University of Cincinnati

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I, Hari Krishna Bharadwaj, hereby submit this original work as part of the requirements for the degree of Master of Science in Chemical Engineering.

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CO2 SEPARATION USING REGENERABLE MAGNESIUM SOLUTIONS DISOLUTION, KINETICS AND VLSE STUDIES

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University of Cincinnati
CO$_2$ SEPARATION USING REGENERABLE MAGNESIUM SOLUTIONS
DISSOLUTION, KINETICS AND VLSE STUDIES

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Graduate School
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by

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ABSTRACT

Fossil fuel power plants are responsible for a considerable amount of total anthropogenic CO$_2$ emissions throughout the world. CO$_2$ capture and sequestration from point source emitters like fossil fuel power plants is essential to mitigate the harmful effects of greenhouse gases. A novel post-combustion CO$_2$ capture technique has been proposed, where CO$_2$ from flue gases can be absorbed by magnesium hydroxide (Mg(OH)$_2$) slurry at 52 °C in a column followed by a regeneration step in a stripper. CO$_2$ absorption in a Mg(OH)$_2$ slurry solution involves physical absorption of CO$_2$ gas into the aqueous phase and subsequent chemical reactions in the aqueous and solid phases. Three critical phenomena influencing the CO$_2$ absorption process, namely: the dissolution of Mg(OH)$_2$ for continuous CO$_2$ absorption, formation of an unwanted by-product magnesium carbonate (MgCO$_3$), and vapor-liquid-solid equilibrium (VLSE) of the system were studied. The dissolution of Mg(OH)$_2$ and the release of magnesium ions into the solution to maintain a level of alkalinity is a crucial step in the CO$_2$ absorption process. The dissolution process was modeled using the shrinking core model and surface chemical reaction was found to be the rate controlling mechanism. The formation of MgCO$_3$ will reduce a regenerative capacity of Mg(OH)$_2$ solvent. The impact of pH control and temperature on the kinetics of magnesium carbonate formation was also studied. The vapor-liquid equilibrium data for a solvent-CO$_2$ system is essential for the design and operating conditions of an absorber and a desorber. It can be used to determine an amount of Mg(OH)$_2$ feed for CO$_2$ absorption and also to determine the operating conditions for CO$_2$ separation and Mg(OH)$_2$ regeneration from a CO$_2$ desorber. These three individual studies will provide a fundamental understanding of CO$_2$ absorption in a Mg(OH)$_2$ slurry solution and basic engineering data for the design and operation of a Mg(OH)$_2$-based CO$_2$ absorption system.
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CHAPTER 1. LITERATURE SURVEY

1.1 Need for CO$_2$ Capture and Sequestration.

The dependence on fossil fuels for achieving the primary energy needs of the world has increased atmospheric emissions of CO$_2$. The combustion of fossil fuels produces CO$_2$, which is a known greenhouse gas believed to be responsible for nearly 60% of the global warming effects. According to the IPCC 2001 report, CO$_2$ contributes to half of the radiative forcing which leads to the greenhouse effect. The percentage of CO$_2$ in the atmosphere has increased by 96% after the industrial revolution. Fossil fuels are very likely to provide nearly 80% of the world’s energy requirements for the coming decades. The use of coal for electricity generation is rapidly increasing because coal is a relatively inexpensive source and electricity generation from coal accounts for 40% of greenhouse gas [GHG] emissions.

One of the first groups of emission sources being targeted for GHG reductions are coal-fired power plants because they are the largest stationary point source emitters of anthropogenic CO$_2$. CO$_2$ emissions in the U.S. from coal combustion have increased over nearly 18% over the period from 1990-2003 with forecasted 54% increase, if no CO$_2$ control were to be applied. If this increase is allowed to happen, the International Panel on Climate Change predicts that by the year 2100, the mean global temperature could have increased by around 1.9°C. This would lead to a sea level increase of 38 m, giving rise to species extinction and unmitigated disaster.
1.2 Various Technologies Involved in CO₂ Capture and Sequestration

CO₂ emissions are a cause of great concern to the world because of the implications to the environment. There are three options to reduce CO₂ emission into the atmosphere - a) to reduce energy intensity, b) to reduce carbon intensity and c) to enhance the sequestration of CO₂. The first option requires efficient use of energy. The second option requires switching to using non-fossil fuels such as hydrogen and renewable energy. The third option involves the development of technologies to capture and sequester more CO₂.

Under the third option we have three technological pathways:

![Block flow diagrams of the three technological pathways for CO₂ capture.](image)

Figure 1. Block flow diagrams of the three technological pathways for CO₂ capture.

a) Pre-combustion capture

In this process, the CO₂ separation takes place before the combustion of the fossil fuel. The fossil fuel is converted into hydrogen by steam reforming or partial oxidation. This is a
very common, well researched, industrial process used in the production of syngas and ammonia. Partial oxidation is more advantageous when compared to reforming because it does not need an additional energy source.

![Diagram of CO shift reaction in post combustion CO₂ capture.](image)

The heated H₂O(g) and synthesis gas streams are fed into the CO-shift converter which operates at 300 ⁰C and 2.14 MPa and CO₂ is produced [CO+H₂O -> CO₂ + H₂]. The CO₂ can be captured by using a physical solvent [Selexol] which is far more energy efficient than other physical and chemical solvents investigated. The CO₂ separated would be sent to a compression unit and the hydrogen generated would be used as an input in a combined cycle to produce electricity. Several advancements are going on in these fields which include development of membrane-based gas separation systems to combine the gas shift reaction and hydrogen separation in one step. This is part of the IGCC [Integrated Gasification Combined Cycle] concept. The main advantage of this capture technique is that high partial pressure CO₂ gas is generated, which results in availability of more driving force for separation. However this system is limited by low availability, high investment and production costs.
b) **Oxy-combustion**

The concept of oxyfuel-combustion for CO$_2$ emission capture was proposed in 1982. The key concept in this process is that nitrogen is totally removed from the combustion air, by means of an air separation unit. A mixture of 95% pure oxygen and recycled flue gas are used. The main reasons for recycling the flue gas are:

a) A gas ready for sequestration is produced which consists mainly of CO$_2$ and H$_2$O

b) Controlling the flame temperature

c) Making up the volume of missing N$_2$ for carrying the heat over to the boiler. CO$_2$ has different properties when compared to N$_2$ [denser than N$_2$ and higher specific heat capacity]. So therefore flue gas recycle ratio and oxygen concentration during the combustion process become key parameters.

![Oxyfuel technology for CO$_2$ capture and storage.](image)

Several investigations carried in pilot plant facilities worldwide have yielded theoretical and design data for oxy-combustion CO$_2$ capture. Very pure CO$_2$ can be produced and this technology has a lot of capability for retrofitting with existing facilities.
Oxyfuel-combustion/sequestration is less efficient per unit of energy produced because it must provide power to several significant unit operations. Large electric power demands must be met to operate cryogenic air separation units for generating pure oxygen. Other problems include corrosion due to buildup of corrosive gases and the need to have high temperature resistant materials.

c) Post-combustion capture

![Diagram of a typical post-combustion CO₂ capture process.]

Figure 4. Typical post combustion CO₂ capture process.

The removal of CO₂ from flue gas after the combustion of coal is referred to as post-combustion capture. Existing fossil fuel powered plants generate a flue gas that is at atmospheric pressure and which has a CO₂ concentration of less than 15%. Therefore the driving force for CO₂ capture is low because the CO₂ partial pressure is less than 0.15 atm.
Despite this problem, post-combustion CO₂ capture has the greatest short-term potential for reducing CO₂ emissions. The reasons are as follows:

1) There are around 5000 pulverized coal combustion power plants worldwide and 600 in the United States of America alone. 25 At least for the coming decades, this will continue to be the type of power plant in operation. 26 Oxy-combustion and pre-combustion capture cannot be applied to these systems, but post combustion capture options can be easily retrofitted into the existing coal-fired power plant technology.

2) Flexibility of operation is available. Post-combustion capture operates as an independent unit and can be shut down in case of a failure. The other two capture processes are very integrated with the plant, so if capture fails, the entire plant must be shut down. 27

3) Post-combustion capture is the only available technology for gas-fired power plants.

4) Commercialization of IGCC technologies has fallen away with time and has not caught on in the way that it was expected to.

1.3 Challenges facing Post-Combustion CO₂ Capture

Post-combustion CO₂ capture has been used for many years in different industrial applications like natural gas treatment. 28 But several challenges have to be overcome in order to have a completely functioning, economic CO₂ capture system to treat the flue gases for an entire plant. The additional energy requirements are as follows:

a) Heat energy from the turbine required for operating the absorption and stripping process

b) Energy requirements for compression, transportation and storage.
Figure 5. Additional energy requirements for CO₂ capture. ²⁹

Two key factors which need to be considered before applying carbon capture and storage technology [CCS] to coal-fired power plants are the energy penalty and efficiency penalty. It is defined in the following two ways: ²⁹

\[
EP = 100 \times \frac{\text{Power output without CCS} - \text{Power output with CCS}}{\text{Power output without CCS}}
\]

\[
EP = \text{Efficiency without CCS} (\%) - \text{Efficiency with CCS} (\%)
\]

For three leading CO₂ capture techniques, the published values are given as follows:

Table 1. Energy & efficiency penalties for various CO₂ capture techniques

<table>
<thead>
<tr>
<th>CO₂ Capture Method</th>
<th>Energy Penalty</th>
<th>Efficiency Penalty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption by MEA</td>
<td>25 -27%</td>
<td>11-13%</td>
</tr>
<tr>
<td>Absorption by KS2</td>
<td>15 - 25 %</td>
<td>6 -10%</td>
</tr>
<tr>
<td>Oxy combustion</td>
<td>21%</td>
<td>9%</td>
</tr>
</tbody>
</table>
The values calculated above are mainly simulated values and for practical CO₂ capture, the energy penalties are much higher (around 40%). The largest application for CO₂ capture is electricity production, but this energy penalty will reduce net electric output by 20-30% below the plants which do not employ CO₂ capture.

Costs for CO₂ capture are reported as ($/tonne) CO₂ captured or ($/tonne) CO₂ avoided. As seen above, the CO₂ capture processes are energy intensive and if implemented, will increase the cost of electricity for operating the coal-fired power plant. The average cost for CO₂ capture and compression has been worked out to be around $58/tonne of CO₂ avoided which results in a 63% increase in electricity cost for the power plant. The process of CO₂ capture accounts for about 70% of total carbon capture and storage cost. This is the reason why most research efforts are directed towards this area. The need for a cost effective, potent, energy efficient CO₂ capture technology is paramount in order to meet the Department of Energy’s CO₂ mitigation technology goal by 2020.
1.4 Post-Combustion CO₂ Capture Pathways

Post-combustion CO₂ capture can be divided into five main categories:

![Diagram showing the five main categories of post-combustion CO₂ capture: Absorption (Chemical and Physical), Membranes, Biological Capture, Other New Techniques, and Post Combustion CO₂ Capture.]

Figure 6. Post Combustion capture pathways.

1.5 Post-Combustion CO₂ Capture using Absorption

Absorption is a physical and/or chemical process in which gas molecules are dissolved in the liquid phase. Absorption is a common process in the chemical industry and is used to treat industrial waste gas or flue gas streams containing acid gases like H₂S, NOₓ, and CO₂. An ideal solvent would have high reactivity towards CO₂, low regeneration costs, high absorption capacity, high thermal stability, low environmental impacts and low solvent costs.

1.5.1 Physical Absorption using Solvents

Physical absorption of CO₂ using solvents takes place at low temperatures and high pressures. The amount of CO₂ absorbed for these systems is directly proportional to its partial pressure following Henry’s law. The desorption can be achieved by increasing the temperature (Temperature Swing Absorption) or lowering the pressure (Pressure Swing Absorption).
interaction between CO$_2$ and the solvent is either weak Van der Waals type or electrostatic, which reduces the energy requirements for regeneration.

Physical absorption has been used commonly in the industry for CO$_2$ removal from syngas in ammonia and methanol production. Some commonly used physical solvents are:

1.5.1.1 Sulfolane

Sulfolane solvent was first developed in the 1960’s by the Shell Oil company and it was used in natural gas purification. Sulfolane has many advantages such as high capacity, low vapor pressure (1.9 kPa at 150 °C), and low enthalpy of vaporization (543 kJ/kg). However, the most beneficial use of sulfolane in CO$_2$ absorption is in the form of a mixed solvent with other amines such as Diisopropyl amine (DIPA), 2-amino-2-methyl-1-propanol or methyl diethanolamine (MDEA). These mixed solvents combine the advantages of physical and chemical solvents such as increased absorption capacity (reducing stoichiometric dependence), higher purity of treated CO$_2$ and lesser recirculation of the solvent. The solvent with sulfolane and DIPA is referred to as Sulfinol D and the solvent with Sulfolane and MDEA is called Sulfinol M. This solvent has many advantages including low solvent recirculation rates and low solvent degradation rates. The operation of a Sulfinol unit is similar to that for an alkanolamine solution but for the addition of a flash tank. The Sulfinol process operates at maximum efficiency at a H$_2$S/CO$_2$ ratio of 1:1 and an acid gas of pressure 110 lb/in$^2$. abs. The flash tank is required to dispose the hydrocarbons that have been absorbed in the solvent and prevent operational difficulties. The main disadvantages with this technique are high hydrocarbon solubility and the high cost of chemicals used in the process.
1.5.1.2 Selexol

The Selexol process uses a physical solvent to remove acid gas from streams of synthetic or natural gas. This solvent has been in use from the 1960’s and is a mixture of dimethyl esters of polyethylene glycol \([\text{CH}_3 (\text{CH}_2\text{CH}_2\text{O})_n \text{CH}_3]\), where \( n \) is between 3 and 49.\(^{43}\) This system is highly suited for the bulk removal of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \). The key driving force for the Selexol process is the acid gas partial pressure. The absorption takes place at low temperatures (0–5 °C) and desorption takes place by pressure reduction or stripping with air or steam.\(^{44}\)

Selexol is best suited for applications with high \( \text{CO}_2 \) content in the acid gas stream. The Selexol solvent is also chemically and thermally stable and it suffers from minimal losses due to its low vapor pressure. This solvent also has preferential solubility for \( \text{H}_2\text{S} \) and therefore it is ideally suited for \( \text{H}_2\text{S} \) removal in the presence of high \( \text{CO}_2 \) content. The limitations of this technique include dependence of efficiency on high pressure and potential hydrocarbon losses due to high affinity of Selexol towards hydrocarbons.

