DIRECT AND INDIRECT AQUEOUS MINERALIZATION USING RED GYPSUM FOR CARBON DIOXIDE SEQUESTRATION

AMIN AZDARPOUR

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Petroleum Engineering)

Faculty of Petroleum and Renewable Energy Engineering
Universiti Teknologi of Malaysia

JANUARY 2015

“To my beloved family”

ACKNOWLEDGEMENT

Thanks to ALLAH, the Most Gracious and the Most Merciful, All praise and glory are to Almighty Allah who gave me the courage and patience to accomplish this research. Without his help and mercy, this wouldn’t be possible.

First and foremost, I would like to express my deep gratitude to my dear supervisor Professor Dr. Radzuan Bin Junin for all his kindness, assistance and guidance. I also want to thank my co-supervisor Dr. Muhammad A. Manan for his encouragements and valuable comments. It has been an honour and a privilege to have the opportunity to work with them.

I wish to thank the Universiti Teknologi Malaysia (UTM) for providing the facilities to advance the project. Indeed, this research project gave me a valuable experience and an excellent insight. I would like to further extend my gratitude to all suppliers and technicians who assisted me directly or indirectly throughout the progress of my project.

I am greatly indebted to Professor Dr. Mohammad Asadullah from Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM) for his supports, assistance and guidance.

Finally, I would like to send my deep appreciations to my lovely wife, mother, father, and sisters who brought me up with love.

ABSTRACT

Carbon capture and storage is gaining prominence as a means of combating climate change. Mineral carbonation is the only known form of permanent and leakage-free carbon storage. The aim of this research was to investigate the suitability and feasibility of utilizing red gypsum as the calcium source for the mineral carbonation process. The physico-chemical analysis of red gypsum showed that calcium and iron are its major constituents, which makes it a highly suitable and potential feedstock for mineral carbonation. The direct carbonation of red gypsum showed that both the purity of the product and the efficiency of the reaction were very low even at elevated reaction temperature and CO_2 pressure. The maximum $CaCO_3$ purity of 23.63% and carbonation efficiency of 41.04% were achieved during direct aqueous carbonation of red gypsum. The red gypsum dissolution studies showed that H_2SO_4 resulted in higher calcium extraction efficiency compared to HCl and HNO_3. Increasing the reaction temperature from 30 °C to 70 °C and also increasing the reaction time from 5 to 120 minutes were found to be effective in enhancing the degree of extraction for all three types of acid used. The maximum of 100% and 84.6% extraction efficiency was achieved for Ca and Fe, respectively. Kinetic analysis found that the dissolution rate of red gypsum is controlled by the combination of product layer diffusion and chemical reaction control. The carbonation efficiency was found to be in direct relationship with CO_2 pressure where the maximum carbonation efficiency of 100% was achieved at 8 bar CO_2 pressure. The pH swing experiments resulted in $CaCO_3$ with a maximum purity of 98%. The pH swing carbonation of red gypsum could be further investigated as a promising method for large scale CO_2 sequestration.

ABSTRAK

Pemerangkapan dan penyimpanan karbon semakin terkenal sebagai satu cara untuk mengatasi masalah perubahan iklim. Pengkarbonan mineral adalah satu-satunya cara yang diketahui sebagai kaedah penyimpanan karbon secara kekal dan bebas daripada kebocoran. Kajian yang dijalankan ini adalah bertujuan untuk mengkaji kesesuaian dan kebolehlaksanaan penggunaan gipsum merah sebagai sumber kalsium untuk proses pengkarbonan mineral. Analisis fisiko-kimia ke atas gipsum merah menunjukkan bahawa kalsium dan ferum adalah juzuk utamanya, yang menjadikan ianya sangat sesuai dan berpotensi sebagai sumber bahan mentah bagi proses pengkarbonan mineral. Proses pengkarbonan langsung ke atas gipsum merah menunjukkan hasil tindakbalasnya adalah sangat rendah terutama darisegi ketulenan produk dan kecekapan tindakbalasnya walaupun tindakbalas dijalankan pada suhu dan tekanan CO_2 tinggi. Dalam proses pengkarbonan berakues langsung pada gipsum merah, didapati ketulenan maksimum sebatian $CaCO_3$ yang dicapai adalah 23.63% manakala kecekapan pengkarbonan adalah sebanyak 41.04%. Kajian kebolehlarutan gipsum merah menunjukkan bahawa H_2SO_4 menghasilkan kecekapan pengekstrakan kalsium lebih tinggi berbanding dengan HCl dan HNO_3. Peningkatan suhu tindak balas daripada 30 °C hingga 70 °C dan juga masa tindak balas dari 5 hingga 120 minit didapati lebih berkesan dalam meningkatkan tahap pengekstrakan kalsium apabila menggunakan ketiga-tiga jenis asid tersebut. Kecekapan pengekstrakan maksimum sebanyak 100% telah dicapai bagi Ca, manakala bagi Fe adalah 84.6%. Analisis kinetik mendapati bahawa kadar kebolehlarutan gipsum merah dipengaruhi oleh gabungan dua faktor iaitu serapan lapisan hasil bahan dan kawalan tindak balas kimia. Kecekapan pengkarbonan didapati mempunyai hubungan secara langsung dengan tekanan CO_2, yang mana kecekapan pengkarbonan maksimum 100% dicapai pada tekanan CO_2 8 bar. Eksperimen pH-berubah dapat menghasilkan sebatian $CaCO_3$ dengan ketulenan maksimum sebanyak 98%. Dengan ini didapati bahawa pengkarbonan pH-berubah ke atas gipsum merah boleh dikaji selanjutnya kerana ianya amat berpotensi sebagai satu kaedah untuk proses pemencilan- CO_2 yang berskala besar.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

GHG - Greenhouse gas
CO_2 - Carbon Dioxide
ppm - parts per million
IPCC - Intergovernmental Panel on Climate Change
Gt - Gigatone
$^{\circ}C$ - Degree Celsius
CCS - Carbon capture and storage
Ca - Calcium
Mg - Magnesium
Fe - Iron
Mg_2SiO_4 - Olivine
$CaSiO_3$ - Wollastonite
$Mg_3Si_2O_5(OH)_4$ - Serpentine
RG - Red gypsum
$FeTiO_3$ - Ilmenite
TiO_2 - Titanium dioxide
$TiOSO_4$ - Titanyl sulphate
$FeSO_4$ - Iron sulphate
$CaSO_4.2H_2O$ - Gypsum
ppmv - parts per million per volume
TGA - Thermogravimetric analysis
DTA - Differential thermal analysis
FESEM - Field emission scanning electron microscopy
ICP-OES - Inductively coupled plasma optical emission spectrometry
FT-IR - Fourier transform infra-red spectroscopy

SEM	-	Scanning electron microscopy
XRD	-	X-ray diffraction
XRF	-	X-ray fluorescence
NaOH	-	Sodium hydroxide
KOH	-	Potassium hydroxide
NH_4OH	-	Ammonium hydroxide
H_2SO_4	-	Sulphuric acid
HCl	-	Hydrochloric acid
HNO_3	-	Nitric acid
rpm	-	Round per minute
mL	-	Millilitre
ln	-	Natural log
Ea	-	Activation energy
K_o	-	Frequency factors
M	-	Molar
HPHT	-	High pressure high temperature
IEA	-	International Energy Agency
C	-	Carbon
ppb	-	parts per billion
Mg_2SiO_4	-	Forsterite
Fe_2SiO_4	-	Fayalite
$Mg_3Si_4O_{10}(OH)_2$	-	Talc
$CaMgSiO_6$	-	Diopside
SiO_2	-	Quartz
$F_2Mg_5(SiO_4)_2$	-	Kondrodite
$H_4Ca_{12}Al_6Si_{10}O_{43}$	-	Vesuvianite
$CaMg_3Si_4O_{12}$	-	Tremolite
BF	-	Blast furnace
LF slag	-	Ladle furnace slags
EAF	-	Electric arc furnace
BOF	-	Basic oxygen furnace
CKD	-	Cement kiln dust
MSW	-	Municipal solid waste ash
BA	-	Bottom ash

