lowered the Mg²⁺ concentration required to precipitate MgCO₃. The solution was then buffered at a pH of 7.7-8.0, resulting in the improvement of absorption of CO₂. NaCl can increase the release of Ca/Mg²⁺ from silicate by creating soluble complexes and thus lowering the activity of Ca/Mg²⁺ in solution, in the other words, thereby increasing the solubility of Ca/Mg-silicates and decreasing the solubility of Ca/Mg carbonates (Fauth et al., 2001). The reactions of olivine in NaHCO₃/NaCl solution are presented below:

\[
\begin{align*}
    \text{Mg}_2\text{SiO}_4(s) + 2\text{HCO}_3^-(aq) & \rightarrow \\
    2\text{MgCO}_3(s) + \text{SiO}_2(s) + 2\text{OH}^-(aq)
\end{align*}
\]

Equation 2-6

The bicarbonate can be regenerated by the reaction of OH⁻ with CO₂(g):

\[
\text{OH}^-(aq) + \text{CO}_2(g) \rightarrow \text{HCO}_3^-
\]

Equation 2-7
It was assumed that the HCO$_3^-$ concentration and pH of the solution were kept constant and the process did not consume NaHCO$_3$. However, experiments conducted by O’Connor et al. (2004), showed that when 0.64 M NaHCO$_3$ solution was used the carbonation conversion measured was 19%. However, when the solution was recycled and reused the final carbonation conversion was only 0.3%-0.7%. These results substantiated that production of magnesium carbonates demand fresh addition of sodium bicarbonate. This provides a considerable limitation as producing sodium bicarbonate (or sodium carbonate) from gaseous CO$_2$ greatly increases the energy and economic penalties for this process.

O’Connor et al. (2005) and Gerdemann et al. (2007) reported a 91% carbonation conversion was achieved in 6 h at 185 °C and 150 P$_{CO_2}$ bar and 15% solid/liquid ratio in 0.64 M NaHCO$_3$ + 1 M NaCl solution for olivine; for heat treated (HT) serpentine, 80% carbonation conversion was achieved in 6 h at 155 °C and 115 P$_{CO_2}$ bar and 15% solid/liquid ratio in 0.64 M NaHCO$_3$ + 1 M NaCl solution; and for wollastonite, 80% carbonation conversion was reached in 1 h at 100 °C and 40 P$_{CO_2}$ bar and 15% solid/liquid ratio in distilled water (O’Connor, 2001; Gerdemann et al., 2007). Wollastonite reacts faster, and a lower CO$_2$ pressure and no additive are required to obtain high conversion compared to Mg-silicates. However, less CO$_2$ can be sequestered per kilo feedstock than Mg-silicates due to the higher molar mass of Ca. In addition, the
worldwide availability of wollastonite is limited compared to Mg-silicates (O'Connor, 2004).

Direct aqueous carbonation is thus far the only process that has shown a detailed energy and economic evaluation (Gerdemann et al., 2007; O'Connor, 2004). The evaluation is based on the ARC’s process using an autoclave reactor. A 27 % energy penalty was reported for a 1.3 GW coal-fired power, where 75 % of the energy penalty was due to the grinding of the feedstock. Seven regions in the U.S. were studied where both large ultramafic ores and large amounts of CO₂ are present. For the best case, the sequestration cost were 54, 91 and 250 US$/t CO₂ sequestered⁶ (78, 112 and 309 US$/t CO₂ avoid⁷) for olivine, wollastonite and HT serpentine, respectively. These costs have to be reduced significantly in order to become economically competitive with other sequestration options.

Due to the non-complete conversion of the minerals, the mineral amounts required significantly exceed the theoretical amount. Gerdemann et al. (2007) reposted that in the best-case scenario 5.3 tonnes of olivine, 6.5–8.9 tonnes of serpentine or around 8.9 tonnes of wollastonite are required for each tonnes of coal. Therefore it is very important to consider the environmental and economic impacts of the products disposal and utilization.

⁶ This cost excludes the chemical make-up.
⁷ Excluding energy consumption from the CO₂ mineralisation process.
In the Netherlands, Huijgen et al. (2006) studied a similar direct aqueous mineral carbonation process using wollastonite and steel slag. For the optimised conditions, a 70 % carbonation conversion was achieved after 15 min at 200 °C, 20 bar CO$_2$ and particle size of <38 µm. The cost evaluation of the process using chemical simulation software (ASPEN PLUS) was reported to be 125 and 93 US$/t CO$_2$ sequestered for wollastonite and steel slag, respectively (Huijgen et al., 2007). The major costs were associated with the feedstock and the grinding and compression. It was suggested that further cost reduction should focus on the liquid/solid ratio and offset by the sale of the carbonated product.

2.3.5.2 Pre-treatment studies and silica passive layer.

High pressure CO$_2$, fine grinding of minerals and high temperature heat treatment in the direct aqueous route are expensive and energy prohibitive. Therefore, research has been performed on understanding the controlling mechanism of reactions. Aqueous carbonation of Ca/Mg silicates occurs in two steps, 1) dissolution of (Ca/Mg)$^{2+}$ from mineral and 2) precipitation of Ca/Mg carbonate. The rate limiting step is the dissolution since a passive layer is formed, which hinders further leaching of Ca/Mg.

A fundamental study of aqueous carbonation was conducted by Wolf et al. (2004), who developed a micro-reaction system with in-situ
observation of aqueous CO₂ mineral carbonation reaction using synchronotron X-ray diffraction and Raman spectroscopy. The experimental results showed that magnesite precipitated directly when the HT serpentine slurry was exposed at 150 bar CO₂ and 150 °C. McKelvy et al. (2004) developed a system of simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) to study the effect of heat treatment on the serpentine mineral lizardite. Meta-serpentine materials were observed to form above 600 °C by removal of 90 % of hydroxide groups and the carbonation from meta-serpentine directly into magnesite was observed. Bearat et al. (2006) found the formation of a passive silica-rich layer around the mineral particles that hindered further dissolution of Mg from mineral matrix and slowed the carbonate formation. Thus, improvement of carbonation conversion could be achieved by maximizing particle interaction and mechanical stirring (attrition or abrasion). It is interesting to find that the demonstration of intergrowth of carbonate minerals within an olivine matrix. In considering the separation of the products from the un-reacted feedstocks, Bearat et al. (2006) observed that the carbonate precipitated as a coating on the minerals hindering further carbonation and making recycling of un-reacted feedstocks very difficult.

The possibility of reducing the expenses associated with particle size reduction by enhancing particle-particle interaction was studied
using a flow-loop reactor, where a mixture of large particles (75-150 μm) and ultrafine particles (<4 μm) were carbonated at the optimum solution and conditions (see Table 2-7) (Penner, 2004). A 53% conversion was achieved compared to 40% in an autoclave reactor since the intensive mixing removed the silica passive layer and enhanced the reaction rate. Further research in new reactor design, such as fluidised bed reactor and continuous pipeline reactor, is expected to further improve the dissolution efficiency and rate.

2.3.5.3 Thermodynamic studies of dissolution rate and precipitation studies.

The dissolution rate of olivine and serpentine in aqueous solutions has been studied extensively (Oelkers, 2001; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Chen and Brantley, 2000). The dissolution of minerals has been found to occur in two stages: first, a rapid dissolution stage, followed by a relatively slow dissolution stage (Hänchen et al., 2006). The latter stage is most relevant to enhance the mineral carbonation process. Dissolution is affected by temperature, CO₂ pressure and pH. Many geochemistry studies have focuses on dissolution of Ca/Mg silicates, but unfortunately, the majority of these studies were performed at ambient conditions (Oelkers, 2001; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Chen and Brantley, 2000). Hanchen et al. (2006), however, critically analysed earlier studies and performed experiments at 90,
120 and 150 °C. Hänchen et al. (2006) developed the shrinking core model\textsuperscript{8} to describe the dissolution of olivine at high temperature (up to 150 °C). Later, Hanchen et al. (2007) developed a population balance model\textsuperscript{9} to better describe the dissolution of olivine and concluded that the previous model could be used as a good approximation for narrow size distributions, while the improved model was able to handle a much wider range of particle sizes. Hanchen et al. (2008) have extensively studied the chemistry of aqueous mineral carbonation of olivine in order to better understand magnesium carbonate precipitation. An H$_2$O-CO$_2$-Na$_2$CO$_3$-MgCl$_2$ system at various temperature and CO$_2$ pressures (25 °C and 1 bar, 120 °C and 3 bar, 120 °C and 100 bar) was investigated. The results concluded that the formation of magnesium carbonate species depended on temperature and pressure. Nesquehonite (MgCO$_3$•3H$_2$O) precipitated from aqueous solutions at ambient temperature, while at higher temperatures (50 and 100 °C), nesquehonite was transformed into hydromagnesite (4MgCO$_3$•Mg(OH)$_2$•5H$_2$O). When the temperature was above 100 °C, hydromagnesite was transformed into magnesite (MgCO$_3$).\textsuperscript{9}

\textsuperscript{8} Shrinking core model describes the particle size and the reacting core shrink simultaneously.
\textsuperscript{9} Particle population balance describes the time-varying particle size distribution. Assuming particles with constant shape, it is possible to describe the particle size evolution using one characteristic length.
2.3.5.4 Additive-enhanced process.

McKelvy et al. (2006) suggested that the reaction rates can be significantly improved by further increasing the bicarbonate (NaHCO₃, KHCO₃) concentration. Adding bicarbonate salts increased the ionic strength of the solution and therefore facilitated the formation of complexes with dissolved Ca or Mg. Thus, the Ca/Mg-activity in solution was lowered and the release of (Ca/Mg)²⁺ ions from the silicate was enhanced. McKelvy et al. (2006) showed that adding 5.5 M KHCO₃ resulted in an increase of the olivine and HT serpentine carbonation to 81% and 92% after 1 hour, respectively, compared to 91% after 6 h for olivine without additives at the same conditions (185 °C, 150 bar CO₂, <38 μm and 1500 rpm). However, Jarvis et al. (2009) reported that, only 63 % conversion was obtained using 5.5 M KHCO₃ after 1 h. Chen et al. (2006) explained the effects of bicarbonate concentration, temperature and pressure to carbonation conversions in fundamental chemistry.

2.3.5.5 Organic acid process.

In order to overcome the pH conflict between dissolution and carbonation, organic acid solutions with neutral pH have been sought to overcome slow dissolution kinetics without inherently being consumed in reactions. Several additives such as acetic acid and citric acid have been studied (Park and Fan, 2004; Lackner, 2002). A combination of orthophosphoric acid, oxalic acid and EDTA
has been reported to increase the dissolution of serpentine most effectively (65 % dissolution efficiency) (Park and Fan, 2004). Krevor et al. (2011) conducted a solvent selection study, including sodium oxalate, EDTA, trisodium citrate, NH₄Cl, NaCl and sodium acetate at the conditions of 0.1 M salt conc., 90 °C, 20 bar CO₂ and 3g serpentine in 1kg water. They reported that 50 % dissolution efficiency was achieved after 6 h for oxalate, EDTA and citrate, and 100 % dissolution efficiency was obtained after 24 h by using citrate. It is important to point out that neutral pH, while enhancing the dissolution rate, inhibits carbonate precipitation due to the formation of strong complexes. Moreover, there is no evidence to prove the feasibility of recycling organic acid solution and the cost of make-up organic acid solutions is expensive. Furthermore, the un-recycled organic solvent may cause serious environmental impacts. Therefore expensive organic solvents can only be applied practically when the complete solvent recycling is achieved.

2.3.6 Indirect aqueous mineral carbonation

Indirect aqueous mineral carbonation comprises several steps, as described here. Normally, the reactive component (Ca/Mg) is first dissolved from the feedstocks and then reacts with CO₂ to form the desired carbonates (see Fig. 2-10). Various additives are used to enhance the reaction rate and efficiency of each step. Indirect
Chapter 2 – Literature review

mineral carbonation has been widely investigated, and the main processes are presented here.

2.3.6.1 NaOH

Blencoe et al. (2004) developed an approach to overcome the disadvantages associated with the elevated temperatures and pressures of the direct aqueous route. Their process using NaOH was tested using various feedstocks. There are four major drawbacks of this process as follows: (1) reaction times reported were too long (3 days) for industrial application, (2) the feedstock needed to be milled to <10 μm resulting in a high energy penalty, (3) process conditions required 200 °C and 15 bar, and (4) large quantities of NaOH were required as recycling of NaOH was not proved. There is no progress of this process reported since 2004.

2.3.6.2 Acetic acid

In order to reduce the energy requirements, the use of acetic acid for the dissolution of calcium from a calcium-rich feedstock was investigated by Kakizawa et al. (2001). The route consisted of two steps, dissolution and carbonation, as described in Eq.2-8 and 2-9, respectively:

\[
\text{CaSiO}_3(s) + 2\text{CH}_3\text{COOH}(l) \rightarrow \text{Ca}^{2+}(aq) + 2\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) + \text{SiO}_2(s)
\]

Equation 2-8
\[
Ca^{2+}(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l) \rightarrow \\
CaCO_3(s) + 2CH_3COOH(l)
\]

Equation 2-9

The acetic acid used in the dissolution step was recovered in the following carbonation step. A schematic diagram of the process is given in Fig. 2-18.

According to Kakizawa’s (2001) experimental results, 48 % Ca dissolution was achieved at 60°C and atmospheric pressure after 250 mins when using 20 µm wollastonite particles. 20 % CaCO_3 conversion was obtained at 30 °C and 30 bar CO_2 after 60 mins. However, there is no study on the recovery of acetic acid.

Teir et al. (2005 and 2007a) studied the process proposed by Kakizawa (2001) to produce precipitated calcium carbonate (PCC) from both wollastonite and steel slags. According to Teir’s energy penalty evaluation results (ASPEN PLUS), PCC production via the conventional route (calcination process) emitted 0.21 kg CO_2 /kg
PCC, whereas PCC production via the acetic acid process route using wollastonite gave a net fixation of 0.34 kg CO₂/kg PCC (Teir et al., 2005). Teir also found that the principal problem of unsuccessful recycling of acetic acid. The complete recycling of the acid is necessary for this process to become feasible in large scale and that has not yet been demonstrated.

Inspired by the concept of CO₂ fixation of wollastonite using acetic acid, Teir et al. (2007a) and Eloneva et al. (2008) investigated a similar process using steelmaking slags, which contain significant amounts of CaO. Teir et al. (2007a) reported that over 84 % Ca can be dissolved from blast furnace slags, steel converter slag, electric arc furnace slag and argon oxygen decarburization (AOD) process slag at 50 °C using 33.3 wt% acetic acid after 20 mins, compared to 41 % from wollastonite under the same conditions. Subsequently,
Eloneva et al. (2008) reported 19 - 74% Ca carbonation efficiency was obtained from blast furnace slag using acetic acid at 1-30 bar CO₂ and 30-70 °C (see Fig. 2-19). However, significant amounts of sodium hydroxide (28 g/l) were required to promote the carbonation. The mass balance of this process showed that 4.4 kg of blast furnace slag, 26 l (100 wt %) of acetic acid, and 3.5 kg of NaOH would be required to bind 1 kg of CO₂, resulting in a maximum of 2.5 kg of 90% pure calcium carbonate. The world steelmaking slag production was estimated to be around 255-345 Mt steel making slags in 2003 (Teir et al., 2007a). Thus, the annual CO₂ storage potential of steelmaking slags is in the order of 70 - 180 Mt CO₂ by using the process investigated by Eloneva (2008). Although the CO₂ sequestration potential for this option compared to the global CO₂ emissions is small, the process could provide a significant alternative solution. Nevertheless, a problem being investigated related to the acetic acid route is the co-leaching of heavy metals, and the demand for NaOH in order to precipitate carbonates. The additional NaOH makes recycling of acetic acid impossible and as a result the chemical costs for this process route are too high.

2.3.6.3 Acid/base pH swing

In order to overcome the different pH requirement for dissolution and carbonation, Park et al. (2004) studied an indirect aqueous

10 22.5 l acetic acid could be recycled after evaporation.
mineral carbonation process called pH swing process. The pH swing process consisted of a first step at low pH to dissolve the Mg from the serpentine by using a combination of organic acids and ammonium bisulphate, and a second step at higher pH by adding ammonia water to form carbonates. Internal grinding in combination with organic acids proved to be the most effective dissolution. The process conditions required to obtain a significant conversion (70 °C and 1 bar) were milder than those for direct aqueous carbonation (185 °C and 150 bar). However, a detailed study of costs and environmental impact was not provided.

Maroto-Valer et al. (2005) proposed another process with serpentine based on acid/base pH swing. However, the chemicals used in this process could not be regenerated. In a follow-up study by Alexander et al. (2007), the effects of reaction time, particle size, temperature and solvent concentration on serpentine dissolution efficiencies were reported under the conditions of atmospheric pressure and low temperatures (25 - 50 °C). The results of Alexander’s study were in agreement with previous findings (Park and Fan, 2004). Magnesium dissolution improved with increasing acid concentration (1.5-5 M) and decreasing particle size (163, 125 and 63 μm).

Teir et al. (2007a, c and 2009) studied the possibility of CO₂ mineral sequestration using serpentinite in Finland, where there is no
suitable geological formation, but there are abundant magnesium silicates. In their serpentine dissolution studies (Teir et al., 2007c), various acids and bases were tested (HCl, H₂SO₄, HNO₃, HCOOH, CH₃COOH, NaOH, KOH, NH₃, NH₄Cl, (NH₄)₂SO₄, and NH₄NO₃). Sulfuric acid was found to be the best dissolution agent of all the chemicals tested, however ammonium salts were able to extract Mg selectively but with low dissolution efficiency. The effect of the particle size in the range of 125 - 500 µm did not influence the Mg dissolution rate significantly in 2 h and at 70 °C. All mineral acids (2 M HCl, H₂SO₄, HNO₃) extracted 100% Mg from the serpentinite sample after 3 h. Product layer diffusion was found to be the rate limiting step for Mg dissolution. In their subsequent work, the process was fully developed and described in Fig. 2-20 (Teir et al., 2007b).

Figure 2-20: Process scheme for production of hydromagnesite from serpentinite using HCl or HNO₃ (Teir et al., 2009)
Firstly, HCl and HNO₃ solution were selected as the dissolution solvents due to their low boiling point (the boiling point for nitric acid is 83 °C, hydrochloric acid is 48 - 110 °C (38 - 20 wt. % and sulfuric acid is 338 °C). 88 % and 93 % of Mg, 37 % and 87 % of Fe were dissolved from serpentine (100 g/l) at 70 °C after 2 h by HNO₃ and HCl, respectively. The residue after dissolution, a high silica by-product, was separated by filtering. The solution was then evaporated to get solid magnesium salts and recover the acids. After dissolving magnesium salts into water, NaOH was added into the solution to raise the pH of solution from dissolution. Magnetite (Fe₃O₄) and goethite (Fe₂O₃•H₂O) precipitated when the pH was controlled to 4-6. After separating the precipitates, CO₂ was bubbled through the solution with pH regulation by adding NaOH, and hydromagnesite (Mg₅(CO₃)₄(OH)₂• 4H₂O) was precipitated at pH 8-11 at 30 °C. A solution pH of 9 was found to be the optimum value for precipitation. At this pH, the highest purity of hydromagnesite (99 wt.%) and lowest net requirements of NaOH (0.9-1.2 g NaOH / g hydromagnesite) were achieved, as well as the highest conversion (94 %) of magnesium ions to carbonate were obtained. Besides, relatively pure iron oxide (88 wt.%) and amorphous silica (82 wt.%) were obtained in this process. So far, this indirect aqueous process is the only one with detailed studies of mass balance, energy and cost evaluation (Teir et al., 2009). The mass balance is presented in Fig. 2-21.
### Table 2-1

<table>
<thead>
<tr>
<th></th>
<th>Amounts when using HNO$_3$ (t)</th>
<th>Amounts when using HCl (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Serpentinite</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>3.6*</td>
<td>-</td>
</tr>
<tr>
<td>HCl</td>
<td>-</td>
<td>2.1*</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.3*</td>
<td>2.3*</td>
</tr>
<tr>
<td>Total</td>
<td>10.0</td>
<td>8.5</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Mg$_6$(CO$_3$)$_4$(OH)$_2$·4H$_2$O</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>-</td>
<td>3.3*</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>4.8*</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Total</td>
<td>10.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>

* Unless regenerated from the spent sodium salt solution, these are the amounts of make-up chemicals required for each ton of CO$_2$ fixed as hydromagnesite.

* Unless used for regeneration of NaOH and acids, these are additional by-products from the process.

Figure 2-21: Mass balance of Teir’s process (Teir et al., 2009).

Teir et al. (2009) reported that the energy required for grinding the serpentinite to below 74 µm is about 160-190 MJ/t (44-53 kWh/t) CO$_2$ sequestered. The evaporation of the water released would require at least 1908 MJ/t (530 kWh/t) CO$_2$ sequestered. Based on the mass balance, the chemical make-up used in this process would cost 1300 US$/t CO$_2$ sequestered for a process based on HCl and 1600 US$/t CO$_2$ sequestered for a process based on HNO$_3$. Teir et al. (2009) proposed that electrolysis could be one option for recycling the resulting aqueous NaCl or NaNO$_3$ solution. In the chlor-alkali industry, NaCl is electrolysed producing chlorine gas, sodium hydroxide and hydrogen gas (see Eq. 2-10 and 2-11):

$$2NaCl(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$$

$\Delta G = 208$ kJ/mol NaCl
\[ H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \]

\[ \Delta H = -352 \text{ kJ/mol} \]

However, this regeneration process suffered from a high energy penalty, where the energy consumption for electrolysis of the NaCl is 3277 kWh/t CO\textsubscript{2} sequestered when using HCl and 4361 kWh/t CO\textsubscript{2} sequestered when using HNO\textsubscript{3}, respectively. Teir et al. (2009) concluded that the process studied might be suitable for producing valuable mineral and metal products from serpentinite, but probably not for CO\textsubscript{2} sequestration. However, the thermal stability study of the hydromagnesite produced shows that it should be a stable storage medium for CO\textsubscript{2} up to 300 °C.

**2.3.6.4 Ammonium salts**

It is imperative to recycle the additives in carbonation processes due to the large scale of any industrial application. Recently, ammonium salts have received growing attention due to their weak base and strong acid properties and the feasibility of recovery with low energy requirements.

Kodama et al. (2008) developed a pH swing CO\textsubscript{2} mineral carbonation process using recyclable ammonium salts. The schematic picture of this process is presented in Fig. 2-22.
Steel slags were firstly dissolved by NH₄Cl to leach Ca and produce ammonia gas (Eq. 2-12). The Ca-rich slurry with ammonia was injected into the absorption tower to absorb CO₂ and produce ammonium carbonate (Eq. 2-13). This is followed by the precipitation of calcium carbonate in another reactor and the recovery of ammonium chloride (Eq. 2-14). In their experimental work, 72 % dissolution efficiency was achieved at 80 °C for 60 mins, and the precipitation was theoretically calculated to be 70 % at 80 °C. The energy input requirement for this process was estimated at around 300 kWh/t CO₂, but the loss of NH₃ presented a problem. More experimental work is need on precipitation and to prove the recovery of ammonium salts.

---

Figure 2-22: schematic picture of a pH swing CO₂ mineral carbonation process using recyclable ammonium salts (Kodama et al., 2008)
Eloneva et al. (2010) studied the CO₂ emissions reduction by mineral carbonation of steel making slags using ammonium salts. In their study, ammonium chloride, ammonium nitrate and ammonium acetic were firstly selected as the most promising solvents. These ammonium salts effectively dissolved 50-80 % Ca at 30 °C and atmospheric pressure. Close to 100 wt% pure calcium carbonate was precipitated from the Ca-NH₄ salt solution by bubbling through CO₂ at 30 °C with conversion efficiencies of 50-70 % after separation of the slag residue. Then, the effects of particle size, solid to liquid ratio and solvent concentration on dissolution efficiencies were experimentally studied. The results indicated that the grain size of the steel converter slag should not be increased to above 500 μm and solid to liquid ratio over 100 g/l (in 2 M solution)
should be avoided. Based on the experimental results, the mass balance of the process was estimated and presented in Fig. 2-23.

Figure 2-23: A simplified process scheme for sequestering 1 t of CO₂ by producing pure calcium carbonate from steel converter (SC) slag using aqueous solution of ammonium salt as a solvent (Eloneva et al., 2010).

1 t of sequestered CO₂ requires 4.7 t of steel converter slag (33 wt % Ca) and produces 2.3 t of CaCO₃, as well as 3.4 t of residue slag. Assuming that 5 wt % of ammonium would be lost, 39 kg of NH₃, 122 kg of NH₄Cl, 182 kg of NH₄NO₃, or 175 kg of CH₃COONH₄ are consumed per tonnes of CO₂ sequestered. The cost for chemical make-up would be 38 US$/t CO₂ sequestered (26 €/t CO₂ sequestered) for NH₄Cl and 58 US$/t CO₂ sequestered (40 €/t CO₂ sequestered) for both NH₄NO₃ and CH₃COONH₄. The energy penalty in grinding, extraction and carbonation was estimated to be 140 kWh/t CO₂ sequestered (<100 μm), 5-200 kWh/t CO₂ sequestered depending on the particle size and 5 kWh/t CO₂ sequestered, respectively. On the other hand, the sale of produced calcium
carbonates as PCC can generate a profit of 329 US$/t CO₂ sequestered (227 €/t CO₂ sequestered) (Nordkaly, 2004) and the selling of CO₂ emission allowance can earn 19 US$/t CO₂ sequestered (13 €/t CO₂ sequestered). Accordingly, this process shows promise to be potentially economical feasible. However, the minimization of ammonium losses is extremely important and the suitability of the products for use as commercial products has to be explored further. In addition, the raw materials studied thus far do not have enough CO₂ storage capacity potential for climate change mitigation purposes.

