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Utilization of CO$_2$ to Mitigate Greenhouse Gas Effect

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in Chemical Engineering

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An Abstract of
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Greenhouse effect is the phenomenon of warming of the earth’s surface and its lower atmosphere due to increased levels of carbon dioxide and other gases, known as Greenhouse Gases (GHGs). It has been suggested that the release of greenhouse gases such as carbon dioxide, water vapor, nitrous oxide, methane, and ozone into the atmosphere by human activities (such as increased fossil fuel production and the growing use of automobiles) will trap more of the solar radiation that is reflected by the earth’s surface, causing rise in the atmospheric temperature over time. This is known as called global warming

A novel and viable solution of mitigating two most important greenhouse gases, viz., carbon dioxide and water vapor by way of converting them into carbon monoxide and water individually or into syngas together has been described in this thesis, and the two gases were converted into carbon monoxide and hydrogen by using an oxide (waste from steel industry) or a metal as the reducing oxide. The resulting product was used as a
fuel in running a single-button SOFC at 650°C with comparable efficiency. The spent oxide was highly magnetic in nature and could be used potentially in making ceramic ferrites for scores of applications.
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Chapter 1

Introduction

1.1 World Energy Consumption

In general, seeking for an alternative energy can be limited to two main reasons: the economical and the environmental. Oil is a global fundamental product for living. The two factors, supply and demand, control the price of crude. In 2008, the oil price went up to $147/barrel. Since 1983, world consumption of crude oil products has grown fairly steadily. The Energy Information Administration (EIA) predicted that world oil use will continue to grow and will reach 118 million barrels per day by 2030\textsuperscript{[1]} It is estimated that about 43\% of this growth in oil consumption will come from developing countries such as China and India. However, United States will remain world’s largest oil consumer; the United States accounts for about 25\% of global oil consumption\textsuperscript{[1]}

1.2 The Greenhouse Effect

The greenhouse effect is caused by an atmosphere containing gases that absorb and emit infrared radiation\textsuperscript{[2]}. Moreover, the greenhouse effect is a phrase used to describe the increased warming of the earth’s surface and lower atmosphere due to
increased levels of carbon dioxide and other greenhouse gases. Some Scientists fear a rise in temperature of about 5°C as early as the middle of the next century; that means the climate will change tens of times faster than the average rate of natural change.

1.3 Greenhouse Gas Effect Mechanism

When the sun's rays hit earth's atmosphere and the surface of the earth, approximately 70 percent of the energy stays on the planet, absorbed by land, oceans, plants and other objects. The other 30 percent is reflected into space by clouds, snow fields, and other reflective surfaces. But even the 70 percent that gets through doesn't stay on the Earth forever (otherwise the earth would become a much warmer than what it is)\[^3\]. In other words, the amount of radiation emitted by the earth is almost exactly balanced by the amount of solar energy absorbed. That means the Earth is in a near state of radiation equilibrium, and that is why the Earth’s temperature changes quite slowly every year. However, as seen in Figure 1.1, about 30 % of the incoming solar energy is reflected back to space and is not available to the earth.
If Earth absorbed more solar energy, it would create a new equilibrium. If earth contains more white surfaces - such as more clouds - it would reflect more solar radiation and absorb less. Therefore, it would cause the plant to be colder. The average surface temperature of the earth during a year is about 14°C. The difference between the apparent temperature of the earth and the actual temperature of the surface is 14°C; this is due to the greenhouse effect of the atmosphere.

1.4 Global Warming

Global warming is the change in earth’s atmospheric temperature observed in recent years. Researchers indicate that the release of greenhouse gases such as water vapor, carbon dioxide, nitrous oxide, methane, and ozone into the atmosphere by human activities (such as increased fossil fuel production and consumption; and the growing use of energy) will trap more of the solar radiation than is reflected by earth’s surface,
causing a rise in the atmospheric temperature. These gases have the potential of absorbing solar radiation reflected from the Earth’s surface, causing a disturbance in the heat balance of the planet, and warming the surface by producing trapped energy. When the greenhouse gases absorb the solar radiation, the stratosphere becomes warmer and eventually re-emits infrared radiation. This radiation ultimately gets back to the troposphere. The greenhouse effect measured in terms of global warming potential (GWP) is expressed with reference to carbon dioxide’s contribution to global warming.

The issue of global warming has emerged from a mild concern to a global reality affecting everyone and everything today. Industries world-wide are beginning to mandate close monitoring of their carbon footprint on environment. Defined as the increase in the average temperature of the earth’s atmosphere, global warming is believed to have already irreversibly changed Earth’s climate by many scientists. The effect of global warming continues to pose dire implications on our planet. Rising sea levels, glacier retreat, arctic shrinkage, rapidly altering agricultural patterns, expansion of tropical diseases and explosion of forest fires are just a few of the many direct effects of global warming; this ultimately poses a great threat to the quality of life.\[4\] Behind this climatic shift are the growing volumes of GHG’s, specifically carbon dioxide and water vapor. While water vapor in earth’s stratosphere is increasing at a rate of ~1%, CO$_2$ concentration is increasing at a rate of 0.6% annually, and is expected to rise. Since these emissions are anthropogenic in nature and result primarily from the combustion of fossil fuels, use of world energy has emerged at the center of the global warming debate. According to the Energy Information Administration (EIA), world energy related CO$_2$ emissions are increasing at an alarming 2% annually, ultimately producing 28.1 billion
metric tons in 2005 which is projected to reach 42 billion metric tons by 2030. In 2008, the Nobel Prize winning Intergovernmental Panel on Climate Change (IPCC) published a landmark report warning of rising sea levels, expanding deserts, more intense storms and the extinction of up to 30% of plant and animal species\(^5\). Recent climate studies, however, suggest that the IPCC report significantly underestimates the severity of global warming over the next 100 years, making the disaster more acute.

1.5 Greenhouse Gases Emissions

Several human activities such as industrialization, power plants, transportation, agriculture, and fossil fuels production and consumption, commercial and residential activities have invariably led to the production of high amounts of greenhouse gases. Greenhouse gas emissions level is an account of the quantity of greenhouse gases added up to or removed from the atmosphere over a specific period of time. They will also give information on the activities that cause emissions and removals. Moreover, knowing them will provide a background on the technique used to Figure out the emissions levels. Environmentalists use the greenhouse gas emissions level to track emission sources, develop strategies and policies, and assess progress\(^6\).

