

MINERAL CARBONATION OF RED GYPSUM FOR
CARBON DIOXIDE SEQUESTRATION

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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 Malaysia

SEPTEMBER 2014

This thesis is dedicated to my beloved Mother, Father, Sisters, and my Wife.

Thank you very much for your kind help and encouragement.

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my deepest gratitude and appreciation to my research supervisor Prof. Dr. Radzuan Junin for his constructive advice, guidance, commitment, and loyal encouragement throughout this research. Besides my advisor, I would like to thank the rest of my thesis committee: Prof. Dr. Ariffin Samsuri (Chairman), Prof. Dr. Kheireddine Aroua (External Examiner), and Assoc. Prof. Khairul Sozana Kamarudin (Internal Examiner), for their encouragement, helpful, and insightful comments. I am really thankful of the Faculty of Petroleum & Renewable Energy Engineering (FPREE), School of Postgraduate Studies (SPS) for complete assistance during all stages of the research.

I would like to extend my appreciation especially to Abu Samah Nasir who helped me during experiments and analyses in all the time of research. My sincere thanks also goes to Dr. Mark Tyrer for making this possible to simulate the analyses and do geochemical modeling.

My appreciation is given to IAU – Mahabad Branch and also my family for financial support during this study. I would like to thank all my friends who participate and encourage me during this study.

ABSTRACT

Reduction of carbon dioxide (CO₂) emissions into the atmosphere is a key challenge in order to mitigate the anthropogenic greenhouse effect. A CO₂ emission causes lots of problems to human health and increases the global warming, CO₂-uptake decreases these environmental issues. Mineral carbonation process is an alternative method during which industrial wastes rich in calcium (Ca) or magnesium (Mg) react with CO₂ to form a stable carbonated mineral. In this research the feasibility of CO₂ mineral carbonation by the use of red gypsum, as a Ca-rich source, was technically evaluated using autoclave mini reactor. For this purpose, the effect of a wide-range of key procedure variables such as reaction temperature, reaction time, particle size, stirring rate, CO₂ pressure, and liquid to solid ratio, on the rate of mineral carbonation were studied. The results show that the maximum conversion of Ca (98.8%) is obtained at the condition that has optimum amount of these variables. Moreover, the results confirmed that red gypsum has high potential to form calcium carbonate (CaCO₃) during the process of CO₂ mineral carbonation. It was concluded that mineral carbonation process using red gypsum could be considered as an attractive and low-cost method in industry to mitigate considerable amount of CO₂ from the atmosphere, which is the main issue in the current and coming years.

ABSTRAK

Pengurangan pelepasan karbon dioksida (CO_2) ke atmosfera merupakan cabaran utama bagi mengurangkan kesan rumah hijau antropogenik. Pelepasan CO_2 menyebabkan banyak masalah kepada kesihatan manusia dan meningkatkan pemanasan global, pengambilan CO_2 akan mengurangkan isu-isu alam sekitar. Proses pengkarbonan mineral adalah kaedah alternatif di mana bahan buangan industri yang kaya dengan kalsium (Ca) dan magnesium (Mg) bertindak balas dengan CO_2 untuk membentuk mineral karbonat yang stabil. Dalam kajian ini kemungkinan, pengkarbonan mineral CO_2 dengan menggunakan gipsum merah, sebagai sumber yang kaya Ca, telah dinilai secara teknikal dengan menggunakan reaktor mini autoklaf. Untuk tujuan ini, kesan pelbagai pembolehubah utama seperti suhu, masa tindakbalas, saiz zarah, kadar pengadukan, tekanan CO_2 , dan nisbah cecair pepejal kepada, terhadap atas kadar pengkarbonan mineral telah dikaji. Hasil kajian menunjukkan bahawa penukaran maksimum Ca (98.8%) diperoleh pada keadaan pembolehubah optimum. Selain itu, keputusan mengesahkan bahawa gipsum merah mempunyai potensi yang tinggi untuk membentuk kalsium karbonat (CaCO_3) semasa proses pengkarbonan mineral CO_2 . Sebagai kesimpulan didapati proses pengkarbonan mineral menggunakan gipsum merah boleh dianggap sebagai kaedah yang menarik dan kos rendah, sehingga boleh diguna kan oleh industri untuk mengurangkan sejumlah besar CO_2 dari atmosfera, yang merupakan isu utama pada masa ini dan masa akan datang.