1.5.1.3 Rectisol

The Rectisol process was one of the earliest used physical solvents for acid gas treatment and has been used for synthesis gas applications. Chilled methanol is used as the solvent and is very complex compared to other physical solvent processes. The high vapor pressure of methanol necessitates the operation of the process at temperatures ranging from 0 °C to -70 °C.\(^{45}\) The solubility’s of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) are high in methanol compared to Selexol and also allow for deep sulphur removal. Regeneration can be easily achieved by flashing the rich solvent at low pressure. Other advantages of this process include removal of carbonyl based compounds and high miscibility of the solvent with water, eliminating foaming losses. The need to refrigerate the solvent and the complex operating scheme are the main disadvantages of this process.\(^ {46}\)
These disadvantages can be offset by the net reduction in solvent flow rate for CO₂ removal compared to other physical solvent processes. ⁴⁷

1.5.1.4 Fluor Process

The Fluor Process uses propylene carbonate as a solvent and is used generally in syngas treatment. It is licensed by Fluor Daniel, Inc. and is particularly useful for treating acid gas streams with high CO₂ partial pressure. Propylene Carbonate (C₄H₆O₃) is a polar solvent which has higher CO₂ solubility compared to any other physical solvent. A typical Fluor process has two stages of flashing and is ideal suited for acid gas streams with an acid gas partial pressure > 60 psi. ⁴⁸ The operating temperature for the Fluor solvent ranges between -18 °C to 65 °C. Despite the vapor pressure of propylene carbonate being higher than Selexol, it has much lesser solvent losses. The Fluor process requires no water wash to recover the solvent because of its low vapor pressure. ⁴⁵ The major drawbacks of this process include need for high solvent recirculation, expensive nature of the solvent and unstable nature of the solvent when H₂S is present in more than trace concentrations. ⁴⁴ ⁴⁵

1.5.2 Chemical Absorption using Solvents

Chemical absorption systems are the most preferred option for post-combustion CO₂ capture because they are ideally suited for treating flue gases with low to moderate CO₂ partial pressure. Absorption using chemical solvents at this point in time offers the highest capture efficiency and lowest energy costs when compared to other existing post-combustion capture systems. ⁴⁹ The flue gas is cooled and brought into contact with the solvent in an absorber/contactor. The absorption takes place due to a chemical reaction between the CO₂ and the solvent. The absorber temperatures are between 40 °C and 60 °C and the CO₂ binds weakly
with the chemical solvent to form an intermediate compound. The CO\textsubscript{2} rich solution is pumped to a stripper vessel and the solvent is regenerated by using high temperatures (100 °C – 140 °C) and pressures.

1.5.2.1 Amine-Based Solvents

One of the most commonly used and studied solvents are the amine-based solvents, particularly monoethanolamine [MEA]. It was developed over 60 years ago as a general, non-selective solvent to remove acidic gas impurities (e.g. H\textsubscript{2}S, CO\textsubscript{2}) from natural gas streams.\textsuperscript{50} Pure unhindered amine reacts with CO\textsubscript{2} to form a water-stable compound called carbamate and half a mole of CO\textsubscript{2} is absorbed per mole of amine.\textsuperscript{51} A conventional MEA would involve cooling the flue gas and contacting it with a lean solvent with a CO\textsubscript{2} loading of 0.1-0.2 mol CO\textsubscript{2}/mol MEA, yielding a rich solvent of about 0.4-0.5 mol CO\textsubscript{2}/mol MEA loading at a temperature of 40-60 °C.\textsuperscript{52} The rich solvent is pumped to a stripper, where it is regenerated at elevated temperatures (100-120 °C) and pressures (1.5-2 atm).\textsuperscript{53,53a} Major problems associated with amines are: a) solvent degradation, b) high energy consumption for regeneration [1900 kJ/kg CO\textsubscript{2}], and c) corrosion.\textsuperscript{54,51}

Several ethanolamine derivatives can be produced by replacing one or more of the alcohol groups by hydrocarbon groups e.g. methyldiethanolamine (MDEA). MEA can react more than MDEA, but MDEA has a greater CO\textsubscript{2} absorption capacity [1 mol of CO\textsubscript{2}/mol amine] and requires lower regeneration energy [1200 kJ/kg of CO\textsubscript{2}].\textsuperscript{55,56,57} Mixed amines and amine blends have been reported to maximize the desirable qualities of the individual amines.\textsuperscript{58} There could be reduction in cost for regeneration of the solvent by up to 20%, if a mixture of MEA and MDEA is used.\textsuperscript{59} This is due to the lower heat of vaporization of MDEA [223 cal/g] when compared to MEA [355 cal/g]. It has also been shown that the addition of a small amount of
MEA to an aqueous solution of MDEA significantly increases the enhancement factor and the rate of CO$_2$ absorption.  

1.5.2.2 Carbonate-Based Solvents

Aqueous-based carbonate solvents comprise the second most popular class of solvents used in acid gas treating. A soluble carbonate reacts with CO$_2$ to form bicarbonate, which when heated, releases CO$_2$ and the solvent is regenerated as a carbonate. A substantial reduction in the energy requirement, compared to amines, is the major advantage of this process. However, their low reaction rates require a use of a promoter like piperazine to increase the rate of reaction.  
Piperazine has a cyclic diamine structure that favors rapid formation of carbamates and it also catalyzes proton extractions in the reaction mechanism. The amine can absorb 2 moles of CO$_2$ for every mole of amine and with potassium carbonate, which has capacity of 1 mol CO$_2$/mol K$_2$CO$_3$ in solution, the blended solvent has potential for high CO$_2$ capacity.  
When piperazine is blended with K$_2$CO$_3$, the amount of amine protonation is reduced by the buffering capacity of the potassium bicarbonate, which leaves more amine free to react with CO$_2$.  
The K$_2$CO$_3$/PZ system (5 molar K; 2.5 molar PZ) has an absorption rate 10–30% faster than a 30% solution of MEA.  
A model was simulated in Aspen plus in which a five-stage absorption-desorption unit was used. Five stages were chosen during modeling because it gave a good compromise between calculation precision, computational effort and convergence behavior of the model. The absorber was operated at 40 °C and stripper was also operated at nearly the same temperature. This is possible because the desired heat of absorption of the promoted potassium carbonate is near or below that of water.
Pure piperazine itself has been investigated as a novel solvent for CO$_2$ absorption. Piperazine has was thought to have limited solubility, but recent research shows that PZ has the capability to be used in very high concentrations when it is partially loaded with CO$_2$. The CO$_2$ absorption rate is twice that of 30% MEA and the thermal degradation also is negligible up to 150 °C. PZ will also require 2 to 3 times less absorber packing than MEA. Piperazine is 3 to 10 times more expensive than MEA, but this cost can be offset by other advantages of piperazine, namely its resistance to oxidative degradation and its corrosion resistance to stainless steel.

1.5.2.3 Ammonia

Ammonia based wet scrubbing systems are very similar in working to the amine based systems. It reacts with CO$_2$ mostly in the form of ammonium carbonate (AC) and ammonium bicarbonate which has lower heats of reactions than amine based systems. An additional advantage for this system is that when it reacts with SO$_2$ and NO$_x$, fertilizers are formed which is a salable by product. A typical removal efficiency can reach 90% with 5% or higher concentration, but if the concentration exceeds 15%, substantial amount of ammonia will volatilize from the solution. The major problems associated with this process are that the flue gas must be cooled to ambient temperature to increase the CO$_2$ uptake and to reduce the ammonia vapor emissions from the absorption column.

Another novel process which involves the use of ammonia is the chilled ammonia process, where the absorption takes place at a very low temperature of 0-10 °C which prevents the ammonia from evaporating. In this process, the CO$_2$ loading concentration of the CO$_2$ lean stream ranges from 0.33-0.67 mol CO$_2$/mol NH$_3$ and CO$_2$ rich stream from 0.5-1 mol CO$_2$/mol NH$_3$. 
The desorber temperature ranges from 50-200 °C and the pressure from 2-136 atm. The energy required for this process [1147 kJ/kg CO\textsubscript{2}] is much lower than the corresponding values for MEA and amines[4215 kJ/kg CO\textsubscript{2}].

1.5.2.4 Dual Alkalis

The Solvay process makes use of two alkalis to sequester CO\textsubscript{2} in the form of sodium carbonate which is a very useful by-product. Since the Solvay process is not efficient, a modified dual alkali approach was proposed. This process involves the reaction of CO\textsubscript{2} with NaCl and NH\textsubscript{3} to produce sodium carbonate. The primary alkali ammonia is recovered by reacting the NH\textsubscript{4}Cl produced, with lime. Lime acts as the secondary alkali and limestone is used as a source of lime. The drawbacks with this system include consumption of limestone, intensive energy requirements and also the release of one mole of CO\textsubscript{2} for every mole of CO\textsubscript{2} captured during the calcination of limestone.

1.5.2.5 Ionic Liquids

Ionic liquids are a broad category of salts, typically containing an organic cation and either an inorganic or organic anion. Ionic liquids are non-flammable, environmentally benign and can exhibit exceptional thermal stability. They are known as designer solvents because their physical properties such as melting point, viscosity and gas solubilization can be controlled by altering the substituents of the cation or anion. The mechanism for capture is based on physisorption and involves weak interaction between the ionic liquids and CO\textsubscript{2} with a heat of absorption around -11kJ/gmol. ILs can dissolve gaseous CO\textsubscript{2} and are stable at temperatures up to several hundred degrees centigrade. Their good temperature stability offers the possibility of recovering CO\textsubscript{2} from flue gas without having to cool it first. Since ionic liquids are physical
solvents, little heat is required for regeneration. However ionic liquids face problems like corrosion, expensive bulk scale production and very high viscosities [66 to 1110 cp at 25 °C]. 74

1.5.3 Absorption using Carbonation/Calcination Cycles

This capture technique involves the reaction of CO₂ with a solid metal oxide yielding a metal carbonate as the product and regeneration of the metal oxide by heating the metal oxide beyond the calcination temperature. This system has several advantages like: a) CO₂ separation can be performed at flue gas conditions without the need for high system pressure/low temperature. b) High equilibrium capacities of the sorbent (393 g of CO₂/kg) compared to the amine process (MEA- 60 g of CO₂/kg). c) Ability of generate pure streams of CO₂ despite the presence of SO₂ and other gases. 75 Calcium oxide has proposed as the sorbent of choice for this method because of its high absorption capacity and cyclic stability. The cyclic CCR (carbonation calcination reaction) process has two reactors: 1) carbonation reactor – where CaO is carbonated to CaCO₃ at 600 °C -700 °C and atmospheric pressure. 2) calcination reactor – where calcination of CaCO₃ takes place to regenerate the sorbent and produce a concentrated stream of CO₂ at high temperatures (> 900 °C). 76 Fluidized beds of CaO have been shown to give excellent CO₂ capture efficiencies from combustion flue gases at high temperatures. 77 Lu et al. 78 demonstrated the applicability of this technology using a pilot scale dual fluidized system, with continuous sorbent looping and achieved high capture efficiency (> 90%) for the first several cycles. The major disadvantage of this technique is the decrease in absorbent activity with the increase in the number of carbonation/calcination cycles. This takes place due to various factors like sintering, sulphation and attrition. Some potential methods for reducing problems caused by sintering include spent sorbent reactivation by air/steam and thermal pretreatment of the sorbent. 79
1.6 Post-Combustion CO$_2$ capture using Adsorption

Adsorption is a heterogeneous process which involves the capture of CO$_2$ molecules on the surface of a solid sorbent. The CO$_2$ interacts with the sorbent via weak Vander waals forces (physisorption) or stronger covalent bonds (chemisorption). The advantages of using such sorbents for CO$_2$ capture include reduced energy costs for regeneration and greater capacity and selectivity. Regeneration of the solid sorbent is done via Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA). Pressure Swing Adsorption is a cyclic process where the adsorption is carried out at a relatively higher pressure compared to the desorption pressure, with a part of the product from the adsorption step. PSA has been used more extensively due to lower energy demand and higher regeneration rate.

Activated carbon based solid sorbents and carbon molecular sieves have been studied extensively for flue gas CO$_2$ capture. Activated carbon based systems operate at close to room temperature and atmospheric pressure. Initial studies indicated that around 70% CO$_2$ removal was achievable using AC’s at 298 K coupled with PSA. Siriwardane et al. demonstrated that activated carbons at higher pressures (>25 psi) show significantly higher CO$_2$ capacity than molecular sieves. Garcia et al. observed that increase in temperature leads to reduction in CO$_2$ capacity and breakthrough time for the activated carbon sorbent. Activated carbons can be produced from a wide variety of sources and thus can be produced at a lower cost on the industrial scale. They also possess other significant advantages such as hydrophobicity and lower energy requirements to carry out regeneration [20 kJ/gmol]. But, these advantages are offset by other problems like low absorption capacity at lower partial pressures of CO$_2$, reduction in capacity with temperature and low selectivity.
Carbon Molecular Sieves (CMS) are a class of microporous carbon materials that are used for separating molecules on the basis of molecular weight or size. These CMC’s must exhibit a highly developed pore network and controlled size opening to differentiate between molecules having similar dimensions. Initial studies performed by Kapoor et al. \(^{85}\) demonstrated the applicability of carbon molecular sieves with PSA for separation of a CH\(_4\)/CO\(_2\) mixture. Burchell et al. \(^{86}\) developed a porous monolithic activated carbon material which has a large micropore volume and achieved a CO\(_2\) uptake of \(>100\) mg/g. Wahby et al. \(^{87}\) prepared a series of CMS’s from petroleum pitch using potassium hydroxide as an activating agent and achieved high capacities of CO\(_2\) absorption (380 mg CO\(_2\)/g sorbent) at 273 K and 1 bar. The major drawbacks of this technique include the need for pretreatment of gases before adsorption, low CO\(_2\)/N\(_2\) selectivity and temperature dependence on adsorption capacity.

### 1.7 Post-Combustion CO\(_2\) Capture using Membranes

Membranes are semi permeable barriers which can selectively remove CO\(_2\) from flue gas through mechanisms like diffusion, ionic transport and adsorption. Membranes can either be constructed by using either polymeric or inorganic material and can be porous or non porous. \(^{44}\) Membrane based processes have generated a lot of interest because it can significantly bring down the cost for regeneration of the sorbent. Membranes have not yet been commercially employed for CO\(_2\) capture from flue gas, but have been used extensively for CO\(_2\) recovery from natural gas. \(^{88}\) Three major variables that play an important role in membrane based separation processes are:

1. Membrane selectivity \((\alpha)\) – intrinsic parameter determined by the ratio of pure gas permeabilities,
2. Pressure ratio \((\psi)\) – is the ratio of pressures between upstream and downstream compartments,
3. Stage cut \((\theta)\) – is the ratio of the permeate flow to the feed flow rate. \(^{89}\)
Membrane process for CO₂ separation can be divided into three main systems: a) non dispersive contact via microporous membranes, b) Gas permeation systems c) Supported liquid membranes. Some of the commonly used membranes in these systems are discussed below:

### 1.7.1 Polymeric Membranes

Polymeric membranes are classified into rubbery, polyolefinic or glassy depending on their operating temperature relative to the glass transition temperature. The major mechanism in the transport of gas molecules through a polymeric membrane is by solution diffusion. The key relation between permeability, diffusivity and solubility for a polymeric membrane is given by

\[ P = DS \]

where \( P \) is the permeability coefficient – a measure of the flux of the membrane (cm³ cm⁻² s⁻¹ cm Hg⁻¹), \( D \) is the diffusivity coefficient (cm² s⁻¹) and \( S \) is the solubility coefficient which measures the solubility of the gas molecules within the membrane (cm³ cm Hg⁻¹).