Water vapor is the dominant greenhouse gas in the atmosphere. However, changes in water vapor concentration are also considered to be a result of climate feedbacks related to the warming of the atmosphere rather than a direct result of industrialization. Water accounts for about 90% of our planet’s greenhouse effect - perhaps 70% due to water vapor and about 20% due to clouds (mostly water droplets). In
some studies, it is reported that water vapor contributes as high as 95% of the total atmospheric greenhouse effect\textsuperscript{[7]}.

Water vapor is the most abundant greenhouse gas. More than 90% of the greenhouse gases are water vapor emission. The human activity contribution in emitting water vapor is around 0.001%. Other greenhouse gases are carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}), nitrous oxide (N\textsubscript{2}O), and miscellaneous other gases (CFC's, etc.)

1.6 Carbon Dioxide Emissions

The overall carbon rotation is made up of large carbon flows and reservoirs. Large amounts of carbon are in the form of carbon dioxide (CO\textsubscript{2}), which is absorbed by oceans and living plants and emitted to the atmosphere through natural processes (evaporation and photosynthesis).

In the past, awareness of the greenhouse effect has focused mainly on carbon dioxide. Each year, nearly six billion tons of CO\textsubscript{2} is released into the atmosphere, mostly as a result of fossil fuel consumption. Measurements made at different locations in the world indicated that the ratio of carbon dioxide in the atmosphere is currently increasing by about 0.4 % each year\textsuperscript{[8]}. Investigation on air trapped in ice indicates that the carbon dioxide mixing ratio was between 275 and 285 ppmv during the seventeenth and eighteenth centuries\textsuperscript{[9]} Since 1958, Dr. Charles David Keeling has been studying the variation in atmospheric CO\textsubscript{2} concentration at the Mauna Loa Observatory. He created a curve called the Keeling Curve which measures the progressive buildup of carbon dioxide. Figure 1.2 shows the carbon dioxide concentration (expressed in ppm by volume) measured at Mauna Loa Observatory from 1958 until 2008.
Figure 1.2: Concentration of Carbon Dioxide in the Atmosphere

The curve shows a steady increase of CO$_2$ concentration in atmospheric from about 315 parts per million by volume (ppmv) in 1958 to 385 ppmv as of June 2008 – an increase of about 120 ppmv per century.

Measurements of CO$_2$ concentration in ancient air bubbles trapped in polar ice cores indicate that the mean atmospheric CO$_2$ concentration has historically been between 275 and 285 ppmv during the Holocene epoch (9,000 BCE onwards); it began to rise fast at the beginning of the 19th century \cite{10}. On the other hand, analyses of stomata frequency in tree leaves indicate that average atmospheric CO$_2$ concentration may have reached 320 ppmv during the medieval warm period and 350 ppmv during the early Holocene \cite{9,11}.

Due to the rapid increase in industrialization and use of fossil fuels, atmospheric CO$_2$ has increased over the past few years and is believed to have played a major role in
global warming. If the CO₂ emission level continue to rise, along with an increase in other greenhouse gases, the results will be disastrous. Even if the greenhouse gas emissions continue at the present rate without any mitigation efforts, the global temperature will rise 5°C or more by the end of the century causing significant irreversible environmental changes that can affect human civilization irreversibly [12].
Chapter 2

Literature Survey

2.1 Carbon Dioxide Mitigation

The combustion of fossil fuels is the main cause of the emission of greenhouse gases (GHGs) and as a result of that it is also the main cause of climate change. With increased efforts in developing technologies to mitigate greenhouse gases, the net emission of these gases can be significantly reduced thereby minimizing the greenhouse effect. Carbon dioxide is considered the second most important GHG in the earth's atmosphere next to water vapor \[13\].

Both in terms of the role of biological processes and the physics of ocean circulation and gas exchange, it is known with certainty that human activities are significantly disturbing the global carbon cycle. This has resulted in a significant increase of carbon dioxide levels in the atmosphere by way of observed flow of CO\(_2\) into oceans. The oceans are considered to be the largest reservoir for CO\(_2\) storage. It is obvious that CO\(_2\) dissolved or disposed into seawater will not be isolated from the atmosphere for an indefinite period \[13\].

Three major concepts of CO\(_2\) sequestration have been put forward, via,
• Ocean sequestration: ‘Injection dissolution’ of CO₂ into water column at depths > 1000 m.
• ‘Lake deposition’ directly onto the sea floor at depths > 3000 m where CO₂ is denser than water and is expected to form a 'lake', delaying emission into the environment.
• Geological sequestration: Gaseous storage in various deep geological formations: unminable coal streams, exhausted oil fields and depleted gas fields.
• Mineral sequestration: Reacting CO₂ with metal oxides to produce stable carbonates

In terms of their technological status and commercial viability, each of these options has some common deficiencies. For example, each of them is extremely expensive, has questionable sequestration efficacy, and more importantly their ancillary environmental and economic costs vs. benefits are debatable.

2.2 Direct Disposal of Carbon Dioxide to Seawater

Disposal of carbon dioxide into oceans has been generally researched on a theoretical basis [14]. The capture method involves absorbing carbon dioxide into a solvent from the flue gases. Transferring the entire outlet gas is not practical since the carbon dioxide percentage ranges from about 3% in the case of gas turbine plant [15]. The percentage of CO₂ from a natural gas combined cycle plant is about 3.6% and for a coal fired power plant, the CO₂ concentration is around 14%. The highest level of CO₂ - around 80% - is found in the case of some specialized petrochemical processes [16]. Disposal of carbon dioxide into oceans relies on three strategies [17]:
1. Flowing liquefied CO$_2$ into deepwater by pipeline
2. Making dry-ice releasing it from a ship
3. Forming liquid CO$_2$ pool in the deep ocean bed.

Figure 2.1 shows the pathway from the very instant of its generation at the power plant to its separation from other gases, to disposal from a pipeline to the depth of 1500 m.

![Figure 2.1: Scheme for carbon dioxide disposal into ocean](image)

**2.3 Limitation of Carbon Dioxide Disposal into the Seawater**

Carbon dioxide disposal in ocean is highly energy intensive. For instance, the reduction in utility output is around 15 to 24% for a gas fired plant and 27 to 37% for a
coal fired plant; for an advanced coal plant, the reduction in utility output is around 13 to 17% \[^{19}\]. These numbers do not take into account the industrial processes such as liquefaction and disposal. These estimates are based on other assumptions \[^{20}\], suggesting that the overall reductions in efficiency could be up to 35%. Furthermore, capturing carbon dioxide in a power plant will reduce the efficiency to around 10% \[^{21}\], indicating that CO\(_2\) capture and liquefaction will require additional energy in order to maintain the plant efficiency. In another word, a power plant would need around 10% of the additional fuel to liquefy, compress, and pump CO\(_2\) at about 150 atm. pressure into the sea. This will result, in turn, in creating more carbon dioxide per unit of energy produced \[^{22}\].