APC - Air pollution control
μm - Micron meter
$MgCO_3$ - Magnesium carbonate
$CaCO_3$ - Calcium carbonate
MPa - Mega Pascal
NaCl - Sodium chloride
$NaHCO_3$ - Sodium bicarbonate
NH_4HSO_4 - Ammonium bisulfate
NH_3 - Ammonia
$(NH_4)_2CO_2$ - Ammonium Carbonite
NH_4Cl - Ammonium chloride
GGBS - Ground granulated blast furnace slag
PS - Phosphorus slag
SS - Steel slag
S/L - Solid to liquid ratio
g/L - Gram per litre
PGM - Platinum group metals
$FeCO_3$ - Siderite
mm - Millimetre
K - Kelvin
Fe_2O_3 - Hematite
CaO - Calcium oxide
S - Sulfur
SO_3 - Sulfur trioxide
MnO - Manganese oxide
TiO_2 - Titanium dioxide
SiO_2 - Silicon dioxide
CO_3^{-2} - Carbonate
mg - Milligram
PSD - Particle size distribution
$CaSO_4$ - Calcium sulphate
H_2CO_3 - Carbonic acid
HCO_3^- - Bicarbonate
K_{sp} - Carbonate solubility product

K_H - Henry’s constant

K_{a1} - First order dissociation of carbonic acid

K_{a2} - Second order dissociation of carbonic acid

Fe^{2+} - Ferrous

Fe^{3+} - Ferric

$FeSO_4$ - Iron(II) sulfate

CH_3COOH - Acetic acid

HCOOH - Formic acid

mg/L - Milligram per litre

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	In this appendix the methodology of solution preparation and molecular weight of compounds and elements are presented	175
B	In this appendix the XRD and TGA analysis of pure materials is presented	178
C	The details of experimental findings of direct carbonation of RG are presented in this appendix	181
D	In this appendix the results of Ca/Fe extraction from red gypsum is presented	188
E	The details of pH swing carbonation experiments are presented in this appendix	212
F	List of Publications	219

CHAPTER 1

INTRODUCTION

1.1 Introduction

It is postulated that the current warming of the global climate is the result of the increase in anthropogenic greenhouse gas (GHG) emissions, particularly carbon dioxide (CO_2) since the beginning of the industrial revolution (IPCC, 2007). The average atmospheric CO_2 has increased from 280 ppm in the 1750s to 389 ppm in 2010 (IPCC, 2005; IPCC, 2007; Bobicki *et al*., 2012). The increase in atmospheric CO_2 over the last two and a half centuries has been attributed to two major anthropogenic forcing fluxes: (i) emissions from fossil fuel combustion and industrial processes and (ii) land use change (Canadell *et al*., 2007; IPCC, 2007; Raupach *et al*., 2007). Because the use and supply of global energy is projected to grow, especially as developing countries pursue industrialization, fossil fuels are expected to maintain their dominance in the global energy mix until 2030 and beyond. If no proactive mitigative action is taken, energy-related CO_2 emissions are likely to be 40-110% higher in 2030 than they were in 2000 (23.5 Gt CO_2 per annum) (IPCC, 2007; IEA, 2011). The latest figures indicate that the world CO_2 emission from fuel combustion was 29.4 Gt in 2008 (IEA, 2011). By 2100, atmospheric CO_2 concentrations could reach 540-970 ppm (IPCC, 2001), resulting in a global mean temperature increase of 1.8–4 ºC (IPCC, 2005). It is recognized that a temperature increase of this magnitude would have wide-ranging and drastic implications for water and food availability, human health, ecosystems, coastlines and biodiversity (Kiehl and Trenberth, 1997; Yamasaki, 2003; IEA, 2003; Feely *et al*., 2004; IPCC, 2005; van Alphen *et al*., 2010a; Bobicki *et al*., 2012).

Reducing the energy intensity, switching to non–fossil fuels, and enhancing CO_2 sequestration by developing technologies to capture and sequester more CO_2 are the available and applicable methods of reducing the CO_2 concentration. However, in a short-to-medium period, CO_2 sequestration methods are necessary to implement to avoid further increase of CO_2 (Raupach *et al*., 2007; Bobicki *et al*., 2012). The contribution of up to 15−55% of the cumulative global climate change mitigation effort by 2100 has been predicted by carbon capture and storage (CCS) methods. Moreover, improvements of CO_2 sequestration methods, the increase of their effectiveness and the change to a carbon-free fuel, such as renewables, are very important to achieve a sustainable energy system (Yamasaki, 2003; IPCC, 2005).

The basic steps of CCS methods consist of post–combustion and pre–combustion CO_2 capture, separation from other gases, transportation to the sites, and CO_2 isolation from the atmosphere via storage. CO_2 sequestration is a process that involves all four steps of CO_2 capture, separation, transportation, and finally storage. Geological CO_2 storage, ocean storage, below seabed storage, and CO_2 mineral sequestration are the practical techniques of CO_2 sequestration (Svensson *et al*., 2004; Gibbins and Chalmers, 2008; Olajire, 2010).

Geological storage is the injection of CO_2 into abandoned underground gas/oil fields or saline formations to improve the oil, gas, and coal bed methane recovery from reservoirs. Several projects operating in Norway (such as the Sleipner project), Canada, Algeria, Australia, and other locations are examples of the use of this method throughout the world. However, the lack of permanency, the risk of leakage and the post–monitoring of the site are the problems and challenges associated with this method (IPCC, 2005). CO_2 injection into the great depth of ocean water results in carbonate production due to the reaction of CO_2 with ocean water and carbonic acid dissociation. Ocean storage is very suitable for CO_2 reduction; however, environmental issues, such as decreasing of water pH and the lack of permanency, have made this method unattractive in recent years (Huesemann, 2006; Bobicki *et al.*, 2012). CO_2 storage below the ocean floor at depths of at least 3,000 m of ocean and several hundred meters of marine sediment is called below seabed storage. The lack of permanency and post–monitoring of the site (negative points of geological and ocean storage) do not exist with below seabed storage method; however, this method is still new and requires further research (House *et al.*, 2006).

Mineral carbon dioxide sequestration is an exothermic chemical reaction of a metal–bearing oxide, usually calcium (Ca), magnesium (Mg), or iron (Fe), with CO_2 to form stable solid carbonates. Carbonation can take place either in-situ or ex-situ (Bobicki *et al.*, 2012). In–situ carbonation is the reaction of CO_2 with Mg and Ca minerals underground where CO_2 is being injected, and ex-situ carbonation is the same reaction taking place above ground in a chemical processing plant (Lackner *et al.*, 1995; Gerdemann *et al.*, 2004). The CO_2 mineralization, or mineral carbonation, is an artificial rock weathering and was first proposed by Seifritz in 1990, whereas natural rock weathering is a geological time-scale process (Seifritz, 1990). Mineral carbonation provides a permanent and leakage–free CO_2 disposal method in that the produced carbonates are environmentally benign and stable (Maroto–Valer *et al.*, 2005). The produced carbonates are also profitable because Ca and Mg carbonates are widely used industrially, such as in papers, paints, plastics, adhesives, sealants, cosmetics, flooring, fireproofing and fire–extinguishing industries (Bobicki *et al.*, 2012).

Alkaline earth metals, such as Ca and Mg, are the most favorable metals for mineral carbonation (Huijgen and Comans, 2003). However, these minerals are usually rare in nature due to their high reactivity, and they usually appear in the form of silicates. The most common natural silicate minerals are olivine (Mg_2SiO_4), wollastonite ($CaSiO_3$), and serpentine ($Mg_3Si_2O_5(OH)_4$) (Lackner *et al.*, 1995; Huijgen and Comans, 2003). In addition to the natural minerals, industrial solid residues and wastes rich in Mg and Ca are also potential materials to be used as carbonation feedstocks. Some more investigated and well–known waste solids, such as waste ashes, waste cement, steelmaking slag, and mining wastes, can also be used as carbonation feedstocks (Bertos *et al.*, 2004; IPCC, 2005; Bonenfant *et al.*, 2008a, Dri *et al.*, 2013; Dri *et al.*, 2014).