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LIST OF SYMBOLS

<i>d</i>	-	Particle size (mm)
<i>T</i>	-	Temperature
$^{\circ}\text{C}$	-	Degree centigrade
<i>t</i>	-	Reaction time
<i>n</i>	-	Stirring rate
$p\text{CO}_2$	-	Partial pressure of carbon dioxide
<i>K</i>	-	Kelvin
<i>ml</i>	-	Milliliter
<i>h</i>	-	Hour
<i>min</i>	-	Minute
<i>s</i>	-	Second
<i>g</i>	-	Gram
<i>kg</i>	-	Kilogram
<i>wt. %</i>	-	Weight percent
$p\text{CO}_2$	-	Partial pressure of carbon dioxide
<i>k</i>	-	Rate constant
<i>L/S</i>	-	Liquid to solid ratio
<i>rpm</i>	-	Revolution per minute
<i>Pa</i>	-	Pascal
<i>atm</i>	-	Atmosphere
<i>psi</i>	-	Pound per square inch

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Carbon dioxide (CO₂), alongside other gases, is released into the atmosphere during fuel combustion, particularly due to the extensive use of fossil fuels for energy production from coal, oil, and natural gas since the industrial revolution (Kwon *et al.*, 2011). The industries, which are major contributors of CO₂, are power plants and steel making industries that burn coal or other fossil fuels as their traditional sources of fuel. Since fossil fuels are in abundance all over the world, it is unlikely that industries can replace them with other sources of fuel in the near future. Fossil fuels, as the essential energy sources, are utilized for more than 85% of the world energy consumption (IEA, 2008). Despite the advantages of fossil fuels, including high energy supply, ease of use and storage, and low cost; the net increase of CO₂ into the atmosphere causes a real challenge related global warming (IPCC, 2005).

Since the industrial revolution, the levels of greenhouse gases (GHGs) and CO₂ in the atmosphere have greatly increased (Bachu, 2000; Mackenzie *et al.*, 2001; Bachu *et al.*, 2007; SRA, 2007). The rise of the global surface temperature is attributed to the increased GHGs and it is estimated that the average annual temperature will rise by 2.0 °C (Bodman *et al.*, 2013). Environmentalists first used the term “greenhouse effect” in early 1800s to describe the impact of trace gases in the atmosphere. Concern on climate change by environmentalists began in the mid-1950s after noticing the slow but steady impact of climate change (IPCC, 2005).

Industrialization and development of countries in the 21st century are estimated to increase the demands of energy by 57% from 2004 to 2030 (IEA, 2008). Figure 1.1 shows the projected energy consumption in different sources from 2004 to 2030.