### 2.4 Effect of Carbon Dioxide on Oceans

Releasing carbon dioxide into seawater will likely decrease the pH near the injection points \[^{23}\]. In studies reported by Herzog et al. \[^{24}\] it was shown that the pH of the seawater near the injection point is less than 5.8 and less than 6.6 within an area 25 km long and 1km wide from the injection point. This has direct repercussions on the ocean chemistry as a whole, for the following reason.

In the presence of oxygen, ammonium ions are readily oxidized to nitrite and nitrate by marine bacteria, by a process called nitrification, The resulting nitrate accumulates in the euphotic zone (that is exposed to the sunlight) where it helps in the growth of phytoplankton.
Therefore, the disposal of CO$_2$ into deep oceans is most likely to interrupt the rate of oxidization of ammonia, resulting in the reduction of pH around the injunction point. Many marine ecosystems will get affected due to this pH variation $^{[23]}$.

2.5 Carbon Dioxide Sequestration by Minerals

Carbon dioxide sequestration by mineral is one of the techniques that have been used by industries in order to sequestrate CO$_2$. Basically, the CO$_2$ captured as a by-product in processes are converted into solid carbonates by either magnesium oxide (MgO) or calcium oxide (CaO) to form stable carbonates, which are then reburied in mines. This technique was originally proposed by Seifritz (Seifritz, 1990). Figure 2.2 shows the CO$_2$ sequestration by mineral

![Figure 2.2: Carbon dioxide sequestrations $^{[25]}$](image)
The main idea of the mineral sequestration process is that the formed mineral carbonates are end products of geologic processes and are known to be stable over geological time periods, but the limitation in such techniques is needs of constructing a mineral carbonation plant close enough from the mine due to the large volumes of material required. Furthermore, more land fields will be required in order to store the newly formed carbonates.

In addition to these limitations, mineral CO$_2$ sequestration technologies have environmental impacts such as the consumption of extra energy. Kakizawa studied the reduction in power plant efficiency. The calculation he made indicated a decrease from 40% to 32% for a thermal power plant when mineral sequestration is applied$^{[25]}$

2.6 Conversion of Carbon Dioxide into Methanol

Hydrogenation of carbon dioxide is yet another approach to moderate its greenhouse gas effect. Conversion of CO$_2$ into compounds, such as methanol, ethanol, and formic acid, has been intensively investigated. In particular, the formation of methanol from the hydrogenation of CO$_2$ has drawn much consideration because of its large demand as a bulk chemical. It has been reported that CO$_2$ is used for methanol synthesis$^{[26]}$. For that reason, there have been great efforts to develop a catalytic system for the CO$_2$ hydrogenation$^{[27][28]}$.

It has been, however, challenging to develop an efficient and economical process to obtain methanol via CO$_2$ hydrogenation$^{[29]}$, the main limitation being the source of hydrogen used in the process and its operational cost.
2.7 Innovation

As shown in the previous sections, so far, no technology has offered a practical solution to the burgeoning problem of global warming. The currently pursued options to mitigate CO₂ emission are mostly concerned with the sequestration of CO₂ alone and are extremely energy intensive, elaborate in design, years away from achieving practical feasibility and above all, exorbitantly expensive. Other less popular options, catalytic methanation, or photo-reduction, require hydrogen and are hardly practical in implication.

This work investigates the question, what if one could convert CO₂ into carbon monoxide (CO), water into H₂ and a mixture of (CO₂+H₂O – the ultimate product of complete combustion of hydrocarbon-based fossil fuels, including biofuels) into syngas (CO+H₂), respectively? Syngas is a valuable precursor for the well-known Fischer-Tropsch process perfected by Germans during WW I to make synthetic fuels since Germany had no oil reserves. All these streams (CO, H₂ and CO+H₂) are also ideal fuels for solid oxide fuel cells (SOFCs). Hence, essentially the waste products of combustion could become a fuel source and can be recycled. Alternatively, if desired, CO could be converted into H₂ via catalytic water-gas-shift reaction which then becomes a feed for PEMFCs.

This thesis describes the results pertaining to the development of inexpensive heterogeneous oxide material systems capable of converting CO₂ and H₂O into CO and H₂, respectively, on a 1:1 molar basis, under mild temperature and atmospheric pressure. These streams when fed into an IT-SOFC at 650°C create a open circuit voltage, quite comparable to that of the same SOFC run with pure H₂ (ideal fuel).
Chapter 3

Theoretical Rationale

Basically, in this work, we used the simple concept of oxidation-reduction reaction (redox) in the solid-gas phase. We considered the following gas-solid redox reactions taking place by using metal / metal oxide.

\[
\text{CO}_2(\text{gas}) + MO_{x}\text{(solid)} \rightarrow MO_{x+1}\text{(solid)} + CO(\text{gas}) \quad \text{(3.1)}
\]

\[
\text{CO}_2(\text{gas}) + M_{\text{(solid)}} \rightarrow MO_{x+1}\text{(solid)} + CO(\text{gas}) \quad \text{(3.2)}
\]

Substituting iron oxide and iron in equation 2.1 and 2.2

\[
\text{CO}_2(\text{gas}) + 2Fe_3O_4\text{(solid)} \rightarrow 3Fe_2O_3\text{(solid)} + CO(\text{gas}) \quad \text{(3.3)}
\]

\[
3\text{CO}_2(\text{gas}) + 2Fe_{\text{(solid)}} \rightarrow Fe_2O_3\text{(solid)} + 3CO(\text{gas}) \quad \text{(3.4)}
\]

In stoichiometry calculations, we assume that reactions run to completion. However, equilibrium takes place when there is a constant ratio between the concentration of the reactants and the products. For every reaction at a certain temperature, there is only one value for K. A large K value (K>1) implies that there are more products than reactants.
and that the equilibrium lies to the right, whereas, a small K value will shift the reaction to the left. Therefore, the K value of equation 3.3 is:

$$CO_2(gas) + 2Fe_3O_4(solid) \rightarrow 3Fe_2O_3(solid) + CO(gas)$$

Table 3.1: Gibbs energy and the enthalpy change

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\circ_{298}$</th>
<th>$\Delta G^\circ_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2(gas)$</td>
<td>-393,509</td>
<td>-394,359</td>
</tr>
<tr>
<td>$CO(gas)$</td>
<td>-110,525</td>
<td>-137,169</td>
</tr>
<tr>
<td>$Fe_3O_4(solid)$</td>
<td>-1,118,400</td>
<td>-1,015,400</td>
</tr>
<tr>
<td>$Fe_2O_3(solid)$</td>
<td>-824,200</td>
<td>-742,200</td>
</tr>
</tbody>
</table>