Red gypsum (RG) is a by-product produced during titanium dioxide (TiO_2) production from ilmenite ($FeTiO_3$) ores. Ilmenite contains approximately 43-65% titanium dioxide and is widely used as raw material for titanium dioxide manufacturing. Titanium dioxide is extracted from ilmenite through stepwise processes. The first step is the chemical reaction of ilmenite with sulfuric acid to digest the ore. In this step, the titanyl sulfate ($TiOSO_4$) and iron sulfate ($FeSO_4$) are produced. The second step is the clarification of produced liquor through solid separation. This is followed by the hydrolyzation of the liquor by steam for TiO_2 precipitation. Finally, the hydrated TiO_2 is separated and washed with water to remove the impurities. The neutralization of the spent sulfuric acid during TiO_2 extraction with limestone and lime produces a by-product named RG ($CaSO_4.2H_2O$). In the next step, the RG is filtered and separated from water, and the produced water is recycled in the process. This waste product is disposed of in landfill areas or left as stacks close to the titanium dioxide industry. RG is rich in Ca and Fe (more than 70%), which makes it a very potential feedstock for mineral carbonation. The titanium dioxide industry in Malaysia produces 400,000 tons of RG annually that could be utilized for CO_2 sequestration (Fauziah *et al.*, 1996, Azdarpour *et al.*, 2014).

1.2 Problem Statement

One main technical parameter makes the mineral carbonation process industrially viable. The process must result in high carbonation efficiency and products purity at low operating conditions, which means at low CO_2 pressure and reaction temperature (Bobicki *et al.*, 2012). The main barriers to the commercial deployment of mineral carbonation are low carbonation conversion and slow reaction kinetics. It has been stated in the literature that carbonation through direct mineral carbonation results in low carbonation efficiency and product purity. This is because the process suffers from thermodynamic limitations, which results in low overall carbonation efficiency (O'Connor *et al.*, 2000a; O'Connor *et al.*, 2000b; Gerdemann *et al.*, 2004). In some of the studies in the literature, moderately high carbonation efficiencies have been reported; however, critical analysis of those studies reveals that relatively high CO_2 pressure and reaction temperature have been utilized. This inherently increases the overall cost and required energy of the project and prevents the project from being implemented in large-scale (Lackner *et al.*, 1997; Fauth *et al.*, 2000; Fauth *et al.*, 2002; Goldberg and Walters, 2002). In some of the studies in the literature, even at relatively high CO_2 pressure and reaction temperature, the overall carbonation efficiency is still low, which hinders the process from being implemented in large-scale (Béarat *et al.*, 2002; Huijgen *et al.*, 2006; Lammers *et al.*, 2011). Another problem arises from mining and pretreatment of feedstocks. The natural minerals require mining activities, energy-intensive pre-treatments, such as fine grinding, heat treatment, and chemical activation with strong acids, to provide adequate conversions and reaction kinetics. These activities increase the overall required energy of the carbonation process (Lackner *et al.*, 1997; O'Connor *et al.*, 2001; Goldberg *et al.*, 2002; Huijgen *et al.*, 2006; Teir *et al.*, 2005; Teir *et al.*, 2007a; Teir *et al.*, 2007b).

Therefore, carbonation through an indirect process has been proposed in this study to improve the carbonation efficiency and product purity. In addition, this research is aimed to utilize the by-product red gypsum, an industrial waste rich in Ca and Fe, as a feedstock for the mineral carbonation process.

1.3 Research Objectives

This research investigated the suitability and feasibility of utilizing RG as the Ca source for mineral carbonation processes. In addition, this research also investigates the effects of different reaction conditions, such as temperature, CO_2 pressure and particle size, on the overall carbonation process in a wide range, not only at certain limited values. Based on the research novelty and also the contributions to the literature, the objectives of this research are defined as follows:

1. To determine physico-chemical properties of red gypsum as the feedstock

2. To evaluate the feasibility of the red gypsum for carbonation through direct carbonation

3. To evaluate the efficiency of calcium and iron extraction from red gypsum by using different acids and bases along with kinetic analysis for indirect carbonation process

4. To determine the effect of CO_2 pressure on the overall carbonation of pH swing process

1.4 Research Scope

In this research, RG ($CaSO_42H_2O$), a by-product from the titanium dioxide industry that is rich in Ca and Fe, is selected as the potential feedstock for mineral carbonation purposes. This research consists of four main steps, including characterization of raw red gypsum in the first step, direct carbonation of RG in the second step, Ca extraction from RG in the third step and, finally, implementation of the pH swing process at different CO_2 pressures. These four main steps are designed and aimed in such a way to cover all objectives of this study.

RG is characterized physically, chemically, and mineralogically using inductively coupled plasma optical emission spectrometry (ICP-OES), flourier transform infrared (FT-IR) spectroscopy, X-ray fluorescence (XRF) analysis, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), particle size distribution (MASTERSIZER 2000) analysis, and X-ray diffraction (XRD) analysis.

For the direct carbonation of RG, different CO_2 pressure of 1 to 70 bar in conjunction with different reaction temperature of 25 to 300 °C applied. In addition, RG with several range of particle size of less than 45 microns, 45-75, 75-100, 100-212, 212-300, 300-400, and 400-500 microns utilized. In these experiments, NH_4OH used as a basic solution in all experiments. All carbonation experiments conducted in a 100 mL autoclave mini reactor capable of withstanding a maximum pressure of 200 bar and maximum temperature of 450 °C.

In the third step of this research, H_2SO_4, HCl and HNO_3 with variable concentrations of 0.1 to 4 M utilized to extract Ca from RG. A stirring rate of 1000 rpm used consistently in all experiments. The reaction temperatures of 25, 30, 50 and 70 °C in conjunction with variable reaction times of 5 to 120 min utilized. All dissolution experiments carried out in a 500 mL spherical glass batch reactor. In addition, the kinetic analyses performed using heterogeneous reaction models and pseudo-homogeneous models. Finally, Arrhenius plot used to calculate the activation energies (Ea).

In the final step, initially 2 M H_2SO_4 was used for RG dissolution at 70 ºC with 60 min reaction time and 1000 rpm stirring rate. NH_4OH was used to remove impurities from the Ca-rich solution. The carbonation experiments performed under CO_2 initial pressure of 1 to 70 bar at a constant reaction temperature of 25 °C. A 100 mL autoclave mini reactor with temperature controller was used for all carbonation experiments.

1.5 Significance of the Study

Increasing anthropogenic greenhouse gas emissions and, in particular, CO_2 have caused the current warming of the global climate (Canadell *et al.*, 2007; IPCC, 2007). Excessive fossil fuel combustion, industrial processes and land use changes are considered as the main causes of increasing the atmospheric CO_2 concentration

(IPCC, 2007; Raupach *et al.*, 2007). In this regard, stabilization of the atmospheric CO_2 concentration is of great importance (Bobicki *et al.*, 2012). CCS involves separation of CO_2 from gaseous wastes, transportation to storage sites and, finally, long term isolation from the atmosphere. CCS has been proposed as a bridging technology that will allow CO_2 emissions to be managed during fossil fuel dependence while the effort for the use of renewable energy sources steadily increases (van Alphen *et al.*, 2010a, van Alphen *et al.*, 2010b). Mineral carbon sequestration of RG is one of the CCS technologies that provide a safe and leakage-free CO_2 isolation. This study is aimed to discover implementations that will reduce the atmospheric CO_2 concentration. This is because RG contains significant amounts of Ca and Fe (more than 33%), which makes it a very potential feedstock for mineral carbon sequestration processes. Therefore, mineral carbonation of RG will be able to play a significant role in reducing the concentration of CO_2 in the atmosphere. The objectives of this study are designed in such a way that the findings can contribute to the literature data significantly.