Achieving a higher permeability and selectivity for CO₂ is the main focus of membrane research and development. Polymeric membranes cannot withstand temperatures above 100 °C and also experience a drop in selectivity with increasing temperatures. So therefore, polymeric membranes are more suited for post-combustion because the flue gas temperature is low. But lower partial pressures of CO₂ necessitate the need for compressors or vacuum systems, which increase the overall cost of the CO₂ capture process. Single stage membrane systems would result in low efficiency, as the permeate would be diluted with nitrogen gas, thereby creating the need for an additional membrane step. Polyamide membranes with the 6FDA group have been researched extensively and give good selectivity for CO₂. Polyethylene oxides (PEO) membranes have also been found to be good candidates for CO₂ absorption owing to strong affinity for the CO₂ molecule by the polar ether oxygen in the polymer chain. The major drawback identified for the PEO membranes is its tendency to crystallize, which causes a
decrease in permeability. Other technologies investigated for improving the performance of the membrane include mixed matrix membranes (incorporation of an inorganic nanoparticle into a polymeric matrix) and facilitated transport membranes (coating the membrane with cross linked polyvinilamine). 96

1.7.2 Zeolitic Membranes

Zeolites are porous, inorganic, crystalline aluminosilicates that have been used extensively to prepare membranes to separate CO₂ from CH₄. Initial studies revealed physisorption to be the dominant process for CO₂ absorption on zeolites. 97 The uniform crystalline nature of zeolites with well-defined pore sizes between 0.5 to 1.2 nm also allows for separation of molecules through the molecular sieving effect. Zeolites have excellent regeneration properties compared to other membranes/sorbents and possess extremely fast adsorption kinetics. Both natural and synthetic zeolites have shown promising results for CO₂ separation from flue gas streams. Siriwardane et al. 98 performed CO₂ absorption studies on five zeolites (4A, 5A, 13 X, APG-II and WE-G 592) at 120 °C and concluded that zeolites 13 X and WE-G 592 showed the best CO₂ absorption capacities (0.7 mol/kg at 1 atm and 1.2 mol/kg at 20 atm). They also concluded that absorption capacity is proportional to the pore diameter and the Na/Al ratio of the zeolites. Further studies showed that zeolite 13X is extremely selective to CO₂, possessing high isosteric heats of adsorption (37.2 kJ/mol). 99 Temperature swing adsorption has been investigated by many research groups for regeneration of the zeolites and zeolites 5A/13X show excellent CO₂ uptake capacity combined with good regeneration capability. However zeolites suffer from a lot of disadvantages including attrition of the zeolites, detrimental effect of water on CO₂ adsorption and decrease in adsorption capacity with temperature.
1.7.3 Membranes in Conjunction with Chemical Solvents

These hybrid membrane-solvent systems are being researched actively because they offer the possibility of achieving high selectivity and high permeabilities. The solvent is supported on the pores of the membrane or introduced inside the pores of the membrane. They provide a high surface area to volume ratio and ensure excellent mass transfer between the gas and the solvent stream. The immobilization of aqueous amine on to a solid support like silica has several advantages like bringing down the energy required for regeneration, reducing the degradation of the amine and cutting down on the corrosion of the absorber. Supported amine adsorbents can be divided into three classes: a) Class 1: porous supports impregnated physically with monomeric or polymeric amines, b) Class 2: amines covalently linked to the supports, c) Class 3: amines which are polymerized in situ from an amine monomer. The most commonly used amine for impregnation is Polyethylenimine (PEI), which is a branched amino polymer or a linear amino polymer with secondary amines. The effect of PEI impregnation was studied on various carbonaceous materials like activated carbons, fly ash, biochar and carbon nanotubes and a substantial increase in CO$_2$ adsorbate interactions were found. However, these methods could result in potential blocking of the pores, whose mechanisms have not yet been fully understood.

Xu et al. developed a novel molecular basket adsorbent (Class 1) by dispersing PEI into pores of mesoporous MCM-41 and selectively achieved CO$_2$ adsorption from flue gas, maintaining the stability of the sorbent after several cycles. PEI-impregnated MCM-41 showed an increase in adsorption capacity with increasing temperature compared to other conventional adsorbents like activated carbons and zeolites. Several other silica supported sorbents have been studied (SBA-15, MCM-48, PE-MCM-41 and SBA-16) and all of these class 1 supported amines show excellent CO$_2$ sorption capacities compared to the pure amines. Although Class 2
supported amines (amine grafted covalently on to the silica support) show improved CO$_2$ adsorption capacities, they suffer from problems like low thermal stability in the presence of water vapor and lower equilibrium CO$_2$ adsorption capacities compared to class 1 supported amines. Class 1 supported amines showed improved performance in the presence of water vapor and can effectively adsorb CO$_2$ with high working capacities of 4 mmol/g. Supported amines show great potential in bringing down the energy requirements for the CO$_2$ capture process, but are very much in the nascent stage of development and require further investigation about the selection criteria and the effect of other gases on these sorbents.

1.8 Post-Combustion CO$_2$ Capture using Biological Methods

500 billion tons of CO$_2$ are fixed annually by terrestrial vegetation and microalgae have the ability to fix CO$_2$ with around 10 times efficiency as that of terrestrial plants. A controlled photosynthesis reaction by the microalgae that fixes CO$_2$ has been investigated as it has additional advantages of high value biomolecule production, production of H$_2$ and reduction in the cost of CO$_2$ capture. Several studies have shown that microalgae are capable of growing rapidly under high CO$_2$ concentrations and also in the presence of SO$_x$ and NO$_x$, which are common components of flue gas. The microalgal strain *Chlorella Vulgaris* shows excellent growth at high temperatures and CO$_2$ concentrations of 15% (which is the average flue gas CO$_2$ partial pressure). A photo bioreactor with *Chlorella Vulgaris* exposed to 1850 ppm of CO$_2$ and short gas residence was able to remove upto 74% of the CO$_2$ in the airstream. However, CO$_2$ mitigation by microalgae would be economically feasible, only when the biomass produced leads to products that have substantial commercial value. Another major disadvantage faced by these microalgae systems are that they require land and water resources in close proximity to the power plant.
1.9 Other Technologies for CO$_2$ Capture

1.9.1 Cryogenics

Cryogenic separation is a novel technique where all other components of the flue gas are removed barring N$_2$ and CO$_2$ are removed and the remaining gas is sent into a chamber where CO$_2$ is liquefied by fractional condensation and distillation at low temperatures. When the system operates at the triple point of CO$_2$ (-56.6 °C and 7.4 atm), the CO$_2$ will liquefy into a concentrated solution and the N$_2$ can be vented out at the top of the chamber. The major advantage of this process is that the liquid CO$_2$ can easily be transported, stored or sent to enhanced oil recovery fields. $^{109}$ Tuinier et al. $^{110}$ demonstrated the applicability of cryogenic capture to post-combustion CO$_2$ by achieving effective separation of CO$_2$/N$_2$ mixtures using dynamically operated packed bed systems. The Cryocell process developed by Cool energy Ltd showed excellent CO$_2$ capture efficiencies from natural gas, comparable to amine based technology and had many advantages like the non-requirement of chemicals, water supply and heating systems. $^{111}$ The potential roadblocks with this technology are the high cost of energy for refrigeration and possible plugging by ice in the feed streams of the cooling units.

1.9.2 Metal Organic Frameworks

Metal organic frameworks (MOF) are a new class of crystalline porous material comprised of metal containing nodes linked by organic ligand bridges and held together by coordination bonds. $^{112}$ The MOF materials have 3D structures with uniform pores and a network of channels that are stable to the elimination of guest molecules (solvents) and can store gases like H$_2$ and CO$_2$. The pore size, topology and chemical composition of the MOF’s can be tuned over a wide range resulting in the maximum reported capacities for CO$_2$ adsorption. Additionally, MOF’s possess fast adsorption rates which are essential for gas separation.
Yazaydin et al.\textsuperscript{113} screened over 14 MOF’s for CO\textsubscript{2} adsorption at flue gas pressures and reported that Mg/DOBDC and Ni/DOBDC show excellent CO\textsubscript{2} capacities at 0.1 atm and 298 K. Liu et al.\textsuperscript{114} compared the performance of Ni/DOBDC and reported that in addition to better performance, Ni/DOBDC can resist the impact of water on adsorption better than zeolites. The major problems to be overcome in this area include high synthesis cost of the MOF’s and improving the stability of the MOF’s towards heat regeneration, water vapor and acid gases.\textsuperscript{115}

1.10 Conclusion

This chapter provided a concise overview of the available technologies for post-combustion CO\textsubscript{2} capture. There is an urgent need to develop technologies and process that are able to achieve DOE’s goal of 90% CO\textsubscript{2} capture with less than 35% increase in cost of electricity. Post-combustion capture using chemical solvents offer the best near term potential for CO\textsubscript{2} capture due to their state of development and commercial viability for integration with power plants. The implications, advantages and process conditions for using magnesium hydroxide solutions as a post combustion solvent will be discussed in the upcoming chapter.
CHAPTER 2. MAGNESIUM HYDROXIDE AS POST-COMBUSTION SOLVENT FOR CO$_2$ ABSORPTION

2.1 Magnesium Hydroxide for CO$_2$ Capture

Amine based solutions are the most widely used and studied systems for post combustion CO$_2$ Capture. A common solvent for reference is 30% weight aqueous MEA [Monoethanolamine], which have been used previously by oil and chemical industries for acid gas removal from natural gas streams. But MEA suffers from several disadvantages which include: a) solvent degradation due to side reactions with SO$_2$ and other flue gases, b) corrosion of the equipment, c) low CO$_2$ loading capacity and d) high regeneration energy. The requirement for a solvent that is non-corrosive, SO$_2$ resistant and has a low binding energy for easy regeneration is paramount.

Magnesium based minerals like serpentine, brucite and olivine have been investigated for permanent CO$_2$ disposal in the form of magnesite, which is an environmentally stable benign carbonate. It can also be used in the form of a slurry solution to absorb CO$_2$ in a packed/bubble column and produce a rich stream of CO$_2$ by recovering the solvent in a regenerator. The idea of using magnesium hydroxide solutions as a potential solvent to scrub CO$_2$ from flue gases was derived from the established practice of Flue Gas Desulphurization using lime or limestone solutions. Magnesium hydroxide was found to give superior continuous absorption capacity compared to other alkaline solutions like NaOH and Ca(OH)$_2$. The process investigated in this study involves CO$_2$ absorption using magnesium hydroxide slurry solutions at 52 °C and regeneration of the solvent at a stripper temperature of 65 °C.
2.2 Process Description

A process flow diagram was developed as shown below in the figure 7. The system requirements for using Mg(OH)$_2$ as a solvent to separate CO$_2$ from flue gas and sequester it with a 95%(mole) purity were estimated based on the molar compositions of 15% CO$_2$, 13% H$_2$O and 3% O$_2$ and the remaining N$_2$ at the inlet of the CO$_2$ absorber with 90% CO$_2$ removal from a typical 500 MW coal fired power plant. 4M Mg(OH)$_2$ (21% wt of Mg(OH)$_2$) was assumed to be used to achieve 90% removal.

![Process flow diagram of the proposed setup.](image)

Here, the flue gas is assumed to enter an absorber section at an adiabatic saturation temperature of 52 °C from the FGD system. The gas stream is contacted with the scrubbing liquor containing the magnesium compounds at a pH which is low enough to allow as much as possible of the magnesium carbonate compounds to be in solution, but high enough to allow for rapid
absorption of CO₂. The rich magnesium slurry containing 1 % (mole) CO₂ is raised from 52 °C to 62 °C after passing through a major heat exchanger (HX1) and further increased by 3 °C from 62 to 65 °C under 5.1 atm with low pressure steam in the stripper.

The operating pressure of the stripper was determined using the Henrys law data that take into account the dissociation of CO₂ in the aqueous phase using PRO II process simulator. The operating pressure of the stripper is created by a pump (P1) and is maintained to have a purity of 95 % (mole) in the CO₂ exiting the stripper. The high operating pressure of 5.1 atm is useful to reduce the amount of water vapor in the CO₂ stream which in turn reduces the load on the LP steam and no additional cooling water is also required to meet the 95 % CO₂ specifications. Also, the subsequent downstream compression and dehydration processes would require much lesser energy.

### 2.3 Advantages of Using Magnesium Hydroxide for CO₂ Capture

As a by-product of magnesium-enhanced FGD systems, the material will be readily available, and its production will not result in the release of additional CO₂ emissions to the atmosphere. The active ingredient Mg(OH)₂ is readily available commercially and can be reclaimed from any lime based FGD systems as all limestone’s have magnesium hydroxide up to some extent, ranging from 4 % to 45 %. The outlet temperatures of most flue gases are around 52 °C. If Mg(OH)₂ is used for CO₂ absorption, no additional heating of the flue gas is required. Regeneration of Mg(OH)₂ takes place at 65 °C in the stripper which implies due to the small temperature difference, lesser energy will be consumed during the stripper operation. CO₂ separation is high with recycle and it has a very favorable chemistry for absorption (ΔG = -9.13 kcal/mol at 25 °C). The scrubber can also react with other acid gases like sulphur oxides (SO₂ and SO₃) coming from the FGD scrubber and can separate sulphur in the form of
CaSO₄. No modification of the existing boiler-heat transfer configuration is required and the system can be easily retrofitted into the existing FGD units or designed as new units in combination with the FGD unit.

2.4 Magnesium Hydroxide Recovery from Magnesium-Enhanced Wet FGD

Low cost magnesium hydroxide for CO₂ capture can be generated from magnesium enhanced wet Flue Gas Desulphurization units originally developed by Carmeuse North America. A magnesium-enhanced process using lime has around 3-6% of MgO in the calcium oxide. The MgO in the lime produces MgSO₃ in the absorber liquid. MgSO₃ is a soluble salt that accumulates in the liquid portion of the slurry and acts as a catalyst, by reducing the resistance to the transfer of SO₂ from the gas to the liquid. The slurry has the various reaction products with SO₂, liquid phase SO₂ and solid calcium hemihydrate. Slurry is pumped from the reaction tank and sprayed into the flue gas. SO₂ reacts with MgSO₃ to form Mg(HSO₃)₂. Slaked lime consisting of Ca(OH)₂ and Mg(OH)₂ react with magnesium bisulfite to get calcium sulfite hemihydrate (CaSO₃·1/2H₂O) and MgSO₃ is regenerated which is then available for continued capture of SO₂ when reaction tank slurry is recirculated.