Calculating the Enthalpies of the reaction, $\Delta H$

$$\Delta H = \sum nH_{(prod.)} - \sum nH_{(react.)}$$  \hfill (3.5)

$$\Delta H = -(3 \times 824200) - 110585 + 393509 + (2 \times 1118400) = -47.184 \text{kJ/mol}$$

Calculating the Gibbs free energy change, $\Delta G$

$$\Delta G = \sum nG_{(prod.)} - \sum nG_{(react.)}$$  \hfill (3.6)
\[ \Delta G = -(3 \times 742200) - 137169 + 394359 + (2 \times 1015400) = -61.390 kJ/mol \]

\( K_\circ \) represents the equilibrium constant at reference temperature \( T = 298K \)

\[
K_\circ = \exp\left( -\frac{\Delta G^\circ}{R \times T_{298}} \right)
\]

\[
K_\circ = \frac{61390 \text{ J/mol}}{8.314 \times 298 \text{ K}} = 5.76 \times 10^{10}
\]

(3.7)

\( K_1 \) supplies the major effect of temperature, such that the product \( K_\circ K_1 \) is the equilibrium constant at temperature \( T \) when the heat of reaction is assumed independent of temperature:

\[
K_1 = \exp\left[ -\frac{\Delta H^\circ}{R \times T_{298}} \left( 1 - \frac{T_{298}}{T_{\text{ran}}} \right) \right]
\]

\[
K_1 = \exp\left[ -\frac{47184}{2477.5} \left( 1 - \frac{298K}{853K} \right) \right] = 4.144 \times 10^{-6}
\]

(3.8)

\( K_2 \) accounts for the much smaller temperature influence resulting from the change of \( \Delta H^\circ \) with temperature. For ideal reaction condition, \( K_2 = 1 \), therefore, the equilibrium constants for equation 2.3 is

\[
K = K_\circ \times K_1 \times K_2 = 5.76 \times 10^{10} \times 4.144 \times 10^{-6} \times 1 = 238 \times 10^3
\]

(3.9)
Clearly the equilibrium constant of the reaction is far greater than 1. This is a typical result, and accounts for the fact that there are more products than reactants and that the equilibrium lies to the right.

In addition of the equilibrium constant of the reaction, the thermodynamic equilibrium oxygen partial pressure ($P_{O_2}$) of the two oxides ($Fe_3O_4$ and $Fe_2O_3$) at 800K is computed to be $1.32 \times 10^{-18}$ atm. For $P_{O_2}$ values greater than $1.32 \times 10^{-18}$ atm., the oxidation of $Fe_3O_4$ into $Fe_2O_3$ will occur. Similar analysis yields a value of $2.22 \times 10^{-27}$ atm. for the $P_{O_2}$ of the oxidation of $Fe$ into $Fe_2O_3$; therefore, at $P_{O_2}$ greater than $2.22 \times 10^{-27}$ atm., the oxidation of $Fe$ into $Fe_2O_3$ will take place.

The oxidation of $Fe/Fe_3O_4$ into $Fe_2O_3$ occurs by the reaction of $CO_2$ into CO.

The partial pressure of oxygen could be computed from the following equation:

$$P_{O_2} = \left( \frac{P_{CO_2}}{P_{CO}} \right)^2 \times \left( \frac{1}{-\Delta G^0} \right)^2$$

$$\left( e^{\frac{RT}{-\Delta G^0}} \right)$$

According to equation (3.10) controlling the concentration ratio of $CO_2$ and CO in the mixture may control the partial pressure of oxygen at given temperature. Table 3.2 shows the computed values of $P_{O_2}$ at 800 K in some $CO_2/CO$ mixtures

Table 3.2 Equilibrium $P_{O_2}$ values at 800 K in some representative $CO_2/CO$ mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$P_{O_2}$ (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$ – 10 ppm CO</td>
<td>$2.81 \times 10^{-18}$</td>
</tr>
<tr>
<td>$CO_2$ – 1 ppm CO</td>
<td>$2.81 \times 10^{-16}$</td>
</tr>
<tr>
<td>$CO_2$ – 0.1 ppm CO**</td>
<td>$2.81 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
It can be seen from Table 3.2 that the equilibrium partial pressure of oxygen generated by CO<sub>2</sub> – CO mixture (2.81 X 10<sup>-14</sup>) is greater than Po<sub>2</sub> of Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> and Fe/Fe<sub>2</sub>O<sub>3</sub>, which indicates that pure CO<sub>2</sub> is capable of oxidizing Fe/Fe<sub>3</sub>O<sub>4</sub> into Fe<sub>2</sub>O<sub>3</sub> which signature the reduction of CO<sub>2</sub> into CO in Equations 3.3 and 3.4.

The reaction of water vapor with metal or metal oxide follows the same thermodynamics equilibrium oxygen partial pressure of Equation 3.3 and 3.4. The Po<sub>2</sub> values at 800K for various H<sub>2</sub>O/H<sub>2</sub> mixtures were computed for the reaction:

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]  

(3.11)

Table 3.3 Equilibrium Po<sub>2</sub> values at 800 K in some representative H<sub>2</sub>O/H<sub>2</sub> mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Po&lt;sub&gt;2&lt;/sub&gt; (atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O – 10 ppm H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.16 x 10&lt;sup&gt;-16&lt;/sup&gt;</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O – 1 ppm H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.16 x 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O – 0.1 ppm H&lt;sub&gt;2&lt;/sub&gt; **</td>
<td>1.16 x 10&lt;sup&gt;-12&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

As can be seen in Table 3.2, the equilibrium partial pressure of oxygen generated by H<sub>2</sub>O/H<sub>2</sub> mixture (1.16 x 10<sup>-12</sup>) is greater than Po<sub>2</sub> of Fe/Fe<sub>3</sub>O<sub>4</sub> into Fe<sub>2</sub>O<sub>3</sub> as per reaction:

\[ H_2O(g) + 2Fe_3O_4(g) \rightarrow 3Fe_2O_3(s) + H_2(g) \]  

(3.12)

For water vapor reacting with metal

\[ 3H_2O(g) + 2Fe(s) \rightarrow Fe_2O_3(s) + 3H_2(g) \]  

(3.13)
This indicates that H$_2$O vapor is capable of oxidizing Fe$_3$O$_4$ and Fe into Fe$_2$O$_3$ and H$_2$

Thus, carbon dioxide and water are converted into carbon monoxide and hydrogen, respectively. The conversion in this work can be considered heterogeneous catalytic reduction [30].