This study presents various major contributions to the literature. This research provides comprehensive details regarding the physical and chemical properties of RG. The findings of RG's characterization can be used as a reference for future works. This study also provides knowledge to determine the most effective acid for maximizing the extraction rate of Ca from RG. In addition, the kinetics involved during Ca extraction from RG are introduced. Moreover, this study provides comprehensive knowledge regarding the feasibility of direct and indirect carbonation of RG. The carbonation efficiency and $CaCO_3$ purity are investigated in direct and indirect carbonation under different operating conditions. These findings can be used as valuable references for designing the most effective and feasible carbonation method with the aim of maximum conversion rate with minimum energy loss.

Another significance of this study is the possibility of waste management. RG is considered a waste of titanium extraction industries that is usually accumulated in landfills. Malaysia is considered one of the major RG producers in the world. Therefore, utilization of this waste as a potential feedstock for mineral carbonation processes, alongside process optimizations for large-scale implementation could be a significant achievement in CO_2 mitigation strategies. In addition, the produced carbonates have some industrial applications, such as in papers, paints, plastics, adhesives, sealants, cosmetics, flooring, fireproofing and fire–extinguishing industries (Eloneva *et al*., 2008; Eloneva *et al*., 2010, Bobicki *et al*., 2012).

1.6 Organization of the Thesis

This thesis is organized into six chapters. A brief outline of the contents of the thesis is as follows:

Chapter 1 presents an introduction to the research problem. It involves the background and significance of the research, as well as the problem statement and contributions.

Chapter 2 is devoted to the literature study that has been carried out in relation to subjects concerning this thesis. Firstly, energy dependency on fossil fuels and, consequently, GHG emissions and the global warming phenomenon are studied. Secondly, CCS as one of the key elements in CO_2 mitigating scenarios is reviewed and discussed. Finally, mineral carbonation as the main focus of this research is critically described and reviewed. Suitable feedstocks, carbonation routes and parameters affecting the overall process are critically addressed.

Chapter 3 focuses on introducing methodologies to achieve the designed objectives of this research. Methodologies to conduct RG characterization, direct carbonation of RG, Ca/Fe extraction from RG, and pH swing carbonation of RG are fully designed and described in this chapter.

Chapter 4 presents the results of RG characterization as well as direct carbonation of RG. The characterization studies include physical and chemical analysis of RG. The results of direct carbonation of RG are expressed in terms of product purity and carbonation efficiency with respect to variable RG particle size, different CO_2 pressure and reaction temperature.

Chapter 5 presents the results of RG dissolution and pH swing carbonation. In the first section, the dissolution results are presented in terms of Ca/Fe extraction efficiency with respect to different reaction temperatures and times. In addition, kinetic analysis results are also provided to support the experimental findings. In the second section, the results of the pH swing carbonation experiments with different CO_2 pressures are provided. The results are expressed in terms of product purity, carbonation efficiency and removal efficiency.

Chapter 6 sums up the research findings and outlines the directions for future research works.

REFERENCES

Ashraf, M., Zafar, Z. I., Ansari, T. M. (2005). Selective leaching kinetics and upgrading of low-grade calcareous phosphate rock in succinic acid. *Hydrometallurgy*. 80: 286–292.

Azdarpour, A., Asadullah, M., Junin, R., Manan, M., Hamidi, H., and Mohammadian, E. (2014). Direct carbonation of red gypsum to produce solid carbonates. *Fuel Processing Technology*. 126: 429–434.

Baldyga, J. Henczka, M. and Sokolnicka, K. (2010). Utilization of carbon dioxide by chemically accelerated mineral carbonation. *Materials Letters*. 64: 702–704.

Bang, J. H., Jang, Y. N., Kim, W., Song, K. S., Jeon, C. W., Chae, S. C., Lee, S. W., Park, S. J., and Lee, M. G. (2011). Precipitation of calcium carbonate by carbon dioxide microbubbles. *Chemical Engineering Journal*. 174(1): 413–420.

Battisti, D. S. and Naylor, R. S. (2009). Historical warnings of future food insecurity with unprecedented seasonal heat. *Science*. 323(5911): 240–244.

Béarat, H., McKelvy, M. J., Chizmeshya, A. V. G., Sharma, R., and Carpenter, R. W. (2002). Magnesium hydroxide dehydroxylation/carbonation reaction processes: Implications for carbon dioxide mineral sequestration. *Journal of the American Ceramic Society*. 85(4): 742–748.

Bernardo, E., Dal Maschio, R. (2011). Glass–ceramics from vitrified sewage sludge pyrolysis residues and recycled glasses. *Waste Management*. 31: 2245–2252.

Bertos, F. M., Simons, S. J. R., Hills, C. D., and Carey, P. J. (2004). A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2. *Journal of Hazardous Materials*. 112:193–205.

Blencoe, J. G., Palmer, D. A., Anovitz, L. M., and Beard, J. S. (2004). *U. S. Patent US20040213705 A1*. Washington DC: U.S. Patent and Trademark Office.

Bobicki, E. R., Liu, Q., Xu, Z., and Zeng, H. (2012). Carbon capture and storage using alkaline industrial wastes. *Progress in Energy and Combustion Science*. 38: 302–320.

Bonenfant, D., Kharoune, L., Sauvé, S., Hausler, R., Niquette, P., Mimeault, M., and Kharoune, M. (2008a). CO_2 sequestration potential of steel slags at ambient pressure and temperature. *Industrial and Engineering Chemistry Research*. 47: 7610–7616.

Bonenfant, D., Kharoune, L., Sauve, S., Hausler, R., Niquette, P., Mimeault, M., and Kharoune, M. (2008b). CO_2 sequestration by aqueous red mud carbonation at ambient pressure and temperature. *Industrial and Engineering Chemistry Research*. 47: 7617-7622.

Böke, H., Akkurt, S., Özdemir, S., Gökturk, E. H., Caner Saltik, E. N. (2004). Quantification of $CaCO_3$-$CaSO_3.0.5H_2O$-$CaSO_4.2H_2O$ mixtures by FT-IR analysis and its ANN model. *Materials Letters*. 58: 723-726.

Canadell, J. G., Le Quéré, C., Raupach, M. R., Field, C. B., Buitenhuis, E. T., Ciais, P., Conway, T. J., Gillett, N. P., Houghton, R. A., and Marland, G. (2007). Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proceedings of the National Academy of Sciences*. 104(47): 18866–18870.

Cannane, N. O. A., Rajendran, M., and Selvaraju, R. (2013). FT-IR spectral studies on polluted soils from industrial area at Karaikal, Puducherry State, South India. *Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy*. 110: 46–54.

Carapellucci, R., and Milazzo, A. (2003). Membrane systems for CO_2 capture and their integration with gas turbine plants. *Proceedings of the Institution of Mechanical Engineers Part A: Journal of Power and Energy*. 217: 505–517.

Casas, J. M., Crisóstomo, G., and Cifuentes, L. (2005). Speciation of the Fe(II)–Fe(III)–H_2SO_4–H_2O system at 25 and 50 ºC. *Hydrometallurgy*. 80: 254–264.

Chai, L., and Navrotsky, A. (1994). Enthalpy of formation of siderite and its application in phase equilibrium calculation. *American mineralogist*. 79: 921–929.

Chang, R., Goldsby, K. (2012). *Chemistry*. 11th Edition, McGraw-Hill publisher.

Chen, Z. Y., O'Connor, W. K., and Gerdemann, S. J. (2006). Chemistry of aqueous mienral carbonation for carbon sequestration and explanation of experimental results. *Environmental Progress*. 25(2): 161–6.

Chen, W. L., Chen, C. K., Lee, J. W., Lee, Y. L., Ju, C. P., and Lin, J. H. C. (2014). Structure, properties and animal study of a calcium phosphate/calcium sulfate composite cement. *Materials Science and Engineering: C*. 37: 60–67.