The reactions involved are

Absorption:

\[ SO₂ + H₂O + MgSO₃ \rightarrow Mg(HSO₃)₂ \]

Precipitation and regeneration:

\[ Mg(HSO₃)₂ + Ca(OH)₂ \rightarrow CaSO₃ \cdot \frac{1}{2} H₂O \text{ (solid)} + MgSO₃ + 1/2 H₂O \]

\[ Mg(HSO₃)₂ + Mg(OH)₂ \rightarrow 2 MgSO₃ \]

Mg(OH)₂ production:

\[ MgSO₄ + Ca(OH)₂ + 2 H₂O \rightarrow CaSO₄·2 H₂O(gypsum) + Mg(OH)₂ \]
One portion of the absorber slurry containing the soluble magnesium sulfite and the insoluble calcium sulfite hemihydrate is sent to an oxidation tower and is further oxidized using compressed air at the bottom of the tower. Calcium sulfite dihydrate is converted to gypsum and magnesium sulfite is converted to magnesium sulfate. Magnesium hydroxide is produced by adding slaked lime to the liquid containing MgSO₄. MgSO₄ undergoes a double decomposition reaction to precipitate as magnesium hydroxide and gypsum.

Figure 8. Schematic of magnesium hydroxide recovery process.¹¹⁸
2.5 Chemistry of the Absorption / Desorption Process.

Carbon dioxide hydrolyzes upon dissolution in water. The product $H_2CO_3^*$ can be considered as the effective carbonic acid value in water due to difficulty in differentiating between dissolved CO$_2$ and carbonic acid. At a pH of 8.4 – 8.6, the formation of the carbonate ion is minimal.

The reactions of interest for magnesium hydroxide solutions exposed to atmospheres containing CO$_2$ are:\(^{119}\)

\[
\begin{align*}
CO_2 + H_2O & \leftrightarrow H_2CO_3^* \\
H_2CO_3^* & \leftrightarrow H^+ + HCO_3^- \\
HCO_3^- & \leftrightarrow H^+ + CO_3^{2-} \\
Mg(OH)_2 & \leftrightarrow Mg^{2+} + 2OH^- \\
Mg^{2+} + CO_3^{2-} & \rightarrow MgCO_3 \\
Mg^{2+} + 2HCO_3^- & \leftrightarrow Mg(HCO_3)_2 \\
Mg(HCO_3)_2 & \leftrightarrow Mg(OH)_2 + CO_2
\end{align*}
\]

The magnesium bicarbonate formed is completely soluble and does not exist as a solid. The solid magnesium carbonate (MgCO$_3$) formation is controlled kinetically and requires more time than the liquid residence time of the system. So for successful operation, the system needs to be operated at a high pH which will allow CO$_2$ absorption, but low enough to nullify the formation of magnesium carbonate.

The objective of this thesis is to investigate three crucial phenomena in this absorption process, namely:
1) The rate of dissolution of magnesium hydroxide and impact of factors like pH, temperature, stirring rate and particle size.

2) Kinetics of magnesium carbonate formation and the impact of pH control and temperature.

3) Vapor-liquid-solid equilibrium of the CO$_2$-H$_2$O-Mg(OH)$_2$ system.
CHAPTER 3. DISSOLUTION RATE STUDIES OF MAGNESIUM HYDROXIDE

3.1 Introduction

One of the most important steps in the CO₂ scrubbing process is the rate at which the magnesium hydroxide dissolves from the solid part of the slurry and becomes available for reaction with the absorbed CO₂. A thorough understanding and prediction of the dissolution rate process under different conditions is required for the successful operation of the CO₂ absorption system.

CO₂ gas absorption into Mg(OH)₂ solution takes place based on the following steps.¹²⁰

1. Diffusion of CO₂ gas through the gas film near the gas liquid interface
2. Dissolution of CO₂ in the liquid phase.
3. The first dissociation of CO₂ [into bicarbonate ions].
4. The second dissociation of CO₂ [into carbonate ions].
5. The dissolution of Mg(OH)₂ from the solid part of the slurry
6. The diffusion and subsequent reaction of inorganic carbon species within the reaction zones of the liquid film.

Step 1 depends on the type of equipment used to bring the gas into contact with the slurry solution. Step 2 – 4 take place instantaneously. Magnesium hydroxide is nearly insoluble in water and has a Ksp value of 5.61 *10⁻¹¹ (mol³/dm⁹). So therefore, the dissolution rate of Mg(OH)₂ is the slowest step in this reaction and therefore very likely to be the rate determining
step of the entire reaction. Thus prediction of the dissolution rate of magnesium hydroxide is essential for the design of the Mg(OH)$_2$ based - CO$_2$ absorption system.

Over the years, several studies have been conducted on the dissolution of limestone (calcium carbonate), which is used as a sorbent for SO$_2$ capture in wet Flue Gas Desulphurization (FGD) systems. Most of the earlier studies focused on the impact of dissolution on geological processes such as evolution of Karst landscapes in limestone areas $^{121, 122}$, effect of calcite dissolution on ocean chemistry $^{123, 124, 125}$, growth and dissolution of sedimentary rocks $^{126, 127}$ and acid fracturing of oil field reservoirs $^{128, 129}$. Plummer et al. $^{130}$ conducted a critical review of the existing work and concluded that dissolution rates were controlled by hydrogen ion diffusion below pH 5 and by surface reaction kinetics above pH 5. More recent studies have focused on estimating dissolution of limestone, lime and other calcium based materials under conditions encountered in wet FGD units.

Chan and Rochelle $^{131}$ measured the dissolution rate of reagent CaCO$_3$ at constant pH using batch titration with HCl and developed a mass transfer model assuming that the calcite particles behaved as spheres in an infinite stagnant solution. Toprac and Rochelle $^{132}$ showed that there is no influence of the type of limestone on the dissolution rate and that dissolution rate depends heavily on the particle size distribution.

Gage and Rochelle $^{133}$ studied the impact of sulfite on dissolution and concluded that, in the presence of sulfite, the dissolution rate was controlled by a combined mass transfer/surface reaction regime. Tseng and Rochelle $^{134}$ also investigated the dissolution rate of calcium sulfite (by product of FGD systems) and showed that under simulated FGD conditions, the dissolution rate solely depends on mass transfer.
Other studies have also discovered that under certain conditions, surface reaction may also influence the dissolution of limestone. Lund and Fogler\(^\text{135}\) studied limestone dissolution in HCl using a rotating disk apparatus and found that at -15.6 °C both mass transfer and surface reaction controls the dissolution rate. Gao Xiang et al.\(^\text{136}\) measured limestone dissolution rate under conditions of pH (4 – 6), temperature (25°C -55 °C) and dissolved sulfite (1mM). They obtained the same trend of results reported by Gage and Rochelle and also concluded that the dissolution rate of limestone is inversely proportional to its crystallinity.

Siagi et al.\(^\text{137}\) investigated the dissolution rate of South African calcium based material using HCl solution to maintain a constant pH and concluded that the dissolution rate was controlled by surface chemical reaction control. Their studies showed that the dissolution rate increased with an increase in temperature and decrease in particle size. The dissolution kinetics of magnesium oxide during the leaching of magnesite was found to be controlled by surface chemical reaction with high values of apparent activation energy (58-64 kJ/gmol)\(^\text{138}\). The dissolution of calcined magnesite was also reported to follow chemical reaction control, which was further supported by a linear relation between the particle size and the apparent rate constant.\(^\text{139}\)

Various studies have also searched for ways to increase the rate of limestone dissolution by using various additives. It was also reported that organic acids with buffering capacity between the pH of the gas/liquid interphase and pH of the bulk liquid phase would provide optimum enhancement.\(^\text{140}\) Chang and Rochelle\(^\text{141}\) investigated the impact of buffering by acetic acid and concluded that as little as 10 to 20mM of acetic acid would provide maximum mass transfer enhancement. Dibasic acid (commercially called AGS), which is a byproduct of adipic was also tested for buffering capabilities. It enhanced limestone scrubber performance as
effectively as adipic acid and is 40-50% cheaper than pure adipic acid. Adipic acid, AGS, glutaric and succinic acid in concentrations of around 5 mM were found to increase the SO₂ removal from 78% to 90%. Limestone dissolution has also been shown to increase with the use of ammonium based salts.

3.2 Motivation in Estimating the Dissolution Rate of Mg(OH)₂

As stated earlier, knowledge and predicting the dissolution rate of any sorbent is essential for the successful operation of any CO₂/SO₂ capture system. Very few dissolution rate studies have been performed for compounds other than limestone and other similar calcium based substances for Flue Gas Desulphurization (FGD) systems. At pH levels greater than 8, dissolution rate occurs slowly and via poorly defined mechanisms. FGD units operate at a pH ranging between 4-6 and therefore the dissolution rates at higher pH values has not received much study.

This study aims to investigate the impact of higher values of pH on dissolution rate of magnesium hydroxide. A system pH of 8.6 was used as a constant value in many experiments for estimation of dissolution rate. The reason behind this is that in the Mg(OH)₂–CO₂ system, a pH of 8.6 has been estimated to be an optimum pH value, where the absorption of CO₂ will take place with minimum solid (MgCO₃) byproduct formation. The objective of this work was to study the impact of pH, temperature and stirring speed on magnesium hydroxide dissolution rate. An experimental correlation was also developed which would predict the rate of dissolution under different conditions. The rate controlling mechanism was determined and conversion time equations were developed using the shrinking core model. Kinetic parameters like rate constant, order of reaction and activation energy was determined. The impact of particle size decrease on the dissolution rate was quantified using the shrinking core model.
3.3 Dissolution Rate Studies – Experimental Techniques

Dissolution rate studies can be divided into the following categories based on the experimental technique used:

- **FREE DRIFT**
  - Rotating Disk/Cylinder Powders
  - Rotating Disk/Cylinder Powders

- **Ph STAT**
  - Rotating Disk/Cylinder Powders
  - Rotating Disk/Cylinder Powders

Figure 9. Different techniques for estimating dissolution rate.

The free drift method has been used more extensively for geology related studies to determine the dissolution rates of calcite and aragonite, which are polymorphic forms of calcium carbonate. It involves suspending the size fractioned particles in solution and measuring the pH/calcium ion concentration change with respect to time. The pH stat technique involves maintaining the bulk solution at a constant pH value by the addition of a mineral acid. The amount of acid per unit time is used to calculate the dissolution rate. The main advantages of the pH stat technique over the free drift technique are: a) minimal variation in the state of solvent saturation, b) reaction is not interrupted during real time, c) other parameters such as temperature can be accurately controlled and thereby, we get more accurate values for the dissolution rate. Sometimes the solid is compressed into a solid disk and made to rotate in the
solution with/without pH control. This is done for those solids whose pH values are very difficult to control in the experimental range of operation. The rotating disk ensures that the mass transfer to and from the surface is well defined and can be altered by changing the rotating speed of the disk. The disk surface can be pretreated and etched to produce reproducible surfaces.

The current study employs the pH stat technique for solids suspended in well stirred solutions. This has been a technique commonly employed for estimating the dissolution rate of limestone for wet FGD applications and is more closely applicable to a practical scenario. The pH and temperature was controlled satisfactorily within the given range using pH stat/controller device and water bath respectively.

3.4 Materials and Methods

3.4.1 Experimental Setup

Magnesium hydroxide dissolution was estimated using a pH stat device [Cole Parmer Chemcadet] where the dissolution rate was correlated to acid consumption required to maintain a preset value of pH. A pH stat device consists of three parts 1) pH Probe 2) pH meter 3) pH controller. The pH controller monitors the reading from the pH meter and when the set value is exceeded, it activates a pump (Walchem Diaphragm Pump, Cole Parmer) This pump delivers acid into the beaker, preventing further increase in pH. The weight of the acid being delivered is recorded by a balance. The pH reading and weight balance readings are monitored continuously by means of data acquisition software [Labview 2011 and Teraterm Pro]. The temperature of the beaker is kept constant by means of a hot water bath (±0.5 °C). The pH values were controlled within ±0.2 during the entire experiment.
Pure distilled water was used in all the experiments. The pH probe was immersed inside a 700 ml beaker filled with 250 ml of distilled water. The pH, temperature and agitation speed were set to preset values and magnesium hydroxide powder (USP/FCC grade, Fisher Scientific) was added to the beaker. The slopes of the acid weight vs. time curves were calculated in the time interval of 5 to 20 minutes. This was done to ensure the pH values were stable and within the control range. The surface area of magnesium hydroxide powders used was estimated using the BET analysis method (TriStar 3000 V6.05).

### 3.4.2 Estimation of Solid Dissolution Flux

Magnesium hydroxide reacts with HCl in a 1:2 stoichiometric ratio as given below.

\[
Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O
\]  

(1)
The weight of acid vs. time curves was used to calculate the rate of acid consumption. The solid dissolution rate flux was calculated using the approach developed by Wang et al. \(^{150}\)

\[
\text{The pure acid mole flow rate} = \frac{10^{-3} C_{\text{acid}} S}{\delta} \text{ (gmol / min)} \tag{2}
\]

Because the solution pH is kept constant, all acid flow is neutralized by solid Mg(OH)\(_2\) dissolution, bringing in the d factor [Stoichiometric ratio of solid: acid] = 1/2

\[
\text{The solid Mg(OH)}_2 \text{ dissolution rate} = \frac{10^{-3} C_{\text{acid}} S d}{60 \delta} \text{ (gmol / sec)} \tag{3}
\]

\[
\text{Dissolution rate of Mg(OH)}_2 \text{ in terms of flux}\left(N_i\right) = \frac{10^{-8} C_{\text{acid}} S d}{6 \text{BET} \delta W_{\text{solid}}} \text{ (gmol / cm}^2\text{sec)} \tag{4}
\]

Where \(W_{\text{solid}}\) = Initial weight of the solid (g) and BET = surface area of the solid at the start (m\(^2\)/g), \(S\) = slope of the acid solution consumption (g/min), \(\delta\) = density of the HCl solution (g/cm\(^3\)) and \(C_{\text{acid}}\) = concentration of the HCl solution used for pH control (mol/liter)

### 3.5 Results and Discussion

Reagent grade magnesium hydroxide from Fisher Scientific was used for most of the experiments. The average BET surface area was estimated to be 5.07 m\(^2\)/g. Hydrochloric acid was used as the medium to control pH because the product formed by reaction between Mg(OH)\(_2\) and HCl is MgCl\(_2\). MgCl\(_2\) is highly soluble in water (54 g/100 mL of water at 20 °C) and does not interfere with the dissolution process of Mg(OH)\(_2\).
Typical pH and HCl consumption vs. time graphs are given below in figures 11 and 12.