The basic reaction consists of passing CO$_2$ and H$_2$O (vapor) over the metal oxide or metal, that produce CO, H$_2$ or syngas (CO+H$_2$), at mild conditions of temperature and pressure [31]. Both iron and iron oxide used in this work are available in large amounts. Earth’s crust is composed of about 5% of iron. The worldwide availability of iron is estimated to be about 800 billion tons as ores that contain more than 230 billion tons of iron [31].

The product (CO and H$_2$) of this technique is called syngas. Syngas can be used in many applications. One of the most useful applications of using syngas is called Fischer-Tropsch process. Ficher-Tropsch process is a catalytic hydrogenation method that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons [31].
Chapter 4

Experimental Section

4.1 Materials

4.1.1 Iron Oxide: Industrial Samples

The raw material mill scale waste iron oxide (Fe$_3$O$_4$) samples were provided from two steel companies: Midrex Technologies Inc. (Charlotte, NC, USA) and Nucor - Yamato Steel coco. (Blytheville, AK, USA). These will be referred to as MID and NY, respectively, throughout the thesis. The MID and NY mill-scale waste, were taken for a ball-milling to crush the materials into fine powder, by using ceramic milling media in isopropanol. Figure 4.1 shows the laboratory set-up of the milling and sieving apparatus. The ratios of the sample to the milling media were 1:3. After the ball-milling, the samples were dried in a vacuum oven to remove all the isopropanol, and then the samples were sieved through a 325 mesh to ensure uniform particle size distribution. Dried and sieved samples from both sources were stored in pre-cleaned plastic bottles, labeled and were used in further processing and characterization. Among all samples, mill scale waste (Fe$_3$O$_4$) received from Midrex Technologies was used in thesis.
4.1.2 Iron Oxide: Commercial Sample

In addition to the iron oxide obtained from MID and NY, an iron powder sample (99%; average particle size ~ 100 nm) was obtained from Alfa-Aesar (Waltham, MA).

4.1.3 Iron: Derived from Millscale Waste

The $\alpha$-iron used in this experiment was prepared from the steel industrial waste iron oxide ($\text{Fe}_3\text{O}_4$). The reduction of $\text{Fe}_3\text{O}_4$ was carried out via solvothermal processing using an autoclave. The autoclave (AutoClave Engineers, PA) stainless steel vessel has a processing capacity of 1L. The internal wall of the vessel coated with zirconiua to prevent corrosion under strongly alkaline conditions. Figure 4.2 shows the autoclave setup in the laboratory.
10 g of mill-scale waste (Fe$_3$O$_4$) powder were mixed with 50 mL of ethanol. 160 mL of hydrazine monohydrate (99%, Alfa Aesar) were added to the mixture. 10g pellets of sodium hydroxide were added to maintain the pH (>12) of the mixture. This mixture was placed in autoclave vessel and purged with pure nitrogen to displace any oxygen in the system. After purging, the system was pressurized to about 1000 psi. The reaction temperature was set to 100°C and the reaction time was 6 hr. The product was washed thoroughly using a centrifuge. Ethanol, water, and acetone were used as washing media to remove any impurities that might be present in the product. The solvothermally
reduced samples were then systematically characterized for their phase and morphology using XRD and SEM, respectively.

### 4.2 Experimental Setup

For both sets of samples, iron oxide powder was packed in a cylindrical Swagelok™ SS filter with a pore size of 5µm. The diameter of the filter was 0.5cm. The iron oxide powder inside the filter was packed with glass wool to avoid the displacement of the bed. The stainless steel filter was placed in the center of the quartz reactor located in the proper zone of the furnace to maintain the propitiate reaction temperature. The furnace used in this experiment was a Lindberg Minimite furnace. The iron oxide powder inside the filter was heated in an inert nitrogen medium up to 580°C. When the reaction temperature (580°C) was reached, a pure carbon dioxide gas (provided from air gas) was flowed at 100 stander cubic centimeter per minute (Sccm). In the case of experiment involving water vapor, carbon dioxide gas was passing through water bath prior it inlet the reactor. The moisture level in the gas stream was varied by changing the temperature of the water bath. The gas mixture which exits the reactor goes to the gas chromatograph or fuel cell. The fuel cell is a single-button Hionic™ solid oxide fuel cell (Ni-GDC || YSZ || LSM-GDC) operated at 650°C. The electrodes of the fuel cell were attached to a multimeter (Kikusui PLZ30F-70UA, Kikusui America Inc.) to monitor the open circuit voltage (OCV; without applying a load) that was produced when passing pure hydrogen/carbon monoxide or by the gas mixture that exit the reactor. Figure 4.3 shows the fuel cell electrodes connected to the multimeter.
In the other case, the exit gas composition was analyzed using a gas chromatograph (Shimadzu GC 2010) equipped with a PDHID detector. Figure 3.2 shows the process flow diagrams of both experimental setups. In the case of using fuel cell, the gas mixture which exits the reactor pass through a water bath before it enters the fuel cell.

Figure 4.3: Flow diagram of experimental setup
4.3 Characterization

4.3.1 X-ray Powder Diffraction

The X-ray diffraction (XRD) technique was used to characterize the phase evolution in the samples. XRD in this work was particularly useful for determination of phase transformation of species from oxide to reduced metal during the autoclave reduction steps of mill scale Fe$_3$O$_4$. Moreover, XRD signatures on the phase transformation of the oxidize metal by carbon dioxide and water vapor. The Bragg
The equation describes the position of X-ray scattering peaks in angular space Bragg’s equation are equivalent in that they both describe the relation between the lattice vectors and the scattering vector for an X-ray reflection to occur. Bragg’s equation is often written in the more popular form $2d \sin \theta_B = n \lambda$ \[32\]

\[
\Delta_1 + \Delta_2 = 2d \cos(90^\circ - \theta) = 2d \sin \theta
\]

Figure 4.5: Visualization of the Bragg’s equation \[32\]

Where, 

- $B$ = full width of half the maximum of the tallest Bragg peak
- $d$ = distance between two adjacent planes
- $\theta$ = diffraction angle
- $\lambda$ = wavelength
- $n$ = reflection order

The X-ray Diffraction equipment used for characterizing the samples called Philips diffractometer system (PW 3050/60 X’pert Pro) using monochromatic CuK$\alpha_1$
radiations ($\lambda = 1.54056$ Å) and Ni filter operated (Generator Settings) at 45 kV and 40 mA. The Minimum step size 2Theta:0.001; and minimum step size Omega: 0.001. The start position [$^\circ \theta$]: 28.0064 and the end position [$^\circ \theta$]: 84.9904.