2.4 Products from CCSM and applications

The successful development of applications of products with marketable value from mineralisation processes can help to offset the cost of CO₂ sequestration. The products of CO₂ mineral sequestration can be utilised in many applications such as building materials or high value commercial products. In addition to the final carbonates, several by-products from the indirect aqueous process, where by-products could be separated, can have industrial applications. However, the purity levels of products from the process, diversity of application, the size of market and market value are significant factors to the successful application of products from CCSM. In addition, the products from CCSM may need post-processing to get smaller particle size and higher purity, and the
energy penalty of CCSM plus post-processing may be higher than that for producing these products by conventional process.

The different CCSM process routes illustrated (Section 2.3.3-2.3.6) produce a range of different products, which can be divided into two main groups: low value mixed products (mixtures of carbonates with silica sand, iron oxides and silicate rock residue in the ARC process) and high value pure products (carbonates, silica and iron oxide like in indirect pH-swing process). Taking Teir’s pH-swing indirect aqueous process route (Teir et al., 2007b) as an example, 1.1 t/t CO$_2$ of silica sand with 82-88% purity, 0.5 t/t CO$_2$ of Iron oxides and 2.7 t/ t CO$_2$ of 99% pure hydromagnesite, with uniformly sized and spherical crystals with a lamellar structure are produced. Due to the limitations on applications and market value of low value mixed products, only high value pure products are investigated in this study.

The main products of CO$_2$ mineralisation are Ca or Mg carbonates, while the by-products include silicon, iron precipitates and other heavy metals. These products could be further post-processed to achieve high purity and increase their commercial value. Table 2-8 presents the main products from CO$_2$ mineralisation and their purity as reported from the literature, as well as the applications, size of current market and commercial values.
Table 2-8: Products from CO₂ mineralisation, and their purity, market size and value of potential applications.

<table>
<thead>
<tr>
<th>Products</th>
<th>Purity</th>
<th>Market size</th>
<th>Applications</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC</td>
<td>&gt;97%</td>
<td>13 Mt¹²</td>
<td>Filler and coating pigment in plastics, rubbers, paints and papers</td>
<td>145-402 US$/t³³</td>
</tr>
<tr>
<td>(CaCO₃)</td>
<td></td>
<td></td>
<td>paper industry, cement industry, civil engineering and production of fire retardant, a reinforcing agent in rubber, a drying agent, a laxative, supplement in food</td>
<td>(fine grade)</td>
</tr>
<tr>
<td>Magnessite or hydromagnesite</td>
<td>&gt;90%</td>
<td>18.3 Mt</td>
<td></td>
<td>200-1200 US$/t</td>
</tr>
<tr>
<td>(MgCO₃)</td>
<td></td>
<td></td>
<td></td>
<td>(technical grade)</td>
</tr>
<tr>
<td>or Silica</td>
<td>82-</td>
<td>112 Mt</td>
<td>electronic, automotive, chemical, and ceramic industries</td>
<td>10-134 £/t</td>
</tr>
<tr>
<td>(SiO₂)</td>
<td>88%</td>
<td></td>
<td></td>
<td>(grain-fine ground grade)</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>36%</td>
<td>1414 Mt</td>
<td>iron industry and the manufacture of pigments</td>
<td>219-235 US$/t (pigment)</td>
</tr>
<tr>
<td>(FeO)</td>
<td></td>
<td></td>
<td></td>
<td>2.12 US$/t (iron ore)</td>
</tr>
</tbody>
</table>

In considering the large amount of CO₂ emissions (around 33 Gt in 2010), the amount of products from CO₂ mineralisation is significantly large, in the order of thousands of Million t per year.

The current market is not large enough to take up these quantities,

and new applications must be found. Recently, Calera Corporation proposed to use the end product of their CO₂ mineralisation process as supplementary cementitious material (SCM). The cement industry produces 5% of the total global CO₂ emissions (Gunning et al., 2010), and if the product from mineralisation could be used as a substitute for cement. The cement industry would be replaced then by the mineralisation industry, which has negative CO₂ emissions and helps to store CO₂ from other sources such as power plants. In addition, the Fe-rich precipitate (iron oxide) from indirect aqueous processes could be used as feedstock for a steel-making plant. If the mineralisation process is scaled up to millions of tonnes per year, the trace elements should be paid more attention. For example, Ni and Mn are valuable metals and are widely used in high efficiency batteries.

2.5 Summary.

There has been an increasing interest in mineral carbonation. Obviously, one of the main advantages of this process is the permanent safe storage of CO₂ due to the thermodynamically stable nature of the solid carbonates formed (Goff, 1998). Moreover, carbonation is an exothermic process, which may reduce the overall energy penalty and costs (Lackner, 2000). However, mineral sequestration also faces some barriers such as low efficiency of mineral dissolution, slow kinetics, and energy intensive pretreatment processes (Lackner et al., 1995). Although, low efficiency
and slow kinetics have been solved by swinging the pH (Teir et al., 2007c; Park and Fan, 2004), the addition of large amounts of acid and base required for the dissolution and subsequent carbonation limit the development of mineral sequestration. Therefore, there is a need to find low cost recyclable solvents that can provide high efficiency of mineral dissolution and carbonation.
Chapter 3. Carbon dioxide capture and storage by mineralisation using recyclable ammonium salts

Ammonium salts have received increasing attention in CCSM due to their properties to form efficient acid and base in dissolution and carbonation reactions and ability of being recycled. Kodama et al. (2008) reported a pH-swing CO₂ mineralisation process with steel slags using recyclable ammonium salts. Pundsack et al. (1967) also reported using a recyclable ammonium salts for serpentine dissolution. In this study, the author developed a new pH-swing mineral carbonation process by using recyclable ammonium salts. The process developed here overcomes the two barriers of low efficiency of mineral dissolution and unrecyclable use of additives.

Moreover, mineral sequestration has been considered as a separate process from capture. In the capture process, the CO₂ is first absorbed by chemicals, such as monoethanolamine or NH₃ (Yang et al., 2008). The CO₂ is then thermally desorbed to recover the sorbents and release concentrated CO₂. The CO₂ is then compressed for transportation; however, compression consumes a lot of energy, which nearly accounts for 25% of the total energy penalty of the whole CCS process (IPCC, 2005). The process developed here combines capture and mineralisation by employing ammonium salts.

In this Chapter, two process routes of CCSM process with recyclable
Chapter 3 – CCSM with recyclable ammonium salts

ammonium salts are described in Section 3.1, the characterization of raw materials used in this study is reported in Section 3.2 and the solvent selection studies is presented in Section 3.3.

3.1 Description of process

In this work, two process routes were developed using different solid to liquid ratio. The first process route is at low solid/liquid ratio (<100 g/l) and three products are obtained (Si rich product with residual serpentine, Fe-rich products and hydromagnesite). The second process applies high solid/liquid ratio (>200 g/l) in order to reduce the water usage and energy requirement in evaporation, and only one product (mixture of residual serpentine and carbonates) is obtained. It is not possible to separate products in the high solid to liquid ratio experiments since MgSO₄ exceeds the solubility limit and precipitates during mineral dissolution. These two process routes are described in the following sections.

3.1.1 CCSM process route at low solid to liquid ratio

The multistep process route with pure products for carbon dioxide capture storage and mineralisation consists of five main steps, and the main reactions are presented in Figure 3-1 and Table 3-1.
Firstly, NH₃ is used to capture CO₂ from power plant’s flue gas and produces NH₄HCO₃. Secondly, the NH₄HSO₄ is used to extract Mg from serpentine at mild heating conditions in the mineral dissolution step. Thirdly, the Mg-rich solution produced from mineral dissolution is regulated to neutral pH by adding NH₄OH; then, the impurities in the leaching solution are removed by adding NH₄OH. After that, the solution reacts with the intermediate product (NH₄HCO₃) from the
CO₂ capture step to precipitate carbonates at mild temperature. Since the formation of carbonate is determined by temperature (Hänchen et al., 2008), nesquehonite (MgCO₃•3H₂O) can be converted to hydromagnesite (4MgCO₃•Mg(OH)₂•4H₂O) above 70°C. With the precipitation of hydromagnesite, the final solution contains mainly (NH₄)₂SO₄. Finally, the (NH₄)₂SO₄ could be recovered by evaporation and subsequently heated up to regenerate NH₃ which returns to the capture step and NH₄HSO₄ which is then reused for the mineral dissolution step.

The thermodynamic data for this process was calculated by using HSC 5.0 thermal calculation software and the enthalpy and Gibbs free energy values for the different steps are presented in Table 3-1. It can be seen that all reactions in this process are spontaneous, with the exception of the regeneration reaction. The dissolution and carbonation reactions are exothermic, while the reaction of carbonate formation is endothermic.

This process is unique in using NH₄HCO₃ instead of direct CO₂ gas for indirect aqueous mineral carbonation. The advantages of using NH₄HCO₃ include avoiding CO₂ desorption in the capture step and subsequent CO₂ compression for transportation that are energy intensive steps of the conventional CCS process (70 % of the total energy penalty in whole CCS process; IPCC, 2005).
3.1.2 CCSM process route at high solid to liquid ratio

The CCSM process route at high solid to liquid ratio also consists of five main steps (see Fig. 3-2), and the main reactions are the same as those presented in Table 3-1.

![Diagram of CCSM process route at high solid to liquid ratio](image)

Figure 3-2: Schematic of CCSM process route at high solid to liquid ratio.

Firstly, NH₃ is used to capture CO₂ from power plant’s flue gas and produces NH₄HCO₃. Secondly, the NH₄HSO₄ is used to extract Mg from serpentine at mild temperature (100 °C) in the mineral dissolution step, where the dissolved Mg ions exist in both the liquid phase and also as precipitated MgSO₄. Thirdly, the mixed slurry produced from mineral dissolution is regulated to neutral pH by adding NH₄OH. After that, the solution reacts in a closed autoclave with the intermediate product (NH₄HCO₃ or (NH₄)₂CO₃) from the CO₂ capture step to precipitate carbonates at mild temperature (80 °C). The pressure evolved from the decomposition of NH₄HCO₃ or (NH₄)₂CO₃ helps the carbonation reaction and transforms...
hydromagnesite into magnesite (Hänchen et al., 2008). After filtering the slurry, the final solution contains mainly (NH₄)₂SO₄ and a mixed product solid consisting of magnesite, residual serpentine and high Fe content impurities. Finally, the (NH₄)₂SO₄ can be recovered by evaporation and subsequently heated up to regenerate NH₃ which goes back to the capture step, while the regenerated NH₄HSO₄ is then reused for the mineral dissolution step.

3.2 Characterization of raw materials

A serpentinite sample from Cedar Hills quarry in southeast Pennsylvania, USA and supplied by Albany Research Center (U.S.), was selected for this study. A batch of 10 kg serpentinite was ground and sieved. A coarse portion of the sample was ground initially in a jaw crusher in order to get small particles. Then, the crushed sample was ground to a smaller particle size using a Tema mill for a short time (30 s). Once the grinding process was completed, the samples were sieved using an automatic shaker to generate sample with particle size fraction of 75-150 μm. Particle size distribution (PSD) tests were performed to measure the particle size. To identify the mineral phases present, 1 gram sample was analyzed using a Philips Analytical 1050 X-Ray Diffraction (XRD) at scan speed 3°20/minute from 5° to 65°under 40 kV / 40 mA. To determine the elemental composition of the serpentinite sample, 0.5 gram sample was completely dissolved using HF solution by
microwave digestion. The solutions were diluted 100-fold and acidified by 10\% HNO$_3$, and then analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (Perkin-Elmer's Optima 3000 series) using two different wave lengths to give a more exact reference number for the concentrations of Mg, Si, Fe, Ca, Al, Ni, Mn, Cr, Cu, Al, Sr, Na, Ti and Ba. The inherent carbonate content of the sample was determined using a thermal gravimetric analyzer (TGA Q500, TA Instrument). Representative samples (10-20 mg) were heated in a ceramic cup under nitrogen atmosphere at 20°C/min from ambient to 950 °C. The weight loss in the temperature region of 450°C to 650 °C was determined to be carbonates (Huijgen et al., 2006). The loss on ignition (LOI) was determined by drying the sample at 950°C for 1 hour in argon. The elemental composition of the original mineral sample determined by microwave digestion and ICP-AES is presented in Table 3-2.

Table 3-2: Elemental analysis of original mineral serpentine

<table>
<thead>
<tr>
<th>Element/Oxide (wt%)</th>
<th>Element, wt% (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>7.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>40.1</td>
</tr>
<tr>
<td>MnO</td>
<td>0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1</td>
</tr>
<tr>
<td>NiO</td>
<td>0.3</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>38.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.1</td>
</tr>
<tr>
<td>Water 1</td>
<td>0.6</td>
</tr>
<tr>
<td>Water, bonded 2</td>
<td>11.9</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
</tr>
<tr>
<td>LOI</td>
<td>13.6</td>
</tr>
</tbody>
</table>

1 Free moisture, measured as the weight loss after 1 hour at 105 °C, in nitrogen.
2 Chemically-bonded water, measured as the difference between the LOI and all other volatiles.
The major elements were Mg (24.0 wt. %), Si (17.8 wt. %) and Fe (5.3 wt. %), and minor elements were Mn, Ca, Al and Ni (concentrations of 0.1–0.3 wt.%). The sample contained trace carbonate (1.1 wt.%). The loss on ignition at 950 °C was 13.6 wt.%, which consists of 0.6 wt.% moisture content (number 1) and 11.9 wt.% chemical-bound water (number 2). This can be confirmed by the TGA analysis (Fig. 3-3).

![TGA graph of the original mineral serpentine sample.](image)

Figure 3-3: TGA graph of the original mineral serpentine sample.

The particle size distribution (PSD) graph of the original mineral serpentine with particle size fraction of 75-150 μm is described in Fig 3-4. The $d_{50}$ is 87 μm and $d_{90}$ is 105.9 μm. In this study, particle size fraction of 75-150 μm is selected as the base line in order to
compare with other researchers’ work, where this same particle size fraction was used (Teir et al., 2007c).

![PSD graph of original mineral serpentine with particle size fraction of 75-150 μm.]

The XRD pattern (Fig. 3-5) reveals that it is mainly serpentine, \(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4\); antigorite), and small amounts of forsterite \(\text{Mg}_2\text{SiO}_4\) and magnetite \(\text{Fe}_3\text{O}_4\). It should be noted that different polymorphic forms may have different dissolution behavior, as already discussed by Van Essendelft et al. (2009a). A summary of the results from serpentine characterization indicate that this serpentine sample is representative and similar to that used in Teir (2007c) and Alexander et al. (2007) studies. The high levels of Mg indicate that this serpentine sample is suitable for CO\(_2\) mineralization.
Chapter 3 – CCSM with recyclable ammonium salts

3.3 Solvent selection studies

In order to find a suitable ammonium salt for leaching Mg from serpentine, NH₄Cl, (NH₄)₂SO₄ and NH₄HSO₄ (which cover a wide range of pKa from -3 to 10) were tested alongside previously used solvents for comparison of dissolution efficiencies. Maroto-Valer et al. (2005) have reported dissolution of serpentine using acids (e.g. HCl, H₂SO₄, HNO₃), where a 2M H₂SO₄ gave the highest dissolution efficiency of Mg, 70 % at 75°C after 6 hours. A batch of 20 g of serpentine (75–150 μm) was dissolved in 400 ml aqueous solutions of 2M concentrations of the respective solvent in a sealed flask. This concentration of solvent was chosen as it represents 100 % excess of the required stoichiometric amount. The solutions were stirred at 800 rpm at a temperature of 70 °C. The solutions were immediately

Figure 3-5: XRD pattern of the original mineral serpentine.
filtered with 0.7 μm Pall syringe filters after 3 hours dissolution. The concentrations of Mg, Fe, and Si in the filtered solutions were measured using ICP-AES.

Since the original mineral sample contained very low concentrations of Ca (0.09 wt%, Table 3-2), only the concentrations of Mg, Fe and Si are reported for the dissolution studies. The Mg dissolution efficiencies (MgDissolution %) using different solvents are shown in Fig. 3-6.

![Figure 3-6: Mg dissolution from serpentine using different ammonium salts and H2SO4 (2M concentration at 70°C for 3 hours)](image)

After 3 hours NH4HSO4 can extract significant amounts of Mg from serpentine (52 %), while NH4Cl and (NH4)2SO4 can only extract smaller amounts (3–5 %). A dissolution experiment using H2SO4 was carried out to compare with that using ammonium salts. The
results indicated that NH₄HSO₄ can extract slightly more Mg than H₂SO₄ acid (52 vs. 47 %). Both NH₄HSO₄ and H₂SO₄ perform better than (NH₄)₂SO₄ and NH₄Cl. This can be due to the pKa values of NH₄HSO₄ and H₂SO₄ that are both -3.00 and much lower than 9.24 and 8.74 for NH₄Cl and (NH₄)₂SO₄, respectively. Moreover, NH₄HSO₄ is preferred over H₂SO₄ because ammonium salts have the potential to be regenerated.

3.4 Summary

The two process routes of CCSM with recyclable ammonium salts were described. The serpentine sample used was characterized by TGA, PSD, XRD and ICP-AES. Solvent selection experiments were carried out to find the suitable ammonium slats and compare with the sulfuric acid.
Chapter 4. CCSM process route at low solid to liquid ratio

4.1 Dissolution of serpentine using recyclable ammonium salts at low solid/liquid ratio

This section presents the dissolution of serpentine using a series of ammonium salts at different temperatures. Therefore, in this work the kinetics of serpentine dissolution were investigated and the rate-limiting step was identified. The understanding of dissolution kinetics can help to improve the dissolution rate. Van Essendelft et al (2009a and 2009b) have found that the dissolution mechanism of serpentine with sulfuric acid changes with particle size as the reaction progresses. Their work suggests that the dissolution rate-limiting step may be a combination of several control factors as the reaction progresses. The author developed a model that considered surface reaction, surface speciation, the electrical double layer, particle size distribution, temperature, concentration and grinding energy input (Van Essendelft et al., 2009b).

4.1.1 Experimental methods

Dissolution experiments were carried out in a 600ml 3 neck glass flask reactor, which was heated by a temperature-controlled silicone
oil bath and equipped with a water-cooled condenser to minimise solution losses due to evaporation (Fig. 4-1). The 400 ml 1.4 M NH₄HSO₄ solution was well mixed by using a magnetic stirrer at 800 rpm. The solution was heated up to the temperature required, and then 20 grams of 75-150 μm fraction of serpentine were added. For the kinetics studies, the t₀ started after adding the solid serpentine sample. After that, 1 ml liquid samples were dissolved with a syringe at given interval times, such as 5 min, 15 min, 30 min, 1 h, 2 h, and 3 h. The samples were immediately filtered using a 0.45 μm syringe filter unit. The Mg, Fe and Si concentrations of the samples were measured using ICP-AES. The dissolution efficiency of a specific element X (Mg, Fe or Si) in solution sample at a given time y (at 5, 15, 30 mins...) was calculated as follows:

\[
X_{\text{Dissolution}}\% = \frac{C_y \times V}{m_{\text{batch}} \times w_x} \times 100\% \quad \text{Equation 4-1}
\]

\(C_y\) is the concentration of element \(x\) in the solution sampled at \(y\) time, \(V\) is the volume of the solution in the reactor (\(V\) is considered constant as only 6ml are dissolved throughout the course of the experiment), \(m_{\text{batch}}\) is the mass of serpentine sample added. \(w_x\) is the initial weight percentage of mass of element \(x\) over the total mass of solid present in the original mineral sample. The reproducibility of the results from the experimental work was approximately 1%. The uncertainty stems from errors in three
measured quantities, i.e., the solvent concentrations, the mass of the solid and the analysis error of liquid sample by ICP-AES.

4.1.2 Results and discussion

Based on the dissolution experiments described previously (Section 3.3), \( \text{NH}_4\text{HSO}_4 \) was selected for further studies. The dissolution rate of serpentine with a particle size fraction of 75–150 \( \mu \text{m} \) was tested at temperatures of 70, 80, 90, and 100 °C. The concentration used was 1.4 M \( \text{NH}_4\text{HSO}_4 \) following earlier work by Pundsack et al (1967), where this represents 40 % excess of the stoichiometric amount. The effect of temperature upon the dissolution of serpentine is shown in Figures 4-2 to 4-4. As expected, temperature has a significant effect upon the solubility of magnesium (and other
elements as well) from serpentine, and higher temperatures yield higher dissolution efficiencies for each element tested. At 100 °C and 3 hours, NH₄HSO₄ was able to extract 100 % of Mg and 98 % of the Fe, but only 17.6 % of Si (Figure 4-2). The Mg:Si ratio remains greater than the stoichiometric 3:2 by more than a factor of 5, as the mineral leaching is an incongruent process, which has also been confirmed by previous work (Bearat et al., 2006). This incongruent leaching is probably due to the secondary precipitation of dissolved silicon back to the surface of particles (Bearat et al., 2006). The formation of a silica-rich passive layer can inhibit the continuous leaching of magnesium and iron from the inside of particles and this probably explains why the dissolution rate slows down over time. The formation of a silica passive layer has been previously reported on direct mineral carbonation, where dissolution and carbonation are studied concurrently (Bearat et al., 2006). They observed that the presence of this passive layer inhibited the dissolution reaction.
Chapter 4 – CCSM process route at low solid to liquid ratio

Figure 4-2: Mg dissolution from serpentine in 1.4 M NH₄HSO₄ solution at 70, 80, 90 and 100°C for 3 hours.

Figure 4-3: Fe dissolution from serpentine in 1.4 M NH₄HSO₄ solution at 70, 80, 90 and 100°C for 3 hours.
Figure 4-4: Si dissolution from serpentine in 1.4 M NH$_4$HSO$_4$ solution at 70, 80, 90 and 100°C for 3 hours.

NH$_4$HSO$_4$ provided a 100 % dissolution efficiency after 3 hours and this value is higher than that of 72 % reported by Park et al (2004) using H$_3$PO$_4$, oxalic acid and EDTA and that of 70 % reported by Alexander et al. (2007) using H$_2$SO$_4$. A 100 % Mg dissolution efficiency has also been reported by Teir et al. (2007c) using HCl and HNO$_3$.

It is anticipated that the dissolution rate (mol/m$^2$/s) can be further improved by increasing the additive concentration in the aqueous solution. Furthermore, pre-treatment of serpentine could further enhance the dissolution rate. For example, studies have shown that heat-treatment at 650 °C increases reactivity greatly (McKelvy et al., 2004). However, physical and thermal activation of the mineral increases considerably the energy demand of the process.
Gerdemann et al. (2007) have studied the energy penalty of pre-treatment of serpentine. The theoretical energy required for the heat-activation process to heat the mineral to 630 °C is up to 326 kWh/t for serpentine. The energy required for the initial crushing step is estimated to be 2 kWh/t and grinding to minus 75 μm adds another 11 kWh/t. Further grinding to minus 38 μm in ball mills is estimated to add 70 kWh/to, and high-intensity grinding in an stirred media detritor adds an estimated 150 kWh/t. The extra energy penalty can increase CO₂ emissions and decrease the net power generated of power plants. More recently, it has been reported that concurrent grinding could effectively remove the silica layer from the particles (Van Essendelft et al., 2009a).

4.1.3 Kinetic analysis

In a liquid-solid reaction, the reaction rate is generally controlled by one of the following sequential steps: diffusion through the fluid film, diffusion through the layer on the particle surface, or the chemical reaction at the surface. The rate of the reaction is controlled by the slowest of these steps (Levenspiel, 1972.).

In order to determine the kinetic parameters, including reaction constant and activation energy, and the rate-limiting step in the dissolution of serpentine using ammonium salts, the experimental data were analyzed according to the standard integral analysis method (Levenspiel, 1972.). The unreacted-core model of constant
size particles (Levenspiel, 1972.) was selected since previous studies have reported incongruent dissolution of serpentine and proved the existence of a silicon layer after dissolution (Fauth et al., 2001). Experimental data were fitted into integral rate equations of film diffusion control, product layer diffusion control, and reaction control for constant size particles (flat plate, cylinder and sphere). The multiple regression correlation coefficients (R) were calculated for each equation and checked graphically. The rate-limiting step of the reaction was identified as that reaction with the highest multiple regression correlation coefficient.

Kinetic analysis was performed using the magnesium dissolution data (Table 4-1). When fitting the experimental data to the integral rate equations, product layer diffusion gave the best match based on the regression correlation coefficients calculated (Figure 4-5).