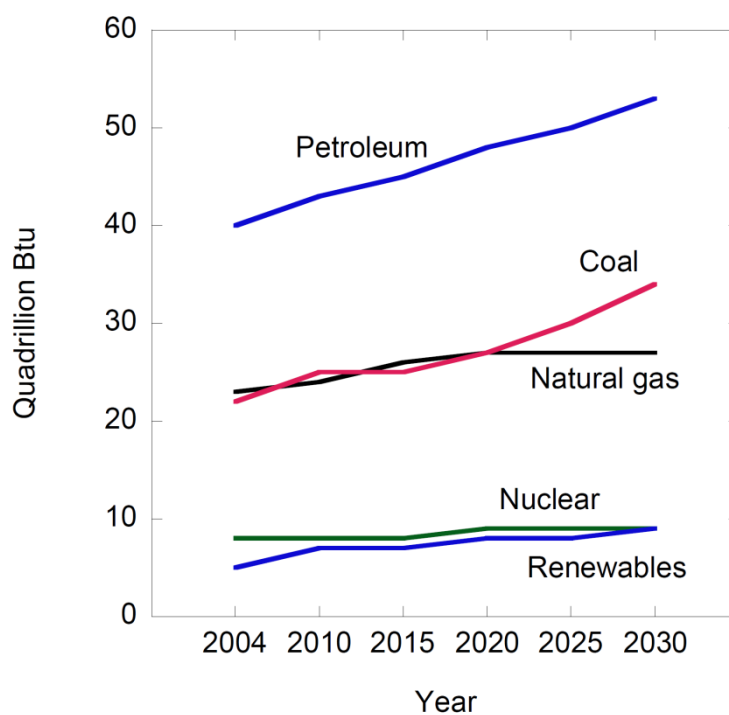


Figure 1.1 Projected energy consumption from 2004 to 2030 (USEIA, 2011)

The concentration of CO₂ in the Earth's atmosphere has been enhanced sharply from 280 ppm in the 1750s to about 389 ppm in 2010 due to the increase in fossil fuel consumption and other human activities (Thoning *et al.*, 2013). Moreover, atmospheric CO₂ has risen recently to about 395 ppm in 2012 (Thoning *et al.*, 2013). Consequently, the increase of CO₂ concentration to average of 943 ppm by the end of the 21st is expected (Sanderson *et al.*, 2011; Bodman *et al.*, 2013).

The term global warming is used to refer to the phenomenon in which the earth's surface temperature increased by about 0.7 °C in the 20th century. This increase can be attributed to the reliance of humans on fossil fuels for more than 85% of their energy needs. This ratio is expected to continue for the next 30 years. The amount of released CO₂ has changed in recent years. Thus, the related global temperature is estimated to exceed 2 °C by 2100 (Bodman *et al.*, 2013) as a direct result of anthropogenic activities and then CO₂ emission to the atmosphere. As a result, the

anthropogenic activities should be minimized to reduce CO₂ emission and climate change.

IPCC (2007) referenced models that predict the earth's surface temperatures will increase by 1.5–5.8 °C between the year 1990 and 2100. This will result to the rising of sea levels and most importantly, changes in the patterns and amounts of precipitation. The impacts of these changes are vast and devastating ranging from droughts, floods, hurricanes, and heat waves to tornadoes. The impact on human life, economic, and financial situations of everyone will be devastating. For this reason, the need to fight climate change is dire and thus should be prioritized.

Some primary alternatives are adopted for moderation of CO₂ emission. These alternatives include use of fuels that are less carbon intensive, improvement of energy efficiency, and sequestration of carbon through various ways of storage and capture (Bachu, 2000; Preston and Jones, 2006; Bachu *et al.*, 2007).

The objective of CO₂ capture and sequestration (CCS) is to aid global decrease of CO₂ emissions through “capturing” the CO₂ produced. Consequently, there has been a rise in the global acknowledgement of the importance of emissions and as a result, the Kyoto Protocol was formulated. This is an agreement signed by the key industrialized nations. It binds about 37 industrialized nations and the European community to cut their emissions by an average of five percent below their levels of emissions in 1990. Its first commitment period started in 2008 and ended in 2012. During the second commitment period, Parties committed to reduce greenhouse gas (GHG) emissions by at least 18 percent below 1990 levels in the eight-year period from 2013 to 2020; however, the composition of Parties in the second commitment period is different from the first.

The reductions required in the emissions can only be attained by simultaneously taking different methods of mitigating emission of CO₂ for example CCS, energy efficiency, fuel switching and renewable energy. Energy efficiency and fuel switching cover the decrease of CO₂ produced at the source; however, there exists a limitation to the alterations, which can be adopted by the establishments, both private and public, without having a cost implication. Despite these changes, production of CO₂ still

occurs. The amount that is produced should be captured and sequestered by decreasing emission at the source and even upon completion of production. There are three key steps involved in sequestration of CO₂. These are:

- (1) CO₂ capture
- (2) mining and transportation of CO₂
- (3) CO₂ sequestration

The point of focus in capture studies has diverted in the recent past towards the use of better solvents like ionic liquid-based materials, aqueous ammonia, and solids, which can absorb CO₂ chemically. All methods used in capture need a control process of CO₂ release and regeneration of the solvents by heating, in an energy-intensive process.