Cizer, Ö., Van Balen, K., Elsen, J., and Van Gemert, D. (2012). Real-time investigation of reaction rate and mineral phase modifications of lime carbonation. *Construction and Building Materials*. 35: 741–751.

CO2CRC. (2007). Cooperative Research Centre for Greenhouse Gas Technologies. http://www.co2crc.com.au/imagelibrary/

Dooley, J. J., Dahowski, R. T., and Davidson, C. L. (2009). The potential for increased atmospheric CO_2 emissions and accelerated consumption of deep geologic CO_2 storage resources resulting from the large-scale deployment of a CCS-enabled unconventional fossil fuels industry in the U.S. *International Journal of Greenhouse Gas Control*. 3(6): 720–730.

Dong, Q., Kumada, N., Yonesaki, Y., Takei, T., Kinomura, N., and Wang, D. (2010). Template-free hydrothermal synthesis of hollow hematite Microspheres. *Journal of Materials Science*. 45: 5685–5691.

Dri, M., Sanna, A., and Maroto-Valer, M. M. (2013). Dissolution of steel slag and recycled concrete aggregate in ammonium bisulphate for CO_2 mineral carbonation. *Fuel Processing Technology.* 113: 114–122.

Dri, M., Sanna, A., and Maroto-Valer, M. M. (2014). Mineral carbonation from metal wastes: Effect of solid to liquid ratio on the efficiency and characterization of carbonated products. *Applied Energy*. 113: 515–523.

Elbeyli, I. Y., and Piskin, S. (2004). Thermal dehydration kinetics of gypsum and borogypsum under Non-isothermal conditions. *Chinese Journal of Chemical Engineering*. 12(2): 302–305.

Eloneva, S., Teir, S., Salminen, J., Fogelholm, C. J., and Zevenhoven, R. (2008). Steel converter slag as a raw material for precipitation of pure calcium carbonate. *Industrial and Engineering Chemistry Research*. 47: 7104–4711.

Eloneva, S., Puheloinen, E. M., Kanerva, J., Ekroos, A., Zevenhoven, R., and Fogelholm, C. J. (2010). Co-utilisation of CO_2 and steelmaking slags for production of pure $CaCO_3$-legislative issues. *Journal of Cleaner Production*. 18: 1833–1839.

Fagerlund, J., Nduagu, E., and Zevenhoven, R. (2011). Recent developments in the carbonation of serpentinite derived $Mg(OH)_2$ using a pressurized fluidized bed. *Energy Procedia*. 4: 4993–5000.

Fauth, D. J., Goldberg, P. M., Knoer, J. P., Soong, Y., O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Walters, R. P., Lackner, K. S., Ziock, H. J., McKelvy, M. J., and Chen, Z. Y. (2000). Carbon dioxide storage as mineral carbonates. *Preprints of symposia-American Chemical Society, Division Fuel Chemistry*. 45(4): 708–712.

Fauth, D. J., Soong, Y., and White, C. M. (2002). Carbon sequestration utilizing industrial solid residues. *Preprints Symposium, American Chemical Society, Division Fuel Chemistry*. 47(1): 37–38.

Fauziah, I., Zauyah, S., and Jamal, T. (1996). Characterization and land application of red gypsum: A waste product from the titanium dioxide industry. *Science of the Total Environment*. 188: 243–251.

Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., and Millero, F. J. (2004). Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans. *Science*. 305: 362–366.

Fouda, M. F. R., Amin, R. E. S., and Abd-Elzaher, M. M. (1996a). Extraction of magnesia from Egyptian serpentine ore via reaction with different acids. I. Reaction with sulfuric acid. *Bulletin of the Chemical Society of Japan*. 69(7): 1907–1912.

Fouda, M. F. R., Amin, R. E. S., and Abd-Elzaher, M. M. (1996b). Extraction of magnesia from Egyptian serpentine ore via reaction with different acids. II. Reaction with nitric and acetic acids. *Bulletin of the Chemical Society of Japan*. 69(7): 1913–1916.

Gázquez, M. J., Bolívar, J. P., García-Tenorio, R., and Vaca, F. (2009). Physicochemical characterization of raw materials and co-products from the titanium dioxide industry. *Journal of Hazardous Materials*. 166: 1429–1440.

Geerlings, J. J. C., Van Mossel, G. A. F., and In't Veen, B. C. M. (2007). *U. S Patent No. US7731921 B2*. Washington DC: U.S. Patent and Trademark Office.

Gerdemann, S. J., Dahlin, D. C., O'Connor, W. K., and Penner, L. R. (2003). *Carbon dioxide sequestration by aqueous mineral carbonation of magnesium silicate minerals*. Technical report, Albany Research Center.

Gerdemann S. J., Dahlin D. C., O'Connor W. K., Penner L. R., and Rush G. E. (2004). Factors affecting ex-situ aqueous mineral carbonation using calcium and magnesium silicate minerals. *The 29th International Technical Conference on Coal Utilization & Fuel Systems.* 13–17 September. Florida, USA.

Gerdemann S. J., O'Connor W. K., Dahlin D. C., Penner, L. R., and Rush H. (2007). Ex situ aqueous mineral carbonation. *Environmental Science and Technology*. 41(7): 2587–2593.

Gharabaghi, M., Irannajad, M., and Azadmehr, A. R. (2013). Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions. *Chemical Engineering Research and Design*. 91: 325–331.

Giammar, D. E., Bruant Jr, R. G., and Peters, C. A. (2005). Forsterite dissolution and magnesite precipitation at conditions relevant for deep saline aquifer storage and sequestration of carbon dioxide. *Chemical Geology*. 217: 257–276.

Gibbins, J., and Chalmers, H. (2008). Carbon capture and storage. *Energy Policy*. 36: 4317–4322.

Goff, F., and Lackner, K. S. (1998). Carbon dioxide sequestering using ultramafic rocks. *Environmental Geosciences*. 5: 89–101.

Goldberg, P., and Walters, R. (2002). A program to develop CO_2 sequestration via mineral carbonation. *The 6th international conference on greenhouse gas control technologies*. 1–4 October. Kyoto, Japan.

Gopi, S., Subramanian, V. K., and Palanisamy, K. (2013). Aragonite-calcite-vaterite: A temperature influenced sequential polymorphic transformation of $CaCO_3$ in the presence of DTPA. *Materials Research Bulletin*. 48: 1906–1912.

Gunning, P. J., Hills, C. D., and Carey, P. J. (2010). Accelerated carbonation treatment of industrial wastes. *Waste Management*. 30: 1081–90.

Hadiko, G., Han, Y. S., Fuji, M., and Takahashi, M. (2005). Synthesis of hollow calcium carbonate particles by the bubble templating method. *Materials Letters*. 59: 2519–2522.

He, L., Yu, D., Lv, W., Wu, J. and Xu, M. (2013). A Novel Method for CO_2 Sequestration via Indirect Carbonation of Coal Fly Ash. *Industrial & Engineering Chemistry Research*. 52: 15138−15145.

Hemmati, A., Shayegan, J., Bu, J., Yeo, T. Y. and Sharratt, P. (2014). Process optimization for mineral carbonation in aqueous phase. *International Journal of Mineral Processing*. 130: 20–27

House, K. Z., Schrag, D. P., Harvey, C. F., and Lackner, K. S. (2006). Permanent carbon dioxide storage in deep-sea sediments. *Proceedings of the National Academy of Sciences*. 103(33): 12291–12295.

Huesemann, M. H. (2006). Can advances in science and technology prevent global warming?. *Mitigation and Adaption Strategies for Global Change*. 11: 539–577.

Huijgen, W. J. J., and Comanas, R. N. J. (2003). *Carbon dioxide sequestration by mineral carbonation: Literature Review*. Technical Report. Energy Research Center of the Netherlands.

Huijgen, W. J. J., Witkamp, G. J., and Comans, R. N. J. (2005). Mineral CO_2 sequestration by steel slag carbonation. *Environmental Science and Technology*. 39: 9676–9682.