Table 4-1: Multiple regression coefficients for experimental kinetic data fitted to constant size particles models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film diffusion</td>
<td>$k_t = X_p$</td>
<td>$-0.279 - 0.2016$</td>
</tr>
<tr>
<td>Product layer diffusion</td>
<td>$k_t = 1 - 3(1 - X_p)^{2/3} + 2(1 - X_p)$</td>
<td>$0.9324 - 0.9643$</td>
</tr>
<tr>
<td>Chemical reaction controls</td>
<td>$k_t = 1 - (1 - X_p)^{1/3}$</td>
<td>$0.4228 - 0.8562$</td>
</tr>
</tbody>
</table>

The results (Figure 4-5) indicate that the rate limiting step for dissolution of serpentine in $\text{NH}_4\text{HSO}_4$ is more likely to be product layer diffusion. Luce (1972) found that a product layer is the rate-controlling mechanism for dissolution of magnesium silicates by using HNO₃ and KOH. Apostolidis and Distin (1978) also found that the rate was limited by diffusion through a silica passive layer when
the magnesium dissolution is above 25% by using H₂SO₄. This study is in agreement with these studies and the finding that low concentration of Si in solution supports the theory of a build up of a product layer of silica on the particles. It should be noted that the rate-limiting control mechanism probably changes with particle size, and if a smaller particle size sample was chosen, pure chemical reaction control may have become dominant.

Figure 4-5: Kinetic analysis of the dissolution of Mg from serpentine using 1.4 M NH₄HSO₄

The apparent rate constant (k) was determined from the slope of the lines in Figure 4-5. The apparent rate constant can be used for determining the activation energy (E) by Arrhenius' law:

\[ k = k_0 e^{-E/RT} \]  
(Eq. 2)
The activation energy was determined by plotting the apparent rate constants for each experiment at different temperatures (Fig. 4-6). As there are no previous studies of dissolution of serpentine using ammonium salts, studies for dissolution of serpentine in strong acids were selected for comparison and the activation energies reported are presented in Table 4. The activation energy found in this study (40.9 kJ mol\(^{-1}\)) is similar to the value calculated by Fouda (1996) for dissolution of serpentine in 3M H\(_2\)SO\(_4\) between 30-75°C (Table 4-2). However, it is much lower than that reported by Teir et al. (2007) when using 2M H\(_2\)SO\(_4\) between 30-70°C (Table 4-2). The difference between Fouda’s and Teir’s work is probably due to heat pre-treatment of samples in Fouda’s work.

Figure 4-6: Arrhenius plot for dissolution of Mg from serpentine using 1.4 M NH\(_4\)HSO\(_4\)
Table 4-2: Data on dissolution of serpentine from literature

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Solution</th>
<th>Activation energy $E$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fouda et al. (1996b)</td>
<td>Serpentine pre-heated at 800°C for 2-3 hours, 3 M H$_2$SO$_4$, T=30-75°C</td>
<td>35.6</td>
</tr>
<tr>
<td>Teir et al. (2007)</td>
<td>Serpentine with particle size fraction of 74-125 µm, 2 M H$_2$SO$_4$, T=30-70°C</td>
<td>68.1</td>
</tr>
<tr>
<td>Present study</td>
<td>Serpentine with particle size fraction of 75-150 µm, 1.4 M NH$_4$HSO$_4$, T=70-110°C</td>
<td>40.9</td>
</tr>
</tbody>
</table>

Teir et al. (2007c) proposed that chemical reaction is the initial rate limiting step, and product layer diffusion gradually becomes rate limiting, because of the build up of a product layer of silica and the decrease of unreacted surface area. The observed activation energy here is higher than the value of typical layer diffusion controlled process, and is roughly one half of that of a pure chemical reaction controlled process (Levenspiel, 1972.). In summary, the rate limiting mechanism of serpentine dissolution with 75-150 µm particle size using NH$_4$HSO$_4$ is a combination of chemical reaction control and product layer diffusion control. This explains the derivations observed from Figure 4-5.

4.1.4 The effect of solvent concentration

The effect of solvent concentration was tested by dissolving 20 g of original mineral serpentine (75-150 µm) in a 400 ml solution of ammonium bisulphate with concentration values of 0.7, 1 (stoichiometric value), 1.4, 2 and 2.8 M at 100 °C for 1 h. The Mg concentrations of the solutions after dissolution were analyzed by
ICP-AES. The equipment and procedure used were same to those described in Section 4.1.1.

Figure 4-7: The effect of solvent concentration on dissolution of Mg from serpentine in aqueous solution of ammonium bisulphate.

According to the stoichiometry of dissolution of Mg and NH₄HSO₄, 2 parts of NH₄HSO₄ is required to dissolve one part of Mg. A 20 g serpentine dissolving in 400 ml solution theoretically contains 0.5 M Mg ions, thus 1 M NH₄HSO₄ aqueous solution is required. However, due to the limitation of the diffusion of NH₄HSO₄ in pore space of mineral particles, only 65.0% Mg dissolution efficiency was obtained when using the 1 M stoichiometry concentration, compared to 41.2, 82.5 and 89.9 % when using 0.7, 1.4 and 2 M, respectively (Fig. 4-7). Therefore, the excess of NH₄HSO₄ concentration can maximise the Mg dissolution efficiency. Although the highest Mg dissolution efficiency (95.5 %) was achieved at highest solvent
concentration (2.8 M), 1.4 M was considered to be the optimized solvent concentration since more excess cannot promote the dissolution efficiency significantly. However, it must be noted that when using excess NH₄HSO₄ more ammonia water was consumed to regulate the pH to neutral value.

4.1.5 The effect of particle size

The effect of particle size was tested by dissolving 20 g of original mineral serpentine in a 400 ml solution of 1.4 M ammonium bisulphate at 90 °C for 2 h. The particle size values selected were <38, 75-150 and 150-300 μm, as these values allow for comparison with previous published work. The Mg concentrations of the solutions after dissolution were analyzed by ICP-AES. The equipment and procedure used were identical to those described in section 4.1.1.

Figure 4-8 shows that dissolution rate of Mg in all three particle size within the first 15 minutes is higher than that after 15 minutes. The smallest particle size (<38 μm) presents the slightly highest Mg dissolution efficiency (68.1 % in 60 mins) (Fig. 4-8). Moreover, the Mg dissolution efficiency does not decrease significantly with increasing particle size, where 67.8 % (60 mins) is achieved when using the 75-150μm compared to 65.4 % (60 mins) for that using 150-300 μm. After 2 h, the Mg dissolution efficiency of that using 75-150 μm is nearly same to that using <38 μm. Alexander et al.
Chapter 4 - CCSM process route at low solid to liquid ratio

(2007) reported 38 and 25 % were obtained in their H₂SO₄ extraction experiments when using 75-150 and 150-300 μm. In terms of energy saving on grinding, the high particle size fraction of 75-150 μm should be used.

![Figure 4-8: The effect of particle size on dissolution of Mg from serpentine in aqueous solution of ammonium bisulphate.](image)

4.1.6 The effect of solid to liquid ratio

High solid to liquid ratio is preferred to reduce water usage and save energy during the evaporation. Accordingly, the dissolution of Mg from serpentine using different solid to liquid ratios was tested by adding a sample (20, 40, 80 and 120 g) of serpentine (75-150 μm) to 400 ml of 1.4 M ammonium bisulphate solution at 100 °C for 3 h. The Mg concentrations of the solutions after dissolution were analyzed by ICP-AES. The equipment and procedure used were identical to those described in Section 4.1.1. For the solid to liquid
ratio above 100 g/l, MgSO₄ precipitated during the dissolution, and excess water was added at the end of dissolution to dissolve all the Mg into the solution. After filtering, the Mg concentration and the volume of solution were measured.

The highest Mg dissolution efficiency (100 %) was reached with the lowest solid to liquid ratio (50 g/l) (Fig. 4-9). The Mg dissolution efficiency did not decrease significantly (91 %) when the solid to liquid ratio increased to 100 g/l. The Mg dissolution efficiency decreased from 91 % to 75 % as the solid to liquid ratio increased from 100 g/l to 200 g/l. However, when solid to liquid ratio continuously increase to 300 g/l, the Mg dissolution efficiency increased to 85 %. Because increasing of high solid to liquid ratio enhances the probability of interactions between particles. Once the product layer is exfoliated by collision of particles, the fresh mineral located below the product layer can react with the reactive reagent (NH₄HSO₄). This results in increasing of dissolution efficiency with increasing the diffusion of reactive reagent in the pore space of particles. The increase of dissolution efficiency by the intensive particle-particle interaction resulted from the removal of silica passive layer have been reported by Bearat et al. (2006) and Park and Fan (2004).
Consequently, the solid to liquid ratio of 50 g/l in the dissolution of Mg from serpentine is favoured and ratios over 100 g/l should be avoided. Application of internal grinding in serpentine dissolution at a fluidised bed is a potential solution to provide intensive particle-particle interaction and thus remove passive layer (Park and Fan, 2004).

4.1.7 Summary
This work reports the dissolution of serpentine using ammonium salts. It has been shown that NH$_4$HSO$_4$ can extract significant amounts of Mg from serpentine and its dissolution efficiency is higher than that reported using H$_2$SO$_4$. The results from dissolution experiments show that at 100 °C 1.4 M NH$_4$HSO$_4$ extracted 100% of
Mg from serpentine in 3 hours, as well as 98% of Fe, but only 17.6% of Si. This incongruent leaching would lead to create a passive silicon layer on the surface of particle that blocks continuous leaching of Mg. In addition, it was found that the Mg dissolution from serpentine increases with higher temperatures.

The dissolution kinetics of serpentine with NH$_4$HSO$_4$ were found to follow the model of constant size particles, where the rate limiting mechanism is a chemical reaction with product layer diffusion control. In this study, the results show that serpentine dissolution with NH$_4$HSO$_4$ is very temperature dependent with activation energy of 40.9 kJ mol$^{-1}$, which is in agreement with the previous kinetic studies of magnesium dissolution from serpentine.

The effect of solvent concentration, particle size and solid to liquid ratio were investigated. The Mg dissolution from serpentine was favoured at when using particle size fraction of 75-150 µm, 1.4 M ammonium bisulfate solution at 50 g/l solid to liquid ratio.

4.2 Production of hydromagnesite with recyclable ammonium salts

The dissolution of serpentine with NH$_4$HSO$_4$ has been reported in Section 4.1. In this section, the carbonation with NH$_4$HCO$_3$ and the regeneration of NH$_4$HSO$_4$ and NH$_3$ are reported. The carbonation experiments were conducted at different molar ratio of Mg-
NH₄HCO₃-NH₃. Finally, the mass balance of all streams in this process is presented.

4.2.1 Experimental methods

4.2.1.1 Preparation of magnesium salt solutions from serpentine using NH₄HSO₄

Previous dissolution experiments conducted have shown that NH₄HSO₄ is suitable for extracting magnesium from serpentine (Section 3.3). The dissolution of magnesium from serpentine using NH₄HSO₄ is presented in Eq. 4-2:

\[
\text{Mg}_3\text{Si}_2\text{O}_5 \cdot (\text{OH})_4(s) + 6\text{NH}_4\text{HSO}_4(aq) \rightarrow 3\text{MgSO}_4(aq) + 2\text{SiO}_2(s) + 5\text{H}_2\text{O}(l) + 3(\text{NH}_4)_2\text{SO}_4(aq)
\]

For the dissolution experiments, the same procedure and serpentine sample was used as in Section 4.1.1. Different temperatures (80 °C, 90 °C and 100 °C) and reaction times (1 h, 2 h and 3 h) were used for the preparation of MgSO₄ solutions. After dissolution, the solution was cooled down to room temperature and filtered using a 0.45 μm Pall syringe filters. The filtrate is referred to as filtrate 1 (Figure 3-1) and was used for the pH regulation studies described in Section 4.2.1.2. The solid residue was dried at 105 °C overnight and is referred to as product 1 (Figure 3-1). The filtrate 1 was analysed by ICP-AES to measure the concentration of dissolved Mg, Fe and Si.
For the purpose of this analysis, filtrate 1 was acidified by 70 wt. % HNO₃ for preventing precipitation of Mg and Fe. The product 1 was sampled and sent for XRF analysis to determine the weight % of Mg, Fe and Si. The reproducibility of these analyses is found to be around 1 % according to duplicate experiments.

### 4.2.1.2 pH regulation and removal of impurities

About 40 % excess NH₄HSO₄ was used for the dissolution of serpentine in order to maximise the magnesium dissolution. After the dissolution, the pH values of the solution were about 0.9～1.2. Because the carbonation reaction is favored at high pH values, it was necessary to increase the pH of the solution to alkaline values. The chemical reaction of the pH regulation is presented in Eq. 4-3:

\[
NH₄HSO₄(aq) + NH₃ \cdot H₂O(aq) \rightarrow (NH₄)_2SO₄(aq) + H₂O(l)
\]

Equation 4-3

The reason of using ammonia water is because the above reaction produces ammonium sulphate, which can be converted back to NH₃ and NH₄HSO₄ in the regeneration step in order to achieve the recycle of the additives (Figure 3-1).

If a high value product (pure magnesium carbonate) is desired, some impurities, such as Fe, Al, Cr, Zn, Cu and Mn, need to be precipitated out from the system firstly by increasing the pH. In order to optimize the removal of impurities, extra ammonia water...
was added into filtrate 1 after pH regulation, and the reactions of impurities removal are presented in Eq. 4-4 and 4-5:

\[
(Fe, Al, Cr)_{2}(SO_4)_3(aq) + 6NH_3 \cdot H_2O(aq) \rightarrow 2(Fe, Al, Cr)(OH)_3(s) \downarrow +3(NH_4)_2SO_4(aq)
\]

Equation 4-4

\[
(Zn, Cu, Mn, Fe)SO_4(aq) + 2NH_3 \cdot H_2O(aq) \rightarrow (Zn, Cu, Mn, Fe)(OH)_2(s) \downarrow + (NH_4)_2SO_4(aq)
\]

Equation 4-5

During the pH regulation and removal of impurities, ammonia water (35 wt. %) was added into filtrate 1 until the pH value was neutral. During this process, the solution was stirred and an in-situ pH probe was used to measure the pH value. The solution was filtered with 0.7 μm Pall syringe filters. The filtrate is referred to as filtrate 2 (Figure 3-1) and was used for the carbonation experiments described in Section 4.2.1.3. The solid residue was dried at 105 °C overnight and is referred to as product 2 (Figure 3-1). The filtrate 2 was analyzed by ICP-AES to quantify the concentration of different elements, including Mg, Si, Fe, Mn, Zn, Cu, Al and Cr. The product 2 was analyzed by XRF and XRD to quantify its composition and identify the mineral phases present.
4.2.1.3 Precipitation of hydromagnesite using NH₄HCO₃

The precipitation of hydromagnesite by reacting MgSO₄ with NH₄HCO₃ and NH₃ is presented in Eq. 4-6 and 4-7:

\[
MgSO_4(aq) + NH_4HCO_3(aq) + NH_3 \cdot H_2O(aq) + 2H_2O(l) \rightarrow MgCO_3 \cdot 3H_2O(s) \downarrow + (NH_4)_2SO_4(aq)
\]

Equation 4-6

\[
5MgCO_3 \cdot 3H_2O(s) \rightarrow 4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O(s) \downarrow + 10H_2O(l) + CO_2(g) \uparrow
\]

Equation 4-7

The formation of magnesium carbonate species depends on temperature and pressure (Hänchen et al., 2008). Nesquehonite (MgCO₃•3H₂O) can precipitate from aqueous solutions at ambient temperature as described in Eq. 4-6, while at higher temperatures (50 and 100 °C), nesquehonite is transformed into hydromagnesite (4MgCO₃•Mg(OH)₂•5H₂O) as presented in Eq. 4-7. For temperatures above 100 °C, hydromagnesite is transformed into magnesite (MgCO₃). In this study, hydromagnesite was produced as the experiments were conducted at 85 °C.

For the carbonation experiments, the filtrate 2 was put in a 500 ml 3 neck glass vessel and heated up to 60 °C using a silicon oil bath. The experimental setup was as previously reported in Section 4.1.1.
The time, temperature and pH values were recorded every 5 mins. Before starting heating, ammonia water (35 wt. %) was added into filtrate 2. When the temperature reached 60 °C, NH₄HCO₃ (as CO₂ source) was added and the solution was heated to 90 °C. After the solution was stabilised at 90 °C, the solution was kept at that temperature for 30 mins. 2 ml aliquots were sampled using a needle syringe at 5, 10, 15, 30, 45 and 60 mins. The liquid samples were filtered by a mini filter unit and acidified with HNO₃ for subsequent ICP-AES analysis to measure the Mg concentration. At the end of the experiment, the solution was cooled down and filtered with 0.7 μm Pall syringe filters and the filtrate is referred to as filtrate 3 (Figure 3-1). The solid residue was dried at 105 °C overnight and is referred to as product 3 (Figure 3-1). The composition of the product 3 was analyzed using XRF and the mineral phases were identified by XRD. Experiments were conducted at different mass ratios of Mg : NH₃ : NH₄HCO₃, where Mg is the mass of Mg in filtrate 2, and NH₃ and NH₄HCO₃ represent the mass of ammonia water and the mass of NH₄HCO₃ added, respectively. In addition, a preliminary experiment was conducted where no NH₃ was added. The matrix of the experiments conducted at different mass ratios is listed in Table 4-3.
Chapter 4 – CCSM process route at low solid to liquid ratio

Table 4-3: Matrix of the molar ratios Mg: NH₄HCO₃: NH₃ and carbonation efficiency (For experiments 3 and 4, ammonia water was added at ambient temperature, therefore double ammonium magnesium was precipitated. For all the other experiments, ammonia water was added when the temperature reached 60 °C)

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>NH₄HCO₃</th>
<th>NH₃</th>
<th>Carbonation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>25.5</td>
</tr>
<tr>
<td>Experiment 1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>71.6</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>1</td>
<td>3</td>
<td>0.5</td>
<td>53.0</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>1</td>
<td>3.5</td>
<td>1.5</td>
<td>46.5</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>1</td>
<td>4</td>
<td>1.5</td>
<td>53.4</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>41.5</td>
</tr>
<tr>
<td>Experiment 6</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>77.9</td>
</tr>
<tr>
<td>Experiment 7</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>89.9</td>
</tr>
<tr>
<td>Experiment 8</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>95.9</td>
</tr>
<tr>
<td>Experiment 9</td>
<td>1</td>
<td>4</td>
<td>1.5</td>
<td>91.5</td>
</tr>
<tr>
<td>Experiment 10</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>91.3</td>
</tr>
</tbody>
</table>

The carbon content of the product 3 was measured by a TGA Q500 analyzer. The temperature programme was from 30 °C to 950 °C at 20 °C/min under nitrogen atmosphere. The carbonation efficiency from soluble magnesium sulphate to hydromagnesite is defined as follows:

\[
\text{Carbonation efficiency (\%) = } \frac{\text{CO}_2 \text{ content (wt\%)} \times 24 \times m_3}{44 \times c_2 \times V_2} \times 100
\]

Equation 4-8

Where \( \text{CO}_2 \text{ content (wt. \%)} \) is the weight loss of product 3 during the temperature range from 300 °C to 500 °C corresponding to carbonate decomposition from the TGA studies (Huijgen et al., 2015).
2006). $m_3$ is the mass (grams) of product 3 from carbonation experiment, $c_2$ is the magnesium concentration in filtrate 2 from ICP-AES and $V_2$ is the volume of filtrate 2, 24 and 44 is the total molecular weight of Mg and CO₂ in hydromagnesite.

### 4.2.1.4 Thermal decomposition of (NH₄)₂SO₄

The filtrate 3 was evaporated by using a rotary evaporator at 60 °C for 15 mins. The solid collected from the rotary evaporator is referred to as product 4. The regeneration of NH₄HSO₄ and NH₃ was conducted by thermal decomposition of product 4 in an oven at 330 °C and the reaction is presented in Eq. 4-9:

$$\text{(NH}_4\text{)}_2\text{SO}_4(s) \rightarrow \text{NH}_4\text{HSO}_4(s) + \text{NH}_3(g) \uparrow$$

Equation 4-9

The thermal decomposition of product 4 was characterised by performing thermal gravimetric studies using a TGA Q500 in the temperature range of 30-530 °C under nitrogen atmosphere. The temperature programme was as follows: from 30 °C to 230 °C at 10 °C/min, hold for 10 mins at 230 °C, up to 330 °C at 10 °C/min, hold for 10 mins at 330 °C and finally up to 530 °C at 10 °C/min. The choice of these three heating steps was to avoid the mixture of products decomposition. In order to ascertain the decomposition from the TGA analysis of product 4, pure (NH₄)₂SO₄ and NH₄HSO₄
were also characterised by TGA analysis using the same heating procedure.

4.2.2 Results and discussion

4.2.2.1 Preparation of magnesium salts solutions from serpentine using NH₄HSO₄

The results from the ICP-AES analyses (Table 4-4) of the filtrate 1 solutions from all experiments show that high concentrations of Mg and Fe were dissolved, while most of the Si remained in the serpentine. The dissolution efficiency is calculated as the percentage of dissolved elements in filtrate 1 solution over elements in original mineral serpentine. The values for the original mineral serpentine are also reported in Table 4-4. Taking experiment 3 as an example, using the data in Table 4-4, the dissolution efficiency of Mg from serpentine was 91 % using 1.4 M NH₄HSO₄ at 100 °C for 2 h. The dissolution efficiency of other elements for experiment 3 is presented in Figure 4-10.
Figure 4-10: Dissolution efficiency of different elements after serpentine dissolution by NH₄HSO₄ (Experiment 3, 100 °C, 2 h)

It was found that 96 % Fe, 17 % Si, 100 % Ni and Mn, and some Ca, Zn, Cu and Al were also dissolved from serpentine. This result is consistent with the previous dissolution studies, where the dissolution efficiencies of Mg, Fe and Si from serpentine were 95 %, 83 % and 17 %, respectively, under the same experimental conditions (Section 4.1.2). The dissolution efficiencies for Ni, Mn, Ca, Zn, Cu and Al were very similar for all experiments conducted. As high purity MgCO₃ is desired, all the other cations are considered as impurities, with Fe and Si being identified as the main impurities and are reported in Table 4-4. In conclusion, Mg was removed from serpentine, leaving behind amorphous silica. This can be explained by incongruent dissolution of Mg and Si as previously discussed (Section 4.1.2), where chemical reaction with product layer diffusion
control was found to be the rate limiting step of serpentine dissolution in NH₄HSO₄.

Table 4-4: Summary from ICP-AES analyses of original mineral serpentine and filtrate samples produced in the experiments (units: mg/l).

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Dissolution</th>
<th>Carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serpentine</td>
<td>11970.0</td>
<td>3680.0</td>
<td>2050.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment 1</td>
<td>Filtrate 1</td>
<td>8851.0</td>
<td>505.2</td>
<td>1179.0</td>
<td>73.8</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>8252.0</td>
<td>74.1</td>
<td>600.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>2347.0</td>
<td>11.2</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Experiment 2</td>
<td>Filtrate 1</td>
<td>9052.0</td>
<td>447.0</td>
<td>1284.0</td>
<td>75.4</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>8290.0</td>
<td>110.0</td>
<td>244.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>3219.0</td>
<td>20.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Experiment 3</td>
<td>Filtrate 1</td>
<td>10957</td>
<td>621.0</td>
<td>1964.0</td>
<td>91.3</td>
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<tr>
<td></td>
<td>Filtrate 2</td>
<td>9629.0</td>
<td>98.0</td>
<td>337.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>2983.0</td>
<td>5.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Experiment 4</td>
<td>Filtrate 1</td>
<td>8497.0</td>
<td>399.0</td>
<td>1131.0</td>
<td>70.8</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>7840.0</td>
<td>105.0</td>
<td>187.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>2914.0</td>
<td>21.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Experiment 5</td>
<td>Filtrate 1</td>
<td>9550.0</td>
<td>411.0</td>
<td>1133.0</td>
<td>79.6</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>8690.0</td>
<td>154.0</td>
<td>145.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>4097.0</td>
<td>35.2</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Experiment 6</td>
<td>Filtrate 1</td>
<td>8261.0</td>
<td>478.0</td>
<td>1175.0</td>
<td>68.8</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>7866.0</td>
<td>132.0</td>
<td>206.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>1625.0</td>
<td>19.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Experiment 7</td>
<td>Filtrate 1</td>
<td>8960.0</td>
<td>463.0</td>
<td>1084.0</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>8123.0</td>
<td>98.0</td>
<td>133.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>865.0</td>
<td>15.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Experiment 8</td>
<td>Filtrate 1</td>
<td>8487.0</td>
<td>422.0</td>
<td>1064.0</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>7679.0</td>
<td>68.5</td>
<td>97.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>889.2</td>
<td>6.9</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Experiment 9</td>
<td>Filtrate 1</td>
<td>6311.0</td>
<td>289.5</td>
<td>738.3</td>
<td>52.6</td>
</tr>
<tr>
<td></td>
<td>Filtrate 2</td>
<td>5784.0</td>
<td>58.5</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>589.8</td>
<td>12.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Experiment 10</td>
<td>Filtrate 1</td>
<td>8264.0</td>
<td>311.0</td>
<td>1135.0</td>
<td>68.9</td>
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<tr>
<td></td>
<td>Filtrate 2</td>
<td>7794.0</td>
<td>82.5</td>
<td>98.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate 3</td>
<td>780.6</td>
<td>8.5</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>
Finally, in order to compare this work with Pundsack’s (1967), carbonation experiments were carried out following his procedure. CO₂ was bubbled into the prepared high Mg concentration solution from serpentine and excess ammonia water was added to adjust the pH until the value of 9. Only 35 % carbonation efficiency was obtained. In comparison, the carbonation efficiency from this work can achieve a maximum of 95.9 % (experiment 8) due to the faster reaction rate between NH₄HCO₃ and Mg.