The CCS process begins when CO₂ is captured and reproduced in a concentrated form to allow convenient storage and transportation. Various methods of CO₂ capture, which are considered, include post-combustion, pre-combustion, and oxy-fuel combustion capture. At present, the technologies show a theoretical efficiency of 90%, that is, eliminates 90% of the emissions from the effluent stream; however, they have not been used on a full-scale power plant level. Two instances of prosperous pilot plants include the Ferry-bridge carbon capture pilot that uses post combustion capture, which is 90% efficient, and the Renfrew oxyfuel project whose efficiency lies between 75-85% (DECC, 2012).

The post-combustion capture refers to the removal of CO₂ from power station flue gas prior to its compression, transportation, and storage in suitable places, as part of the CCS. The use of amine-based solvent for post-combustion capture has attracted considerable interest and led to significant progress in CO₂ capture (Bui *et al.*, 2014). This is in fact the most advanced technology for CO₂ capture to date and it is likely to be the first carbon capture technology to be deployed worldwide on a large scale. The post-combustion pilot plants already demonstrate the feasibility of CO₂ removal with amine solvent from flue gas albeit at modest scale (Folger, 2009; Bui *et al.*, 2014).

At pre-combustion capture, there is the separation of CO₂ prior to combustion, which takes place into streams of hydrogen, and CO₂, by reacting the fuel with air or steam to produce hydrogen. The most common technique used for the separation is steam reforming. The oxy-fuel combustion process is same as the pre-combustion CO₂ capture in principle. The process of oxy-fuel combustion involves the burning of a fossil fuel energy source in the presence of pure oxygen. Burning fuel in the presence of oxygen removes contaminants, including nitrogen, from the exhaust stream resulting in water and CO₂ being easier to capture. This technique still is being investigated since the temperatures necessary for the process of pure oxygen combustion to take place are very high (about 3500 °C). In theory, the flue gas upon stripping of the extra pollutants like SO₂ and NO₂ may be recycled back to the reaction unit to lower the reaction temperature.

Water, which contains high concentrations of dissolved CO₂, is very acidic (pH = ~3). Minimal quantities of this if present in the atmosphere may corrode steel (Cole *et al.*, 2011). To avoid loss and damage of mechanical integrity of pipes, water is eliminated from the CO₂ stream. The separation occurs in vapor-liquid separator drums, initially through gravity separation then through pressurizing the CO₂ stream to 20-40 bars (Cole *et al.*, 2011).

Because fossil fuels are abundant all over the world, it is unlikely that industries can replace them with other sources of fuel in the near future and it is necessary to find ways to reduce concentration of CO₂ in the atmosphere. Therefore, numerous researchers have focused on mitigation of GHGs released into the atmosphere (Holloway, 2001; Herzog, 2002; Kaszuba *et al.*, 2003; Carapellucci and Milazzo, 2003; Yamasaki, 2003; Palandri and Kharaka, 2004; Bachu *et al.*, 2005; Maroto-Valer *et al.*, 2005; Metz *et al.*, 2005; Xu *et al.*, 2005; Flaathen *et al.*, 2009; Gislason *et al.*, 2010; King *et al.*, 2010; Qafoku *et al.*, 2012). As a result, some available and feasible methods such as geological storage, aquifer storage, deep sea or ocean storage, and mineral carbonation have been proposed to mitigate the amount of GHGs, especially CO₂ in the atmosphere.

Storing CO₂ in geological formations, such as in depleted oil and gas reservoirs, is one of proposed solutions. These reservoirs contain hydrocarbon at high pressure over the geological period, which prove that they have the potential to be used for storage of CO₂. However, this technique has its own challenges. The most important issues are the possibility of release of CO₂, the determination of mineral reaction kinetics, and the understanding characterization of storage formations (Jun *et al.*, 2013). Furthermore, the lack of permanency, the risk of leakage, and the post-monitoring of the site are other problems and challenges associated with this method (Metz *et al.*, 2005).