Huijgen, W. J. J., Witkamp, G. J., and Comans, R. N. J. (2006). Mechanisms of aqueous wollastonite carbonation as a possible CO_2 sequestration process. *Chemical Engineering Science*. 61(13): 4242–4251.

Huijgen, W. J. J. (2007). *Carbon dioxide sequestration by mineral carbonization*. PhD Thesis, Energy research Centre of the Netherlands, The Netherlands.

IEA. (2003). *World Energy Investment Outlook (EIA2003)*. International Energy Agency, Paris.

IEA. (2011). *World Energy Outlook (EIA2011)*. International Energy Agency, Paris.

IEA. (2012). *The Annual Energy Outlook 2012 with projection to 2035 (AEO2012)*. International Energy Agency, Paris.

Iizuka, A., Fujii, M., Yamasaki, A., and Yanagisawa, Y. (2004). Development of a new CO_2 sequestration process utilizing the carbonation of waste cement. *Industrial & Engineering Chemistry Research.* 43(24): 7880–7887.

IPCC. (2001). *Climate change 2001. The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on*

Climate Change. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

IPCC. (2005). *IPCC special report on carbon dioxide capture and storage*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

IPCC. (2007). *Climate change. The Physical science basis (4th assessment)*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.

Jia, L., Anthony, E. J., Lin, W., Ruan, Y., and Gora, D. (2004). Carbonation of magnesium silicate minerals: an experimental study. *Canadian Journal of Chemical Engineering*. 82: 1289–1295.

Jing, G., Tang, S., and Li, X. (2013). Effect of HPAM on Calcium Carbonate Crystallization. *Journal of the Korean Chemical Society*. 57(3): 365–369.

Jo, H., Jo, H. Y., and Jang, Y. N. (2012). Effect of extraction solutions on carbonation of cementitious materials in aqueous solutions. *Environmental Technology*. 33(12): 1391–1401.

Jo, H., Park, S. H., Jang, Y. N., Chae, S. C., Lee, P. K. and Jo, H. Y. (2014). Metal extraction and indirect mineral carbonation of waste cement material using ammonium salt solutions. *Chemical Engineering Journal*. 254. 313–323

Johnston, M., Clark, M. W., McMahon, P., and Ward, N. (2010). Alkalinity conversion of bauxite refinery residues by neutralization. *Journal of Hazardous Materials*. 182: 710–715.

Kakizawa, M., Yamasaki, A., and Yanagisawa, Y. (2001). A new CO_2 disposal process via artificial weathering of calcium silicate accelerated by acetic acid. *Energy*. 26: 341–354.

Katsuyama, Y., Yamasaki, A., Iizuka, A., Fujii, M., Kumagai, K., and Yanagisawa, Y. (2005). Development of a process for producing high-purity calcium carbonate ($CaCO_3$) from waste cement using pressurized CO_2. *Environmental Progress*. 24(2): 162–170.

Kavaliauskaite, I., Uibu, M., Teir, S., Kuusik, R., Zevenhoven, R., and Denafas, G. (2005). Carbon dioxide long-term emissions and its storage options in the Baltic region. *The 5th International Conference on Ecosystems and Sustainable Development*. 3–5 May, Cadiz, Spain.

Khoo, H. H., and Tan, R. B. H. (2006). Life cycle evaluation of CO_2 recovery and mineral sequestration alternatives. *Environmental Progress*. (25): 208–217.

Kiehl, J. T., and Trenberth, K. E. (1997). Earth's Annual Global Mean Energy Budget. *Bulletin of the American Meteorological Society*. 78: 197–208.

Kodama, S., Nishimoto, T., Yamamoto, N., Yogo K., and Yamada, K. (2008). Development of a new pH-swing CO_2 mineralization process with a recyclable reaction solution. *Energy*. 33(5): 776–784.

Kohlmann, J., and Zevenhoven, R. (2001). The removal of CO_2 from flue gases using magnesium silicates, in Finland. *The 11th International Conference on Coal Science (ICCS 11)*. September 30– October 5, San Francisco, USA.

Kojima, T., Nagamine, A., Ueno, N., and Uemiya, S. (1997). Absorption and fixation of carbon dioxide by rock weathering. *Energy Conversion and Management*. 38: 461–466.

Koljonen, T., Siikavirta, H., Zevenhoven, R., and Savolainen, I. (2004). CO_2 capture, storage and reuse potential in Finland. *Energy*. 29: 1521–1527.

Kong, B., Yu, J., Savino, K., Zhu, Y., and Guan, B. (2012). Synthesis of α–calcium sulfate hemihydrate submicron-rods in water/n-hexanol/CTAB reverse microemulsion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 409: 88–93.

Kontogeorgos, D. A., and Founti, M. A. (2012). Gypsum board reaction kinetics at elevated temperatures. *Thermochimica Acta*. 529: 6–13.

Lackner, K. S., Wendt, C. H., Butt, D. P., Joyce, E. L., and Sharp, D. H. (1995). Carbon-Dioxide Disposal in Carbonate Minerals. *Energy*. 20(11): 1153–1170.

Lackner, K. S., Butt, D. P., Wendt, C. H., Goff, F., and Guthrie, G. (1997). *Carbon dioxide disposal in mineral form: Keeping coal Competitive Tech*. Technical Report No: LA-UR-97-2094. Los Alamos National Laboratory.

Lackner, K. S. (2002). Carbonate Chemistry for Sequestering Fossil Carbon. *Annual Review of Energy and the Environment*. 27(1): 193–232.

Lackner, K. S. (2003). A guide to CO_2 sequestration. *Science*. 300: 1677–1678.

Lammers, K., Murphy, R., Riendeau, A., Smirnov, A., Schoonen, M. A. A., and Strongin, D. R. (2011). CO_2 Sequestration through Mineral Carbonation of Iron Oxyhydroxides. *Environmental Science & Tec*hnology. 45: 10422–10428.

Lee, J. K., and Dong, W. K. (2005). Characteristic study of Korean magnesium silicates for CO_2 mineral carbonation. *The 22nd annual international Pittsburgh coal conference*. 12–15 September, Pittsburgh, USA.

Lee, M. G., Jang, Y. N., Ryu, K. W., Kim, W., and Bang, J. H. (2012). Mineral carbonation of flue gas desulfurization gypsum for CO_2 sequestration. *Energy*. 47: 370–377.

Leiva, C., García Arenas, C., Vilches, L. F., Vale, J., Gimenez, A., Ballesteros, J. C., and Fernández-Perei, C. (2010). Use of FGD gypsum in fire resistant panels. *Waste Management*. 30: 1123–1129.

Lekakh, S. N., Rawlins, C. H., Robertson, D. G. C., Richards, V. L., and Peaslee, K. D. (2008). Kinetics of aqueous leaching and carbonization of steelmaking slag. *Metallurgical and Materials Transactions B*. 39: 125–134.

Levenspiel, O. (1972). *Chemical Reaction Engineering*. (2nd ed) John Wiley & Sons, New York.

Li, L. Y. (2001). A study of mineral transformation to reduce red mud tailings. Waste *Management*. 21: 525–534.

Li, X., Fernández Bertos, M., Hills, C. D., Carey, P. J., and Simon, S. (2007). Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste Management*. 27(9): 1200–1206.

Li, G., Li, Z., and Ma, H. (2013). Synthesis of aragonite by carbonization from dolomite without any additives. *International Journal of Mineral Processing*. 123: 25–31.

Lin, H., Fujii, T., Takisawa, R., Takahashi, T., and Hashida, T. (2008). Experimental evaluation of interactions in supercritical CO_2/water/rock minerals system under geologic CO_2 sequestration conditions. *Journal of Materials Science*. 43: 2307–2315.

Ling, Y., Wang, G., Wheeler, D. A., Zhang, J. Z., and Li, Y. (2011). Sn-Doped Hematite Nanostructures for Photoelectrochemical Water Splitting. *Nano Letters*. 11: 2119–2125.