4.2.2.2 pH regulation and removal of impurities

It was found that after adding ammonia water (35 wt. %) to the filtrate 1 solution, some particles precipitated. After filtering and drying overnight at 105 °C, the resulting solid and filtrate were labelled as product 2 and filtrate 2 (Figure 3-1), respectively. Ammonia water (35 wt. %) was then added to filtrate 2 until the pH value reached 8.5. Table 4-5 presents the XRF results of the products and the mass balance for Mg, Si and Fe will be discussed in Section 4.2.2.6. Taking experiment 7 as an example, it can be seen that product 2 consists of 19 % Fe, 8 % Si and 3 % Mg. The XRD pattern of product 2 for the experiment 7 (Figure 4-11) identified double ammonium salts, (NH₄)₂Fe₂(SO₄)₂•6H₂O, (NH₄)₂Mg₂(SO₄)₂•6H₂O and (NH₄)₂Zn₂(SO₄)₂•6H₂O, to be the major phases. The presence of these double ammonium salts resulted from the excess of ammonia water. Hot water flashing can
decompose these double ammonium salts into ammonium sulphate and insoluble hydroxide salts (Everingham, 1976).

Table 4-5: XRF analyses of solids produced in the experiments (units: wt. %), and the CO₂ content from TGA analysis. The mass balance for Mg, Si and Fe for the three products in relation to patent serpentine is also presented as mass ratio (%).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Serpentine</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
<th>Experiment 4</th>
<th>Experiment 5</th>
<th>Experiment 6</th>
<th>Experiment 7</th>
<th>Experiment 8</th>
<th>Experiment 9</th>
<th>Experiment 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product 1</td>
<td>23.9</td>
<td>10.5</td>
<td>9.8</td>
<td>11.8</td>
<td>12.5</td>
<td>11.7</td>
<td>11.7</td>
<td>12.5</td>
<td>11.7</td>
<td>12.5</td>
<td>11.7</td>
</tr>
<tr>
<td>Mass ratio (%)</td>
<td>100</td>
<td>26.2</td>
<td>24.6</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
<td>29.2</td>
</tr>
<tr>
<td>Mg</td>
<td>100</td>
<td>86.3</td>
<td>43.6</td>
<td>83.1</td>
<td>42.4</td>
<td>42.8</td>
<td>88.8</td>
<td>42.4</td>
<td>42.8</td>
<td>42.4</td>
<td>42.4</td>
</tr>
<tr>
<td>Si</td>
<td>10.0</td>
<td>5.6</td>
<td>5.3</td>
<td>3.0</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Fe</td>
<td>5.7</td>
<td>20.4</td>
<td>21.2</td>
<td>27.5</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
<td>21.3</td>
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<tr>
<td>Mass ratio (%)</td>
<td>100</td>
<td>22.2</td>
<td>6.3</td>
<td>11.7</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
<td>11.0</td>
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</tr>
<tr>
<td>CO₂</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4-4 clearly shows that the concentration of Fe in filtrate 2 decreased significantly compared to filtrate 1. This decrease of Fe concentration indicates that Fe precipitates. The results of XRF, ICP-
AES and XRD analysis in Tables 4-4 and 4-5 and Figure 48 are consistent with this observation, indicating that a high Fe content precipitate was produced. Some Mg also precipitated during this procedure, causing filtrate 2 to contain 5% less dissolved magnesium than filtrate 1. All experiments presented similar XRF, ICP-AES and XRD results on product 2 and filtrate 2 samples. Moreover, the Fe content of product 2 was measured by XRF to be between 16 wt. % to 28 wt. % (Table 4-5). Furthermore, the picture of product 2 could be seen in Figure 4-11.

Figure 4-11: XRD pattern of product 2 of experiment 7.

4.2.2.3 Precipitation studies

10 precipitation experiments were carried out at different mass ratio of Mg:NH₃:NH₄HCO₃, as shown in Table 4-3. The observations and
findings from these 10 experiments were similar in terms of carbonation and morphology of the product 1, 2, 3 and 4 (Pictures of products can be seen in Figure 4-12). Taking product 3 of experiment 7 as an example, Figure 4-13 shows the presence of magnesium carbonate. This corresponds to the decrease of Mg concentration in solution for ICP-AES results presented in Table 4-4.

Figure 4-12: Pictures of original mineral sample and products in the process route. (A. patent serpentine; B. product 1; C. product 2; D. product 3; E. product 4)

Figure 4-13 shows the Mg concentration variation with time and temperature for experiment 7. The starting time is recorded when heating starts. It can be seen that the pH of filtrate 2 decreased from 8.5 to 7.3 when the temperature increases during the first 20 mins. When the temperature reached 60 °C, NH₄HCO₃ was added and the pH increased slightly to 7.6. No precipitate was formed
before adding NH₄HCO₃. The concentration of magnesium started to 
drop when the temperature went up to 70°C at 25 minutes. In the 
following 5 mins, half of the Mg ions precipitated at a very high rate 
of 33.3 mmol/min. When the temperature was stabilised at 85 °C 
after the 40 minutes, the pH became stable and the Mg precipitated 
at a constant rate of 7.9 mmol/min. After 25 mins counted from the 
addition of NH₄HCO₃, the concentration of Mg in solution became 
constant and finally went below 1000 mg/l.

Figure 4-13: Temperature, time, pH and concentration of Mg in solution during 
the course of a typical carbonation experiment (Experiment 7)

For product 3 of experiment 7, the XRD pattern of product 3 (Figure 
4-14) showed that the Mg precipitated as hydromagnesite, 
Mg₅(CO₃)₄(OH)₂•4H₂O. Combining the results from XRF of product 3 
(Table 4-5) and ICP-AES of filtrate 3 (Table 4-4), it can be
concluded that product 3 is a 80% purity hydromagnesite with only 0.79 wt. % of Fe and 0.29 wt. % Si.

---

Figure 4-14: XRD pattern of product 3 of experiment 7

The carbon content of product 3 can be calculated from the TGA profiles (Figure 4-15 (a)), as described in the experimental methods (Section 4.2.1.3). All samples presented one carbonate phase according to the XRD studies. Therefore, the mass of the identified carbonate phase was estimated based on the corresponding weight loss from the TGA studies. As an example, Figure 4-15 (a) shows two peaks, where the first peak below 250 °C is about 12 wt. % and corresponds to the release of crystal water (Huijgen et al., 2006). The second peak located between 250 °C to 500 °C accounts for 37 wt. % and is due to the decomposition of hydromagnesite (Hänchen et al., 2008). Finally, based on the CO₂ content (Table 4-5) and the
Mg concentration in filtrate 2 (Table 4-4), it can be calculated that the carbonation efficiency of experiment 7 is 90%.

![TGA profiles of product 3 and product 4 from experiment 7, NH₄HSO₄ and (NH₄)₂SO₄](image)

**Figure 4-15: TGA profiles of product 3 and product 4 from experiment 7, NH₄HSO₄ and (NH₄)₂SO₄**

**Improving carbonation by adding NH₃**

During the carbonation step, the Mg ions firstly react with HCO₃⁻ to form Mg(HCO₃)₂ (Eq. 4-11) that then thermally decomposes into insoluble nesquehonite at above 70 °C, followed by the transformation of nesquehonite into hydromagnesite (Eq. 4-8). It must be pointed out that in the thermal decomposition reaction of

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Mg(HCO₃)₂ into MgCO₃·3H₂O (Eq. 4-12), 1 mole of Mg(HCO₃)₂ is converted into 1 mole of insoluble MgCO₃·3H₂O and 1 mole of CO₂. This means that the maximum stoichiometry carbonation efficiency from soluble Mg(HCO₃)₂ into precipitated MgCO₃·3H₂O is only 50%.

As an example, in the preliminary experiment where no NH₃ was used (Table 4-3), the carbonation efficiency was only 25.5%. However, the joint use of ammonia water and NH₄HCO₃ can improve the carbonation as described by the reactions presented in equations 4-10 – 4-17:

\[
\text{MgSO}_4(aq) + \text{NH}_4\text{HCO}_3 \rightarrow \text{Mg(HCO}_3)_2(aq) + \text{NH}_4\text{SO}_4(aq)
\]

Equation 4-10

\[
\text{Mg(HCO}_3)_2(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{MgCO}_3\cdot3\text{H}_2\text{O}(s) \downarrow + \text{CO}_2(g) \uparrow
\]

Equation 4-11

\[
\text{NH}_3(g) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4\text{HCO}_3(aq)
\]

Equation 4-12

\[
\text{NH}_3(g) + \text{NH}_4\text{HCO}_3(aq) \rightarrow (\text{NH}_4)_2\text{CO}_3(aq)
\]

Equation 4-13

\[
\text{MgSO}_4(aq) + (\text{NH}_4)_2\text{CO}_3(aq) + 3\text{H}_2\text{O}(l) \rightarrow \\
\text{MgCO}_3\cdot3\text{H}_2\text{O}(s) \downarrow + (\text{NH}_4)_2\text{SO}_4(aq)
\]

Equation 4-14
Ammonia captures CO$_2$ to produce NH$_4$HCO$_3$ (Eq. 4-12), as known in CO$_2$ capture technology (Zhang Yun, 2003; Kim et al., 2008). Ammonia can convert NH$_4$HCO$_3$ into (NH$_4$)$_2$CO$_3$ (Eq. 4-13), which can directly produce MgCO$_3$ (Eq. 4-14). Ammonia can also react with MgSO$_4$ to form insoluble Mg(OH)$_2$ when the pH value is above 10, as shown in equation 4-15 (Teir et al., 2007b). Once the CO$_2$ is released from the decomposition of Mg(HCO$_3$)$_2$ (Eq. 4-11), Mg(OH)$_2$ can react with CO$_2$ to form Mg(HCO$_3$)$_2$ (Eq. 4-16). Moreover, the Mg(OH)$_2$ can also react with Mg(HCO$_3$)$_2$ directly to precipitate MgCO$_3$ (Eq. 4-17). Therefore, the carbonation efficiency can be improved by addition of ammonia water to the high Mg concentration solution. This is the case of experiments 1 - 10, where ammonia water was added in all experiments, the carbonation efficiency reached 95.9 % (Table 4-3).
Prevention of precipitation of magnesium ammonium carbonate

The precipitation of magnesium ammonium carbonate (MgCO₃•(NH₄)₂CO₃•4H₂O) can reduce the carbonation efficiency, as MgCO₃•(NH₄)₂CO₃•4H₂O is generated from the reaction of NH₃ and NH₄HCO₃ with Mg ions at temperatures below 60 °C (Eq. 4-18) (Cesca, 1971). It can be seen from Figure 4-16 that the Mg concentration decreased until the temperature reached 60 °C during the first 15 mins. However, MgCO₃•(NH₄)₂CO₃•4H₂O decomposes quickly to produce Mg(HCO₃)₂, and NH₃ gas when the temperature is above 60 °C (Eq. 4-19).

![Graph showing the change in Mg concentration, temperature, and pH over time](image)

Figure 4-16: Temperature, time, pH and concentration of Mg in solution during the course of a carbonation experiment when double ammonium carbonate precipitates (Experiment 4)
MgSO₄(aq) + NH₄HCO₃(aq) + NH₃ • H₂O
+3H₂O → MgCO₃ • (NH₄)₂ CO₃ • 4H₂O(s) ↓

Equation 4-18

MgCO₃ • (NH₄)₂ CO₃ • 4H₂O(s) →
Mg(HCO₃)₂(aq) + 2NH₃(g) ↑ +5H₂O(l)

Equation 4-19

It can be seen from equation 4-19 that NH₃ is produced and this would decrease the carbonation efficiency due to shortage of NH₃. Therefore, the precipitation of MgCO₃ • (NH₄)₂ CO₃ • 4H₂O should be prevented in order to maintain high carbonation efficiency. Taking experiment 4 as an example, the precipitation of MgCO₃ • (NH₄)₂ CO₃ • 4H₂O is indicated on the top left corner of Figure 4-16. When the temperature increased above 60 °C, the Mg concentration increases, indicating the decomposition of MgCO₃ • (NH₄)₂ CO₃ • 4H₂O. The subsequent decrease of Mg ions after 30 minutes indicates the precipitation of hydromagnesite. The carbonation efficiency of experiment 4 is as low as 53.4 % due to the shortage of NH₃ gas which escaped from the reaction system during the thermal decomposition of MgCO₃ • (NH₄)₂ CO₃ • 4H₂O. Comparing experiments 4 and 9 using the same mass ratio of Mg-NH₄HCO₃-NH₃ and same experimental conditions, the carbonation efficiency decreased from 91.5 % to 53.4 % when there was
precipitation of MgCO$_3$•(NH$_4$)$_2$CO$_3$•4H$_2$O (Table 4-3). Therefore, in order to prevent low carbonation efficiency caused by precipitation of magnesium ammonium carbonate, NH$_4$HCO$_3$ should preferably be added into solution above 60°C.

4.2.2.4 Thermal decomposition of (NH$_4$)$_2$SO$_4$

Product 4 is obtained from the carbonation step by evaporating the filtrate 3 (Figure 3-1). The product 4 was used to generate NH$_3$ and NH$_4$HSO$_4$ by thermal decomposition in oven at 330 °C for 20 mins. The released gas (NH$_3$) was collected using water to produce ammonia water. The solid residue after heating was NH$_4$HSO$_4$. These results were verified by conducting TGA studies, as described here. Studies of thermal conversion of ammonium sulphate to ammonium bisulphate can be found in several patents (Brennan, 1975; Bretherick, 1975 and Montgomery, 1962). As an example in this work, the thermal decomposition of product 4 from experiment 7, as studied by TGA, is shown in Figure 4-15 (b). The TGA profile shows two peaks, where the first weight loss below 330 °C is about 21.7 wt. %, corresponding to the release of NH$_3$ and the formation of NH$_4$HSO$_4$. The second weight loss between 350 °C and 500 °C is 75.8 wt. % and is due to further decomposition of NH$_4$HSO$_4$. In total, the weight loss of product 4 is 97.5 wt. %, and the residual 2.5 wt % is due to the presence of MgSO$_4$ which did not react during carbonation. The TGA profile of pure (NH$_4$)$_2$SO$_4$ (purchased from
Fisher Scientific) is presented in Figure 4-15 (c), where two peaks appear at the same temperature range as those for the TGA profile of product 4 (Figure 4-15 (b)). The TGA curve of NH₄HSO₄ is presented in Figure 4-15 (d) and shows only one peak between 330 °C and 500 °C due to decomposition into NH₃, H₂O and SO₃. The NH₄HSO₄ and NH₃ regeneration efficiency from (NH₄)₂SO₄ has been reported to be nearly 97 % (Brennan, 1975; Bretherick, 1975 and Montgomery, 1962). In this work, the regeneration efficiency of NH₄HSO₄ and NH₃ from product 4 is 95 %. These TGA results indicate that the reaction of thermal decomposition of (NH₄)₂SO₄ should not be conducted above 330 °C to avoid further decomposition, since NH₄HSO₄ can decompose into NH₃, SO₃ and H₂O above 330 °C.

4.2.2.5 The effect of mass ratio of Mg-NH₄HCO₃-NH₃ to carbonation

The mass ratio of Mg:NH₄HCO₃:NH₃ is the key factor controlling carbonation efficiency. The stoichiometric mass ratio of Mg:NH₄HCO₃ is 1:2, but experiment 5 shows that when the stoichiometric ratio 1:2 is used, the carbonation efficiency is only 41.5 % (Table 4-3). Increasing the Mg: NH₄HCO₃ ratio can improve the carbonation efficiency, as presented in Table 4-3, where the carbonation efficiency increase to 72%, 78 % and 90 %, when the ratio of Mg:NH₄HCO₃:NH₃ is 1:3, 1:4 and 1:5, respectively. This can
be explained by the thermal decomposition of NH₄HCO₃ (Eq. 4-20), and reported by Zhang et al. (2003). NH₄HCO₃ can regenerate NH₃ and release CO₂ when the temperature is above 70 °C. The two reactions (Eq. 4-6 and Eq. 4-20) compete for NH₄HCO₃, and this may cause low carbonation efficiency due to the shortage of NH₄HCO₃.

\[
NH₄HCO₃(aq) \rightarrow NH₃(g) \uparrow +CO₂(g) \uparrow +H₂O(l)
\]

Equation 4-20

Moreover, adding ammonia water can increase the carbonation efficiency, as discussed in Section 4.2.2.3. In comparison with the preliminary experiment, experiments 1 and 2 show that carbonation efficiencies increase from 25.5 % to 53 % and then 71.6 % when the mass ratio of Mg: NH₄HCO₃: NH₃ increases from 1:3:0 to 1:3:0.5 and then 1:3:1, respectively. This trend was also found in experiments 6, 8 and 9. However, when the ratio increases to 1:4:3, the carbonation efficiency does not increase any further.

In this work, the optimum mass ratio of Mg: NH₄HCO₃: NH₃ was determined. A 3D graph (Figure 4-17) is used to show the relationship of the four variables, including mass of Mg, mass of NH₄HCO₃, mass of NH₃ and carbonation efficiency. Figure 4-17 clearly shows that a low summit of 71.6 % carbonation efficiency appears when the mass ratio of Mg: NH₄HCO₃: NH₃ is 1:3:1 and a
high summit of 95.9% carbonation efficiency appears when the mass ratio of Mg:NH₄HCO₃:NH₃ is 1:4:2. Continuously increasing both NH₄HCO₃ and NH₃ does not result in a further significant rise of the carbonation efficiency. However, an optimum amount of NH₄HCO₃ and NH₃ are needed to achieve the highest carbonation efficiency due to the loss of CO₂ and NH₃ in an open system.

![Figure 4-17: Plotted data of carbonation efficiency vs. molar ratio of Mg-NH₄HCO₃-NH₃](image)

The process studied here presents higher carbonation efficiency than that reported by other researchers' work (Gerdemann et al., 2007; Teir et al., 2007b). For example, in Gerdemann et al. work (2007), 64 % carbonation efficiency was achieved in direct carbonation of heat treated serpentine at 155 °C and 115 bars in 0.64 M NaHCO₃ and 1 M NaCl solution. In Teir's work (2007b), the
conversion of magnesium ions to hydromagnesite was 94% using HNO₃ and 79% using HCl at pH value of 9 with addition of NaOH (1.1 g NaOH / g precipitate). In this study, the highest carbonation efficiency is 95.9% at 85 °C and ambient pressure within 30 mins by using NH₄HCO₃ and NH₃.

4.2.2.6 Mass balance

To examine the distribution of Mg released from serpentine in the solids formed in the process (products 1, 2 and 3) and filtrate 3, a mass balance was constructed based on the XRF and ICP-AES and the results are presented in Fig 4-18. It can be seen that most of the Mg from the original mineral serpentine ends up in the precipitated hydromagnesite (product 3). The use of additives at the optimized ratio to improve carbonation conversion results in less Mg remaining in the final solution after carbonation (filtrate 3, experiments 6-10). Longer dissolution times may leach more Mg from the serpentine and therefore reduce the amount present in product 1 (Park and Fan, 2004). In addition, the presence of Mg in product 2 can be minimised by hot water washing (Everingham, 1976). The mass balance for Si and Fe is presented in Table 4-5, as the concentration of these two elements in filtrate 3 is very small. It can be seen that most of the Si remains in the residue after dissolution (product 1). In contrast, most of the Fe ends up in both the residue after dissolution (product 1) and the precipitate after
pH-swing (product 2) depending on the dissolution efficiency. The concentration of Si and Fe in filtrate 3 is negligible (Table 4-4). The total mass balances of Mg from filtrate 3 and product 1, 2 and 3 are 99-100% of the mass of Mg in original mineral is accounted for.

![Mass balance of Mg in product 1, 2 and 3 and filtrate 3 in relation to serpentine](image)

Figure 4-18: Mass balance of Mg in product 1, 2 and 3 and filtrate 3 in relation to serpentine

Considering that the dissolution efficiency can achieve 90% at 100 °C and 2 h and that the carbonation efficiency is 95.9% when the molar ratio of Mg:NH₄HCO₃:NH₃ is 1:4:2, the net conversion of serpentine to hydromagnesite is calculated to be 86.3%. Taking this into account, about 2.63 t of serpentine, 8.48 t of NH₄HSO₄, 2.31 t of NH₄HCO₃ and 0.5 t of NH₃ are required to sequester 1 t CO₂, and 2.95 t of hydromagnesite is produced. If the 95% regeneration efficiency of NH₄HSO₄ and NH₃ is considered, 0.12 t of
NH₄HSO₄ and 0.025 t of NH₃ is consumed to sequester 1 t CO₂. All the chemicals used in this process can be obtained from (NH₄)₂SO₄. Considering the current price for (NH₄)₂SO₄ is 90 US$/t (ICIS, 2010), the cost for make-up chemicals of this process is estimated to be 18 US$/t CO₂. However, in Teir’s work (2007b), the cost for make-up chemicals is 1300 US$/t CO₂ when using HCl and 1600 US$/t CO₂ when using HNO₃. Moreover, the cost could be reduced by using high solid/liquid ratio and this will be the focus of future work.

**4.2.3 Summary**

In the Section 4.2, the precipitation of hydromagnesite from prepared high Mg concentration solution by using NH₃ and NH₄HCO₃ and the regeneration of NH₃ and NH₄HSO₄ were studied. In conclusion, pure hydromagnesite can be produced from serpentine with regenerated ammonium salts with a net conversion of 86.3%. Amorphous silica can be obtained from the dissolution step. By-products with maximum 27.5 wt. % Fe content were obtained from the pH regulation and removal of impurities step. The additives used, NH₄HSO₄ and NH₃, can be regenerated by thermal decomposition of (NH₄)₂SO₄ at 330 °C. The addition of ammonia water before carbonation could significantly improve the carbonation efficiency. It must be pointed out that NH₄HCO₃ should be added into solution after 60 °C to prevent the production of magnesium ammonium carbonate. The mass ratio of Mg:NH₄HCO₃:NH₃ is the key factor to
control the carbonation efficiency, and it was found that when the mass ratio of Mg:NH₄HCO₃:NH₃ was 1:4:2, the carbonation efficiency achieved 95.9 %. From the TGA studies, the regeneration efficiency of NH₄HSO₄ in this process was found to be 95 %. According to the mass balance, about 2.63 t of serpentine, 0.12 t of NH₄HSO₄, 2.31 t of NH₄HCO₃ and 0.025 t of NH₃ are required to sequester 1 t CO₂, and 2.95 t of hydromagnesite is produced.
Chapter 5. CCSM Process route at high solid to liquid ratio condition

In Chapter 4, the author discussed the CCSM process route at low solid to liquid ratio condition (50 g/l) using recyclable ammonium salts, where 90% dissolution efficiency at 90 °C for 3 h, and 90% carbonation efficiency at 80 °C for 1h were achieved. Based on these results and the used solid to liquid ratio (50 g/l), 50-56 t of water is required to sequester 1 t CO₂. Since water evaporation is the most energy intensive step in the process (typical energy consumption for mechanical vapour recompression (MVR) evaporator system is 10-36 kWh/t evaporated water (Karasek, 2010), the water usage need to be minimised to make this process economically feasible. Therefore, the CCSM process was investigated at high solid liquid ratio (above 200 g/l). The process was described in Section 3.1.2 and the schematic of the process is presented in Figure 3-2. In this section, the autoclave pressure reactor was used to solve problems such as volume expansion and the loss of ammonia vapour. The effects of using different solid to liquid ratios on the dissolution efficiency and carbonation conversion were investigated. The comparison of carbonation conversions using different ammonium salts, the amount of residual NH₄HSO₄ after
dissolution and the pH increase were studied. Finally, the mass balance of all streams is reported.

5.1 Experimental methods

5.1.1 Dissolution of serpentine using recyclable ammonium salts at high solid/liquid ratio

In Section 3.4, the author showed that NH$_4$HSO$_4$ is suitable for dissolving magnesium from serpentine, as presented in Eq. 4-2.

Magnesium sulfate's solubility in water is reported to be 33.7 g/100 g water at 20 °C and increased to 52.9 g/100 g water at 90 °C (Solubility Database, 2011). Therefore, magnesium sulfate (MgSO$_4$) would precipitate in the dissolution of serpentine using NH$_4$HSO$_4$ when the solid to liquid ratio is above 280 g/l. However, MgSO$_4$ was found to precipitate when the solid to liquid ratio was above 100 g/l (Section 4.1.6). This is explained as the solubility of MgSO$_4$ is lower in a mixture solution than in pure water solution due to the activity of other dissolved species, such as NH$_4^+$ and SO$_4^{2-}$ and HSO$_4^-$. In this study, solid to liquid ratio values of 200 g/l and 300 g/l were used.

In this study, the same serpentine sample with particle size fraction between 75-150 μm was used as in Chapter 4. The dissolution

---

\[ 33.7 \text{ g/100 g water} \times 1000\text{g water} \times \frac{24}{120/24} \times 24\% \text{, 1000 g water is 1 litre water, 24 and 120 is molecular weight of Mg and MgSO}_4, 24\% \text{ is the weight \% of Mg in serpentine, assuming 100 \% dissolution efficiency} \]
experiments were carried out in a stirred 300 ml T316 stainless steel autoclave reactor from Parr Instrument Company. The reactor system (shown in Figure 5-1) includes a heating system with heating mantel, and a temperature control box (Parr 4843 controller) to accurately maintain a stable heating environment from ambient to 225°C, mechanical stirring and a cooling water system. The solutions were mixed by using mechanical stirring. A pressure of 1 bar during the experiment was generated due to the water vapour from solution.