Alternatively, Litynski *et al.* (2009) have mentioned three ways for reduction of the GHGs, especially CO₂, emissions as follow:

- (1) Achieving the same economic production using less energy,
- (2) Utilizing carbonless energy sources,
- (3) CO₂ sequestration

As a result, there are three main issues in relation to the CCS methods, including high-energy consumption, high expense, and low separation efficiency. Therefore, it is necessary to develop technologies to trap CO₂ in the reservoir permanently, as well as monitoring the long-term fate of CO₂ in the reservoir. One option for reducing and even eliminating the risks associated with the geological storage of CO₂ is sequestering it into more stable forms. Ex-situ or in-situ mineral carbonation is the ideal technology for reducing the emission of CO₂. The minerals, rocks, and industrial wastes rich in calcium (Ca) and magnesium (Mg) are usually considered as feedstock candidates due to their availability, low cost, and environmentally benign (Lackner *et al.*, 1995; Herzog, 2002; Maroto-Valer *et al.*, 2005; Metz *et al.*, 2005; King *et al.*, 2010). In this method, first CO₂ reacts with water to produce carbonic acid (hydration reaction). Then, carbonic acid dissociates to bicarbonate and carbonate ions. At the end, carbonate ion reacts with the cation and produces a carbonate mineral. Therefore, mineral CO₂ carbonation is considered as one of the most interesting and attractive methods due to simplicity of operation with low cost of adsorption.

Thermodynamically, CO₂ can be bounded as a carbonate (Lackner *et al.*, 1995) with many metals. In many instances, these carbonates dissolve in water; however, calcium (as well as magnesium) carbonate is stable as a solid. The chemical reactions in the mineral carbonation process are exothermic in nature (Lackner *et al.*, 1995), leading to the formation of thermodynamically stable carbonate (Equation 1.1). According to Lackner *et al.* (1997), these reactions are very slow at ambient conditions. Two pretreatment processes have been used to accelerate the carbonation rate: acid and heat treatments (Herzog, 2002; Maroto-Valer *et al.*, 2005; Kwon *et al.*, 2011). These processes take long time and extensive energy, which has made this approach less interesting. However, the reaction rate accelerates with increasing surface area and temperature (Lackner *et al.*, 1995; McGrail *et al.*, 2006; Oelkers *et al.*, 2008; Matter *et al.*, 2009; Schaef *et al.*, 2009; Gislason *et al.*, 2010) and the process becomes attractive (Olsson *et al.*, 2012):



As mentioned before, many natural minerals (e.g., olivine, gypsum, and wollastonite) and industrial wastes (e.g., lignite fly ash, mining waste, and steel slag), containing large amounts of Ca²⁺ and Mg²⁺ have been evaluated as feedstock candidates in mineral carbonation process (Lackner, 1995; O'Conner *et al.*, 2002; Huijgen *et al.*, 2006; Teir *et al.*, 2007a; Kwon *et al.*, 2011; Cárdenas-Escudero *et al.*, 2011; Lee *et al.*, 2012).

According to Lee *et al.* (2012), industrial waste gypsum is classified into three main categories: flue gas desulfurization (FGD) gypsum, phosphogypsum, and red gypsum. These industrial by-products contain approximately 32.5% CaO (Lee *et al.*, 2012) that make them a potential feedstock for mineral carbonation purposes. The produced FGD gypsum could be directly used in the mineral carbonation without any grinding process since it is in a fine powder form (Chou *et al.*, 2005). According to Lee *et al.* (2012), the SO_x elimination process from power plant flow gas is the main source FGD gypsum. However, phosphogypsum is sourced from phosphate rocks to produce phosphate fertilizer by acid treatment. According to Claisse *et al.* (2008), red gypsum containing around 75% gypsum and 25% iron, is an omnipresent feedstock in

industrialized societies. Red gypsum is a by-product of titanium dioxide (TiO_2) production using sulphate process (Claisse *et al.*, 2008). The addition of limestone to FGD gypsum and acid neutralization are considered as the main sources for red gypsum production (Claisse *et al.*, 2008).