Liu, Q., and Maroto-Valer, M. M. (2010). Investigation of the effect of a typical host rock and buffer solution on CO_2 sequestration in synthetic brines. *Fuel Processing Technology*. 91: 1321–1329.

Liu, Q., and Maroto-Valer, M. M. (2012) .Studies of pH buffer systems to promote carbonate formation for CO_2 sequestration in brines. *Fuel Processing Technology*. 98: 6–13.

Lu, B., Li, P., Liu, H., Zhao, L. Y., Wei, Y. (2011). Preparation and mechanism of formation of hematite particles in the Fe-HNO_3 system. *Journal of Physical and Chemistry of Solids*. 72: 1032–1036.

Maroto-Valer M. M., Fauth D. J., Kuchta M. E., Zhang Y., and Andrésen J. M. (2005). Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. *Fuel Processing Technology*. 86(14–15): 1627–1645.

Mattila, H. P., Grigaliūnaitė, I., Said, A., Fogelholm, C. J., and Zevenhoven, R. (2012). Production of papermaking grade calcium carbonate precipitate from steelmaking slag product quality and development of a larger scale process. *Proceedings of 4th International Conference on Process Development in Iron and Steelmaking*. 10–13 June. Lulea, Sweden.

Meyer, N. A., Vogeli, J. U., Becker, M., Broadhurst, J. L., Reid, D. L., and Franzidis, J. P. (2014). Mineral carbonation of PGM mine tailings for CO_2 storage in South Africa: A case study. *Minerals Engineering*. 59: 45–51.

Montes-Hernandez, G., Pérez-López, R., Renard, F., Nieto, J. M., and Charlet, L. (2009). Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly-ash. *Journal of Hazardous Materials*. 161: 1347–1354.

Mori, Y., Enomae, T., and Isogai, A. (2009). Preparation of pure vaterite by simple mechanical mixing of two aqueous salt solutions. *Materials Science and Engineering C*. 29: 1409–1414.

Myers, R.L. (2003). *The basics of chemistry (Basics of the hard sciences)*. 1st edition, Greenwood publisher.

O’Connor, W. K., Dahlin, D. C., Turner, P. C., and Walters, R. P. (1999). Carbon Dioxide Sequestration by Ex-Situ Mineral Carbonation. The 2nd International Dixy Lee Ray Memorial Symposium. August 29–September 2, Washington, DC.

O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Rush, G. E., Walters, R. P., and Turner, P. C. (2000a). CO_2 storage in solid form: a study of direct mineral carbonation. The *5th international conference on greenhouse gas technologies.* 12–15 August. Cairns, Australia.

O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Walters, R. P., and Turner, P. C. (2000b). Carbon dioxide sequestration by direct mineral carbonation with carbonic acid. The *25th international technical conference on coal utilization and fuel systems*. 6–9 March. Clearwater, Florida.

O'Connor W. K., Dahlin D. C., Nilsen D. N., Walters R. P., and Turner P. C., (2001). Carbon dioxide sequestration by direct aqueous mineral carbonation. *Proceedings of the 25th International Technical Conference on Coal Utilization & Fuel Systems.* 6–9 March. Clearwater, Florida.

O'Connor W. K., Dahlin D. C., Nilsen D. N., Gerdemann S. J., Rush G. E., Penner L. R., Walters R. P., and Turner P. C. (2002). Continuing studies on direct aqueous mineral carbonation for CO_2 sequestration. *The 27th International Technical Conference on Coal Utilization & Fuel Systems.* 4–7 March. Florida, US.

O'Connor W. K., Dahlin D. C., Rush G. E., Gerdemann S. J., and Penner L. R. (2005a). Energy and economic evaluation of ex situ aqueous mineral carbonation. *Greenhouse Gas Control Technologies*. 7: 2011–2015.

O'Connor W. K., Dahlin D. C., Rush G. E., Gerdemann S. J., Penner L. R., and Nilsen D. N. (2005b). *Aqueous mineral carbonation: Mineral availability, pretreatment, reaction parametrics, and process studies*. Technical Report No. DOE/ARC-TR-04-002. Albany Research Center.

Oikonomopoulos, I. K., Perraki, M., Tougiannidis, N., Perraki, T., Frey, M. J., Antoniadis, P., and Ricken, W. (2013). A comparative study on structural differences of xylite and matrix lignite lithotypes by means of FT-IR, XRD, SEM and TGA analyses: An example from the Neogene Greek lignite deposits. *International Journal of Coal Geology*. 115: 1–12.

Olajire, A. A. (2010). CO_2 capture and separation technologies for end-of-pipe applications-a review. *Energy*. 35: 2610–28.

Park, A. H., Jadhav, R., and Fan, L. S. (2003a). CO_2 Mineral sequestration: chemically enhanced aqueous carbonation of serpentine. *Canadian Journal of Chemical Engineering*. 81(3–4): 885–890.

Park, Y. S., Shin, H. N., Lee, D. H., Kim, D. J., Kim, J. H., Lee, Y. K., Sim, S. J., and Choi, K. B. (2003b). Drying Characteristics of Particles using Thermogravimetric Analyzer. *Korean Journal of Chemical Engineering*. 20(6): 1170–1175.

Park A. H. A. and Fan, L. S. (2004). CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process. *Chemical Engineering Science.* 59 (22–23): 5241–5247.

Park A. H. A. (2005). *Carbon dioxide sequestration: chemical and physical activation of aqueous carbonation of mg-bearing minerals and pH swing process*. PhD dissertation, The Ohio State University.

Pérez-López, R., Montes-Hernandez, G., Nieto, J. M., Renard, F., and Charlet, L. (2008). Carbonation of alkaline paper mill waste to reduce CO_2 greenhouse gas emissions into the atmosphere. *Applied Geochemistry*. 23(8): 2292–2300.

Raupach, M. R., Marland, G., Ciais, P., Le Quéré, C., Canadell, J. G., Klepper, G., and Field, C. B. (2007). Global and regional drivers of accelerating CO_2 emissions. *Proceedings of the National Academy of Sciences.* 104(24):10288–10293.

Rendek, E., Ducom, G., and Germain, P. (2006). Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash. *Journal of Hazardous Materials.* 128(1): 73–79.

Riahi, K., Rubin, E. S., Taylor, M. R., Schrattenholzer, L., and Hounshell, D. (2004). Technological learning for carbon capture and sequestration technologies. *Energy Economics*. 26(4): 539–564.

Sahoo, S. K., Agarwal, K., Singh, A. K., Polke, B. G., and Raha, K. C. (2010). Characterization of γ- and α-Fe_2O_3 nano powders synthesized by emulsion precipitation-calcination route and rheological behaviour of α-Fe_2O_3. *International Journal of Engineering, Science and Technology*. 2(8): 118–126.

Sahu, R. C., Patel, R. K., and Ray, B. C. (2010). Neutralization of red mud using CO_2 sequestration cycle. *Journal of Hazardous Materials*. 179: 28–34.

Saikia, J. and Das, G. (2014). Framboidal vaterite for selective adsorption of anionic dyes. *Journal of Environmental Chemical Engineering*. 2: 1165–1173.

Sanna, A., Dri, M. and Maroto-Valer, M. M. (2013). Carbon dioxide capture and storage by pH swing aqueous mineralization using a mixture of ammonium salts and antigorite source. *Fuel*. 114: 153–161.

Sanna, A., Uibu, M., Caramanna, G.,Kuusik, R., and Maroto-Valer, M. M. (2014a). A review of mineral carbonation technologies to sequester CO_2. *Chemical Society Reviews*. DOI: 10.1039/C4CS00035H.

Sanna, A., Lacinska, A., Style, M., and Maroto-Valer, M. M. (2014b). Silicate rock dissolution by ammonium bisulphate for pH swing mineral CO_2 sequestration. *Fuel Processing Technology*. 120: 128–135.