![Figure 5-1: Schematic diagram of autoclave reactor used in this study.](image)

The concentration of NH₄HSO₄ in this study was established based on the stoichiometric amount, where 2 parts of NH₄HSO₄ are consumed to dissolve 1 part of Mg from serpentine. For example, 40 g of serpentine (containing 24 wt % of magnesium) required ammonium bisulfate as follows:
Therefore, 4 mol/l \( \text{NH}_4\text{HSO}_4 \) was used for experiments where the solid to liquid ratio was 200 g/l. Thus 6 mol/l \( \text{NH}_4\text{HSO}_4 \) was used for the experiments where the solid to liquid ratio was 300 g/l.

The matrix of dissolution experiments conducted at different conditions is listed in Table 5-1. In order to compare the dissolution efficiency when using different types of reactors (glass and autoclave), two experiments were conducted using the glass reactor for the two solid to liquid ratios. The same procedure was used as presented in Section 4.1.1 for these two experiments. Typical dissolution experiments in the autoclave reactor were performed as follows. A serpentine sample was placed into a vessel with 200 ml \( \text{NH}_4\text{HSO}_4 \) solution at the corresponding concentration depending on the solid to liquid ratio used. The reactor was then sealed and the stirring was started at the speed of 800 rpm. Once reaching 100 °C, the reaction time was started for 3 h. At the end of the experiment, the vessel was cooled down quickly to room temperature by immersing the vessel in an ice bath. Once the reactor was opened, the slurry was washed and transferred into a 1500 ml glass beaker, where Millipore water was used to dissolve the precipitated MgSO_4_. After 30 mins, the slurry was filtered using a 0.45 µm syringe filter.
unit. The filtrate was prepared in a 10% HNO₃ solution for Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) analyzer for determining the concentrations of Mg, Ca, Fe, Al and Si.

Table 5-1: Matrix of dissolution experiments at different conditions.

<table>
<thead>
<tr>
<th>Expt no.</th>
<th>reactor</th>
<th>Solid/liquid ratio (g/l)</th>
<th>Stirring</th>
<th>Sample weight (g)</th>
<th>Conc. of NH₄HSO₄ (mol/I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>glass</td>
<td>200</td>
<td>1500 rpm</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>D2</td>
<td>glass</td>
<td>300</td>
<td>1500 rpm</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>D3</td>
<td>autoclave</td>
<td>200</td>
<td>mechanical</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>D4</td>
<td>autoclave</td>
<td>300</td>
<td>no</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>D5</td>
<td>autoclave</td>
<td>300</td>
<td>mechanical</td>
<td>80</td>
<td>6</td>
</tr>
</tbody>
</table>

For the carbonation experiments, the same dissolution experiment procedure as described above was followed to prepare Mg-rich slurry. The reactor vessel was moved to a fume cupboard for pH regulation after dissolution (see Section 5.1.2).

5.1.2 Measuring the amount of residual NH₄HSO₄ and pH regulation

After the dissolution, the pH values of the solution were acidic (0.9~1.2) due to the presence of residual NH₄HSO₄. Because the carbonation reaction is favourable at high pH values, it was necessary to increase the pH of the solution to alkaline values by
adding ammonia water (see Eq. 4-3). The reason for using ammonia water is that the acid/base reaction produces ammonium sulphate, which can be converted back to NH₃ and NH₄HSO₄ in the regeneration step in order to realize the recycling of the additives (Figure 3-2). Some impurities, such as Fe, Al, Cr, Zn, Cu and Mn, can also react with the added ammonia water to produce some solid products (see Eq.4-4 and 4-5).

Typical pH-swing experiments were performed as follows. Ammonia water (35 wt. %) was added into the slurry from the dissolution step until the pH value was neutral. The ammonia water consumed was recorded by reading the scale (ml) on a buret. During this process, the solution was stirred and an in-situ pH probe (Orion 720APlus pH meter) was used to measure the pH value. The residual amount of NH₄HSO₄ in the slurry was determined from the stoichiometric amount of ammonia water consumed in the acid/base reaction. The concentration of residual NH₄HSO₄ in slurry was calculated as follows:

\[
C_r = \frac{1000 \rho (g/ml) \times w\%}{M(g/mol)} \times \frac{V_1(ml)}{V_2(ml)}
\]

Equation 5-2

\(C_r\) is the concentration of residual NH₄HSO₄ in the slurry. \(V_1\) is the volume of the ammonia water used to regulate the pH to neutral. \(V_2\) is the volume of slurry as 200 ml. \(\rho\) is the density of ammonia.
water (0.88 g/ml). w% is the weight percentage of ammonia in ammonia water (35%). M is the molecular weight of ammonia (35 g/mol). The overall uncertainty from the measured data is estimated to be ~1% as determined from the duplicate experiments. The uncertainty stems from errors in four measured quantities, i.e., the evaporation of ammonia water in storage, the loss of slurry, the reading of V₁ on buret and the analysis error of the pH meter.

5.1.3 Production of magnesite using NH₄HCO₃ or (NH₄)₂CO₃

The reaction of the production of magnesite by reacting MgSO₄ with NH₄HCO₃ and (NH₄)₂CO₃ is presented in Eq. 5-3 and 5-4. Once the dissolved aqueous MgSO₄ was consumed in these carbonation reactions, the suspended solid MgSO₄ dissolved into aqueous MgSO₄ (shown in Eq. 5-5) to supply the consumed MgSO₄.

\[
MgSO₄(aq) + 2NH₄HCO₃(aq) + 2H₂O(l) \rightarrow MgCO₃ \cdot 3H₂O(s) \downarrow + (NH₄)₂SO₄(aq) + CO₂(g) \uparrow
\]

Equation 5-3

\[
MgSO₄(aq) + (NH₄)₂CO₃(aq) + 3H₂O(l) \rightarrow MgCO₃ \cdot 3H₂O \downarrow (s) + (NH₄)₂SO₄(aq)
\]

Equation 5-4

\[
MgSO₄(s) \rightarrow MgSO₄(aq)
\]
Chapter 5 – CCSM process route at high solid to liquid ratio

Equation 5-5

\[ 5\text{MgCO}_3 \cdot 3\text{H}_2\text{O}(s) \rightarrow 4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O}(s) \downarrow +10\text{H}_2\text{O}(l) + \text{CO}_2(g) \uparrow \]

Equation 5-6

\[ 4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 4\text{H}_2\text{O}(s) + \text{CO}_2(g) \rightarrow 5\text{MgCO}_3 \downarrow(s) + 4\text{H}_2\text{O}(l) \]

Equation 5-7

The formation of magnesium carbonate species depends on temperature and pressure (Hänchen et al., 2008). Nesquehonite (\text{MgCO}_3\cdot3\text{H}_2\text{O}) can precipitate from aqueous solutions at ambient temperature, as described in Eq. 5-6 and 5-7, while at higher temperatures (50 and 100 °C), nesquehonite is transformed into hydromagnesite (4\text{MgCO}_3\cdot\text{Mg(OH)}_2\cdot5\text{H}_2\text{O}), as presented in Eq. 5-6. For temperatures above 100 °C or high pressure (>20 bar), hydromagnesite is transformed into magnesite (\text{MgCO}_3) as presented in Eq. 5-7 (Sandengen et al., 2008). In this study, magnesite was produced as the experiments were conducted at 80 °C and a pressure above 20 bar.

The pressure in these experiments was caused by the decomposition of \text{NH}_4\text{HCO}_3 and (\text{NH}_4)_2\text{CO}_3. The increase of pressure was accompanied with an increase in temperature and stabilized once the temperature was constant. The reactions of the
decomposition of NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$ are presented in Eq. 5-8 and 5-9.

\[(\text{NH}_4)_2\text{CO}_3(aq) \rightarrow \text{NH}_4\text{HCO}_3(aq) + \text{CO}_2(g)\uparrow\]

Equation 5-8

\[\text{NH}_4\text{HCO}_3(aq) \rightarrow \text{NH}_3(g) + \text{CO}_2(g) + \text{H}_2\text{O}(l)\]

Equation 5-9

After carbonation, the temperature was cooled down and the pressure was decreased with the drop of temperature. The pressure also decreased resulting from the reaction between NH$_3$ and CO$_2$ gases and water (Eq. 5-10 and 5-11).

\[\text{NH}_3(g) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4\text{HCO}_3(aq)\]

Equation 5-10

\[\text{NH}_4\text{HCO}_3(aq) + \text{CO}_2(g) \rightarrow (\text{NH}_4)_2\text{CO}_3(aq)\]

Equation 5-11

For the carbonation experiments, after pH regulation the corresponding mass of NH$_4$HCO$_3$ or (NH$_4$)$_2$CO$_3$ was added. The mass of NH$_4$HCO$_3$ or (NH$_4$)$_2$CO$_3$ was weighed to established the stoichiometric amount according to the carbonation reaction (Equation 5-3 and 5-4). For example, for the 200 g/l solid to liquid ratio, assuming 100% dissolution efficiency, 2 mol/l Mg$^{2+}$ required
2 mol/l \((\text{NH}_4\text{)}_2\text{CO}_3\). The matrix of carbonation experiments conducted at different conditions is listed in Table 5-2.

Table 5-2: Matrix of dissolution experiments at different conditions.

<table>
<thead>
<tr>
<th>Expt. no</th>
<th>Solid liquid ratio (g/I)</th>
<th>Ammonium salts</th>
<th>Conc. of salts (mol/I)</th>
<th>Temperature (°C)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>200</td>
<td>(\text{NH}_4\text{)}_2\text{CO}_3</td>
<td>2</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>300</td>
<td>(\text{NH}_4\text{)}_2\text{CO}_3</td>
<td>3</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>C3</td>
<td>200</td>
<td>\text{NH}_4\text{HCO}_3</td>
<td>2</td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>C4</td>
<td>300</td>
<td>\text{NH}_4\text{HCO}_3</td>
<td>3</td>
<td>80</td>
<td>1</td>
</tr>
</tbody>
</table>

In order to compare the carbonation efficiency using different ammonium salts, the same amount of \text{NH}_4\text{HCO}_3 was used in experiments C3 and C4. After addition of ammonium salts, the vessel was sealed and heated to the required temperature. When the temperature was stabilized, the solution was kept at that temperature for 1 h. At the end of the experiment, the vessel was cooled down to room temperature using an ice bath and the residual pressure was released through a gas outlet valve. The reacted slurry was filtered with 0.45 μm Pall syringe filters and the filtrate is referred to as filtrate 1 (Figure 3-2). The solid residue was dried at 105 °C overnight and is referred to as product 1 (Figure 3-2). The composition of the product 1 was analyzed using XRF and the mineral phases were identified by XRD. The filtrate 1 was acidified.
with HNO₃ for subsequent ICP-AES analysis to measure the concentration of elements such as Mg, Fe and Si.

The carbon content of the product 1 was measured by a Flash EA 1112 series elemental analyzer. The carbon fixation efficiency of the original mineral serpentine to magnesite is defined as follows:

\[
\text{Carbon fixation efficiency (\%) = } \frac{\text{C content (wt\%) \times 24 \times m}}{12 \times m_{\text{batch}} \times w_{Mg}} \times 100
\]

Equation 5-12

Where C content (wt. %) is measured by the elemental analyzer (EA). m is the mass (grams) of product 1 from carbonation experiment, \(m_{\text{batch}}\) is the mass of serpentine sample added. \(w_x\) is the initial weight percentage of mass of element x over the total mass of solid present in the original mineral sample. 24 and 12 are the molecular weight of Mg and C in magnesite, respectively.

5.2 Results and discussion

5.2.1 Dissolution of serpentine using recyclable ammonium salts at high solid/liquid ratio

The dissolution efficiencies of Mg, Si, Fe and Ca from serpentine using NH₄HSO₄ at high solid to liquid ratio (experiments D1-D5) are presented in Figure 5-2.
Figure 5-2: The effect of solid to liquid ratio to dissolution efficiencies of elements from serpentine (D1 and D3 are 200 g/l, D2 and D5 are 300 g/l).

It is found that around 64-72 % Mg was dissolved, while most of Si, Fe and Ca remained in the serpentine. Taking D5 (300 g/l solid to liquid ratio in the autoclave reactor) as an example, the dissolution efficiency of Mg from serpentine was 71.3 % at 100 °C for 3 h. However, only 5.5 % Si, 5.1 % of Fe and 12.3 % of Ca were dissolved in this experiment. This result is different with the previous dissolution studies at low solid to liquid ratio, where the dissolution efficiencies of Mg, Si and Fe from serpentine were 100 %, 17.6 % and 98 %, respectively, under the same temperature and
Chapter 5 – CCSM process route at high solid to liquid ratio

reaction time and using 50 g/l solid to liquid ratio (Figure 4-2 in Section 4.1.2). The decrease of dissolution efficiencies at high solid to liquid ratio is probably due to the precipitated MgSO₄ on the surface of mineral particles. With the progress of serpentine dissolution, the concentration of aqueous MgSO₄ continuously increases. When the concentration of aqueous MgSO₄ exceeds its solubility, the aqueous MgSO₄ precipitate as solid MgSO₄ (Reverse reaction of Eq. 5-5). The solid MgSO₄ precipitates onto to the surface of mineral particles, thus blocking the diffusion of NH₄HSO₄ in to the pore space of mineral particles. In addition, the stoichiometric molar ratio between NH₄HSO₄ and Mg (2:1) used for these dissolution experiments in this section can also cause the decrease of Mg dissolution in comparison with previous dissolution experiments in Section 4.1.2, where the excess mole ratio (2.8:1) was used.

The dissolution efficiency of serpentine is therefore influenced by the solid to liquid ratio used. The comparison of dissolution efficiencies of Mg, Si, Fe and Ca at different solid to liquid ratios (200 and 300 g/l) is also presented in Figure 5-2. It is found that the dissolution efficiencies of all elements increase slightly when the solid to liquid ratio increased from 200 g/l to 300 g/l. For example, the dissolution efficiency of Mg increased from 65.6 % to 71.3 % when using the autoclave reactor and from 66 % to 70.2 % for the experiments conducted in the glass reactor. This may be due the
intensive particle-particle interaction at high solid to liquid ratio. More collision at high solid to liquid ratio may break down particles or remove the product layer, and thus increasing the diffusion of NH₄HSO₄ into the pore space of the mineral particles. The effect of intensive particle-particle interaction at high solid to liquid ratio is probably similar to the effect of internal grinding reported by Park and Fan (2004). It can be seen from Figure 5-2 that the dissolution efficiency using different reactors is very similar. The main experimental difference between both reactors is the pressure, where 1 bar water vapour was obtained in the autoclave reactor. Thus the small pressure increase does not affect the dissolution of elements from serpentine.

In addition, the dissolution efficiency of serpentine is influenced by stirring. The comparison of dissolution efficiencies of Mg, Si, Fe and Ca at different stirring conditions is presented in Figure 5-3. It can be seen that dissolution efficiencies of the experiment with mechanical stirring (D5) is higher than that without stirring (D4) for the same solid to liquid ratio of 300 g/l. This indicates that the effect of stirring is probably similar to the particle-particle interaction, in that removal of the product layer and thus improves the dissolution efficiency (Bearat et al., 2006).
Figure 5-3: The effect of stirring to dissolution efficiencies of elements from serpentine (D1 used 1500 rpm stirring rate, D4 didn’t use stirring and D5 used mechanical stirring).

At high solid to liquid ratio, the deposition of precipitated MgSO$_4$ on the surface of particles was thought to be the main reason for decreasing the dissolution efficiency (see the XRD results of product 1 from dissolution in Figure 5-8). It is believed that this problem can be overcome to some extent by intensive internal grinding (Park and Fan, 2004).

5.2.2 Measuring the amount of residual NH$_4$HSO$_4$ and pH regulation

It was found that after adding ammonia water (35 wt. %) to the slurry from the dissolution step, no particles precipitated. The presence of double ammonium salts ((NH$_4$)$_2$Fe$_2$(SO$_4$)$_2$•6H$_2$O,
(NH₄)₂Mg₂(SO₄)₂•6H₂O and (NH₄)₂Zn₂(SO₄)₂•6H₂O) have been reported in previous Section 4.2.2.2. But in this study, due to the lower dissolution of impurities such as Fe, Ca and other metal elements, the double ammonium salts did not precipitate and the ammonia water reacted with residual NH₄HSO₄ to form (NH₄)₂SO₄ and increased the pH. The residual concentrations of NH₄HSO₄ were measured by titration with ammonia water after the dissolution step. The comparison of initial and residual concentrations of NH₄HSO₄ is presented in Figure 5-4. The concentration of NH₄HSO₄ decreased from 6 mol/l to 1.6-1.7 mol/l at 300 g/l and from 4 mol/l to 1.1-1.2 mol/l at 200 g/l after dissolution. Therefore, around 70-72.8 % of NH₄HSO₄ was consumed in the dissolution step compared to the stoichiometric value of 100 %, probably because of the blockage of the diffusion of NH₄HSO₄ in the pore space of inner fresh mineral caused by the deposition of precipitated MgSO₄.
After regulating the pH value to 7, NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$ were added into the slurry. The pH change of the slurry is presented in Figure 5-5. It is found that the pH increased from 7 to 8.2-8.5 when using (NH$_4$)$_2$CO$_3$ and was constant at the value of 7 when using NH$_4$HCO$_3$ because of the higher alkalinity of (NH$_4$)$_2$CO$_3$ (pH of 1 M solution is around 8.5) than that of NH$_4$HCO$_3$ (pH of 1 M solution is around 7.5). The higher pH value will be helpful for the subsequent carbonation reactions as the CO$_3^{2-}$ ions are dominant when the pH is above 6.5. The CO$_3^{2-}$ ions can directly react with Mg$^{2+}$ to precipitate MgCO$_3$, while HCO$_3^-$ ions firstly react with Mg$^{2+}$ to form Mg(HCO$_3$)$_2$ and then convert into MgCO$_3$ when heated. The amount of NH$_4$HCO$_3$
and \((\text{NH}_4)_2\text{CO}_3\) added is based on the stoichiometric amount required in the carbonation reaction assuming 100% dissolution of Mg ions from the original mineral serpentine. However, only 70% Mg dissolution efficiency was achieved, and therefore, there will be excess of \(\text{NH}_4\text{HCO}_3\) and \((\text{NH}_4)_2\text{CO}_3\) in the carbonation. The excess of \(\text{NH}_4\text{HCO}_3\) and \((\text{NH}_4)_2\text{CO}_3\) can improve the carbonation efficiency, as a high content of reactive component enhances the probability of interaction between molecules.

Figure 5-5: pH change of slurry at high solid liquid ratio condition. (pH A was measured after dissolution, pH B was 7 and measured after pH-regulation, pH C was measured after adding \(\text{NH}_4\text{HCO}_3\) or \((\text{NH}_4)_2\text{CO}_3\) before carbonation and pH D was measured after carbonation.)
5.2.3 Production of magnesite using NH$_4$HCO$_3$ or (NH$_4$)$_2$CO$_3$

Four carbonation experiments were carried out using different solid to liquid ratios of 200 and 300 g/l and different additives of NH$_4$HCO$_3$ and (NH$_4$)$_2$CO$_3$, as shown in Table 5-3. The carbon content of product 1 and Mg concentrations of filtrate 1 from carbonation experiments are presented in Table 5-3 as well. The carbonation efficiency was calculated based on the following equation:

\[
\text{Carbonation efficiency} = \frac{\text{Carbon Fixation efficiency}}{\text{Dissolution efficiency}} \tag{5-13}
\]

Table 5-3: Carbon contain of product 1, Mg concentration of filtrate 1, fixation efficiency, dissolution and carbonation efficiencies in experiment C1-C4.

<table>
<thead>
<tr>
<th>Expt No.</th>
<th>Carbon % (EA)</th>
<th>Mg conc. in filtrate 1 (mol/l)</th>
<th>Fixation efficiency %</th>
<th>Dissolution efficiency %</th>
<th>Carbonation efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>3.3</td>
<td>601.0</td>
<td>44</td>
<td>66</td>
<td>67</td>
</tr>
<tr>
<td>C2</td>
<td>2.8</td>
<td>361.5</td>
<td>47</td>
<td>71</td>
<td>65</td>
</tr>
<tr>
<td>C3</td>
<td>1.3</td>
<td>1238.5</td>
<td>18</td>
<td>66</td>
<td>27</td>
</tr>
<tr>
<td>C4</td>
<td>1.7</td>
<td>530.6</td>
<td>22</td>
<td>71</td>
<td>31</td>
</tr>
</tbody>
</table>

It can be seen from Table 5-3 that the highest fixation efficiency of 47% was achieved for the experiment C2, where the solid to liquid ratio was 300 g/l and using (NH$_4$)$_2$CO$_3$. The fixation efficiency of

\(^{15}\) The carbon fixation and dissolution efficiencies are defined in Equation 5-12 and 4-1, respectively.
experiment C1 is relatively lower than that of C2 of 44 %. However, when NH₄HCO₃ was used for experiment C3 and C4, the fixation efficiency decreased to 18 % and 22 %, respectively. In order to understand the reason for the high fixation efficiency using (NH₄)₂CO₃, the thermodynamic properties of the reactions of MgSO₄ with (NH₄)₂CO₃ and NH₄HCO₃ were determined by using HSC 5.1 software and the results are presented in Table 5-4. The enthalpy of reaction of MgSO₄ with (NH₄)₂CO₃ is negative, which means that the reaction is exothermic and releases 36.15 kJ/mol. However, the enthalpy of reaction of MgSO₄ with NH₄HCO₃ is positive, which means that the reaction is endothermic and needs 53.06 kJ/mol. For the Free Gibbs energy, the reaction of MgSO₄ with (NH₄)₂CO₃ releases heat at 54.96 kJ/mol, which is higher than for the reaction of MgSO₄ with NH₄HCO₃ (47.28 kJ/mol). In addition, the reaction rate (Log K) of MgSO₄ with (NH₄)₂CO₃ is faster than reaction of MgSO₄ with NH₄HCO₃. Thus, the carbon fixation efficiency is significantly improved when using (NH₄)₂CO₃ compared to that using NH₄HCO₃.

Table 5-4: Thermodynamic properties of reactions of MgSO₄ with (NH₄)₂CO₃ and NH₄HCO₃

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T(°C)</th>
<th>ΔH(kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄(aq) + (NH₄)₂CO₃(aq) → MgCO₃↓ + (NH₄)₂SO₄(aq)</td>
<td>80</td>
<td>-36.15</td>
</tr>
<tr>
<td>MgSO₄(aq) + 2NH₄HCO₃(aq) → MgCO₃↓ + (NH₄)₂SO₄(aq) + H₂O(l) + CO₂↑</td>
<td>80</td>
<td>53.06</td>
</tr>
</tbody>
</table>
Chapter 5—CCSM process route at high solid to liquid ratio

The XRD results of product 1 from C2 and C3 are presented in Figures 5-6 and 5-7, respectively. Magnesite and lizardite (mineral phase of serpentine) were identified in product 1 from C2. However, additional phases of \((\text{NH}_4)_2\text{SO}_4\) and \((\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2\cdot6\text{H}_2\text{O}\) as mascagnite and boussingaultite, respectively, were identified in product 1 from C3. The reason for the presence of these solid sulfate salts is because of the low carbonation efficiency (27-30 %) of the experiments using \text{NH}_4\text{HCO}_3. Magnesite was found for the high solid to liquid ratio experiments (C1 and C2) instead of hydromagnesite for the low solid to liquid ratio experiments (C3 and C4). This can be explained by the \text{CO}_2 pressure (>20 bar, see Figure 5-8), as reported by Hanchen et al. (2008). The pressure increased due to the decomposition of \((\text{NH}_4)_2\text{CO}_3\) and \text{NH}_4\text{HCO}_3 at a temperature above 60 °C, as described in Eq. 5-8 and 5-9. The pressure change of C1-C4 was recorded and presented in Figure 5-8. It can be found that for C1 and C2, where \((\text{NH}_4)_2\text{CO}_3\) was used, the pressure raised sharply from 0 to 320 psi when the temperature was increased from ambient to 80 °C, and then went up continually from 320 psi to 440 psi after 60 mins and finally decreased to 125 psi when the temperature cooled down to ambient. However, for C3 and C4, where \text{NH}_4\text{HCO}_3 was used, the pressure raised from 0 to 602 psi when the temperature increased from ambient to 80 °C, and then went up continually from 602 psi to 758 psi after 60 mins and finally decreased to 424 psi when the temperature cooled down.
to ambient. The higher pressure obtained when NH$_4$HCO$_3$ was used compared to that using (NH$_4$)$_2$CO$_3$ can be explained by the CO$_2$ produced from the carbonation reaction of MgSO$_4$ with NH$_4$HCO$_3$. It has been reported that high pressure can help the carbonation reaction due to the high solubility of CO$_2$ at high pressure (O'Connor, 2004; Alexander et al., 2007). However, since the carbonation rate limiting step in this study is thought to be the diffusion of undissolved MgSO$_4$ and ammonium salts ((NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$) in liquid phase, the high pressure will not help the carbonation reaction.

![Graph](Image)

Figure 5-6: XRD of product 1 from C2.
Chapter 5 – CCSM process route at high solid to liquid ratio

![XRD of product 1 from C3.]