As mentioned earlier, red gypsum contains approximately 32.5% CaO, which could be considered as a feedstock candidate in mineral CO_2 sequestration. Therefore, red gypsum has been selected as a new feedstock candidate for further studies to enhance the conversion of Ca into carbonate form and produce stable calcium carbonate (CaCO_3) in mineral carbonation process.

1.2 Statement of Problem

Reduction of CO_2 emissions into the atmosphere is a key challenge in order to mitigate the anthropogenic greenhouse effect. Increasing CO_2 and other GHGs in the atmosphere have caused to rise the mean global surface temperature. The average global warming has increased about 1 °C since industrial revolution. Moreover, growth of energy demand increases the fossil fuel consumption about 1.7% per year until 2030 (IEA, 2008). Subsequently, increasing the GHGs emission will be more than 70% until 2030. It is estimated that CO_2 emission contributed more than 40% of GHGs emission. Therefore, mitigation and reducing of CO_2 concentration in the atmosphere caused by anthropogenic activities are essential problems in the world, which is the most important preferment of this study.

Alternatively, CO_2 can be removed directly from the power plant flue gas by reaction with alkaline minerals or wastes by mineral carbonation (Huijgen *et al.*, 2006; Costa *et al.*, 2007; Oelkers *et al.*, 2008; Rubin, 2008; Lammers *et al.*, 2011). The natural minerals such as olivine, gypsum, and wollastonite, which are rich in Ca^{2+} or Mg^{2+} , are usually considered as feedstock candidates for mineral carbonation.

However, despite the rapid carbonation of waste and its open structure, mostly the previous carbonation studies have focused on the natural minerals containing Mg

[e.g., Zevehoven *et al.* (2008), Boerrigter (2009), Dufaud *et al.* (2009), Krevor and Lackner (2009), Li *et al.* (2009), Bonfils *et al.* (2010), Zhao *et al.* (2010), Kwak *et al.* (2010), Wang and Maroto-Valer (2011)].

Indeed, some industrial wastes such as lignite, fly ash, mining waste, and steel slag containing large amounts of $\text{Ca}^{2+}/\text{Mg}^{2+}$ have been evaluated as potential raw materials for CO_2 sequestration processing. However, specifically, red gypsum is a new feedstock with a rate of dissolution and carbonation in the mineral carbonation process that no study until now has investigated its mineral carbonation process. Moreover, information about the control and determination of rates of both the dissolution and carbonation stages, which are not mentioned in previous studies, is essential to optimize the mineral carbonation process in this study. Therefore, in this study red gypsum has been selected as a new feedstock candidate for further studies in mineral carbonation process.

1.3 Research Objectives

The main objectives of the current study are:

- (1) To develop a technically applicable and feasible process for CO_2 mineral carbonation by the use of red gypsum based on its mineral composition verified by X-ray fluorescence (XRF), X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM) instruments.
- (2) To determine the rate of dissolution and carbonation of red gypsum in order to optimize the process of mineral CO_2 sequestration based on possible effective variables, including reaction temperature and time, particle size, stirring rate, and liquid to solid ratio.
- (3) To determine the cost and energy required in dissolution and carbonation process of red gypsum and assess its environmental issues associated with mineral CO_2 sequestration.

1.4 Scope of the Study

In this study, red gypsum is selected to reduce CO₂ concentration in the atmosphere by applying mineral carbonation process. This process is conducted using a mini reactor that is designed at the maximum working temperature of 315 °C (600 °F) and pressure of 2900 psi (~200 bar). To this aim, different kinds of experiments are performed at various conditions.