### 4.3.2 Electron Microscopy

The surface features of the samples (Topography) and the shape and size of the particles (Morphology) of the samples in this work were examined using scanning Electron Microscopy (SEM). The SEM was detecting the samples features to a 500 nanometers. The SEM is also prepared with Energy Dispersive X-ray Spectroscopy (EDS) that can provide semi quantitative compositional analysis by the interaction of the primary beam with atoms in the sample.

Both sets of samples were taken to electron microscopy before and after the reaction to create an enlarged view of an object such that we can observe detailed changes in crystal structure of the samples.

### 4.3.3 Scanning Electron Microscopy

The samples were examined by using Hitachi S-4800 High Resolution Scanning Electron Microscope. The S-4800 is a cold field emission high resolution scanning electron microscope that can guarantee high resolution (1.0 µm) at low voltage. The accelerating voltage on the S-4800 is around 0.5 - 30 kV (variable at 0.1kV/step). The S-4800 has a specimen stage $X = 0^\circ 110$mm and $Y = 0^\circ 110$mm.

Because the SEM utilizes vacuum conditions and uses electrons to form a high image resolution, special preparations was done to the samples. All samples, before and
after the reaction, were totally dried from moisture to avoid the vaporization in the vacuum. Moreover, all samples were coated with a thin layer of conductive material (gold). This coating process was done by using a device called a "sputter coater."

The sputter coater uses an electric field and argon gas. The sample was placed in a vacuumed chamber. Argon gas was used as a purging medium. Argon gas and an electric field in the sputter enhance the electron to be removed from the argon, causing the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions push the gold atoms from the surface of the gold foil. These gold atoms drop and settle onto the surface of the sample producing a thin gold coating.

4.3.4 Gas Chromatograph

A Shimadzu gas chromatograph (GC), Model 2010 was used in this experiment. The GC operated with Pulse Discharge Helium Ionization Detector (PDHID) and Flame Photometric Detector (FPD) was used to analyze the effluent gas.

The outlet gas mixture of the reaction was analyzed using a gas chromatography (GC) to separate volatile components of the gas mixture. A small amount of the gas mixture that exits the reactor was drawn be analyzed via syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the sample is injected. The injector is set to a temperature higher than the boiling points of the reactor outlet gas mixture. Thus, components of the gas mixture evaporate into the gas phase inside the injector. The GC was operated in temperature programmed mode to separate gases in 15
minutes. In this experiment, the carrier gas used was helium. The helium flows through the injector and pushes the gaseous components of the sample onto the GC column. Supelco’s Carboxen 1010 Plot column (Supelco # 25467) was used to analyze gases which required detection by PDHID detector. The gas component separation takes place inside the column, and then after, the components of the gas mixture pass through the GC column. The GC operated in automatic continuous acquisition mode from the beginning of the experiment until the end.

### 4.3.5 Magnetic Measurements

All materials respond in one way or the other to an applied magnetic field. The term “magnetic material” means one that maintains a magnetic polarization in the absence of an applied field. If the material is initially completely demagnetized, and the applied field is increased to some intermediate value and then reversed, the sample is said to be remanence. If no further increase in magnetization results as the field is increased, the material is said to be saturated. Magnetic measurement were carried out to measure the magnetic properties of the samples before and after CO$_2$ beneficiation with the metal and the metal oxide both to assess the nature of conversion the reductnats go through in this process. For this purpose, the technique of vibrating sample magnetometry (VSM) was employed. VSM measures the magnetic moment by moving the sample between two pick-up coils at a frequency of 1 to 100Hz, in a magnetic field strength of up to 160 kAmp/m (20000 Oe).
Chapter 5

Results and Discussion

5.1 Raw Material Characterization

5.1.1 Industrial Oxide Sample

Of the two iron oxide wastes (MIDREX and Nucor-Yamamoto) supplied by the steel industries, the one from MIDREX was used as the conversion reactant in this work. Figure 5.1 shows images of the as-received and ball milled and sieved MID sample.

![MID samples: as-received (left) and ball-milled and sieved through 325 mesh screen (right)](image)

Figure 5.1: MID samples: as-received (left) and ball-milled and sieved through 325 mesh screen (right)
X-ray diffractometry was conducted on the ball milled and sieved sample was for phase identification and the XRD signature is shown in Figure 5.2.

Figure 5.2: XRD pattern of the raw mill-scale waste (MID)

Three major phases, magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$) and wüstite (FeO) were identified. From the peak ratio measurements, magnetite was found to be the most dominant phase in the MID sample followed by hematite a small fraction of wustite. Figure 5.3 shows the morphological features in the processed MID sample; the energy dispersive spectroscopic (EDS) analysis of the same is shown in Figure 5.4; EDS provides rapid semi-quantitative analysis of the sample composition.
The EDS of the mill-scale waste was taken at 5 micron in this work. The sample was placed on stub by using a carbon tape. The sputter coater time was set to be 40 sec. The peak positioned at 2.2 keV was belonging to the gold that has been used to coat the sample in the sputter coater.
From the EDS analysis, the atomic percentages of oxygen and iron (of mill-scale waste) were computed to be 64.18 and 35.85 respectively.

Figure 5.5 shows the magnetic property of the mill-scale waste (MID)

![Magnetic Properties of mill-scale waste (MID)](image)

Figure 5.5: Magnetic Properties of mill-scale waste (MID)

Table 5.1: Magnetic Properties of Raw Material (MID)

<table>
<thead>
<tr>
<th>Hysteresis Loop</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation Magnetization [Ms (emu/g)]</td>
<td>26.8</td>
</tr>
<tr>
<td>Remanent Magnetization [Mr (emu/g)]</td>
<td>3.48</td>
</tr>
<tr>
<td>Coercive Field [Hc Oe]</td>
<td>6328.4</td>
</tr>
</tbody>
</table>
5.1.2 Commercial Iron Oxide Sample

Figure 5.6 and 5.7 shows the XRD and SEM collected on the iron oxide (Fe$_3$O$_4$) sample procured from Alfa-Aesar; hematite is present in trace amounts.