Figure 11. Sample pH vs. time. (pH = 8.6, temperature = 52 °C and rpm = 700)

Figure 12. Weight of HCl solution vs. time. (pH = 8.6, temperature = 52 °C and rpm = 700)
Table 2. Summary of dissolution rate results

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Slope[S] (g/min)</th>
<th>pH</th>
<th>Rpm</th>
<th>Solid Dissolution rate (gmol/cm²·sec)</th>
<th>Grade of Mg(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.5</td>
<td>4.07</td>
<td>7.6</td>
<td>700</td>
<td>4.621 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>22.5</td>
<td>3.08</td>
<td>8.6</td>
<td>700</td>
<td>3.497 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>22.5</td>
<td>1.26</td>
<td>9.6</td>
<td>700</td>
<td>1.430 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>32.0</td>
<td>5.2</td>
<td>8.6</td>
<td>700</td>
<td>5.905 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>42.0</td>
<td>7.14</td>
<td>8.6</td>
<td>700</td>
<td>8.108 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>52.0</td>
<td>9.43</td>
<td>8.6</td>
<td>700</td>
<td>1.070 * 10⁻¹⁰</td>
<td>Fisher</td>
</tr>
<tr>
<td>22.5</td>
<td>0.77</td>
<td>8.6</td>
<td>700</td>
<td>1.008 * 10⁻¹¹</td>
<td>Industrial</td>
</tr>
<tr>
<td>52.0</td>
<td>9.25</td>
<td>8.6</td>
<td>1110</td>
<td>1.050 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>52.0</td>
<td>8.01</td>
<td>8.6</td>
<td>500</td>
<td>9.096 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
<tr>
<td>22.5</td>
<td>3.74</td>
<td>8.6</td>
<td>1110</td>
<td>4.247 * 10⁻¹¹</td>
<td>Fisher</td>
</tr>
</tbody>
</table>

3.5.1 Effect of pH

The effect of pH was investigated keeping the temperature at 23 °C, stirring speed at 700 rpm, acid and magnesium hydroxide concentration [0.01 M HCl and 0.01 M Mg(OH)₂] constant. Most dissolution experiments for limestone have been conducted in the pH range of 4 to 6. Plummer et al. 125 demonstrated linear dependence on H⁺ ion concentration with the dissolution rate for limestone. The drop in dissolution rate with increasing pH is more drastic at lower pH values. Chan and Rochelle 151 showed that the dissolution rate of limestone at room temperature decreases by a factor of 6.7 from 4 to 5. It is evident from figure 13 that increasing the pH
results in a lower dissolution rate for magnesium hydroxide. Increasing the pH results in lowering the H\(^+\) ion concentration and consequently lower values of dissolution rates.

\[ \text{ln } N_s \] vs. pH

<table>
<thead>
<tr>
<th>Model</th>
<th>Polynomial</th>
<th>Adj. R Square</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-41.7748</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>B1</td>
<td>4.7025</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>B2</td>
<td>-0.3075</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Figure 13. ln Ns (solid dissolution flux) vs. pH.

### 3.5.2 Effect of Temperature

Figure 14 presents the effect of temperature on reagent grade Mg(OH)\(_2\), which was estimated keeping all other process variables constant. The Mg(OH)\(_2\) dissolution rate increases with increasing temperature and this effect seems to be quite significant. A diffusion controlled process is only moderately dependent on temperature and a chemical reaction controlled process is strongly dependent on temperature. The reason is that diffusion coefficient D is linearly dependent on temperature, while chemical reaction constant is exponentially related to temperature as given by the Arrhenius law. Figure 15 shows that dissolution rates for Mg(OH)\(_2\) at a pH of 8.6 demonstrates an excellent fit for the Arrhenius equation i.e. [Solid
dissolution rate \[ N_s = A e^{-\frac{E_a}{RT}} \]. This result would be used in the experimental model for predicting the effect of temperature on the dissolution rate.

Figure 14. Solid dissolution flux vs. temperature.

Figure 15. Arrhenius plot of \( \ln N_s \) (solid dissolution flux) vs. \( 1/T \).
3.5.3 Effect of Agitation Speed

Figure 16 illustrates the effect of agitation speed on Mg(OH)$_2$ under pH control and temperature of 52.°C. The dissolution flux increases with increasing the stirring speed in the range from 500 to 700 rpm. Moo Young and Calderbank$^{153}$ had studied that impact of agitation on liquid mass transfer between liquid and suspended particles and arrived at the conclusion that convective mass transfer resulting from mixing is independent of particle size and is affected by specific agitation power. The increase in stirring speed increases the convective mass transfer between the solid Mg(OH)$_2$ and liquid. The dissolution rate was found to be independent of the agitation speed after 700 rpm at higher temperatures. Agitation speeds below 500 rpm resulted in unstable pH control by the pH stat and therefore, most of the experiments were carried out at 700 rpm.

![Figure 16. ln Ns (solid dissolution flux) vs. ln \( \omega \).](image-url)
3.5.4 Experimental Model

An experimental correlation was developed by Meserole et al.\textsuperscript{154} for limestone dissolution

\[
\ln N_s = a - b_1 \left( \frac{1}{T} \right) + b_2 (pH) + b_3 \ln (\omega) + b_4 \ln (At) + b_5 \ln (Mg).
\]

Where

\( N_s \) = the dissolution rate flux of calcium or magnesium

\( T \) = Solution temperature (K), \( pH \) = Solution pH and \( \omega \) is the stirring rate in the reactor (rpm).

Based on the experimental data obtained above for magnesium hydroxide, a similar correlation was developed, which had the following form

\[
\ln N_s = -32.894 - \frac{3592.4}{T} - 0.3075(pH)^2 + 4.7025(pH) + 0.5025\ln (\omega)
\]

This correlation is valid for the following ranges

\( pH \) between 7.6 to 9.6

Temperatures ranging from 22 °C to 52 °C

Rpm ranging from 500 to 700

This dissolution flux model was compared with experimentally derived flux values and the results are in good agreement with each other as seen in figure 17.
Figure 17. Comparison between the experimental and predicted values of the dissolution flux.

3.6 Kinetic Analysis and Shrinking Core Model

3.6.1 Selection of Rate Controlling Mechanism

The shrinking core model was chosen because of its ability to identify the rate controlling step and to provide essential kinetic parameters for the dissolution reaction like rate constant, order of reaction and activation energy. It is useful to describe situations in which solid particles are being consumed either by dissolution or reaction. The magnesium hydroxide particle is nonporous and spherical and dissolves according to shrinking core model. For this reaction, the following steps happen in succession:

a) Diffusion of the reactant H\(^{+}\) ions from the main body of the liquid through the liquid film to the surface of the solid.

b) Reaction on the surface between H\(^{+}\) and the solid particle.
c) Diffusion of the reaction products from the surface back into the bulk of the liquid. The particle shrinks continuously and there is no ash layer present.

The rate controlling step for dissolution reactions are surface chemical reaction controlled or liquid film diffusion controlled. The selection of the appropriate rate controlling mechanism is essential for the development of conversion equations using the shrinking core model. A common approach is to plot the kinetic data of \( r_c/r_0 \) (radius of particle at time \( t \)/initial radius) vs. \( t/\tau \) (time taken for particle to reach radius of \( r_c \)/time taken for complete dissolution) and compare the results with predicted curves for reaction and diffusion control.

Magnesium hydroxide dissolution rates were tested without pH control at 52 °C at 700 rpm using with 15 and 30 strokes/min of 0.01 M HCl solution, till all the particles were completely dissolved. 700 rpm was chosen as an optimum value, since the dissolution rate does not increase further with an increase in mixing speed beyond 700 rpm. The two flow rates cover a range of the HCl solution used for all experiments under pH control. The shrinking particle size was measured at every 5 or 10 min over the entire dissolution process in the absence of pH control by using a laser particle size analyzer (Spectex PC-2000). Figure 18 and Figure 19 clearly show the predominance of chemical reaction control over film diffusion control.
Figure 18. Rate controlling mechanism at temperature = 52 °C/ 700 rpm / HCl stroke rate = 15.

Figure 19. Rate controlling mechanism at temperature = 52 °C/ 700 rpm / HCl stroke rate = 30.
3.6.2 **Conversion-Time Equations and Determination of Apparent Rate Constant**

The conversion-time expressions for a chemical reaction controlled process are derived based on the principle that the rate is proportional to the available surface area of the particle. In the reaction \( \text{Mg(OH)}_2 + 2\text{HCl} \rightarrow \text{MgCl}_2 + 2 \text{H}_2\text{O} \), \( \text{Mg(OH)}_2 \) is given the subscript ‘b’ and HCl as ‘a’.

\[
\frac{dN_b}{dt} = -\frac{1}{4\pi r^2} b \frac{dN_a}{dt} = b k^* C_{al}
\]  

(5)

where \( k^* \) is the overall rate constant for the surface reaction (assumed to be first order for now) and \( C_{al} \) is the concentration of \( \text{H}^+ \) ion in the liquid phase (mol/m\(^3\)).

The number of moles of \( \text{Mg(OH)}_2 \) and HCl are related stoichiometrically as follows:

\[
-dN_b = -b dN_a = -\rho_b dV = -4\pi \rho_b r_c^2 dr_c
\]  

(6)

Where \( b \) is the stoichiometric constant, \( \rho_b \) is the molar density of magnesium hydroxide (mol/m\(^3\) of solid) and \( r_c \) is the radius of the unreacted magnesium particle (m).

Substituting (6) in (5)

\[
-\rho_b \frac{dr_c}{dt} = b k^* C_{al}
\]  

(7)

Integrating (7)

\[
t = \frac{2\rho_b r_o}{k^* C_{al}} \left(1 - \frac{r_c}{r_o}\right)
\]  

(8)

The time required for complete dissolution is given at \( r_o = 0 \)

\[
\tau = \frac{2\rho_b r_o}{k^* C_{al}}
\]  

(9)

Fractional conversion and radius of the particle are related by

\[
1 - X_b = \frac{\text{Volume of unreacted core}}{\text{Total volume of the particle}} = \frac{r_c^3}{r_o^3}
\]  

(10)
From (8) (9) and (10)

\[ \frac{t}{\tau} = (1 - (1 - X_B)^{1/3}) \]  

(11)

\[ tk_r = (1 - (1 - X_B)^{1/3}) \]

(12)

\[ k_r = \frac{1}{\tau} = \frac{k \cdot C_{al}}{2 \rho_b r_o} \]

(13)

\[ \tau \]

The values of \( k_r \) can be calculated from the slope obtained by plotting time vs. \((1 - (1 - X_B)^{1/3})\) for various pH and temperature values. The slope is calculated from 5 to 20 minutes, which is the region where the pH is brought to a constant value.

Fractional conversion \( X_B \) can be calculated using the formula

\[ X_B = \frac{\text{Weight of HCl consumed at time } t}{\text{Weight of HCl required for complete dissolution}} \]

(14)

A sample plot of \((1 - (1 - X_B)^{1/3})\) vs. time, is shown in Figure 20. It shows a good fit with a coefficient of determination \((R^2)\) value of 0.989. The value of \( k_r \) for the absorber operating at a pH of 8.6 and temperature of 52 °C was estimated to be \(1.1 \times 10^{-1} \text{ min}^{-1}\). The effect of temperature on dissolution rate can provide information on the dominant reaction mechanism for the process. Activation energy values at the desired operating pH of 8.6 can be obtained by using the Arrhenius equation \( k_r = k_o e^{Ea/RT} \), where \( k_o \) is the pre-exponential factor, \( E_a \) is the activation energy (J/gmol), \( R \) is the gas constant (8.314 J/gmol K) and \( T \) is the temperature (K). When the temperature was raised from 22 °C to 52 °C, the apparent reaction rate constant \((k_r)\) increased by a factor of 5.4 as shown in the Arrhenius plot in Figure 21. Diffusion controlled
reactions have activation energies lower than 20 kJ/gmol and surface controlled reactions have activation energies between 40 to 80 kJ/gmol. The activation energy for Mg(OH)$_2$ dissolution at a pH of 8.6 was calculated to be 42 ± 6 kJ/gmol. This was comparable with the values obtained (45 kJ/gmol) at similar temperatures for a South African magnesium-based material, whose rate determining step was found to be controlled by surface chemical reaction. This result proves that surface reaction plays a dominant role in the dissolution of Mg(OH)$_2$ at the high pH regime.

Figure 20. Sample plot of (1-(1-$X_B$)$^{1/3}$) vs. Time (min) for pH = 8.6 and temperature = 52 °C.
3.6.3 Order of Reaction and Overall Activation Energy for Mg(OH)$_2$ Dissolution

The values of $k_r$ calculated from experimental data at same temperature and different H$^+$ ion concentrations should yield the same value of $k''$, which is the overall reaction constant. It is found however, that the value of $k''$ differs with changes in the $C_{al}$ value. This implies that rate of dissolution is not directly proportional to the concentration of H$^+$ ion in the liquid and the order of reaction is not first order.

Equation 9 was modified as follows:

$$k_r = \frac{k'' C_{al}^n}{2 \rho_b r_o}$$  \hspace{1cm} (15)

Where $n$ is the fractional order of reaction.

Taking natural logarithm on both sides of equation (15)

$$\ln k_r = \ln z + n \ln C_{al} \hspace{1cm} \text{where} \hspace{1cm} z = \frac{k''}{2 \rho_b r_o}$$  \hspace{1cm} (16)
The value of n was calculated by plotting the $k_r$ values at four different temperatures ($22 \, ^\circ\text{C}$, $32 \, ^\circ\text{C}$, $42 \, ^\circ\text{C}$ and $52 \, ^\circ\text{C}$) and different $H^+$ ion concentrations calculated from the constant pH values (figure 22). The reaction order (n) values determined were 0.22 at $22 \, ^\circ\text{C}$, 0.20 at $32 \, ^\circ\text{C}$, 0.23 at $42 \, ^\circ\text{C}$, and 0.31 at $52 \, ^\circ\text{C}$, from which the arithmetic average n value was found to be 0.24. The reaction rate constant ($k''$ with a unit of $\text{min}^{-1}(\text{mol/m}^2)_{k^{-}}(\text{mol/m}^3)$) determined from the intercept values were $8.26 \times 10^{-12}$ at $22 \, ^\circ\text{C}$, $1.66 \times 10^{-11}$ at $32 \, ^\circ\text{C}$, $3.42 \times 10^{-11}$ at $42 \, ^\circ\text{C}$ and $1.43 \times 10^{-10}$ at $52 \, ^\circ\text{C}$. From the intrinsic/overall reaction rate constant, the true activation energy and frequency factor were found to be $76 \pm 11 \, \text{kJ/gmol}$ and $220 \, \text{min}^{-1}(\text{mol/m}^2)_{k^{-}}(\text{mol/m}^3)$ from the Arrhenius equation (figure 23). These results are in agreement with values reported for other calcium and magnesium based minerals.
Fredd and Fogler studied the dissolution rates of calcite in acetic acid solutions and concluded that above 3.7, the dissolution rate is influenced primarily by chemical reaction. The dissolution of mineral oxides in an aqueous environment has been studied for its potential applications in environmental remediation, corrosion, and drug design. Previous studies have shown that the magnesium oxide dissolution exhibits a fractional order $n$ which is frequently in the range between $(0 < n < 0.6)$.\textsuperscript{158,159} Rachman and Frodrocova\textsuperscript{160} investigated the dissolution of periclase (sintered polycrystalline MgO) in dilute HCl solutions. They reported fractional orders of reaction (0.4 to 0.7) and high values of activation energies (93-101 kJ/mol). The measured dissolution rates were up to two orders of magnitude lower than the rate of external mass transfer, which indicated that the dissolution mechanism was controlled by surface chemical reaction control. A similar study performed on the dissolution kinetics of MgO for the effect of pH (ranging from 2 - 4) and different acid anions also showed the predominance of surface reaction control and that a fractional order for the reaction with H\textsuperscript{+} ions coupled with high values of
activation energies serve as an indicator for this type of reaction control. The dissolution kinetics of chrysotile (magnesium silica based hydroxide (white asbestos) – \( \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \)) was investigated due to public health significance of contamination in drinking water and exhibited a fractional dependence on pH (\( n = 0.24 \)) at pH values ranging from 7 to 10 at 25 °C. Fruhwith et al. reported an activation energy value of approximately 70 kJ/gmol for MgO dissolution at pH values >7 with temperatures ranging from 25 to 75 °C. However, there was no experimental justification provided about the impact of pH on the dissolution rate and the information was provided about the nature of the reaction control regime was not clear. Nevertheless, these findings substantiate the existence of a fractional order, high activation energies and dominance of surface chemical reaction for the dissolution of magnesium hydroxide at higher pH regimes, which has not been explored much in previous studies.