**Figure 5-7:** XRD of product 1 from C3.

![Pressure change vs. reaction time in C1-C4.]

**Figure 5-8:** Pressure change vs. reaction time in C1-C4.
5.2.4 Mass Balance

When the solid to liquid ratio of 300 g/l was used, the carbon fixation efficiency was 46.6 %, with dissolution efficiency and carbonation efficiencies of 71.2 and 65.4 %, respectively. Taking this into account, about 4.9 t of serpentine, 11.3 t of NH₄HSO₄, 4.7 t of (NH₄)₂CO₃ and 16 t of water are required to sequester 1 t CO₂, as presented in Figure 5-9. If 95 % regeneration efficiency of NH₄HSO₄ and NH₃ is considered as for previous Section 4.2.2.4, then 0.6 t of NH₄HSO₄ is consumed to sequester 1 t CO₂. In comparison with the results from Section 4.2.2.6, 0.5 t of NH₄HSO₄ is required and 36.6 t of water can be saved at high solid to liquid ratio conditions.

![Figure 5-9: A simplified process scheme for sequestering 1 t of CO₂ by CCSM process at 300 g/l solid to liquid ratio.](image-url)
5.3 Summary

In this chapter, the author has studied the CCSM process route with recyclable ammonium salts at high solid to liquid ratio conditions. In conclusion, the increase of dissolution efficiency when the solid to liquid ratio increased from 200 g/l to 300 g/l could be explained by particle-particle interaction. Magnesite instead of hydromagnesite was found due to the CO₂ pressure caused by the decomposition of ammonium salts at high temperature. The carbon fixation efficiency was significantly improved by using (NH₄)₂CO₃ compared to NH₄HCO₃ for the same concentration. At solid to liquid ratio of 300 g/l, the highest carbon fixation efficiency achieved was 46.6 %. According to the mass balance, about 4.9 t of serpentine, 0.6 t of NH₄HSO₄, 4.7 t of (NH₄)₂CO₃ and 16 t of water are required to sequester 1 t CO₂.
Chapter 6. Process evaluation and optimization

In this chapter, a preliminary evaluation was conducted to evaluate the OPEX\textsuperscript{16} of the two process routes described in Chapters 4 and 5. A block diagram of the process scheme is shown in Figure 6-1. Firstly, the hot flue gas at a temperature of 900-1300 °C (depend on the fuel used and combustion technologies applied, 900 °C is used in this study) from the combustor passes through the thermal decomposition tower, where ammonium sulfate is decomposed into ammonium bisulfate and ammonia gas. After passing through a heat exchanger, ammonia gas and water vapour are condensed as aqueous ammonia and the flue gas is sent into an adsorption tower, where CO$_2$ is absorbed by a high concentration of aqueous ammonia into CO$_2$ containing ammonium salts (NH$_4$HCO$_3$, (NH$_4$)$_2$CO$_3$ and NH$_4$NH$_2$CO$_2$). The mineral is grinded to particle size between 75-150 μm and mixed with water from the mechanical vapour recompression (MVR) evaporator and NH$_4$HSO$_4$ from the thermal decomposition tower. The Mg ions are dissolved from the mixed slurry in the dissolution reactor. After filtering the solid residue (consisting mainly of amorphous silica), the pH of the Mg-rich solution is regulated by adding ammonia water to a pH value of 7 and a Fe-rich precipitate is produced with increasing pH. After

\textsuperscript{16} Including energy consumption, chemical cost and mineral cost
filtering the Fe-rich precipitate, the Mg-rich solution reacted with CO₂ containing ammonium salts from the capture step to precipitate magnesite. After filtering the carbonate product, the remaining solution consisting mainly of ammonium sulfate is sent to the MVR evaporator. Dry ammonium sulfate solid is collected for the thermal decomposition and water is recycled.

Figure 6-1: Block diagram of the CCSM process with recyclable ammonium salts.

The steps of capture, filtering, water evaporation and regeneration of ammonium salts are not the focus of this study. The technologies regarding these steps are mature and have been demonstrated in large scale projects (Kothandaraman, 2010). Therefore, a literature review was conducted to assess the potential applicability of these technologies to this study and identify the energy consumption for these steps in the process (Section 6.1). A preliminary cost
evaluation of the two process routes studied in Chapters 4 and 5 was conducted based on the mass balance from the experimental work and energy consumption from the literature review (Section 6.2). The conditions related to the cost reduction of the process, such as solid to liquid ratio and reaction time, were determined by using the results from the preliminary evaluation. Finally, the optimization experiments were conducted to further reduce the energy and cost of the process (Section 6.3).

6.1 Literature review of technologies regarding carbon dioxide capture, filtering, water evaporation and regeneration of ammonium salts

6.1.1 Carbon capture step

As described in Chapter 3, ammonia water was used to absorb CO₂ and produce (NH₄)₂CO₃ or NH₄HCO₃ in solid or liquid phase. The solid or liquid ammonium salts are then reacted with alkaline metal ions such as Mg/Ca to permanently store CO₂ as carbonate. In comparison with conventional aqueous ammonia carbon capture process, the energy intensive thermal regeneration of CO₂ and the high pressure CO₂ compression for transportation are avoided. Since the aqueous ammonia carbon capture has been intensively studied in recent years, there is a large body of publications available to assess the potential applicability of the aqueous ammonia process to
this study (Zhang et al., 2003; Kim et al., 2008; Kothandaraman, 2010; Huang, 2002; Corti, 2004; GAL, 2006). However, some variations in the capture step need to be investigated in order to match the requirements of the CCSM process with recyclable ammonium salts. For example, the output concentration of (NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$ in the stream from the CO$_2$ capture step is a very important factor for the carbonation reaction. 2 mol/l NH$_4$HCO$_3$ and 3 mol/l (NH$_4$)$_2$CO$_3$ are required in the process studied in Chapters 4 and 5. In considering the reduction of water usage in order to minimise the energy consumption of water evaporation, (NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$ are preferred to be either solid phase or high concentration of liquid phase. Therefore, high initial concentration of NH$_3$ is necessary for the capture step in this study. In addition, the output streams from the capture step typically contain both (NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$, where the proportion of products is dependent on the process parameters (reaction time, CO$_2$ loading, flow rate of CO$_2$ and reaction temperature) (Zhang, 2003, Kim et al., 2008).

6.1.1.1 High concentration of NH$_3$

The CO$_2$ absorption efficiency is closely related to the concentration of NH$_3$. Zhang et al. (2003) investigated the relationship between CO$_2$ absorption efficiency and NH$_3$/CO$_2$ molar ratio, where the absorption efficiency of CO$_2$ increased with higher NH$_3$
concentrations. The CO$_2$ absorption efficiency was reported to be improved from 76 % to 92 %, when the initial concentration of NH$_3$ increased from 1.8 mol/l to 2.4 mol/l, respectively. Besides, the high concentration of NH$_3$ can prolong the residence time of NH$_3$ in the absorber and increase the CO$_2$ absorption capacity. Kim et al. (2008) showed that increasing the NH$_3$ concentration can result in longer breakthrough times, where the time to achieve 95 % CO$_2$ removal efficiency doubled from 2 h to 4 h when using 7 wt. % and 17 wt. % of NH$_3$ solutions, respectively. Kim et al. (2008) also investigated the change of CO$_2$ sorption capacity with different aqueous ammonia concentration. It was reported that 13 wt. % (6.7 mol/l) aqueous ammonia was thought as the optimum concentration to maximise CO$_2$ sorption capacity (2.8 mol/kg).

6.1.1.2 Output concentration of (NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$
concentration and composition in the stream from CO$_2$ capture step

According to Kim et al. (2008), the output concentration of total CO$_2$ containing species from CO$_2$ absorption with 13 wt. % aqueous ammonia can achieve 3.4 mol/l, containing 35 % ammonium carbamate, 41 % ammonium bicarbonate and 24 % ammonium carbonate. It is thought that the higher concentration of aqueous ammonia used in absorption can generate higher concentration of CO$_2$ containing species.
6.1.1.3 Ammonia loss

Resnik et al. (2004) found that ammonia is lost to the gas phase during absorption, and the higher the initial concentration of aqueous ammonia increases the relative loss of NH₃ in capacity. For environmental reasons, the loss of ammonia must be kept to a minimum.

6.1.1.4 Energy consumption of current CO₂ ammonia process

CO₂ capture with aqueous ammonia has been studied at laboratory scale (Zhang et al., 2003; Kim et al., 2008). However there is no published information about energy consumption. A similar process using chilled ammonia has been successfully demonstrated for coal-fired power plants in a collaborative project by Alstom, the Electric Power Research Institute (EPRI) and We Energies in 2007 (0.1 Mt CO₂/year) (GAL, 2006). According to the study of Kothandaraman (2010), the energy consumption for 85% of capture of CO₂ in the chilled ammonia system was estimated to be 477 kWh/t CO₂, where 44% of the energy consumption from using the chilled ammonia system arises from the refrigeration process, 27 % of the energy consumption comes from the cooling of ammonia in the absorption process and 25 % of the energy consumption was due to the compression process. For the CCSM process with recyclable ammonium salts, the energy consumption of the capture step is 19
kWh/t CO$_2$, which is only 4 % of the energy required in the chilled ammonia system because compression, cooling and desorption are not necessary (considering that 4 % of 477 kWh/t).

6.1.2 Filtering, water evaporation and regeneration of ammonium salts

The two most energy intensive steps of CCSM with recyclable ammonium salts process are water evaporation and thermal decomposition. Both of the two steps are related to water usage, which is controlled by the solid to liquid ratio used. In this section, suitable technologies for filtering, water evaporation and thermal decomposition for CCSM within the recyclable ammonium salts process are identified and described, and their energy consumption is estimated.

6.1.2.1 Filtering

The slurries after dissolution, pH regulation and carbonation require separation of the solid from the liquid. The costs of filtering are related to the particle size and the concentration of the slurry. Large particles and a higher concentration of slurry can reduce the costs. It is reported that the energy required to dewater a magnesite concentrate from the beneficiation of taconite is 0.2 kWh/t of water removed (Eimco water technologies, 2011).
The filtering step of the CCSM process with recyclable ammonium salts process can be regarded as similar to filtering/dewatering in the mining processing Industry. Hydrocyclones are therefore considered suitable for the CCSM process, since the particle sizes required for CCSM are matched with the working particles size range of hydrocyclone from 75 to 300 μm (Eimco water technologies, 2011). For the other choice of filtering equipment can be investigated in future work, such as the gravity filtering.

6.1.2.2 Water evaporation

CCSM wet technologies require a final drying step, which is a water thermal evaporation process. Thermal removal of water from slurries is a highly energy intensive technique. The new Mechanical Vapour Recompression (MVR) technology provides a low energy solution with typical power consumption of 8-12 kWh/t of clean water (Karasek, 2010; Windsor MVR Evaporation System, 2011).

MVR evaporators have been applied in food, paper and chemical industries (Karasek, 2010; Windsor MVR Evaporation System, 2011). Therefore, MVR are considered suitable for the CCSM process with recyclable ammonium salts.

6.1.2.3 Thermal decomposition of ammonium slats

Ammonium sulfate can be converted into ammonium bisulfate and ammonia gas by heating, as shown in the following equation:
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\[(NH_4)_2SO_4(s) \rightarrow NH_3 \uparrow + NH_4HSO_4(s)\]

Equation 6-1

It is essential to control the temperature above 250 °C to initiate the decomposition, and no higher than 500 °C to prevent the formation of pyrosulfate \(((NH_4)_2S_2O_7)\), which further decomposes into ammonia gas, sulphur dioxide and nitrogen at above 500 °C. The decomposition rate of \((NH_4)_2SO_4\) is slower when the temperature is below 300 °C. Moreover, the decomposition reaction is endothermic, absorbing 110 KJ/mol heat (value calculated using HSC 5.1). Finally, numerous processes for the thermal decomposition processes for ammonium sulphate have been suggested (Brennan, 1975; Montgomery, 1962; Bretherick, 1975).

The single step water evaporation and thermal decomposition of ammonium sulphate designed by Albert et al. (1972) proposed to inject a fluid mixture comprising of ammonium sulphate and water into a stream of hot flue gas (1300 °C) in an evaporation zone, where water is evaporated. The mixture of hot flue gas (500 °C), water vapor and ammonium sulphate flow into a decomposition zone, where ammonium sulphate was converted into ammonium bisulphate and ammonia.

In addition of the wet method described above, a dry method has been reported by Brennan (1975) and Furkert (1973), where 99-
100% NH₄HSO₄ was produced from a mixture of salts comprised of 50 % NH₄HSO₄, steam inlet temperature of 450-470 °C and liquid to gas ratio from 0.66 to 1. The mixture of ammonium bisulfate with ammonium sulphate in the feed has been reported to improve the conversion rate of ammonium sulphate to ammonium bisulfate (Welty, 1972; Montgomery, 1962; Furkert, 1973).

There is no data reported in the literature for the energy consumption of thermal decomposition of ammonium sulphate. However, a similar thermal process using rotary kiln for production of Portland cement can be considered as a comparable example. Worrell et al. (2008) reported that the thermal energy consumption for a rotary kiln is generally 3.1 GJ/t (1450 °C) and the power consumption for pumping was 6 to 9 kWh/t (IEA, 2010b). Taking this into consideration, the thermal decomposition of ammonium sulphate is estimated to require 0.85 GJ/t (400 °C). This heat penalty is high and makes the CCSM process costly. Recovering waste heat from flue gas from a power plant can reduce this heat penalty. Currently, the waste heat from flue gas from a power plant is only used in air pre-heater, and the majority of waste heat is not recovered. In contrast, a heat recovering system has been applied in the steel industry successfully (Hualwei and Xin, 2011; Rautenbach et al., 1979). The heat capacity the flue gas (10 vol. % of CO₂) leaving the boiler at 900 °C is around 1.3 KJ/Nm³, or in other words, 1 t CO₂ can provide 30 GJ of heat. Therefore, the heat
from the flue gas is sufficient for the thermal decomposition step, and only 6 to 9 kWh of power consumption for pumping is needed to decompose 1 t of ammonium sulphate. The use of waste heat from flue gas in power plant is very important for the CCSM process, and if this is not used the theoretical value of energy consumption for thermal decomposition of ammonium salts would rise to 236 kWh per tonne ammonium sulphate (value obtained from HSC software simulation). In order to supply enough heat for thermal decomposition of ammonium salts, a heat exchanger, such as shell and tube, should be placed after boiler (900 °C) and before selective catalyst reduction (SCR), where the minimum operation temperature of SCR is ~280 °C (Williams, 2009). For the other existing air pollution control system (APCs), electrostatic precipitator (ESP) and flue gas desulphurisation (FGD) do not have specific temperature requirements (Shanthakumar et al., 2008). Additionally, the aqueous ammonia capture step of the CCSM process has the potential to convert SO₂ and NOₓ into ammonium salts, and this may resolve the heat requirement of both thermal decomposition of CCSM and SCR. The integration of SO₂, NOₓ and CO₂ capture by ammonia has already been reported by Powerspan (2011) and Cansolv (2011).
6.2 Preliminary cost analysis

A preliminary cost analysis of OPEX, including energy consumption, chemical consumption and feedstock cost, was developed based on the experimental results discussed in Chapters 4 and 5 (see Table 6-1). For the analysis, several assumptions were made based on the experimental results were made to simplify the work.

- The analysis was based on sequestering 1 t of CO₂.
- Serpentine consists of 24 wt. % of Mg.
- For the low solid to liquid ratio scenario, the 50 g/l was used. According to the results from Chapter 4, the total CO₂ fixation efficiency is 77 %, with 100 % and 96 % of dissolution and carbonation efficiencies, respectively.
- For the high solid to liquid ratio scenario, the 300 g/l was used. According to the results from Chapter 5, the total CO₂ fixation efficiency is 47 %, with 71 and 65 % are the dissolution and carbonation efficiencies, respectively.

The conditions applied for each step of the process are summarised in Appendix 1. The input and output of the two process routes were calculated and are presented in Table 6-1. The input and output streams of each step are listed in Appendix 2.
Table 6-1: Mass balance of the two process routes described in Chapters 4 and 5.

<table>
<thead>
<tr>
<th></th>
<th>50 g/l (t)</th>
<th>300 g/l (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Serpentine</td>
<td>3.0</td>
<td>4.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>-4.2₁</td>
<td>-0.7₁</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.2</td>
<td>-0.3₁</td>
</tr>
</tbody>
</table>

| **Output** |            |             |
| NH₄HCO₃/(NH₄)₂CO₃/NH₄NH₂CO₂ | 2.2 | 2.2 |
| MgSO₄      | 0.2        | 1.4         |
| (NH₄)₂SO₄  | 0.1        | 0.1         |
| Product 1  | 1.3        |             |
| Product 2  | 0.3        |             |
| Residual solid | 3.1 |        |
| Hydromagnesite | 2.8 |          |
| Magnesite   |            | 1.9         |

¹Negative values indicate these chemicals are produced from the process.

According to the mass balance, the energy consumption for each step was calculated (Table 6-2) based on the following energy penalties. The details can be seen in Appendix 2.

- Grinding: 13 kWh/t is used to grind mineral to 75 -150 μm particle size (O’Connor, 2005).
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- CO₂ capture: 19 kWh is used to capture 1 t CO₂ in the aqueous ammonia capture step with recyclable ammonium salts process (Section 6.1.1).

- Water evaporation: MVR evaporator was selected and 8 kWh/t water evaporated (Section 6.1.2.2).

- Filtering: Hydrocyclone was selected and 0.2 kWh/t solution filtered (Section 6.1.2.1).

- Pumping: 1.47 kWh/t solution pumped.

- Thermal decomposition: 6 kWh/t ammonium salts for pumping, cooling and preheating for the thermal decomposition of ammonium salts, if heat recovered from the flue gas is applied (Section 6.1.1).

- The electricity price is 0.03 US$/kWh

Table 6-2: Energy consumption (kWh) of the two process routes.

<table>
<thead>
<tr>
<th></th>
<th>50 g/l (kWh)</th>
<th>300 g/l (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>39</td>
<td>63</td>
</tr>
<tr>
<td>CO₂ capture</td>
<td>95</td>
<td>28</td>
</tr>
<tr>
<td>MVR evaporation</td>
<td>701</td>
<td>169</td>
</tr>
<tr>
<td>Filtering</td>
<td>49</td>
<td>19</td>
</tr>
<tr>
<td>Pumping</td>
<td>76</td>
<td>78</td>
</tr>
<tr>
<td>Thermal decomposition</td>
<td>128</td>
<td>43</td>
</tr>
<tr>
<td><strong>Total energy</strong></td>
<td>1088</td>
<td>400</td>
</tr>
</tbody>
</table>
The chemical requirements for the two process routes are presented in Table 6-3. It is assumed that (NH₄)₂SO₄ is supplied to produce NH₄HSO₄ and NH₃ by thermal decomposition with 95% efficiency. Any excess NH₄HSO₄ or NH₃ can be used in the process, and this is considered in the calculation of chemical costs.

Table 6-3: Chemical requirements (t) and costs (US$) of the two process routes.

<table>
<thead>
<tr>
<th></th>
<th>Amount in 50 g/l scenario (t)</th>
<th>Amount in 300 g/l scenario (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄HSO₄</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>NH₃ (capture + mineralisation)</td>
<td>0.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ (equal, 99% purity)</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td>NH₃ (generation from (NH₄)₂SO₄)</td>
<td>0.0</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

NH₄HSO₄ cost (US$) 172.1 154.5
Cost of NH₃ (US$) 0.0 -84.3
Cost of NH₄HSO₄ (US$) -127.4 0.0
Total Chemical cost (US$) 44.7 70.2

---

a Price of NH₃ is 180 US$/t.
b Price of NH₄HSO₄ is 90 US$/t.
c Price of (NH₄)₂SO₄ is 90 US$/t.
d Negative value means excess amount is produced.

The OPEX of the two process routes is shown in Table 6-4.
Table 6-4: OPEX of the two process routes.

<table>
<thead>
<tr>
<th></th>
<th>50 g/l scenario</th>
<th>300 g/l scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(US$/tCO₂ sequestered)</td>
<td>(US$/tCO₂ sequestered)</td>
</tr>
<tr>
<td><strong>Energy cost</strong></td>
<td>33</td>
<td>12</td>
</tr>
<tr>
<td><strong>Chemical cost</strong></td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td><strong>Mineral cost</strong></td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td><strong>Transport cost (100km)</strong></td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td><strong>Total cost</strong></td>
<td>100</td>
<td>119</td>
</tr>
</tbody>
</table>

*Electricity price is 0.03 US$/kWh.*  
*Price of serpentine is 5 US$/t.*  
*Transportation cost is 2.5 US$/t for 100 km.*

The total costs for sequestering 1 t CO₂ are 100 US$ and 119 US$ t at 50 g/l and 300 g/l solid to liquid ratios, respectively. In both cases, the highest cost come from the chemical and accounting for 59-65 % of the total cost. The MVR evaporation is the most energy intensive step, with up to 702 kWh/t CO₂ sequestered for the 50 g/l case. The costs of feedstock are closely related to the carbon fixation efficiency, where increasing efficiency can reduce the feedstock cost. In addition, it can be seen that the solid liquid ratio has a strong influence on the energy consumption. Low solid to liquid ratio resulted in a large amount of water evaporated that subsequently needs to be filtered and pumped. However, both dissolution and carbonation efficiencies decreased at high solid to liquid ratio, and therefore, more serpentine and chemicals are required. Moreover, dissolution efficiency influences the required
amount of serpentine and the amount of products, while carbonation influences the required net amount of NH$_3$ and NH$_4$HSO$_4$ and the energy consumption on CO$_2$ capture.

Based on this preliminary cost analysis the following recommendations are made for the process to improve its economical viability. The low solid to liquid ratio case is better than the high solid to liquid ratio scenario in terms of total cost. However, the solid to liquid ratio should be maximised without exceeding the solubility limit of ammonium sulphate. The input of ammonium salts should be reduced, but the carbonation efficiency should be maintained. In addition, it is also suggested that the carbonation step should be conducted using an autoclave reactor instead of an open glass reactor to produce magnesite instead of hydromagnesite (Section 5.2.3). Another important parameter to be considered is the reaction time, where longer reaction times give high dissolution efficiency, but they demands a large reactor size and therefore increase the capital cost. It is also important to limit the dissolution time to 1 h considering the trade off between the cost and the efficiency.

The carbon footprint of production of the chemical used and mining of raw materials need to be considered, it is suggested to do the life cycle carbon footprint assessment of the CCSM process in future work.
6.3 Process optimization

According to the suggestions from the previous section, optimization experiments were carried out to reduce the total cost of the proposed CCSM process with recyclable ammonium salts. The data shown in Section 6.2 suggested that the low solid liquid ratio case gave better performance on cost evaluation. In the boundary of low solid to liquid ratio (without exceeding the solubility), the maximise value of solid to liquid ratio is 100 g/l (this value was obtained from dissolution experiments in Section 4.1.6), and this value was selected as the optimum value. 40 % excess of NH₄HSO₄ (2.8 M) was used for the dissolution experiments, as for the previous studies described in Chapter 4. Serpentine with 75-150 μm particle size was dissolved at 100 °C for 1 h. A mixture of NH₄HCO₃ and (NH₄)₂CO₃ solution was used instead of NH₄HCO₃ aiming at simulating the different CO₂ containing ammonium salts solution coming from the CO₂ capture step. The mixture solution used contains 1.7 M NH₄HCO₃ and 1.7 M (NH₄)₂CO₃ (see Section 6.1.1), where the output concentration of total CO₂ containing species from aqueous ammonia was 3.4 mol/l. Finally, an autoclave reactor was used for the carbonation step.

6.3.1 Experimental methods

The dissolution step for the optimization experiments was conducted following by the procedure presented in Section 5.1.1. The solid to
liquid ratio was increased to 100 g/l, and the concentration of NH₄HSO₄ to 2.8 M, while the reaction time was reduced to 1 h. The pH regulation step and carbonation steps were carried out following the methods described in Section 4.2.1.2. and 5.1.3., respectively. The mixture solution of 1.7 M NH₄HCO₃, 1.7 M (NH₄)₂CO₃ and ammonia water (13 wt. %) was added to the solution obtained from the dissolution step. The amounts of mixture solution of NH₄HCO₃ or (NH₄)₂CO₃ and ammonia water were determined by the molar ratio of Mg ions in filtrate 2: CO₂ containing ammonium salts: NH₃. The matrix of carbonation experiments conducted at different ratios is listed in Table 6-5.

Table 6-5: Matrix of carbonation experiments conducted at different ratios

<table>
<thead>
<tr>
<th></th>
<th>OP1</th>
<th>OP2</th>
<th>OP3</th>
<th>OP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg in filtrate 2 : CO₂ containing ammonium salts</td>
<td>1:1</td>
<td>1:1.5</td>
<td>1:1</td>
<td>1:1.5</td>
</tr>
<tr>
<td>Mg in filtrate 2 : NH₃</td>
<td>1:1</td>
<td>1:1</td>
<td>1:2</td>
<td>1:2</td>
</tr>
</tbody>
</table>

6.3.2 Results and discussions

According to the results from the ICP-AES analyses of the filtrate 1 from OP1-OP4, the dissolution efficiency of Mg is around 80 % (see Table 6-6), compared to 100 % for the dissolution experiments presented in Section 4.1.2. The decrease of dissolution efficiency at 100 g/l solid to liquid ratio is probably due to the Si passive layer on the surface of the serpentine particle, as the rate limiting step is
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Product layer diffusion control at this solid to liquid ratio (see Section 4.1.3).