![Figure 5.6: XRD pattern of the commercial iron oxide (Alfa-Aesar)](image)
As can be seen, the commercial iron oxide consists of small particles with uniform particle size that gives it a uniform morphology structure.

5.2 Iron: From Mill-scale Reduction

The mill-scale iron oxide waste received from MIDREX was reduced to nanoscale iron by using hydrazine (N₂H₄) as the reducing agent at 1000 psi pressure and temperature of 100°C in an autoclave. In this work, reduced mill-scale waste is referred to as α-iron. The XRD signature and SEM images of α-iron derived from MID mill-scale is shown in Figures 5.8 and 5.9, respectively.
Figure 5.8: XRD pattern of α-iron derived mill-scale reduction in hydrazine
Figure 5.9: SEM images of α-iron derived from mill-scale reduction in hydrazine
Figure 5.10 shows the EDS α-iron. Quantitative analysis shows the formation pure Fe.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 5.10: EDS signature of α-iron

In the process of reduction of mill-scale waste (MID) it was noticed that the product (α-iron) exhibited higher degree of magnetism than the starting material which was evidenced by its magnetization (M-H) curve.

### 5.3 Conversion of Carbon Dioxide over MIDREX Waste

After ball-milling and sieving, 2g of the MIDREX mill-scale waste was taken in a stainless steel filter (and packed with glass wool. The filter was placed inside quartz reactor tube which in turn was placed in split tube furnace in a uniform temperature zone so as to be at the reaction temperature of 580°C. Carbon dioxide flowing from a compressed gas cylinder at a flow rate of 100 Sccm was made to flow over the millscale sample; the stream exiting the reactor was fed into the gas chromatograph for the identification and quantification of the gaseous products.
Figure 5.11 shows the signals for CO$_2$ and CO both which corroborates the concept of CO$_2$ reduction into CO. At the beginning of the reaction, CO yield was around 7% which further strengthens theoretical assumption of stated in Ch. 3.

Figure 5.11: GC evidence of CO$_2$ conversion into CO over MID sample (size: 2g)

Theoretically, increasing the amount of reactant would increase the yield of CO in the exits stream. Therefore, in the second run 6g of mill-scale waste was used, keeping all other parameters unchanged. The results are shown in Figure 5.12
As predicted, 6g of the mill-scale waste yielded ~ 29% of CO. This experiment was repeated several times for consistency and reproducibility. The results obtained in each case showed reproducible and consistent behavior. Also, it can be readily seen from Figures 5.11 and 5.12 that there is an asymptotic decrease in CO concentration with time. This trend could be explained in terms of steady consumption of the reactant with time. Moreover, in Figure 5.12, the CO level decreased to about 50% of its peak value after about an hour on the stream, whereas the total consumption of the mill-scale waste (MID) takes about 4 hours. This is possibly due to the active reaction of magnetite during the early part of the process. Figure 5.13 shows the XRD pattern collected on the used sample reaction with CO₂.
Figure 5.13: XRD pattern collected on MID sample after the reaction

The microstructural features and energy dispersive spectrum (EDS) of the used sample are shown in Figure 5.14 and 5.15, respectively. It can be readily seen that the morphological features of the used sample are quite different from those in the starting material. Moreover, the EDS analysis yields an elemental distribution that is close to the formula $\text{Fe}_2\text{O}_3$.

Figure 5.14: SEM images of the mill-scale waste after reaction with $\text{CO}_2$
Equation (3.3) shows that magnetite ($\text{Fe}_3\text{O}_4$) transforms into hematite ($\text{Fe}_2\text{O}_3$). However, a comparison of the XRD pattern shown in Figure 5.13 with that for the as-received MIDREX waste (Figure 5.2) does not suggest if the mill-scale sale ($\text{Fe}_3\text{O}_4$) has undergone the envisaged phase transformation after reacting with CO$_2$. Thus, by merely comparing the two XRD patterns, it was not enough to conclude that the resulting compound is hematite in nature. Moreover, the resulting compound was found to be more magnetic than the starting materials. It is well known that hematite is weakly paramagnetic. Therefore, the exceptionally high magnetization characteristic of the product is reminiscent of the possibility that it could be maghemite ($\gamma\text{-Fe}_2\text{O}_3$) rather than hematite ($\text{Fe}_2\text{O}_3$).
Maghemite ($\gamma$-Fe$_2$O$_3$) has the same chemical formula as hematite (Fe$_2$O$_3$) but belongs to the crystal structure of magnetite (Fe$_3$O$_4$) - an inverse spinel with a cubic structure$^{[33]}$. A ready comparison of the magnetic properties of these two phases is made in Table 5.2. The saturation magnetization ($M_s$) of maghemite (product) is about 3 times and the remnant magnetization ($M_r$) two times of the starting material.
Table 5.2: Magnetic properties of the raw oxide material (MID) before and after reaction.

<table>
<thead>
<tr>
<th>Property</th>
<th>Magnetite</th>
<th>Maghemite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation Magnetization [M_s (emu/g)]</td>
<td>26.8</td>
<td>78.70</td>
</tr>
<tr>
<td>Remnant Magnetization [M_r (emu/g)]</td>
<td>3.48</td>
<td>8.21</td>
</tr>
<tr>
<td>Coercive Field [H_c (Oe)]</td>
<td>6328.4</td>
<td>4718.4</td>
</tr>
</tbody>
</table>

5.4 Conversion of Carbon Dioxide over α-Iron Derived From Mill-Scale Waste

2g of α-iron were placed in porous SS filter (pore diameter 6 µm) packed loosely with glass wool and placed in the center of a quartz reactor. The reaction was carried out at 580°C by flowing 100 Sccm of CO_2 through the reactor. The exit stream of the reactor was connected to GC for continuous monitoring of the exit gas composition. Figure 5.17 shows the time dependence of exit gas composition (% CO) in the exit, showing the capability of iron to reduce CO_2 as per the theoretical rationale proposed in Chapter 3.
Figure 5.17: GC evidence of CO$_2$ conversion into CO over α-iron (size: 2g)