### 3.6.4 Modified Rate of Dissolution Expression Based on the Shrinking Core Model

The fractional order of reaction results in modification of equation (5), as follows

\[
r_b = -\frac{1}{4\pi r^2} \frac{dN_b}{dt} = -\frac{1}{4\pi r^2} \frac{b dN_a}{dt} = b^k C_{al}^n
\]

(17)

\[
r_b = -\frac{1}{S_a} \frac{dN_b}{dt} = b k C_{al}^n
\]

(18)

\[
C_{bl} = b C_{al} \rightarrow C_{al}^n = b^{-n} C_{bl}^n
\]

(19)

The flux expression for \( \text{Mg(OH)}_2 \) dissolution in terms of concentration of the solid is given by

\[
r_b = -\frac{1}{S_a} \frac{dN_b}{dt} = b^{1-n} k^* C_{bl}^n = b^{1-n} k_0 \exp\left(\frac{-E_a}{RT}\right) C_{al}^{n-130} \exp\left\{\frac{9.192}{T}\right\} C_{bl}^{0.24} \left[\frac{\text{gmol}}{m^2 \cdot \text{min}}\right]
\]

(20)
3.6.5 Effect of Decreasing Particle Size During the Dissolution Reaction.

From the shrinking core model we have

\[ r_e = r_o \left(1 - \frac{k''C_{Al}^n t}{2 \rho r_o} \right) \]  

(21)

The radius of the particle at any time t can be calculated by the above formula and using the values of n and k'' calculated previously. It compares well with the measured data calculated by equation 22 for the intrinsic dissolution period (20 minutes) as seen in figure 24.

\[ \frac{r_e}{r_o} = (1 - X_B)^{1/3} \]  

(22)

An experiment was run for 60 minutes at pH = 8.6 and temperature = 52 °C. The values obtained were verified experimentally by taking samples out at fixed time from the dissolution experiment. The samples were washed with water and the particle size was analyzed using the particle size analyzer with a base dilution of $10^7$. Figure 25 shows a representative particle size distribution for the sample taken at 0 min. The system deviates from the intrinsic region after 20 minutes as seen by the figure 26. This is due to the system attaining an equilibrium value beyond which the Mg(OH)$_2$ does not dissolve further.
Figure 24. Comparison of measured data with shrinking core model at pH = 8.6 and temperature = 52 °C.

Figure 25. Particle size distribution for sample taken at 0 min.
The same analogy for particle radius can be extended to the area occupied by a single particle. The dissolution rate decreases with decreasing particle size and for a single particle, the area at any time $t$ can be calculated by

$$\frac{A_x}{A_0} = \frac{r_c}{r_o}$$  \hspace{1cm} (23)

Substituting (23) in (22)

$$A_x = A_0 (1 - X_B)^{2/3}$$  \hspace{1cm} (24)

It can be seen from figure 27 that the about 60% of the area of the particle is unreacted at time $t = 20$ min and the decrease in area is linear. But as time progresses the decrease in the area of the particle affects the dissolution rate.

Figure 26. Average particle size vs. time using SCM model and experimental data.
The slope of HCl consumed vs. time deviated increasingly away from the linear region with time as shown by figure 28. The value calculated up to 20 minutes is called the intrinsic dissolution rate or the maximum dissolution rate, up to which the dissolution rate is unaffected by the shrinking particle size. The duration of this period will depend upon operating conditions like pH, temperature, concentration and stirring/agitation speed. The change in the average size of the particle with respect to normalized time is illustrated by figure 29. It can be seen that when the average particle size gets reduced to 60% of its initial value, the system deviates from its intrinsic chemical reaction control regime, which would result in a decrease in the dissolution rate. The rate of CO₂ removal would be maximum if the Mg(OH)₂ slurry in the CO₂ absorber is made to dissolve at this intrinsic rate. Particle size analysis of Mg(OH)₂ particles intermittently would be a good tool to predict whether the slurry needs to be recirculated or replaced for optimum performance.
Figure 28. Weight of HCl consumed vs. time for pH = 8.6, temperature = 52 °C for 60 min.

Figure 29. Plot showing the effect of particle size on the rate controlling mechanism
3.6 Conclusion

The dissolution rate of magnesium hydroxide under different operating conditions of pH, temperature and stirring rate was measured using a pH stat apparatus. An experimental correlation was developed which can predict intrinsic Mg(OH)$_2$ dissolution rates as a function of pH, temperature and stirring rate. The dissolution of magnesium hydroxide particles was modeled using the shrinking core model and the rate of dissolution was found to be dependent on surface chemical reaction control. The value of the apparent reaction constant was determined to be $1.1 \times 10^{-1}$ min$^{-1}$ for a pH value of 8.6 and temperature of 52 °C, which are the absorber conditions in the current system. The effect of temperature on the apparent rate constants was found to follow Arrhenius equation and was estimated to be $42 \pm 6$ kJ/gmol at a pH value of 8.6. The dissolution of Mg(OH)$_2$ was found to exhibit fractional dependence on the H$^+$ ion concentration. The order of reaction was found to have a range of $0.20 < n < 0.31$. An activation energy value of $76 \pm 11$ kJ/mol was estimated using the overall/intrinsic rate constants over the entire operational pH range. The particle radius of Mg(OH)$_2$ particles at different times was estimated using a particle size analyzer and the values obtained match with theoretical values obtained using the shrinking core model. A reduction to 60% of its initial average particle size for Mg(OH)$_2$ under the absorber conditions of pH = 8.6 and temperature = 52 °C would lead to deviation from the intrinsic dissolution rate, controlled by surface chemical reaction control.
CHAPTER 4. KINETICS OF MgCO$_3$ FORMATION.

4.1 Introduction

Magnesium carbonate is a crystalline solid formed when magnesium hydroxide reacts with CO$_2$. Figures 30 and 31 show the equilibrium distribution of carbonate and magnesium species which are distributed as a function of pH.

Figure 30. Distribution of dissolved magnesium species as a function of pH.

Figure 31. Distribution of dissolved carbonate species as a function of pH.
This was estimated by running MINEQL which is a chemical equilibrium modeling package for phase equilibrium determination. At a pH between 8 and 9 which is the optimum pH range, the ionic species are dominated by the bicarbonate ion. This would ensure that the formation of magnesium carbonate is minimized. Magnesium carbonate formation would reduce the lifetime for solvent in the chemical cycle between the absorber and the stripper. Dissociation of MgCO\(_3\) would require very high temperatures [\(>250\) °C], as shown in the following TGA diagram for pure MgCO\(_3\).

![TGA curve for MgCO\(_3\).](image)

Figure 32. TGA curve for MgCO\(_3\).

Previous studies have been done in estimating the crystal growth rate of calcium sulfite and calcium sulfite hemihydrate, which are the main reaction products of a flue gas desulphurization unit. Calcium sulfite crystallization affects several factors such SO\(_2\) absorption, limestone dissolution and solution composition, in a manner analogous to MgCO\(_3\). Tseng and Rochelle et al.\(^{164}\) studied the kinetics of calcium sulfite hemihydrate growth using a pH stat
apparatus in an aqueous solution of pH 3.5 to 6.5 and found that the growth was a function of relative supersaturation and strongly inhibited by the dissolved sulfate. Boke et al. developed a quantitative analysis using FTIR to distinguish between limestone(CaCO₃), calcium sulfite hemihydrate (CaSO₃·0.5 H₂O) and gypsum(CaSO₄·2H₂O). The method employed in this study involves using TGA-MS and HCl titration to estimate the distribution of carbon among the solid and liquid phases. The effects of pH control and the heating, on the kinetics of magnesium carbonate formation were investigated. Figure 30 shows that maintaining a pH of 8.6 is conducive to prevent the formation of magnesium carbonate and ensuring that the carbon stays in the liquid phase and interacts with the magnesium in the liquid phase. This would help in the regeneration of the magnesium hydroxide solution in the stripper phase. Also the effect of higher temperatures employed [52 °C and 65 °C] in the process needed to be investigated.

4.2 Experimental Setup and Procedure

A 1M Mg(OH)₂ was prepared by adding 29.15 g of Mg(OH)₂ to 500 ml of water. A total inorganic concentration of X_iic = 0.01 was simulated by adding 0.56 moles of sodium bicarbonate to the Mg(OH)₂ solution. Sodium bicarbonate [NaHCO₃] was used as a source of carbonate and bicarbonate ions to simulate CO₂ in the liquid phase. A pH stat with a set point of 8.6 was connected to pump containing HCl of 1N. The pH stat monitors the pH in the batch setup and prevents it from going above 8.6. A temperature probe was used to monitor the temperature of the solution and a hot plate/stirrer was used to set the temperature of the batch system.
Samples were taken out at different time intervals and immediately centrifuged for the shortest possible time to separate the solid from the liquid. The liquid was filtered with a 0.45 μm filter and analyzed for liquid carbon concentration by HCl titration method. The solids were dried under vacuum at 60°C for 24 hrs. till the solid became dry. The solids were then analyzed for carbon content using the TGA–MS.

4.2.1 **Solid Analysis using the Thermo-gravimetric Analyzer - Mass Spectrometer.**

The solid samples were analyzed for carbon content by using a Thermo gravimetric analyzer [TA Instruments TGA Q5000IR] coupled with a Mass Spectrometer [Pfeiffer-Vacuum Thermostar]. Percent weight loss and detected spectra vs. temperature/time were used to quantify the CO₂ present in the solid sample. Oxygen was used as a carrier gas with the high flow rate of 100 ml/min to ensure complete combustion with approximately 10 ~ 25 mg of sample. Ramp rate used was 5 °C/min up to a target temperature of 800 °C. The calibration curve was obtained using known samples of calcium oxalate powder. The calibration curve for
CO₂ and the TGA-MS curves for a sample experiment are shown below in figures 34, 35 and 36 respectively.

Figure 34. Calibration curve for CO₂ measurement using the TGA-MS.

Figure 35. Sample TGA-MS curve for pH control and temperature 65 °C at 0 min.
4.3 Results and Discussion

The mass balance tables with pH control using HCl and without pH control at three different temperatures are presented below. Bar graphs show the partitioning of the carbon between the bicarbonate ion in the liquid $[\text{HCO}_3^-]$, carbonate ion in the liquid $[\text{CO}_3^{2-}]$ and the solid carbon over different time intervals.

Figure 36. Sample TGA-MS curve for pH control and temperature 65 °C at 15 min.
4.3.1 **No pH control and Temperature of 52 °C**

Table 3. Mass balance for no pH control and temperature of 52 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO$_3^{2-}$ (g)</th>
<th>Carbon in HCO$_3^-$ (g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.16</td>
<td>2.89</td>
<td>0.23</td>
<td>3.28</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.22</td>
<td>2.84</td>
<td>0.50</td>
<td>3.56</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.32</td>
<td>2.48</td>
<td>0.88</td>
<td>3.68</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>0.38</td>
<td>2.32</td>
<td>0.84</td>
<td>3.54</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.44</td>
<td>2.20</td>
<td>0.80</td>
<td>3.44</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>0.48</td>
<td>2.19</td>
<td>0.75</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Theoretical – 3.36 g carbon input, Error range – 2% to 8%

Figure 37. Carbon content vs. time for no pH control at 52 °C.
The mass balance table (table 3) and the bar graphs (figure 37) show the increasing evolution of carbon in the solid phase with time. The drop in the bicarbonate concentration from 1 to 15 minutes is around 20%. It is also seen that the carbonate concentration in the liquid phase is increasing with time.

![Figure 3. pH vs. time graph for no pH control at 52 °C.](image)

Figure 38. pH vs. time graph for no pH control at 52 °C.

There was a decrease in the initial pH of the Mg(OH)\_2 from around 10 to 9.2, due the increase in temperature from 24 °C to 52 °C (figure 38). The pH dropped quickly at the start, because sodium bicarbonate, being soluble in water, released H\(^+\) ions and brought down the pH. Then the pH increased slowly till around 3.5 minutes. In this region, the H\(^+\) ions reacted with the OH\(^-\) ions (released from the dissociation of Mg(OH)\_2) and formed water. This region also included the initiation of solid carbon formation, which continued into the next zone upto 10 minutes. After this period, the pH increased rapidly and went back up to the starting pH. This
was mainly due to the dissolution of magnesium hydroxide, which released OH⁻ ions, thereby increasing the basicity of the solution.

### 4.3.2 pH control at 8.6 and temperature of 52 °C

Table 4. Mass balance for pH control at 8.6 and temperature at 52 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO₃²⁻ (g)</th>
<th>Carbon in HCO₃⁻ (g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.13</td>
<td>3.04</td>
<td>0.33</td>
<td>3.50</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.19</td>
<td>2.82</td>
<td>0.66</td>
<td>3.67</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.22</td>
<td>2.40</td>
<td>0.94</td>
<td>3.56</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>0.17</td>
<td>1.90</td>
<td>1.01</td>
<td>3.08</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.14</td>
<td>1.56</td>
<td>1.15</td>
<td>2.85</td>
</tr>
</tbody>
</table>

![Carbon content vs. time for pH control at 52 °C.](image)

Figure 39. Carbon content vs. time for pH control at 52 °C.
The data for the pH control and temperature 52 °C (table 4 and figure 39) showed a dramatic decrease in the bicarbonate carbon concentration, when compared to the no pH control case. The drop in the bicarbonate carbon concentration from 1 minute to 10 minutes is around 48% for the pH control case, compared to 23% bicarbonate carbon concentration drop, for the same time period, in the experiment with no pH control. This drop in bicarbonate concentration is explained by the following sequence of steps.