The overall reaction for the carbonation step is presented below:

\[ 2\text{MgSO}_4 + \text{NH}_4\text{HCO}_3 + (\text{NH}_4)_2\text{CO}_3 + \text{NH}_3 \rightarrow 2\text{MgCO}_3 \downarrow + 2(\text{NH}_4)_2\text{SO}_4 \]

\[ \Delta H = -43.59 \text{ KJ}, \Delta G = -102.99 \text{ KJ (80 °C)} \quad \text{Equation 6-2} \]

The enthalpy and Gibbs free energy of this reaction are both negative, indicating that it is an endothermic reaction. Due to the low thermal stability of ammonium bicarbonate and ammonium carbonate (decomposition happens at 80 °C), it is necessary to supply excess amount of ammonium bicarbonate and ammonium carbonate for the carbonation reaction to be completed. The presence of ammonia can slow down the decomposition reaction and help the carbonation reaction by maintaining a pH above 8 for precipitation, reacting with CO\(_2\) to regenerate ammonium bicarbonate and then to regenerate ammonium carbonate.

Table 6-6 also shows that the molar ratio of Mg: NH\(_4^+\) salts: NH\(_3\) is the key factor controlling carbonation efficiency. When the molar ratio of Mg: NH\(_4^+\) salts: NH\(_3\) is 1:1:1 (Experiment OP 1), the carbonation efficiency is 80.9 % (Table 6-6). Increasing the Mg: NH\(_4^+\) salts ratio to 1:1.5 (Experiment OP 2) can improve carbonation efficiency to 85.9 %. Further increasing the Mg: NH\(_3\)
ratio to 1:2 (Experiment OP 3) can improve the carbonation efficiency to 89.7%. The improvement of carbonation efficiency by adding ammonia water has been discussed in Section 4.2.2.3. It is thought that ammonia water can react with NH₄HCO₃ into (NH₄)₂CO₃ and thus increases the carbonation efficiency. The comparison between the reaction kinetics of (NH₄)₂CO₃ with MgSO₄ and NH₄HCO₃ with MgSO₄ was also discussed in Section 5.2.3. The highest carbonation efficiency of 96% was obtained when the molar ratio of Mg: NH₄⁺ salts: NH₃ was 1:1.5:2 (Experiment OP 4).

Table 6-6: ICP-AES results of Mg concentration from OP1-4.

<table>
<thead>
<tr>
<th>Filtrate 1 (ppm)</th>
<th>Filtrate 2 (ppm)</th>
<th>Filtrate 3 (ppm)</th>
<th>Dissolution efficiency %</th>
<th>Carbonation efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP1 19149</td>
<td>18999</td>
<td>3605</td>
<td>79.8</td>
<td>80.9</td>
</tr>
<tr>
<td>OP2 18908</td>
<td>18778</td>
<td>2652</td>
<td>78.8</td>
<td>85.9</td>
</tr>
<tr>
<td>OP3 19012</td>
<td>18891</td>
<td>1939</td>
<td>79.2</td>
<td>89.7</td>
</tr>
<tr>
<td>OP4 19201</td>
<td>19083</td>
<td>761</td>
<td>80.0</td>
<td>96.0</td>
</tr>
</tbody>
</table>

The CO₂ from the decomposition of ammonium bicarbonate and ammonium carbonate can increase the pressure of the system. The XRD pattern of product 3 from experiment OP 4 in Figure 6-2 confirms that magnesite is produced from the carbonation step. Therefore, hydromagnesite is transformed into magnesite at high pressure condition.
Figure 6-2: XRD pattern of product 3 from experiment OP 4.

The process was re-evaluated and the cost analysis was estimated based on the optimization experimental work. The input and output streams in each step, energy consumption and chemical cost are presented in Appendix 3. The OPEX of the four optimization experiments is shown in Table 6-7. It can be seen that Experiment OP 4 shows the lowest total cost.

Table 6-7: OPEX of four optimization experiments.

<table>
<thead>
<tr>
<th>Unit</th>
<th>OP1</th>
<th>OP2</th>
<th>OP3</th>
<th>OP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>US$/t_{CO2} sequestered</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy cost</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Chemical cost</td>
<td>55</td>
<td>46</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>Mineral cost</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Transport cost (100km)</td>
<td>9</td>
<td>8</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Total cost</td>
<td>98</td>
<td>88</td>
<td>77</td>
<td>63</td>
</tr>
</tbody>
</table>
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A simplified process scheme of the best case is presented in Figure 6-3, where approximately 3.0 t of serpentine, 0.2 t of NH₄HSO₄ and 0.1 t of NH₃ are required to sequester 1 t of CO₂ and 1.9 t of magnesite, 1 t of high Si contain by-product and 0.3 t of high Fe contain product are produced.

![Diagram of process scheme](image)

Figure 6-3: A simplified process scheme for sequestering 1 t of CO₂ by CCSM process at optimized condition.

Table 6-7 shows that the total cost to sequester 1 t CO₂ decreased from 98 US$ to 63 US$ with the increase of carbonation efficiency at different molar ratio of Mg: NH₄⁺ salts: NH₃. Taking the OP 4 as an example, the cost of energy consumption is 532 kWh or 16 US$ (see Appendix 3), which accounts for 25 % of the total cost. The feed stock cost is 22 US$ (35 % of the total), while the cost of chemical represented the highest cost (40 % of the total), as presented in Figure 6-4. For the energy consumption shown in Figure 6.5 and Appendix 3, MVR evaporation consumes the largest
energy of 312 kWh, which accounts for 59% of the total. Then in increasing order of energy consumption, there is pumping, thermal decomposition, grinding, CO$_2$ capture and filtering. It is confirmed that increasing the carbonation efficiency can significantly reduce the chemical cost, while increasing the solid to liquid ratio can largely reduce the energy consumption. In comparison with other researchers’ work, the energy consumption of this study is relatively lower than the best result of 1009 kWh/t CO$_2$ from Gerdemann et al. (2007), where serpentine was sequestered at 155 °C and 115 bar (Gerdemann et al., 2007). The chemical cost of this study is significantly lower than Teir et al. reported 1300-1600 US$/t CO$_2$ sequestered using serpentine and un-recyclable HCl or HNO$_3$ and NaOH (Teir et al., 2007b).

Figure 6-4: Percentages accounted of energy, chemical, mineral and transport in total cost.
6.4 Summary

Most of the process units used are mature technologies. Additionally, it was found that the using waste heat from flue gas to supply the heat required for the thermal decomposition of ammonium salts is very important for the success of the CCSM process with recyclable ammonium salts.

The preliminary cost analysis evaluated the OPEX of the two process routes in terms of energy consumption, chemical costs and feedstock cost. It was found that the solid liquid ratio has a large influence on the energy consumption cost. The results show that the total cost to sequestering 1 t CO₂ is 100 US$ at 50 g/l case and 119 US$ at 300 g/l case. Using low solid to liquid ratio (50 g/l) resulted in large streams in the process, and thus resulting in a high energy
consumption. However, high solid to liquid ratio (300 g/l) decreases the dissolution and carbonation efficiencies.

The optimization experiments were conducted according to the recommendations from the preliminary cost analysis. The dissolution efficiency of Mg from serpentine using 2.8 M NH₄HSO₄ at 100 g/l solid to liquid ratio for 1 h was around 80 %. The decrease in dissolution efficiencies is because of the Si passive layer on the surface of serpentine particle. The molar ratio of Mg: NH⁴⁺ salts: NH₃ is the key factor controlling carbonation efficiency, and when using the molar ratio of Mg: NH⁴⁺ salts: NH₃ is 1:1.5:2, the carbonation efficiency was 96 %.
Chapter 7 Cost evaluation

Chapter 6 described the optimization of the operating variables of the CCSM process using recyclable ammonium salts. The variables studied included reaction temperature (T), reaction time (t), particle size of feedstock (d), solid to liquid ratio (S/L) and molar ratio of Mg$^{2+}$:NH$_4^+$:NH$_3$ (R). It was shown that serpentine can be dissolved (80% efficiency) and subsequently carbonated (96% efficiency) within 1 h. The cost of additives and energy consumption were reduced to 25 US$ and <532 kWh, respectively. Chapter 7 describes the cost evaluation (CAPEX$^{17}$ and OPEX) to assess the economic feasibility of the CCSM process with recyclable ammonium salts.

There are several papers published on the costs of mineral carbonation (Gerdemann et al., 2007; Huijgen et al., 2007; Teir et al., 2009). Huijgen’s study represents the most comprehensive cost evaluation, including investment cost, energy cost, chemical cost and feedstock cost. However, Huijgen used wollastonite and steel slags as feedstock, which have limited capacity. Gerdemann et al. (2007) reported that the energy costs for olivine and serpentine were 54 and 250 US$/t CO$_2$ sequestered, respectively. These costs seem substantially higher than other CCS technologies (e.g. costs of geological storage are typically 0.7-8 US$/t CO$_2$ sequestered (IPCC,

$^{17}$Capital cost including purchase equipments, construction, labour and other surcharge
2005). Gerdemann et al. (2007) assumed that the NaHCO₃ and NaCl were recycled in their process; however, this has not been proved. Teir et al. (2009) reported that the cost of chemicals was estimated to be 1300-1600 US$/t CO₂ sequestered using serpentine and un-recyclable HCl or HNO₃ and NaOH. These costs are significantly high, but Teir mentioned the potential for beneficial use of the products made from his process.

The aim of this chapter is therefore to assess the economic feasibility of CO₂ capture and storage costs by CCSM process with recyclable ammonium salts. A basic design of the process by Aspen plus was made to estimate CAPEX cost, including investment and depreciation costs and fixed costs (e.g. labour and maintenance). Finally, a sensitivity analysis was performed to investigate how the process conditions and assumptions may affect the costs and to identify opportunities for cost reduction.

7.1 CCSM process with recyclable ammonium salts

Aspen plus 11.1 flow sheeting software was used in this study. The CCSM process with recyclable ammonium salts requires several classical unit operations, including crusher, heat exchanger, autoclave reactor with stirrer, absorber, mixer and feed pump. Figure 7-1 shows a simplified Aspen flow diagram of the CCSM process with recyclable ammonium salts. The process was designed to sequester CO₂ emitted from a 100 MW power plant (assuming
CO₂ emission of 0.60 kg/kWh and operation time of 8000 h/yr). The simulation was performed using the experimental results from the optimization study described in Chapter 6 (80% and 90% dissolution and carbonation efficiency, respectively). In addition, the process conditions used for dissolution were d (particle size) = 75-150 μm, t= 1 h and T=100°C, while for carbonation, S/L=100 g/l, t=1 h, T=80°C and Mg²⁺:NH₄⁺:NH₃ (R) was 1:1.5:2.

Figure 7-1: Simplified Aspen flow diagram of CCSM process with recyclable ammonium salts

The resulting composition and physical properties of the streams (stream numbers are presented in Figure 7-1) are given in Table 7-1. It was found that the CO₂ removal efficiency was 93% (CO₂ input and output 60 and 4 t, respectively). The heat and power consumptions (unit names are given in Figure 7-1) are shown in Table 7-2. The flue gas from the boiler typically contains 1800 GJ of heat (assuming 900 °C, 10 vol. % CO₂ and 1.2667 kJ/Nm³ of flue
gas) (Coskun, 2009). The total heat consumed in the process was 697.9 GJ (Table 7-2). The demand heats of regenerator and heat exchanger (698 GJ) are only 39 % of the heat of flue gas (1800 GJ). Therefore, using waste heat from flue gas can fully compensate the required heat of the process. The total power consumption was 30 MW representing around 30 % of the 100 MW plant with 93 % of CO₂ removal efficiency.

Table 7-1: Properties (temperature and pressure) and composition of the streams of the CCSM process with recyclable ammonium salts

<table>
<thead>
<tr>
<th>Stream number</th>
<th>T (°C)</th>
<th>P[bar]</th>
<th>H₂O</th>
<th>CO₂</th>
<th>Mg₅Si₂O₇(OH)</th>
<th>MgSO₄</th>
<th>Silate</th>
<th>NH₄HSO₄</th>
<th>NH₄₃SO₄</th>
<th>NH₄</th>
<th>NH₄HCO₃/(NH₄)₂CO₃</th>
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<tbody>
<tr>
<td>Flue gas</td>
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<td>1</td>
<td>60</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>25</td>
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<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
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<tr>
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<td>14</td>
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<td>108.9</td>
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</table>
Table 7-2: Heat and power consumption of CCSM process with recyclable ammonium salts

<table>
<thead>
<tr>
<th>Power flow (MW)</th>
<th>Heat flow input (GJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerator</td>
<td>4</td>
</tr>
<tr>
<td>MVR</td>
<td>18</td>
</tr>
<tr>
<td>Feed pump</td>
<td>3</td>
</tr>
<tr>
<td>Crusher</td>
<td>2</td>
</tr>
<tr>
<td>Heat exchanger</td>
<td></td>
</tr>
<tr>
<td>Absorber</td>
<td>2</td>
</tr>
<tr>
<td>Dissolution</td>
<td></td>
</tr>
<tr>
<td>Carbonation</td>
<td></td>
</tr>
<tr>
<td>HYCYC1,2,3&lt;sup&gt;18&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>30</td>
</tr>
</tbody>
</table>

7.2 Cost evaluation

On the basis of the simulated process shown in Figure 7-1 and the flow sheeting in Table 7-1, the variable and fixed capture and storage costs of all the operation units were estimated.

7.2.1 CAPEX costs

The CAPEX costs were estimated using a detailed factorial cost estimation method as described by Sinnott (1997). The price of

<sup>18</sup> Hydrocyclone 1, 2 and 3
each major unit operation in the process was calculated taking into consideration the following:

- Because of possible corrosion due to the use of ammonia water and ammonium bisulfate, AISI 316 stainless steel was selected for the construction of MVR, regenerator, feed pump heat exchanger, condenser, absorber, HYCYC1 and carbonation reactor. The crusher, water tank and HYCYC 2, 3 are made of stainless steel, while the dissolution and pH reactors are made of glass. The NH3 tank is made of linear low-density polyethylene (LLDPE).

- Reference equipment was selected for which price information was available in the public literature (DACE, 2005). The size of the reference equipment was chosen as close as possible to the actual designed equipment size.

- The cost of the reference equipment was adjusted for the actual size of the equipment type using an apparatus-specific scale factor, which was calculated from the costs data available in the public literature (Peters, 1991).

- The price of the scaled reference equipment was corrected for the operating pressure as well as the materials of construction. On the basis of data presented in Huijgen’s work (Huijgen et al., 2007), prices given for equipment operating at ambient pressure were corrected by a factor of 1.6 in an operating pressure of around 35 bar. In this study, the operation
pressure is 1 bar except for the carbonation reactor, where a maximum pressure of 35 bars is used.

Table 7-3: Surcharge factors used for various equipment (Sinnott, 1997)

<table>
<thead>
<tr>
<th>Direct associated investments (% of equipment cost)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment erection</td>
</tr>
<tr>
<td>Instrumentation</td>
</tr>
<tr>
<td>Piping</td>
</tr>
<tr>
<td>Process building</td>
</tr>
<tr>
<td>Storages</td>
</tr>
<tr>
<td>Utilities</td>
</tr>
<tr>
<td>Ancillary building</td>
</tr>
<tr>
<td>Site development</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Indirect associated investments (% of equipment cost)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design and engineering</td>
</tr>
<tr>
<td>Contractor’s fee</td>
</tr>
<tr>
<td>Contingency</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
</tr>
</tbody>
</table>

After calculation of the costs for the major process equipment units, these costs were multiplied individually with specific factors to include direct associated costs (Table 7-3). For each major unit operation, the sum of direct associated costs was determined to be 215 % of equipment cost and the sum of indirect associated costs was determined to be 40 % of equipment cost. The total direct associated costs and indirect associated costs were added, resulting
in the total fixed capital costs. Finally, 10 % of the total fixed capital costs was reserved as working capital. The investment costs of the mineral carbonation plant were determined as the sum of the fixed and working capital.

Table 7-4 shows the calculation of the CAPEX costs of the process, including the costs of the reference equipment selected for the major unit operations and possible scale and correction factors used. The total CAPEX costs of a mineral carbonation plant with a CCSM process with recyclable ammonium salts are 39 million US$, of which 35.6 million US$ is fixed capital. Total equipment costs are 10 MUS$, of which the most expensive equipment units are the carbonation reactor (2.6 million US$), MVR evaporator (1.3 million US$) and HYCYC 3 (1.2 million US$). The costs of feed pump, absorber, water tank and NH₃ tank are small compared to the other investment costs. Taking into consideration 8000 operating h/yr and the depreciation time of 10 years, the CAPEX cost is 9 US$/t CO₂ sequestered.

A number of units contribute to a small extent to the total CAPEX cost. For example, the total cost contribution for the crushers, feed pump, absorber, condenser, NH₃ tank and water tank is approximately 11 % (Figure 7-2). These common components present therefore very little opportunity for cost reduction and optimization.
The cost of HYCYC 1, 2 and 3 can be significant and accounts for up to 30% of total CAPEX cost (Figure 7-2). The cost of HYCYC is controlled by the amount of slurry processed per tonne of CO₂. The increase of solid to liquid ratio or fixation efficiency can reduce the required size of HYCYC. HYCYC equipment has been utilized in industry for a long time and its performance has been largely optimized. Therefore, there is little opportunity for cost reduction and optimization on this unit.

Figure 7-2: CAPEX Cost structure of CCSM process.

The cost of the carbonation reactors is primarily controlled by the residence/hold time; therefore, faster carbonation kinetics enables lower cost. The cost of the carbonation reactors is also dependent on the solid to liquid ratio, where increasing the solid to liquid ratio from 50 g/l to 100 g/l lowers by 50% the carbonation reactor cost.
Pressure also effects the cost, where as an example the cost decreases from 2583 kUS$ to 260 kUS$ when the pressure decreases from 34 bars to 1 bar (Table 7-4). Overall, the cost of the carbonation reactor takes account for the major CAPEX cost, and therefore the enhancement of carbonation kinetics and conditions optimization, such as S/L ratio and pressure, present significant cost reduction opportunities.
### Chapter 7 – Cost evaluation

Table 7-4: CAPEX costs for CCSM process with recyclable ammonium salts

<table>
<thead>
<tr>
<th>Name of unit</th>
<th>Reference equipment from the literature</th>
<th>Flow-sheeting results</th>
<th>Cost calculation</th>
<th>Price (kUS$)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Equipment</td>
<td>Price</td>
<td>Relevant materials</td>
<td>Relevant size</td>
</tr>
<tr>
<td></td>
<td>type</td>
<td>(kUS$)</td>
<td>size</td>
<td>size</td>
</tr>
<tr>
<td><strong>Crusher</strong></td>
<td>Cone crusher</td>
<td>65</td>
<td>Stainless steel</td>
<td>168.72</td>
</tr>
<tr>
<td><strong>MVR</strong></td>
<td>Leke MVR evaporator</td>
<td>92</td>
<td>AISI 316</td>
<td>2838.03</td>
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<td><strong>Regenerator</strong></td>
<td>Welded plate heat exchanger</td>
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<td>AISI 316</td>
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<td><strong>Water tank</strong></td>
<td>SMC water tank</td>
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<td>Stainless steel</td>
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19 PCE: Purchase cost of equipment
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<tr>
<th>Feed pump</th>
<th>Single stage centrifugal pump</th>
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<td></td>
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</tr>
<tr>
<td>Heat exchanger</td>
<td>Shell and tube heat exchanger</td>
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<tr>
<td>Condenser</td>
<td>Shell and tube heat exchanger</td>
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</tr>
<tr>
<td>Absorber</td>
<td>Ammonia scrubber</td>
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<td></td>
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<tr>
<td>NH₃ tank</td>
<td>Ammonia tank</td>
<td></td>
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</tr>
<tr>
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<td>CSTR</td>
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<td>Hydrocyclone separator</td>
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<tr>
<td><strong>pH reactor</strong></td>
<td><strong>CSTR</strong></td>
<td>10</td>
<td>120 m³</td>
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7.2.2 CO₂ capture and storage costs

The total CO₂ capture and storage costs for the CCSM process with recyclable ammonium salts are listed in Table 7-5, including the CAPEX, energy, chemical and feedstock costs. The total cost is 72 US$/t CO₂ sequestered, when excluding product sale. The largest costs are associated with chemical costs (35 %) (Figure 7-3), followed by energy costs (22 %) and feedstock costs (21 %). In comparison, CAPEX costs (12 %) and transportation costs (10 %) are relatively small. The amount of feedstock required not only has an influence on the costs of feedstocks, but also affect the transportation costs. Also, the value of the products from the process is an important parameter for the costs, since the mass of products is 3.8 times larger than the mass of CO₂ sequestered (212.5 t products compared to 56 t CO₂). However, the value of the products and the market size are uncertain, since no assessment of possible markets have been reported so far. If product sale of 20 US$/t of product 1 (>46.9 wt. % Si), 130 US$/t of product 2 (>60 wt. % Fe) and 400 US$/t of magnesite are included, this would reduce the total costs substantially (e.g. from spend of 71.79 US$/t CO₂ sequestered to a profit 681.30 US$/t CO₂ sequestered) (see Table 7-5). It should be noted that the current market sizes of these products is relatively small compared to the large amounts produced by the CCSM process.
Table 7-5: CO₂ capture and storage costs for CCSM process with recyclable ammonium slats

<table>
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<th>Costs (US$/t CO₂)</th>
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<tr>
<td>CAPEX cost US$/t CO₂</td>
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<td>Total cost exclude product sale</td>
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<td>Magnesite</td>
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<tr>
<td>Total profit from product sale</td>
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<tr>
<td>Total cost include product sale</td>
<td>-681 a</td>
</tr>
</tbody>
</table>

a Negative value means the profit from the sale of products.

Figure 7-3: Pie chart of costs in CCSM process with recyclable ammonium salts
7.3 Sensitivity analysis and influence of the process conditions

A sensitivity analysis was conducted and the results are presented in Table 7-6 and Figure 7-4. Three different values have been selected for each parameter (standard, minimum and maximum values). The effect of these different parameter values on the total cost/t$_{CO2}$ sequestered (including CAPEX and OPEX) can be seen clearly. Within the ranges studied, the largest variables on the reported costs are associated with the value of the carbonation efficiency (72-109 US$/t), molar ratio of Mg:NH$_4$ salts: NH$_3$ (72-101 US$/t), dissolution efficiency (63-87 US$/t), electricity price (61-82 US$/t), price of feedstock (63-81 US$/t) and solid to liquid ratio (72-86 US$/t). Table 7-7 shows the influence of solid to liquid ratio, reaction time, particles size, molar ratio of Mg:NH$_4$ salts: NH$_3$ and excess of NH$_4$HSO$_4$ on the dissolution efficiency and carbonation efficiency. The economically optimum set of process conditions is presented in Table 7-6 (scenario 1). However, the economically optimum set of process conditions may not be the most efficient set (scenarios 7 and 9).
Table 7-6: Parameters studied with a standard, minimum and maximum value.

<table>
<thead>
<tr>
<th>#</th>
<th>Parameters</th>
<th>Standard</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dissolution efficiency (%)</td>
<td>80</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Carbonation efficiency (%)</td>
<td>96</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Solid to liquid ratio (g/l)</td>
<td>100</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Reaction time (h)</td>
<td>1</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>Mg: NH₄ salts: NH₃ (molar ratio)</td>
<td>1:1.5:2</td>
<td>1:1:1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Particle size (μm)</td>
<td>75-150</td>
<td>&lt;38</td>
<td>150-300</td>
</tr>
<tr>
<td>7</td>
<td>Feedstock (US$/t)</td>
<td>5</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>Cost of (NH₄)₂SO₄ (US$/t)</td>
<td>90</td>
<td>70</td>
<td>110</td>
</tr>
<tr>
<td>9</td>
<td>MVR energy cost (kWh/t)</td>
<td>8</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>Thermal decomposition (kWh/t)</td>
<td>6</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>CO₂ capture (kWh/t)</td>
<td>19</td>
<td>10</td>
<td>28</td>
</tr>
<tr>
<td>12</td>
<td>Electricity (US$/kWh)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>13</td>
<td>Operation time (hr/yr)</td>
<td>8000</td>
<td>7500</td>
<td>8500</td>
</tr>
<tr>
<td>14</td>
<td>Depreciation time (yr)</td>
<td>10</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

Combining the information about the effect of parameters on cost (Figure 7-4) and the effect of parameters on efficiency (Table 7-7), it is found that the carbonation efficiency is the most important parameter. Increasing the carbonation efficiency from 81 to 96 %
Chapter 7 – Cost evaluation

results in cost reduction from 109 to 72 $/t CO$_2$ sequestered. Although, addition of NH$_3$ in carbonation (from 0 to 0.07 t) is required in order to get high carbonation efficiency, it can save consumption of NH$_4$HSO$_4$ from 0.71 to 0.20 t.