To understand the efficacy of using this technology in real-time scenarios, the experiment was scaled up with higher batch size of the reactant. Based on the reaction stoichiometry, it was anticipated that higher batch size of reactant would yield higher level of CO. Thus, experiments were carried out with larger batch size (15g) keeping all other experimental parameters identical. Figure 5.18 shows the conversion of the CO$_2$ by 15g of α-iron.
To preserve phase integrity and prevent oxidization of α-iron, the reactor was ramped up to reaction temperature in an inert background by flowing 100 Sccm of N₂. The reaction was carried out till the % CO concentration in the exit dropped to <1%. The reactor was cooled down to room temperature. An inert medium (100 Sccm of N₂) was flown through the reactor during cooling down stage to preserve phase integrity and facilitate retrieval of the post-reacted sample for accurate phase and microstructural characterization. The post-reacted sample was washed two times with water, followed by two washes in ethanol medium, and one wash with acetone.
5.5 Utilization of Carbon Dioxide via Mill-Scale Waste Iron Oxide

It was stated in Chapter 3 that magnetite (Fe₃O₄) and iron (Fe) could potentially convert carbon dioxide and water vapor into a mixture of CO and H₂ (syngas). The ability of α-iron (made from mill-scale waste) to reduce CO₂ to CO has been demonstrated by means of the above experiments. Figure 5.19 shows the schematic of the setup used for the conversion of CO₂ and H₂O into syngas which was subsequently used as a feed for a single-button SOFC operating at 650°C.

Figure 5.19: Schematic of the setup used for conversion of CO₂ and H₂O into syngas

CO₂ gas was bubbled through water bath whose temperature could be manipulated to vary the amount of water vapor (and hence its vapor pressure) in the gas stream, before it enters the reactor containing either the metal or the metal oxide. All parameters were kept identical to the previous experiments. The stream exiting the reactor was led into the single-button SOFC maintained at 650°C and the open circuit voltage (OCV) was monitored. The efficiency of the SOFC running on the fuel from CO₂ and H₂O conversion was compared with that running on streams of H₂ and CO.

Figure 5.20 shows the performance of the SOFC running on the stream exiting the reactor through which humidified CO₂ stream was passed.
Figure 5.20: Performance of a button-cell on the humidified CO$_2$ stream converted into syngas

The same reaction condition was applied on the commercial iron. Figure 5.21 shows the SOFC performance using commercial iron.
In Figure 5.21, the SOFC output initially reached its theoretical limit with syngas as the feed and was only slightly different from that with pure H\textsubscript{2} feed. The maximum OCV of the SOFC using H\textsubscript{2} was 0.98V. When the reactor downstream (CO + H\textsubscript{2}) was fed to the fuel cell, the OCV was 0.96V. This indicates that the fuel cell reached its maximum efficiency when it was running with syngas.

To further evaluate the validity of the concept in a real-world-like conditions, exhaust of a 600 cc Honda engine was fed to a reactor packed with the magnetite powder and the exit stream was led into the anode of a single button SOFC operated at 650°C. The experimental setup used for this evaluation is shown in Fig. 5.22.
5.6 Evidence of Water Conversion into Hydrogen

The study evaluating the performance of the SOFC using pure hydrogen produced via metal steam reforming reaction. In this work, the hydrogen was generated by passing a water vapor into the reactor using α-Fe as the reactant. The outlet of the reactor (H$_2$) was fed to the SOFC. Figure 5.23 shows the performance of SOFC as a function of time using water vapor from a water bath.
The SOFC output was increased as the water bath temperature increased. At
60°C, the OCV was almost 0.5 V. By increasing the water bath to 75°C, the OCV value
reached more than 0.95 V.
A comparison of the fuel cell output under engine exhaust conditions with those using
other feeds is presented in Figure 5.24; the fuel cell operated at 83.9% efficiency with the
engine exhaust. The first and second bars on the Figure are pure H₂ and CO. Both gases
were fed to the fuel cell direct from the tank to maintain theoretical values of the fuel cell
efficiency.
In all the above cases, the fuel cell response under „no load’ condition (OCV) was continuously monitored, and as could be seen, it shows a good correlation of the operational efficiency of the reactant. The higher OCV in the case of humidified CO₂ stream could be attributed to the reduction of water vapors; presence of H₂ in the gas stream, though in small concentration, accentuated the cell performance. Thus, it is reasonable to conclude that a mixture of CO₂ and H₂O (both of which are potent greenhouse gases and are the final products of a combustion process) could be converted into syngas (CO+H₂) – which can either be used as a combined feed for SOFC or can be catalyzed into liquid fuel via Fischer-Tropsh synthesis.
Chapter 6

Conclusions and Recommendations

The raw material (mill-scale) that has been used in this work was a low cost item. Moreover, mill-scale can account for up to about 6 weight percent of the total iron used in the process of making steel. Mill-scale is very plentiful; during one year, around 18.6 million Metric tons were produced. Around 80% of the mill-scale goes to landfills. Using a material like mill-scale to mitigate green house gas can reduce the operational cost of the process. On the other hand, mill-scale waste showed a great conversion of CO$_2$ into CO. The conversion was 1:1 molar basis. Based on the equation 2.3 and 2.4, every 1MMt of the mill scale waste can convert 2MMt of CO$_2$ into 1.2MMt of CO.

By comparing the purities of mill-scale waste with the Fe$_3$O$_4$ received by Alfa-Aesar, we found that both samples are most likely identical in phase identity. The mill scale waste treatment was ball-milling and sieving, which does not add much to the process cost. The difference between the samples was in the morphology. This difference was due to the particle size and the production process.

A study has been made by Kaplan to convert CO$_2$ into CO by electrolysis of molten lithium. He mentioned that during a period of hundreds of hours, the Faradaic efficiency of the process at 900°C was close to 100\%$^{[34]}$. 
In our work, both mitigation and utilization was made at reaction temperature of 580°C. Mill-scale waste from the steel industry succeeded in mitigating CO₂ gas at 580°C. Moreover, the reduced mill-scale (α-Fe) was able to convert greenhouse gas (CO₂ and H₂O) into syngas (CO and H₂). The syngas that was fed to the SOFC which operated without load at 650°C was able to produce 0.98 OCV. This indicates that this concept can partially feed itself by utilizing the SOFC output. The consumed reactant in this process was found to be maghemite (γ-Fe₂O₃). Maghemite can be used for biomedical applications, magnetic recording, magnetic refrigeration, sensing, and catalysis. In addition, the spent reactant could be regenerated under mild reduction using low quality syngas. Moreover, it could be used in the manufacturing of ferrite (MFe₂O₄) components, due to its highly magnetic behavior.

The value of this investigation could be increased by doing a feasibility analysis on power plants using coal or syngas as their feeds. It is suggested a systematic study be carried out by doing a market analysis of the amount of CO₂ released by a typical utility company on an annual basis and outlining the size and cost of an auxiliary system that would beneficiate CO₂ by the technique developed in this work.
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