A series of possible effective variables in mineral carbonation studies such as reaction temperature and time, particle size, stirring rate, and liquid to solid ratio are considered at specific ranges. The reaction temperature range is from 25 °C to 150 °C. The reaction time is limited up to 3 hours to investigate the optimum reaction time in carbonation experiments. Moreover, the particles size of red gypsum samples is categorized in four ranges, including <75 μm, 75-125 μm, 125-200 μm, and >200 μm. Furthermore, the stirring rate from 100 rpm to 600 rpm is considered to improve the dissolution and carbonation rates in mineral CO₂ sequestration. Finally, different amounts of liquid to solid ratio up to 300 ml/g are applied as the target ratio for carbonation studies. Characterization of fresh red gypsum samples and then products is done using XRF, XRD, and FESEM instruments.

1.5 Significance of the Study

Global warming, a phenomenon resulted from enormous fossil fuel consumption and CO₂ emission into the atmosphere, is one of the main concerns in the 21st century. Increasing GHGs concentration, and especially CO₂, is the main cause of increasing Earth's temperature. The findings of this study, which tries to sequester CO₂ via mineral carbonation, are helpful to prevent further damage caused by GHGs, and stabilize concentration of CO₂ by reducing CO₂ emission into the atmosphere. In other words, CO₂ uptake mitigates environmental effects that are problematic for human health and increase the global warming.

Mineral carbonation is considered as a significantly new and interesting method that involves the process by which CO₂ is eliminated from the atmosphere and is sequestered as formed stable minerals. CO₂ mineral carbonation in comparison with other methods of CCS that are geologic storage and ocean storage, is considered as one of the most attractive methods due to simplicity of operation with low cost of adsorption. Moreover, there are fewer limitations in its performance and no monitoring is needed.

Using industrial wastes rich in Ca (or Mg) are favored in mineral carbonation process. Therefore, red gypsum, as a Ca-rich source and a new feedstock, which has not been addressed for mineral carbonation process yet, is selected from this category for advanced research. This study has focused on the mineral carbonation of red gypsum, which is an industrial waste that has high Ca content. Industrial wastes are likely to have more advantages over the natural minerals and rocks because of which red gypsum is selected. For instance, they are available at industrial places, they are cheaper and geochemically unstable (e.g., ash and slag), hence, industrial wastes would be more reactive (Torróntegui, 2010; Olajire, 2013). Therefore, carbonation of industrial like red gypsum is expected to be a rapid process compared to minerals containing Mg that are mostly used. Moreover, the structure of industrial wastes is relatively open and the surface area for reaction is likely larger than natural minerals.

In the process of mineral carbonation, no mining is needed, and therefore, the amount of energy consumption from mining is negligible. Moreover, chemical stability of red gypsum reduces the effects of waste products on the environment significantly. Furthermore, in addition to CO₂ uptake, the reuse of produced wastes in mineral carbonation process of red gypsum is able to diminish the environmental impact.

The low cost and small amount of energy required in the use of red gypsum and less environmental issues could be advantages to the CO₂ sequestration process.

In short, it could be concluded that the findings of this study could be useful in resolving problem of GHGs and global warming with the lowest cost and less environmental issues. Therefore, this method could be considered as a significant method for reducing the CO₂ in the atmosphere.

1.6 Overview of the Thesis

According to main research objectives, this thesis involves some main tasks as follow. At the first task, the process of mineral carbonation is identified for detailed analysis in Chapter 2. Subsequently, a review of the existing literature in mineral carbonation process is discussed in relation to CO₂ sequestration. At the second tasks, the necessary materials for mineral carbonation, approaches of the analysis, and steps of the mineral carbonation are explained in Chapter 3. At the third task, dissolution and carbonation experiments of red gypsum are investigated at different conditions, which addressed in Chapter 4. At the fourth task, the cost of mineral CO₂ sequestration and required energy consumption are evaluated in relation to conducted experiments and the environmental issues associated with mineral CO₂ sequestration are assessed. At the last task, the main conclusions of this study in addition to its implementations are addressed in Chapter 5.

- (3) To reduce the reaction time by using direct mineral carbonation route instead of aqueous indirect mineral carbonation route.
- (4) To investigate the reuse of stable carbonated mineral, i.e., calcite, as supplementary cementation material to make cement or other construction materials.
- (5) To determine the life cycle assessment of red gypsum in mineral carbonation process.

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