Figure 7-4: Sensitivity analysis of CO$_2$ capture and storage costs for CCSM process with recyclable ammonium salts (1. Dissolution efficiency (%), 2. Carbonation efficiency (%), 3. Solid to liquid ratio (g/l), 4. Reaction time (h), 5. Mg: NH$_4$ salts: NH$_3$ (molar ratio), 6. Particle size (µm), 7. Feedstock (US$/t), 8. Cost of (NH$_4$)$_2$SO$_4$ (US$/t), 9. MVR energy cost (kWh/t), 10. Thermal decomposition (kWh/t), 11. CO2 capture (kWh/t), 12. Electricity (US$/kWh), 13. Operation time (hr/yr), 14. Depreciation time (yr); there is no maximum value for 2, 3 and 5, since the selected standard value is already high, the detail information can be seen in Table 7-6)

The dissolution efficiency is affected by reaction time, solid to liquid ratio and particle size of feedstock. The high dissolution efficiency needs a small amount of feedstock, thus decreasing the feedstock,
transportation costs and reducing the amount of additive (NH₄HSO₄) used. Normally, high dissolution efficiency requires longer reaction time (3 h), low solid to liquid ratio (50 g/l) and small particle size. When decreasing S/L from 100 to 50 g/l, the dissolution efficiency increases from 80 % to 90 %. However, low S/L resulted in larger streams of materials and thereby requires a larger size of equipment and high energy consumption. For example, when the amount of water input increases from 39 to 64.7 t, the size of all equipment nearly doubles. Besides, low S/L increases the energy consumption for water evaporation and the amount of additives used. It can be seen from Figure 7-4 (Parameter 3) that the cost/tCO₂ sequestered decreases from 94 to 72 US$/t, when the solid to liquid ratio increases from 50 to 100 g/l.

Table 7-7: Influence of process conditions on dissolution and carbonation efficiency.

<table>
<thead>
<tr>
<th>Scenario #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid to liquid ratio (g/l)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Reaction time (h)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>75-</td>
<td>75-</td>
<td>75-</td>
<td>75-</td>
<td>38</td>
<td>150-</td>
<td>75-</td>
<td>75-</td>
<td>75-</td>
<td>75-</td>
</tr>
<tr>
<td>Mg:NH₄ salts: NH₃ (molar)</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
</tr>
<tr>
<td></td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
<td>1.5-</td>
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<tr>
<td></td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
When increasing the reaction time from 1 to 3 h, the dissolution efficiency raised slightly from 80 % to 90 %. However, long reaction times significantly increase the size of equipment by as much as 3 times and the investment costs will increase from 9 to 26 US$/t. Small particle size (<38 μm) increases the dissolution efficiency slightly (3 %), but raises the grinding power consumption from 13 to 83 kWh/t, and thus increasing the total cost to 76 US$/t. Therefore, small particle size and long reaction time are not preferred in terms of cost reduction.

The energy consumptions of several steps, such as CO₂ capture, MVR evaporation and thermal decomposition present small variations on cost (no more than 10 US$), because the technologies used in these steps have been optimized and their energy penalties are relatively low. The electricity price has a large influence on the total costs (61-82 US$/t CO₂ sequestered) and this is dependent on the types of fuel source (coal or natural gas) and the technologies.
applied (coal-fired, IGCC, supercritical combustion and NGCC). It was assumed that electricity is supplied from the power plant to the mineral carbonation plant at a low price (0.03 US$/kWh). The long depreciation time reduces the total costs, since the investment costs are spread out over long time periods.

7.4 Comparison to other cost analysis

This section compares the costs of the studies process with other reported mineralisation processes (Table 7-8). For the direct aqueous mineral carbonation process using serpentine, the Albany Research Center (ARC) calculated total costs of 250 US$/t CO$_2$ sequestered excluding chemical cost and investment cost. The main difference between the ARC process and this study is due to the large energy consumption of the heat treatment of serpentine (283 kWh/t serpentine) and high energy consumption resulting from high temperature and high pressure applied (155 °C and 115 bar) (Gerdemann et al., 2007). For the Indirect aqueous mineral carbonation process using serpentine, Teir et al. (2009) calculated total costs of 1300-1600 US$/t CO$_2$ sequestered using serpentine and un-recyclable HCl or HNO$_3$ and NaOH, excluding energy cost and investment cost. The high costs of Teir's work resulted from the unrecyclable nature of the chemicals used. The direct aqueous mineral carbonation using wollastonite and steel slags studied by Huijgen (2007) resulted in costs of 86 and 64 US$/t CO$_2$
sequestered (Table 7.8). Additionally, the costs reported by all the other processes exclude the carbon capture step.

Table 7-8: Comparison of costs reported for mineral carbonation and other carbon capture and storage technologies

<table>
<thead>
<tr>
<th>Costs mineral carbonation (US$/t CO₂ sequestered)</th>
<th>Feedstock</th>
<th>Process route</th>
<th>Chemical used</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 Serpentine</td>
<td>Direct aqueous</td>
<td>NaHCO₃ and NaCl</td>
<td>Gerdemann et al., 2007</td>
<td></td>
</tr>
<tr>
<td>54 Olivine</td>
<td>Direct aqueous</td>
<td>NaHCO₃ and NaCl</td>
<td>Gerdemann et al., 2007</td>
<td></td>
</tr>
<tr>
<td>91 Wollastonite</td>
<td>Direct aqueous</td>
<td>water</td>
<td>Gerdemann et al., 2007</td>
<td></td>
</tr>
<tr>
<td>1300-1600 Serpentine</td>
<td>Indirect aqueous</td>
<td>HCl (HNO₃) and NaOH</td>
<td>Teir et al., 2009</td>
<td></td>
</tr>
<tr>
<td>86 Wollastonite</td>
<td>Direct aqueous</td>
<td>Water</td>
<td>Huijgen et al., 2007</td>
<td></td>
</tr>
<tr>
<td>72 (including capture) serpentine</td>
<td>Indirect aqueous</td>
<td>Ammonium salts</td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>

Overall, the CCSM process with recyclable ammonium salts has the lowest costs of 72 US$/t CO₂ sequestered among the current available mineral carbonation processes using serpentine. The CO₂ capture costs are included in the total cost of the CCSM process. Representative CO₂ capture cost reported for different types of power plants range from 25-75 US$/t CO₂ (IPCC, 2005). Therefore, the integration of the mineral carbonation process with the CO₂
capture process into the CCSM process with recyclable ammonium salts successfully lower the overall costs of CO$_2$ capture and storage costs.

7.5 Summary

A comprehensive cost evaluation (CAPEX and OPEX) of the CCSM process with recyclable ammonium salts has reported 72 US$/t CO$_2$ sequestered. The major costs were found to be associated with chemical costs, energy costs and feedstock costs. Sensitivity analysis have shown that influential parameters in the total costs are the possible value of products, carbonation efficiency, molar ratio of Mg:NH$_4$ salts: NH$_3$, dissolution efficiency, electricity price, price of feedstock and solid to liquid ratio. Generally, total costs were affected by the dissolution efficiency and carbonation efficiency. Carbonation efficiency was affected by molar ratio of Mg: NH$_4$ salts: NH$_3$. Dissolution efficiency was affected by the solid to liquid ratio, reaction time and particle size. The optimized process conditions were determined in this study to obtain the lowest total costs.

Research on cost reduction should focus on carbonation reactor, which is the major CAPEX cost contributor identified in this study. The faster carbonation kinetics can significantly reduce the residence time, thus reducing the CAPEX cost of the carbonation reactor.
Chapter 8. Conclusions and future work

8.1 Conclusions
Carbon dioxide capture and storage by mineralisation (CCSM) is considered as one of the main solutions for reducing anthropogenic CO₂. However, low efficiency of mineral dissolution and unrecyclable use of additives are two key barriers for the development of CCSM. In this thesis, a novel pH-swing mineral carbonation process has been developed to improve the dissolution and carbonation efficiencies using a recyclable ammonium salts. This process is unique in using CO₂ containing ammonium salts from aqueous ammonia capture technology, instead of direct CO₂ gas. The advantages of using CO₂ containing ammonium salts include avoiding CO₂ desorption in the capture step and subsequent CO₂ compression for transportation that are energy intensive steps of the conventional CCS process. The integration of carbon capture and mineral carbonation in this process has not been explored before. Two process routes at different solid to liquid ratios were developed to couple the aqueous ammonia carbon capture step with the subsequent carbonation step. Hence, this thesis provides novel information on the dissolution and carbonation experiments with recyclable ammonium salts at different parameters as well as the
regeneration of ammonium salts. And the reaction conditions were carefully selected to maximize the efficiencies.

8.1.1 Serpentine dissolution with ammonium salts

The dissolution of serpentine using ammonium salts was investigated (Section 4.1). The incongruent leaching of Mg and Si created a passive silicon layer on the surface of the particles preventing further leaching of Mg. The applications of internal grinding and fluidized bed are expected to remove the product layer. The solvent concentration, particle size and solid to liquid ratio was carefully selected through the experimental studies. The Mg dissolution from serpentine achieved 100% in 3 hours when dissolving serpentine with particle size fraction of 75-150 μm and using 1.4 M ammonium bisulfate solution at 50 g/l solid to liquid ratio.

8.1.2. Carbonation with ammonium salts

The precipitation of hydromagnesite from prepared high Mg concentration solution was studied by using NH₃ and NH₄HCO₃ in the multistep process route with pure products (Section 4.2). Pure hydromagnesite, amorphous silica and iron by-products were obtained. The integration of carbon capture with mineralization was successful and show high efficiency. The mass ratio of Mg: NH₄HCO₃: NH₃ was the key factor controlling carbonation efficiency. The additives used, NH₄HSO₄ and NH₃, were regenerated
by the thermal decomposition of \((\text{NH}_4\text{)}_2\text{SO}_4\) at 330 °C with 95 % efficiency.

### 8.1.3. CCSM process route at high solid to liquid ratio

The dissolution and carbonation experiments with recyclable ammonium salts at high solid to liquid ratio conditions were studied in Chapter 5. The dissolution efficiency increased when the solid to liquid ratio increased from 200 g/l to 300 g/l due to particle-particle interactions; magnesite instead of hydromagnesite was found after the carbonation step due to the CO\(_2\) pressure evolved (20 bar); and the carbon fixation efficiency was significantly improved by using \((\text{NH}_4\text{)}_2\text{CO}_3\) rather than using \(\text{NH}_4\text{HCO}_3\).

### 8.1.4. Preliminary cost evaluation

Most of the process units are mature technologies, excluding the unit for thermal decomposition of ammonium salts. Additionally, it was found that the use of waste heat from flue gas to supply the heat required for the thermal decomposition of ammonium salts is very important for the success of the CCSM process with recyclable ammonium salts.

A preliminary cost analysis of the developed CCSM process was conducted to evaluate the OPEX of the two process routes (high and low solid-to-liquid ratio) in terms of energy consumption, chemical costs and feedstock cost (Section 6.2). It was found that high solid to liquid ratios resulted in less streams in the process, and thus
lower energy consumption, but it also decreases the dissolution and carbonation efficiencies. It was suggested that dissolution and carbonation efficiencies at the low solid to liquid ratio scenario was better than those at the high solid to liquid ratio.

8.1.5. Optimization work and cost evaluation

The optimization process conditions were determined according to the results from the process evaluation (Section 6.3). A series of experiments were then conducted at the optimization process conditions to maximize the efficiencies. The dissolution efficiency of Mg from serpentine using 2.8 M NH₄HSO₄ at 100 g/l solid to liquid ratio for 1 h was 80 %. The carbonation efficiency was 96 % when the molar ratio of Mg: NH₄⁺ salts: NH₃ was 1:1.5:2. Finally, a comprehensive cost evaluation (CAPEX and OPEX) of the CCSM process with recyclable ammonium salts was made by using Aspen plus software (Chapter 7). It was found that 93 % of the CO₂ can be sequestered by the process with an energy consumption of 30 %. The total capture and storage costs were calculated to be 72 US$/t CO₂ sequestered in this process. The reaction time and equipment cost still have potential to be reduced. The full life cycle carbon footprint of this CCSM process is needed to show the net CO₂ reduction.
Chapter 8 – Conclusions and future work

8.2 Future work

Based on the results and conclusions from this research, there are several areas that are worthy of further investigation which could contribute significantly to the development of the CCSM process with recyclable ammonium salts.

a) To investigate the dissolution experiments in a fluidized bed reactor or pipeline looping reactor, where particle-particle interactions can improve the dissolution efficiency;

b) To improve the carbonation efficiency in the high solid to liquid ratio conditions by adding ammonia water, which can enhance the carbonation kinetics;

c) To investigate the potential use of a continuous process instead of batch process to reduce the reaction time;

d) To measure the species of CO₂ containing ammonium salts at higher NH₃ concentration (>13 wt. %) in the CO₂ absorption step;

e) To investigate the thermal decomposition of ammonium salts with hot gas which mimics the temperature and chemical composition of flue gas from a boiler in a power plant;

f) To use waste materials from industries instead of serpentine with the CCSM process with recyclable ammonium salts.

g) To investigate the re-use of products from the process, especially, the re-use of carbonate products as supplementary
cementitious material (SCM) to make cement or other construction materials;

h) To investigate the co-removal of $\text{SO}_2$, $\text{NO}_x$ and $\text{Hg}$ in the capture and the carbonation steps.

i) To do the full life cycle carbon footprint of this CCSM process is needed to show the net $\text{CO}_2$ reduction.

j) The choice of equipment for filtering, drying and the other steps need to be investigated to reduce the cost.
References


References


References


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References


ZEVENHOVEN, Ron, JOHAN FAGERLUND, INES ROMAO, JAMES HIGHFIELD, BU JIE (2010) Assessment & improvement of a stepwise magnesium silicate carbonation route via MgSO₄ & Mg(OH)₂. *ACEME 10*. Turku, Finland.

Appendix 1:
The detail of conditions applied in the modelling of mass flow

Dissolution step
For 50 g/l scenario, 1.4 mol/l NH₄HSO₄ (15 wt. %) was used to dissolve serpentine with particle size of 75-150 μm. The Mg dissolution efficiency achieved 100 % after 3 h at 100 °C. 90 % of Fe was dissolved. Product 1 (contain 46.9 wt. % of Si) was filtered after dissolution.

For 300 g/l scenario, 6 mol/l NH₄HSO₄ (53 wt. %) was used to dissolve serpentine with particle size of 75-150 μm. The dissolution efficiency achieved 71 % after 3 h at 100 °C.

pH swing step
1 mol NH₄HSO₄ react with 1 mol NH₃ to produce 1 mol (NH₄)₂SO₄. Assuming that the iron ions precipitate does not consume ammonia water. 13 wt. % NH₃ was used.

Product 2 (60 wt. % Fe) was filtered after pH-swing at 50 g/l scenario.

Capture step
According to Kim’s work, 13 wt. % of NH₃ used in aqueous ammonia CO₂ capture can achieve 95 % absorption efficiency and produce 3.4 mol/l total CO₂ containing ammonium salts (41 % NH₄HCO₃, 24 % (NH₄)₂CO₃ and 35 % NH₄NH₂CO₂, molecular weight is 82.52) after breakthrough point of 6 h (Kim et al., 2008). In the other way, capturing 1 t CO₂ requires 0.76 t NH₃ and 5.01 t H₂O and produces 1.88 t of CO₂ containing ammonium salts (where contains 35 % ammonium carbamate, 41 % ammonium bicarbonate and 24 % ammonium carbonate).
## Appendix 2

Input and output streams in each step of the two process routes.

<table>
<thead>
<tr>
<th></th>
<th>Mass at 50 g/l</th>
<th>Mass at 300 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>scenario (t)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Serpentine</td>
<td>2.96</td>
<td>4.88</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>9.54</td>
<td>11.22</td>
</tr>
<tr>
<td>H₂O</td>
<td>54.91</td>
<td>10.16</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO₄</td>
<td>3.55</td>
<td>4.17</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3.91</td>
<td>4.59</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>2.73</td>
<td>3.23</td>
</tr>
<tr>
<td>H₂O</td>
<td>55.80</td>
<td>11.20</td>
</tr>
<tr>
<td><strong>Product 1 (46.9 wt. % Si)</strong></td>
<td>1.27</td>
<td>0.00</td>
</tr>
<tr>
<td>Serpentine</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Residual solid (including serpentine and SiO₂)</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgSO₄</td>
<td>3.55</td>
<td>4.17</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3.91</td>
<td>4.59</td>
</tr>
<tr>
<td><strong>pH-swing step</strong></td>
<td>2.73</td>
<td>3.23</td>
</tr>
<tr>
<td>H₂O</td>
<td>58.49</td>
<td>14.40</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>NH₃ for pH-swing</td>
<td>0.40</td>
<td>0.48</td>
</tr>
<tr>
<td><strong>Residual solid output</strong></td>
<td>3.07</td>
<td></td>
</tr>
</tbody>
</table>
### Appendix

<table>
<thead>
<tr>
<th>Material</th>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄</td>
<td>3.55</td>
<td>4.17</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>7.04</td>
<td>8.30</td>
</tr>
<tr>
<td>H₂O</td>
<td>58.39</td>
<td>14.40</td>
</tr>
<tr>
<td>Product 2 (60 wt. % Fe)</td>
<td>0.25</td>
<td>0.00</td>
</tr>
<tr>
<td>Residual solid</td>
<td>3.07</td>
<td></td>
</tr>
</tbody>
</table>

#### Capture step

**Input**

- CO₂: 4.99/1.46
- NH₃ (13 wt. %): 3.82/1.12
- H₂O: 24.21/7.10

**Output (95 % efficiency, 6 h)**

- NH₄HCO₃/(NH₄)₂CO₃/NH₄NH₂CO₂: 9.36/2.75
- NH₃: 0.76/0.22
- H₂O: 23.05/6.76
- CO₂: 0.61/0.18

#### Carbonation ion step

**Input**

- MgSO₄: 3.55/4.17
- (NH₄)₂SO₄: 7.04/8.30
- NH₄HCO₃/(NH₄)₂CO₃/NH₄NH₂CO₂: 9.36/2.75
- NH₃ for carbonation: 1.01/0.00
- Residual solid: 3.07

**Output**

- H₂O: 88.18/21.16

- (NH₄)₂SO₄: 10.79/11.30
- Hydromagnesite: 2.75
- NH₃: 0.52
- MgSO₄: 0.15/1.44
- NH₄HCO₃/(NH₄)₂CO₃/NH₄NH₂CO₂: 7.12/0.56

**NH₃**
<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td></td>
<td>1.91</td>
</tr>
<tr>
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</tr>
<tr>
<td>H₂O</td>
<td>87.67</td>
<td>21.16</td>
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**Input**

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<tbody>
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<td>(NH₄)₂SO₄</td>
<td>10.79</td>
<td>11.30</td>
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<td>H₂O</td>
<td>87.67</td>
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**Regener**

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<tr>
<td>NH₄HSO₄</td>
<td>9.30</td>
<td>9.74</td>
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<tr>
<td>NH₃</td>
<td>1.38</td>
<td>1.44</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.11</td>
<td>0.11</td>
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<td>H₂O</td>
<td>87.67</td>
<td>21.16</td>
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**Serpentine**

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<td>-0.70</td>
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<td>NH₃</td>
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<td>-0.25</td>
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<td>NH₄HCO₃/(NH₄)₂CO₃/NH₄NH₂CO₂</td>
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**Sum**

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<tbody>
<tr>
<td>MgSO₄</td>
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<td>0.11</td>
</tr>
<tr>
<td>Product 1</td>
<td>1.27</td>
<td></td>
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<tr>
<td>Product 2</td>
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<tr>
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<td>hydromagnesite</td>
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<td>2.75</td>
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Appendix 3.

Input and output streams in each step, the energy consumption, and chemical cost of the four optimization experiments,

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<thead>
<tr>
<th></th>
<th>OP 1</th>
<th>OP 2</th>
<th>OP 3</th>
<th>OP 4</th>
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<tr>
<td><strong>Input</strong></td>
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<td>Serpentine</td>
<td>3.50</td>
<td>3.32</td>
<td>3.15</td>
<td>2.96</td>
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<tr>
<td>NH₄HSO₄</td>
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<td>10.69</td>
<td>10.14</td>
<td>9.53</td>
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<td>H₂O</td>
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<td>26.16</td>
<td>24.83</td>
<td>23.33</td>
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<tr>
<td><strong>Output</strong></td>
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<tr>
<td>MgSO₄</td>
<td>3.36</td>
<td>3.19</td>
<td>3.02</td>
<td>2.84</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3.69</td>
<td>3.50</td>
<td>3.33</td>
<td>3.12</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
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<td>4.35</td>
<td>4.08</td>
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<td>H₂O</td>
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<td>26.96</td>
<td>25.58</td>
<td>24.04</td>
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<td><strong>Mineral dissolution step</strong></td>
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<td>Product 1 (46.9 wt. % Si)</td>
<td>1.16</td>
<td>1.10</td>
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<td>0.98</td>
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<td>Serpentine</td>
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<td>0.63</td>
<td>0.59</td>
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<tr>
<td>Fe²⁺</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
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<tr>
<td><strong>Residual solid</strong></td>
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<tr>
<td>(including serpentine and SiO₂)</td>
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</tr>
<tr>
<td>MgSO₄</td>
<td>3.36</td>
<td>3.19</td>
<td>3.02</td>
<td>2.84</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>3.69</td>
<td>3.50</td>
<td>3.33</td>
<td>3.12</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>4.83</td>
<td>4.58</td>
<td>4.35</td>
<td>4.08</td>
</tr>
<tr>
<td>H₂O</td>
<td>33.19</td>
<td>31.49</td>
<td>29.88</td>
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<tr>
<td>Fe²⁺</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
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<tr>
<td>NH₃ for pH-swing</td>
<td>0.71</td>
<td>0.68</td>
<td>0.64</td>
<td>0.60</td>
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<td><strong>Residual solid</strong></td>
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<td>output</td>
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<td>------------------------------------------</td>
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<tr>
<td>MgSO₄</td>
<td>3.36 3.19 3.02 2.84</td>
<td></td>
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<tr>
<td>(NH₄)₂SO₄</td>
<td>9.24 8.76 8.31 7.81</td>
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<tr>
<td>H₂O</td>
<td>33.07 31.37 29.77 27.98</td>
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<tr>
<td>Product 2 (60 wt. % Fe)</td>
<td>0.30 0.28 0.27 0.25</td>
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<tr>
<td>Residual solid</td>
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<tr>
<td>CO₂</td>
<td>1.18 1.68 1.06 1.50</td>
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<td>NH₃ (13 wt. %)</td>
<td>0.90 1.28 0.81 1.14</td>
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<td>H₂O</td>
<td>5.72 8.14 5.15 7.26</td>
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<tr>
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<th>Captur output</th>
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<tr>
<td>NH₄HCO₃/(NH₄)₂CO₃/NH</td>
<td>2.21 3.15 1.99 2.81</td>
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<tr>
<td>4NH₂CO₂</td>
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<tr>
<td>NH₃</td>
<td>0.18 0.25 0.16 0.23</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.44 7.75 4.90 7.02</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.14 0.21 0.13 0.07</td>
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<table>
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<tr>
<td>MgSO₄</td>
<td>3.36 3.19 3.02 2.84</td>
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<tr>
<td>(NH₄)₂SO₄</td>
<td>9.24 8.76 8.31 7.81</td>
</tr>
<tr>
<td>NH₄HCO₃/(NH₄)₂CO₃/NH</td>
<td>2.21 3.15 1.99 2.81</td>
</tr>
<tr>
<td>4NH₂CO₂</td>
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<td>NH₃ for carbonation</td>
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<td>H₂O</td>
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<td>(NH₄)₂SO₄</td>
<td>12.24 11.76 11.31 10.81</td>
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<td>Hydromagnesite</td>
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<td>NH_{4}HCO_{3}/(NH_{4})<em>{2}CO</em>{3}/NH</td>
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<tr>
<td>4NH_{2}CO_{2}</td>
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<td>NH_{3}</td>
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<td>H_{2}O</td>
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/\[\text{H}_{2}O\]/input

/\[\text{(NH}_{4}\text{)}_{2}\text{SO}_{4}\]/Regen output

/\[\text{NH}_{4}\text{HSO}_{4}\]/output

/\[\text{NH}_{3}\]/output

/\[\text{(NH}_{4}\text{)}_{2}\text{SO}_{4}\]/output

/\[\text{H}_{2}O\]/output

/\[\text{Serpentine}\]/Regen output

/\[\text{H}_{2}O\]/output

/\[\text{NH}_{4}\text{HSO}_{4}\]/output

/\[\text{NH}_{3}\]/output

/\[\text{(NH}_{4}\text{)}_{2}\text{SO}_{4}\]/output

/\[\text{H}_{2}O\]/output

/\[\text{Product 1}\]/output

/\[\text{Product 2}\]/output

/\[\text{NH}_{4}\text{HCO}_{3}/(NH}_{4}\text{)_{2}CO_{3}/NH\]/output

/\[\text{4NH}_{2}CO_{2}\]/output

/\[\text{MgSO}_{4}\]/output

/\[\text{(NH}_{4}\text{)}_{2}\text{SO}_{4}\]/output

229
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<tr>
<td>(NH₄)₂SO₄ (equal, 99%)</td>
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<td>0.63</td>
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<tr>
<td>Cost of (NH₄)₂SO₄</td>
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<td>56.57</td>
<td>39.91</td>
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<td>0.00</td>
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<td>-23.29</td>
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<td><strong>Chemical cost (US$)</strong></td>
<td>54.74</td>
<td>45.85</td>
<td>37.48</td>
<td>24.90</td>
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