When pH control was applied, most of the carbon remained in the liquid phase as bicarbonate ion, and reacted with magnesium ions to form magnesium bicarbonate [Mg(HCO$_3$)$_2$]. In addition, the acid used for pH control was of high concentration [1N] and this might have caused more extensive dissolution of the magnesium hydroxide, leading to greater production of magnesium ions and higher reactivity with the bicarbonate ions in the solution.\textsuperscript{166} The drop in bicarbonate concentration evident during liquid phase titration occurs due to two possible reasons: a) The [Mg(HCO$_3$)$_2$] in the liquid phase reacts with HCl giving rise to soluble MgCl$_2$ and CO$_2$ gas, b) Some portion of the magnesium bicarbonate also ends up with the solids when the supernatant liquid was separated for liquid phase titration. It was reported that magnesium bicarbonate can be converted into a hydrated form of magnesium carbonate, when the slurry was separated and dried under vacuum.\textsuperscript{167} This was further proved by the appearance of more carbon in the solids upon analysis. However, this experiment proves that under conditions of pH control at 52 °C, the formation of [Mg(HCO$_3$)$_2$].is enhanced ,which appears as a drop in bicarbonate concentration during the mass balance analysis.
The pH stat maintained the pH at 8.6 throughout the experiment.

### 4.3.3 No pH control and temperature of 65 °C

Table 5. Mass balance for no pH control and temperature of 65 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO$_3^-$ (g)</th>
<th>Carbon in HCO$_3^-$ (g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.15</td>
<td>3.28</td>
<td>0.44</td>
<td>3.87</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.28</td>
<td>2.88</td>
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</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.36</td>
<td>2.66</td>
<td>1.10</td>
<td>4.12</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>0.42</td>
<td>2.52</td>
<td>1.17</td>
<td>4.11</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.46</td>
<td>2.48</td>
<td>1.10</td>
<td>4.04</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>0.48</td>
<td>2.48</td>
<td>1.15</td>
<td>4.11</td>
</tr>
</tbody>
</table>
Figure 41. Carbon content vs. time for no pH control at 65 °C.

The increase in temperature resulted in the accelerating the kinetics of solid carbon formation as seen in figure 41 and table 5. When compared to the sample taken at 3 minutes for the experiment performed with no pH control and 52 °C, there was almost a 50% increase in the solid carbon formation for no pH control and 65 °C. This effect reduced during the entire experimental run and the percentage difference in the solid carbon formation came down to 34%, when the samples taken at 15 minutes were compared.
The pH of the solution decreased further from its equilibrium room temperature value when the temperature is increased to 65 °C as seen in figure 42. The time period where the pH increased slowly was much shorter for this experiment when compared to the experiment conducted at 52 °C. This occurred because with the increased temperature, the reaction between the various ions occurred almost instantaneously.
4.3.4 pH control at 8.6 and temperature of 65 °C

Table 6. Mass balance for pH control at 8.6 and temperature of 65 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO$_3^{2-}$ (g)</th>
<th>Carbon in HCO$_3^-$ (g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.12</td>
<td>3.14</td>
<td>0.63</td>
<td>3.89</td>
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<td>3.84</td>
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<tr>
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</tr>
<tr>
<td>4</td>
<td>7</td>
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<td>1.97</td>
<td>4.07</td>
</tr>
<tr>
<td>5</td>
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<td>0.12</td>
<td>1.62</td>
<td>1.92</td>
<td>3.64</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>0.11</td>
<td>0.90</td>
<td>2.66</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Figure 43. Carbon content vs. time for pH control at 65 °C.

Same trend was observed as in the previous experiment with 52 °C, with and without pH control as seen in table 6 and figure 43. The effect was even more pronounced at higher temperatures as shown in these experiments with 65 °C. After 15 minutes, the percentage of
available bicarbonate ion was almost 75% more in the no pH control case. This validates our hypothesis that during the process of pH control, the bicarbonate ion predominates and leads to an increased formation of $\text{Mg(HCO}_3\text{)}_2$. This increase is also helped by the enhanced dissolution of $\text{Mg(OH)}_2$ on reacting with HCl. The higher values of magnesium bicarbonate formed during the course of the reaction appears during the liquid phase carbon analysis in the form of bicarbonate concentration and these values are lesser than the value obtained at the same time for the non pH control case. This drop can be attributed to the conversion of $\text{Mg(HCO}_3\text{)}_2$ to $\text{CO}_2$ during the course of the reaction with HCl or to hydrated magnesium carbonate during the solid phase carbon analysis, which is substantiated by the increase in solid carbon content.

![Graph](image)

Figure 44. pH vs. time for pH control at 65 °C.

The pH stat kept the pH stable at 8.6 without any fluctuation.
4.3.5 No pH control and room temperature [24 °C]

Table 7. Mass balance for no pH control and temperature of 24 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO$_3^{2-}$ (g)</th>
<th>Carbon in HCO$_3^-$ (g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
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<tbody>
<tr>
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<td>3.75</td>
</tr>
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</tr>
<tr>
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<td>5</td>
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</tr>
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<td>10</td>
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<td>0.39</td>
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<tr>
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<td>2.28</td>
<td>1.20</td>
<td>3.94</td>
</tr>
</tbody>
</table>

Figure 45. Carbon content vs. time for no pH control at 24°C.

The rate of solid formation (table 7 and figure 45), when compared to the experiments run at elevated temperatures and no pH control was slow. For example, the amount of solid
carbon formed at 10 minutes is 64% less than solid carbon formed at 65 °C for the same time period.

Figure 46. pH vs. time for no pH control at 24 °C.

The initial pH of Mg(OH)$_2$ slurry solution is ~10, and starts to drop due to the dissolution and equilibration of HCO$_3^-$ in NaHCO$_3$ with CO$_3^{2-}$ as shown in figure 46. After some of CO$_3^{2-}$ is consumed to form MgCO$_3$ (which is warranted by a constant pH region between 5 and 20 minutes), OH$^-$ starts to be released to return to the initial pH value, ~10.
4.3.7  pH control at 8.6 and room temperature [24 °C]

Table 8. Mass balance for pH control and temperature of 24 °C

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Time(min)</th>
<th>Carbon in CO₃²⁻(g)</th>
<th>Carbon in HCO₃⁻(g)</th>
<th>Solid phase Carbon(g)</th>
<th>Actual Mass Balance(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.14</td>
<td>2.88</td>
<td>0.24</td>
<td>3.26</td>
</tr>
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<td>2.86</td>
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<tr>
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<td>5</td>
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<td>0.11</td>
<td>2.17</td>
<td>0.80</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Figure 47. Carbon content vs. time for pH control at 24 °C.

The data for the no pH control and room temperature showed a gradual increase in the solid carbon concentration with time and after 30 minutes almost 30% of the carbon was in the
solid phase. But when pH was controlled to 8.6 (table 8 and figure 47), the amount of bicarbonate carbon decreases, compared to the no pH control case. This decrease is not substantial, when compared to the other experiments at higher temperatures. Consequently, the difference in the amount of carbon in the solid is not significant, despite pH control. This is because the process takes place at room temperature and thereby the net amount of solid formed is also less, when compared to the experiments at higher temperature.

![Figure 48. pH vs. time for pH control at 24 °C.](image)

### 4.4 Conclusion

A mass balance analysis was carried out to estimate the distribution of carbon among the different phases for the Mg(OH)$_2$-H$_2$O-NaHCO$_3$ system and the mass balance was closed satisfactorily. The effect of temperature on MgCO$_3$ formation was investigated and the results showed that the increase in reaction temperature would lead to an increase in MgCO$_3$ formation. MINEQL software predicted that for minimizing the carbonate formation, the system needs to be
operated at a pH of 8.6. The impact of pH control at three different process temperatures was investigated and it was found that pH control at 8.6 leads to the formation of magnesium bicarbonate, which is highly beneficial for the regeneration of the Mg(OH)₂ solvent. The drop in bicarbonate concentration in the liquid over time and the concurrent increase in solid carbon justifies our results. But as seen even with pH control, over the course of time, the system tends to move towards the more stable state of solid carbonate formation. This can be offset by utilizing chemicals that might block that growth of carbonate crystal, employing shorter contact times in the absorber or by regular replenishment of the solvent.
CHAPTER 5. VAPOR-LIQUID-SOLID EQUILIBRIUM (VLSE) STUDIES

5.1 Introduction

Vapor-liquid-solid equilibrium (VLSE) data for the CO\textsubscript{2}–water–Mg(OH)\textsubscript{2} system at various temperatures, pressures and concentrations have a vital role in the design and optimization of the flue gas treating process\cite{paper}.\textsuperscript{168} The equilibrium solubility of CO\textsubscript{2} determines the amount of solvent feed solution that needs to be circulated to treat a given feed gas.\textsuperscript{169} It also determines the maximum concentration of CO\textsubscript{2} which can be left in the regenerated solution in order to meet the treated gas specifications.\textsuperscript{170} Physical and chemical equilibria also play a crucial role in defining the boundary conditions for partial differential equations that describe the mass transfer coupled with chemical reactions. VLE data would also be essential to estimate solvent degradation at elevated temperatures. There are hardly any studies on VLSE which were found in literature which exactly mirror the chemistry that is found in the current system of interest i.e. [CO\textsubscript{2}–water–Mg(OH)\textsubscript{2}]. Most studies have been performed on amines like MEA (Monoethanolamine), DEA (Diethanolamine) and MDEA (Monodiethanolamine) piperazine and mixtures of amines with piperazine. This data has been summarized in the form of a table (Table 9). This table contains information about the system under consideration, reaction conditions and additional information investigated by various authors.
Table 9. Literature review of VLE estimation

<table>
<thead>
<tr>
<th>Source</th>
<th>System under Consideration</th>
<th>Temperature range</th>
<th>Pressure range (partial pressure of CO₂)</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma’mun et. al. 171</td>
<td>30 % mass MEA and 50 % mass MDEA</td>
<td>MEA – [120 °C]</td>
<td>MEA - 7 to 192 kPa</td>
<td>Enthalpy of solution of CO₂ in the aqueous MDEA solution was estimated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MDEA – [55, 70 and 85 °C]</td>
<td>MDEA – 66 to 813 kPa</td>
<td></td>
</tr>
<tr>
<td>Aronu et al. 172</td>
<td>15, 30, 45 and 60 mass % MEA</td>
<td>40 – 120 °C</td>
<td>MEA – 0.0035 kPa to 1243.41</td>
<td></td>
</tr>
<tr>
<td>Chakma et al. 173</td>
<td>MDEA [4.28 M and 1.69 M]</td>
<td>100 °C to 200 °C</td>
<td>MDEA – 138 to 4930 kPa</td>
<td></td>
</tr>
<tr>
<td>Liu et al. 174</td>
<td>Piperazine (0.17 kmol/m³ to 1.55 kmol/m³) + MDEA (1.35 to 4.77 kmol/m³)</td>
<td>30 ºC to 90 ºC</td>
<td>13.16 to 935.3 kPa</td>
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</tr>
<tr>
<td>Derks et al. 175</td>
<td>Piperazine [0.2 to 0.6 M]</td>
<td>25, 40 and 70 °C</td>
<td>0.3 to 111 kPa</td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Components</td>
<td>Temperature Range</td>
<td>Pressure Range</td>
<td>Conditions</td>
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<td>-----------------------------------------------------------------------------</td>
<td>-------------------</td>
<td>----------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Dash et al. 168</td>
<td>Piperazine [0.2 to 4.5 M]</td>
<td>25, 35, 45 and 55°C</td>
<td>0.1 to 1500 kPa</td>
<td></td>
</tr>
<tr>
<td>Shen et al. 176</td>
<td>12 wt % MEA + 18 % MDEA, 24 wt% MEA + 6 wt% MDEA</td>
<td>40, 60, 80, 100°C</td>
<td>1 to 2000 kPa</td>
<td></td>
</tr>
<tr>
<td>Austgen et al. 177</td>
<td>2.5 kmol/m³ MEA, 2.0 kmol/m³ MDEA, 4.28 kmol/m³ MDEA + 2.0 kmol/m³ DEA</td>
<td>40 °C and 80 °C</td>
<td>0.05 to 309.3 kPa</td>
<td></td>
</tr>
<tr>
<td>Puxty et al. 178</td>
<td>1 mol/L of MEA, AMPD, two novel amines (A1 and A2)</td>
<td>40 °C</td>
<td>0.3 to 908 kPa</td>
<td>Large Scale screening process was carried out in identifying amines having best CO₂ absorption.</td>
</tr>
<tr>
<td>Dash et al. 179</td>
<td>2-aminoo-2 –methyl-1-propanol (2.2 to 4.9) mol dm³</td>
<td>25 °C to 55 °C</td>
<td>0.4 to 1500 kPa</td>
<td></td>
</tr>
</tbody>
</table>

The parameters in vapor-liquid equilibrium measurement are temperature, pressure, $x_i$ [liquid phase mole fraction of component $i$] and $y_i$ [vapor phase mole fraction of component]. The value of $i$ ranges from 1 to $n$ where $n$ is the number of components. The most commonly fixed variable in VLE measurement is temperature, which is held constant by means of a water bath or a temperature controller. Additionally fixed variables may include the amount of solvent, amount of component loading in the liquid phase and partial pressure of volatile components in
the vapor phase. The most widely employed method for studying VLE is the static method, in which a thermostated system having a set empirical composition, is brought into thermodynamic equilibrium and the phase compositions and the pressure are directly determined. This usually achieved by bringing an aqueous amine solution(solvent) in contact with CO$_2$ or H$_2$S in a cell and waiting till equilibrium is achieved. The indication for onset of equilibrium can be a constant value pressure or pH. Some experimental designs also allow for analysis of the liquid and vapor phases of the desired component by sampling. The current study uses a static method for measurement of vapor-liquid-solid equilibrium data.

5.2 Experimental Setup and Procedure

A high pressure Parr reactor [model 4768] with a working volume of 1 liter was used. This has an inlet valve with a dip tube for the gas which can double up as a liquid collection valve and an outlet valve. The relief valve was preset to 200 psi. A lecture bottle with a volume of 440 ml was used to transfer the CO$_2$ to the reactor. A magnetic stirrer was used to keep the slurry in a well-mixed state. A thermocouple connected to a temperature controller inserted into the reactor to monitor the temperature. Heating plate/water bath were used to raise the temperature of the reactor when needed.
5.2.1 Experimental Procedure

The lecture bottle was a small pressurized gas cylinder, used to transfer CO₂ gas from a main CO₂ gas cylinder. It was equipped with a pressure gauge with a range of 0 to 200 psig. The weight of the lecture bottle was recorded before transferring CO₂ gas to the Parr reactor. A magnesium hydroxide slurry solution was added to the vessel. The vessel was closed and connected to a vacuum pump in order to vacuum residual air and water vapor occupied in the head space of the vessel. After a vacuum was created, CO₂ gas was transferred to the reactor containing Mg(OH)₂ slurry solution until the pressure reached a desired total pressure. As CO₂ gas dissolved in the Mg(OH)₂ slurry solution, the total pressure decreased and additional CO₂ gas was added to the reactor. CO₂ gas was continued to be added to the reactor until a desired pressure was reached. This typically took about a day. After an equilibrium condition was established, the lecture bottle was disconnected from the reactor.
The total amount of CO\textsubscript{2} gas transferred to the reactor was measured and estimated by the weight and final pressure of the lecture bottle after the experiment.