Santos, R. M., Bouwel, J. V., Vandevelde, E., Mertens, G., Elsen, J., and Gerven, T. V. (2013). Accelerated mineral carbonation of stainless steel slags for CO_2 storage and waste valorization: Effect of process parameters on geochemical properties. *International Journal of Greenhouse Gas Control*. 17: 32–45.

Schmidt, C. and Romanosky, B. (2001). *Program Overviews: CO_2 Mineral Sequestration*. presented at Mineral Carbonation Workshop, Pittsburgh, USA.

Schott, J., Pokrovsky, O. S., and Oelkers, E. H. (2009). The link between mineral dissolution/precipitation kinetics and solution chemistry. *Reviews in Mineralogy and Geochemistry*. 70: 207–258.

Seifritz, W. (1990). CO_2 Disposal by Means of Silicates. *Nature*. 345(6275): 486–486.

Sipilä, J., Teir, S., and Zevenhoven, R. (2008). *Carbon dioxide sequestration by mineral carbonation Literature review update 2005–2007*. Technical Report, Åbo Akademi University.

Spanos, N. and Koutsoukos, P. G. (1998). Kinetics of precipitation of calcium carbonate in alkaline pH at constant supersaturation. Spontaneous and seeded growth. *The Journal of Physical Chemistry B*. 102(34): 6679–6684.

Stasiulaitiene, I., Denafas, G., and Sliaupa, S. (2007). Lithuanian serpentines as potential carbon dioxide binders. *The Proceedings of the 32nd International Technical Conference on Coal Utilization & Fuel Systems*. 10–15 June. Florida, USA.

Svensson, R., Odenberger, M., Johnsson, F., and Strömberg, L. (2004). Transportation systems for CO_2-application to carbon capture and storage. *Energy Conversion and Management*. 45: 2343–2353.

Teir, S., Eloneva, S., and Zevenhoven, R. (2005). Production of precipitated calcium carbonate from calcium silicates and carbon dioxide. *Energy Conversion & Management*. 46(18–19): 2954–2979.

Teir, S., Revitzer, H., Eloneva, S., Fogelholm, C. J., and Zevenhoven, R. (2007a). Dissolution of natural serpentinite in mineral and organic acids. *International Journal of Mineral Processing*. 83(1–2): 36–46.

Teir, S., Kuusik, R., Fogelholm, C. J., and Zevenhoven, R. (2007b). Production of magnesium carbonates from serpentinite for long-term storage of CO_2. *International Journal of Mineral Processing*. 85(1-3): 1–15.

Teir, S., Eloneva, S., Fogelholm, C. J., and Zevenhoven, R. (2009). Fixation of carbon dioxide by producing hydromagnesite from serpentinite. *Applied Energy*. 86: 214–218.

Telesca, A., Marroccoli, M., Calabrese, D., Valenti, G. L., and Montagnaro, F. (2013). Flue gas desulfurization gypsum and coal fly ash as basic components of prefabricated building materials. *Waste Management*. 33: 628–633.

Teramura, S., Isu, N., and Inagaki, K. (2000). New building material from waste concrete by carbonation. *Journal of Materials in Civil Engineering*. 12: 288–293.

Uibu, M., Velts, O., and Kuusik, R. (2010). Developments in CO_2 mineral carbonation of oil shale ash. *Journal of Hazardous Materials*. 174: 209–214.

Uliasz-Bochenczyk, A., Mokrzycki, E., Piotrowski, Z., and Pomyka1a, R. (2009). Estimation of CO_2 sequestration potential via mineral carbonation in fly ash from lignite combustion in Poland. *Energy Procedia*. 1: 4873–4879.

van Alphen, K., Hekkert, M. P., and Turkenburg, W. C. (2010a). Accelerating the deployment of carbon capture and storage technologies by strengthening the innovation system. *International Journal of Greenhouse Gas Control*. 4(2): 396–409.

van Alphen, K., Noothout, P. M., Hekkert, M. P., and Turkenburg, W. C. (2010b). Evaluating the development of carbon capture and storage technologies in the United States. *Renewable and Sustainable Energy Reviews*. 14: 971–86.

Van Herk, J., Pietersen, H. S., and Schuiling, R. D. (1989). Neutralization of Industrial Waste Acids with Olivine-The Dissolution of Forsteritic Olivine at 40–70 °C. *Chemical Geology*. 76: 341–352.

Verma, S. K., Deb, M. K., Suzuki, Y., and Tsai, Y. I. (2010). Ion chemistry and source identification of coarse and fine aerosols in an urban area of eastern central India. *Atmospheric Research*. 95: 65–76.

Wang, W., Hu, M., Zheng, Y., Wang, P., and Ma, C. (2011). CO_2 Fixation in Ca^{2+}-/Mg^{2+}-Rich Aqueous Solutions through Enhanced Carbonate Precipitation. *Industrial & Engineering Chemistry Research*. 50: 8333–8339.

Wang, X., Maroto-Valer, M. M. (2011). Integration of CO_2 Capture and Mineral Carbonation by Using Recyclable Ammonium Salts. *Chem Sus Chem*. 4: 1291–1300.

Wang, X., Liang, B., Lü, L., Wu, P., Li, C., and Ma, J. (2012). Simultaneous oxidation and extraction of iron from simulated ilmenite hydrochloric acid leachate. *Hydrometallurgy*. 129–130: 105–110.

Wei, Y., Shimaoka, T., Saffarzadeh, A., and Takahashi, F. (2011). Alteration of municipal solid waste incineration bottom ash focusing on the evolution of iron-rich constituents. *Waste Management*. 31: 1992–2000.

Wu, J. C. S., Sheen, J. D., Chen, S. Y., and Fan, Y. C. (2001). Feasibility of CO_2 fixation via artificial rock weathering. *Industrial and engineering chemistry research*. 40(18): 3902–3905.

Xuan, S., Chen, M., Hao, L., Jiang, W., Gong, X., Hua, Y., and Chen, Z. (2008). Preparation and characterization of microsized $FeCO_3$, Fe_3O_4 and Fe_2O_3 with ellipsoidal morphology. *Journal of Magnetism and Magnetic Materials*. 320: 164–170.

Yadav, V. S., Prasad, M., Khan, J., Amritphale, S. S., Singh, M., and Raju, C. B. (2010). Sequestration of carbon dioxide (CO_2) using red mud. *Journal of Hazardous Materials*. 176:1044–1050.

Yamasaki, A. (2003). An overview of CO_2 mitigation options for global warming - Emphasizing CO_2 sequestration options. *Journal of Chemical Engineering of Japan*. 36(4): 361–375.

Yang. H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E., and Wright, I. (2008). Progress in carbon dioxide separation and capture: A review. *Journal of Environmental Sciences*. 20: 14–27.

Yogo, K., Teng, Y., Yashiima, T., and Yamada, K. D. (2004). Development of a new CO_2 fixation/utilization process (1): Recovery of calcium from steelmaking slag and chemical fixation of carbon dioxide by carbonation reaction. *The 7th international conference on greenhouse gas control technologies*. 5–9 September. Vancouver, Canada.

Zevenhoven, R., Teir, S., and Eloneva, S. (2008). Heat optimization of a staged gas-solid mineral carbonation process for long-term CO_2 storage. *Energy*. 33(2): 362–370.

Zhang, J., Zhang, R., Geerlings, H., and Bi, J. (2012). Mg-Silicate Carbonation Based on an HCl- and NH_3- Recyclable Process: Effect of Carbonation Temperature. *Chemical Engineering & Technology*. 35(3): 525–531.

Zhao, L., Sang, L., Chen, J., Ji, J., and Teng, H. H. (2010). Aqueous carbonation of natural brucite: relevance to CO_2 sequestration. *Environmental Science and Technology*. 44: 406–11.

Zhong, Y., Su, L., Yang, M., Wei, J., and Zhou, Z. (2013). Rambutan-Like $FeCO_3$ Hollow Microspheres: Facile Preparation and Superior Lithium Storage Performances. *ACS Applied Materials & Interfaces*. 5(21): 11212–11217.