### 5.2.2 Calculation Procedure

- The total number of moles of CO\textsubscript{2} transferred to the reactor \( n_{\text{CO}_2}^{\text{tot}} \) was measured by the weight difference in the lecture bottle before and after the experiment.
- The CO\textsubscript{2} partial pressure was estimated by taking the difference between the total system pressure \( P^{\text{tot}} \) and water vapor pressure \( P_{\text{H}_2\text{O}}^v \) at the temperature \( P_{\text{CO}_2} = P^{\text{tot}} - P_{\text{H}_2\text{O}}^v \).
- The number of moles of CO\textsubscript{2} in the vapor phase was estimated using the ideal gas law. \( n_{\text{CO}_2}^v = \frac{P_{\text{CO}_2}V}{RT} \).
- The moles of dissolved CO\textsubscript{2} in the liquid phase was calculated by taking the difference between the total number of moles of CO\textsubscript{2} transferred to the reactor and the number of moles of CO\textsubscript{2} present in the vapor phase (i.e. \( n_{\text{CO}_2}^{\text{l}} = n_{\text{CO}_2}^{\text{tot}} - n_{\text{CO}_2}^v \)).

### 5.3 Results and Discussion

#### 5.3.1 Room Temperature Data

Experimental data were obtained at room temperature using supernatant Mg(OH)\textsubscript{2} solution, 0.1 M, and 1 M Mg(OH)\textsubscript{2} solutions as summarized in Tables 10-12 and Figure 50.

<table>
<thead>
<tr>
<th>CO\textsubscript{2} added (mole)</th>
<th>P\textsubscript{CO}_2 (kPa)</th>
<th>CO\textsubscript{2} in the vapor phase (mole)</th>
<th>CO\textsubscript{2} in the liquid phase (mole)</th>
<th>CO\textsubscript{2} Mole fraction in the liquid phase ((x_{\text{CO}_2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0434</td>
<td>77.85</td>
<td>0.0261</td>
<td>0.0172</td>
<td>0.0012</td>
</tr>
<tr>
<td>0.0981</td>
<td>215.65</td>
<td>0.0725</td>
<td>0.0256</td>
<td>0.0018</td>
</tr>
<tr>
<td>0.1522</td>
<td>346.56</td>
<td>0.1165</td>
<td>0.0356</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.2295</td>
<td>484.36</td>
<td>0.1629</td>
<td>0.0666</td>
<td>0.0047</td>
</tr>
<tr>
<td>0.2925</td>
<td>622.16</td>
<td>0.2093</td>
<td>0.0831</td>
<td>0.0059</td>
</tr>
</tbody>
</table>
The solution obtained at the end of the experiment was very clear indicating all the magnesium hydroxide had been consumed completely. The distribution of CO$_2$ between gas and liquid phases also show that the CO$_2$ is primarily in the gas phase and gradually the amount of CO$_2$ in the gas phase increases with the pressure. Deionized water was tested at the same pressure and the VLSE data followed the same pattern, which suggests the presence of the slurry is essential for high performance CO$_2$ absorption.

Table 11. CO$_2$ equilibrium data for 0.1 M Mg(OH)$_2$ solution

<table>
<thead>
<tr>
<th>CO$_2$ added (mole)</th>
<th>P$_{CO2}$ (kPa)</th>
<th>CO$_2$ in the vapor phase (mole)</th>
<th>CO$_2$ in the liquid phase (mole)</th>
<th>CO$<em>2$- Mole fraction in the liquid phase (x$</em>{CO2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.151</td>
<td>153.64</td>
<td>0.0516</td>
<td>0.0999</td>
<td>0.0071</td>
</tr>
<tr>
<td>0.254</td>
<td>263.88</td>
<td>0.0087</td>
<td>0.1657</td>
<td>0.0117</td>
</tr>
<tr>
<td>0.294</td>
<td>408.57</td>
<td>0.1374</td>
<td>0.1573</td>
<td>0.0112</td>
</tr>
</tbody>
</table>

It can be seen that the number of moles of CO$_2$ in the liquid phase reaches a maximum at a certain pressure i.e. [around 40 psia/275 kPa] and after which even if the pressure rises, the amount of CO$_2$ that can be stored in the liquid reaches a plateau. This is best illustrated by figure 50. Also with using slurry, the amount of available magnesium increases and the pH of the sample varied from 6.45 to 6.74. The solution obtained at the end of experiments was slightly yellow with blackish solids which were the impurities present in Mg(OH)$_2$. 

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Table 12. CO$_2$ equilibrium data for 1 M Mg(OH)$_2$ solution

<table>
<thead>
<tr>
<th>CO$_2$ added (mole)</th>
<th>P$_{CO2}$ (kPa)</th>
<th>CO$_2$ in the vapor phase (mole)</th>
<th>CO$_2$ in the liquid phase (mole)</th>
<th>CO$<em>2$ Mole fraction in the liquid phase ($x</em>{CO2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.453</td>
<td>174.31</td>
<td>0.0586</td>
<td>0.3950</td>
<td>0.0276</td>
</tr>
<tr>
<td>0.513</td>
<td>312.11</td>
<td>0.1049</td>
<td>0.4081</td>
<td>0.0285</td>
</tr>
</tbody>
</table>

The 1 M solution can hold a lot more CO$_2$ in the liquid phase than 0.1 M and it has a limiting pressure of somewhere around 30 psia/206 kPa. At the end of the experiment, the residue was found to be milky carbonated slurry.

![Graph](image.png)

Figure 50. VLSE data for Mg(OH)$_2$-CO$_2$-H$_2$O at room temperatures.

From above graph we come to an understanding about the limiting pressure needed for maximum absorption of CO$_2$ by the magnesium hydroxide solution. For the supernatant liquid,
higher the system pressure better is the absorption. For 0.1 M slurry solution, the optimum pressure is somewhere around 40 psi. 1 M Mg(OH)$_2$ solution showed a higher CO$_2$ equilibrium capacity than 0.1 M Mg(OH)$_2$ solution.

5.3.2 VLSE Data at 40 °C and 52 °C

Experimental data was obtained at 40 °C and 52 °C using 0.1M and 1M Mg(OH)$_2$ solutions and the data was summarized in the following tables and figures:

Table 13. CO$_2$ equilibrium data for 0.1 M Mg(OH)$_2$ solution at 40 °C

<table>
<thead>
<tr>
<th>CO$_2$ added (mole)</th>
<th>P$_{CO2}$ (kPa)</th>
<th>CO$_2$ in the vapor phase (mole)</th>
<th>CO$_2$ in the liquid phase (mole)</th>
<th>CO$<em>2$- Mole fraction in the liquid phase ($x</em>{CO2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0972</td>
<td>130.864</td>
<td>0.0396</td>
<td>0.0576</td>
<td>0.00413</td>
</tr>
<tr>
<td>0.1127</td>
<td>168.785</td>
<td>0.0510</td>
<td>0.0617</td>
<td>0.00443</td>
</tr>
<tr>
<td>0.1454</td>
<td>241.180</td>
<td>0.0729</td>
<td>0.0724</td>
<td>0.00519</td>
</tr>
</tbody>
</table>

Table 14. CO$_2$ equilibrium data for 0.1 M Mg(OH)$_2$ solution at 52 °C

<table>
<thead>
<tr>
<th>CO$_2$ added (mole)</th>
<th>P$_{CO2}$ (kPa)</th>
<th>CO$_2$ in the vapor phase (mole)</th>
<th>CO$_2$ in the liquid phase (mole)</th>
<th>CO$<em>2$- Mole fraction in the liquid phase ($x</em>{CO2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0970</td>
<td>125.70</td>
<td>0.0386</td>
<td>0.0584</td>
<td>0.00419</td>
</tr>
<tr>
<td>0.1281</td>
<td>215.27</td>
<td>0.0661</td>
<td>0.0620</td>
<td>0.00444</td>
</tr>
<tr>
<td>0.1413</td>
<td>246.27</td>
<td>0.0756</td>
<td>0.0656</td>
<td>0.00471</td>
</tr>
</tbody>
</table>
The solution obtained at the end of the experiment is a clear bubbly liquid. This is a consequence of the low pH which is created due the high operating pressure. The influence of pressure forces the magnesium ions dissociate and go into the solution as magnesium bicarbonate. A commonly observed trend in VLE measurement with amine based solutions is that with an increase in temperature, the equilibrium shifts more towards the vapor phase. This trend is observed in the plot of CO$_2$ partial pressure (kPa) vs. $x_{CO_2}$ (mole fraction in the liquid phase) at 40 °C and 52 °C. The mole fraction values in the liquid phase indicate if the system is operated at higher temperature than 52 °C, it would result in a reduction in the amount of absorbed CO$_2$ in the liquid phase.
Table 15. CO$_2$ equilibrium data for 1 M Mg(OH)$_2$ solution at 52 °C

<table>
<thead>
<tr>
<th>CO$_2$ added (mole)</th>
<th>P$_{CO2}$ (kPa)</th>
<th>CO$_2$ in the vapor phase (mole)</th>
<th>CO$_2$ in the liquid phase (mole)</th>
<th>CO$<em>2$- Mole fraction in the liquid phase ($x</em>{CO2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2606</td>
<td>113.29</td>
<td>0.0348</td>
<td>0.2258</td>
<td>0.01601</td>
</tr>
<tr>
<td>0.2984</td>
<td>187.71</td>
<td>0.0576</td>
<td>0.2407</td>
<td>0.01704</td>
</tr>
<tr>
<td>0.3415</td>
<td>253.17</td>
<td>0.0777</td>
<td>0.2638</td>
<td>0.01865</td>
</tr>
</tbody>
</table>

Figure 52. VLSE data for Mg(OH)$_2$-CO$_2$-H$_2$O at 52 °C and different concentrations.

The increase in the concentration of the solution from 0.1 M to 1M at 52 °C resulted in a fourfold increase in the amount of CO$_2$ captured at comparable pressures. This validates the usage of high magnesium hydroxide concentrations in the absorber for maximum sustained CO$_2$ removal.
Vapor-liquid equilibrium (VLE) data in the case of CO₂ capture solvents are generally represented in the form of CO₂ partial pressure vs. CO₂ loading (moles of CO₂/moles of solvent). CO₂ loading values represent the capacity of the solvent and are directly proportional to the absorption capacity of the solvent. Figure compares VLE data available in literature for well-known solvents like MEA [Monoethanolamine], MDEA [Monodiethanolamine], AMP [2-amino-2-methyl-1-propanol] and piperazine at elevated temperatures, with the experimental values obtained for 1M magnesium hydroxide at 52 °C. Magnesium hydroxide has a superior CO₂ loading capacity compared to the other solvents as demonstrated by this graph. CO₂ loading capacities for most solvents decrease with temperature and increase with pressure. Monoethanolamine at different concentrations show lesser CO₂ loading capacities than 1M Mg(OH)₂ at 52 °C. Magnesium hydroxide exhibited a 40 % increase in CO₂ loading compared to 50 % MDEA at 55 °C.
Piperazine [0.8 M] displayed comparable performance with Mg(OH)$_2$ at 52-55 $^\circ$C, but the high cost of piperazine limits its application as a standalone solvent.

5.4 Conclusion

It is highly essential to have equilibrium solubility data over various temperatures, pressures and concentrations for efficient design of the treating units. A static synthetic method was used to determine the vapor-liquid-solid equilibrium data for the CO$_2$–water–Mg(OH)$_2$ system. Experiments were conducted at room temperature for Mg(OH)$_2$ solutions at various concentrations and the need to have a substantial amount of slurry for sustained absorption was established. Experiments were performed at higher temperatures (40 $^\circ$C & 52 $^\circ$C) and the shift in equilibrium towards the vapor phase was observed. The CO$_2$ loading capacities of Mg(OH)$_2$ at the proposed absorption temperature of 52 $^\circ$C were compared to the values found in literature for various solvents like MEA, MDEA and piperazine at standard operating temperatures respectively. Magnesium hydroxide at 1M at 52 $^\circ$C was found to give excellent CO$_2$ loading capacities close to 1 (mol of CO$_2$/mol of solvent) compared to 0.6 (mol of CO$_2$/mol of solvent) for 30 % MEA at 40 $^\circ$C, which is a standard amine concentration used as a benchmark for absorption.
CHAPTER 6. CONCLUSION

Three important phenomena influencing CO$_2$ capture using magnesium hydroxide solutions were investigated, namely: 1) Dissolution rate of magnesium hydroxide, 2) Kinetics of magnesium carbonate formation 3) VLSE of the Mg(OH)$_2$-H$_2$O-CO$_2$ system. Dissolution rate flux was determined using a pH stat apparatus at different operating conditions. An increase in the operational pH decreases the dissolution rate of magnesium hydroxide. The variation of dissolution rate with an increase in temperature was found to follow an Arrhenius type expression, which was used to develop an empirical expression to predict the intrinsic dissolution rate. The dissolution process was modeled using the shrinking core model and surface chemical reaction was found to be the rate controlling step. The apparent reaction rate constant was estimated to be $1.1 \times 10^{-1}$ min$^{-1}$ for an operating pH of 8.6 and temperature of 52 °C. Mg(OH)$_2$ was found to exhibit a fractional rate order which are in the range of $(0.20 < n < 0.31)$. The overall/intrinsic rate constants was determined over the temperature range of 22 to 52 °C using the apparent rate constant values at different constant pH conditions. Activation energy for the entire process was calculated to be $76 \pm 11$ kJ/mol, using the overall rate constants. High values of activation energy and fractional reaction orders offer proof for the surface chemical reaction controlled dissolution rate of Mg(OH)$_2$. The dissolution flux expression was modified to incorporate the fractional reaction order and this expression would used in future work in modeling the entire process of CO$_2$ absorption with Mg(OH)$_2$ slurry solutions. Dissolution rate decreases with time due to a decrease in particle size and this decrease is quantified with the help of the particle size values obtained from the shrinking core model. The dissolution rate starts decreasing from its intrinsic value when the average particle size reduces to 60% of its initial value at a pH = 8.6 and temperature = 52 °C. Regular monitoring of the Mg(OH)$_2$ slurry for
estimating particle sizes is recommended to ensure that dissolution takes place at the intrinsic rate, which is essential for sustained CO₂ absorption. MINEQL results indicated that operating the absorber at pH of 8.6 would be beneficial to prevent the formation of magnesium carbonate, which is a detrimental byproduct for continuous operation of the slurry. Kinetic analysis of MgCO₃ formation was performed using the mass balance method with solid phase carbon analysis by TGA-MS and liquid phase carbon analysis by HCl titration. The results indicate operating the system at a pH of around 8.6 favors the formation of magnesium bicarbonate, which is helpful for regeneration of the slurry in the stripper phase. Vapor-liquid-solid equilibrium studies were performed by using a static analytical device for the CO₂-H₂O-Mg(OH)₂ system. The results validate the importance of the slurry in the absorption process and higher the slurry used, better is the performance. Experiments performed at higher temperatures (40 °C and 52 °C) indicate the shift in equilibrium towards the vapor phase. Mg(OH)₂ gives better CO₂ loading at 52 °C compared to amines and other solvents at similar temperatures. Further research in pilot scale CO₂ absorption in packed/bubble columns is being carried out, which will demonstrate the applicability of this system on a large scale.
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