STUDY OF OXIDATION AND REDUCTION REACTIONS IN IRON-SILICA MAGNETICALLY STABILIZED POROUS STRUCTURES

By

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<td>$E_a$</td>
<td>Activation energy</td>
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<tr>
<td>$\alpha$</td>
<td>Apparent volume fraction</td>
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<td>$h$</td>
<td>Bed height</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
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<td>$f(x)$</td>
<td>Dimensionless function defining reaction mechanism</td>
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<td>$h_0$</td>
<td>Initial bed height</td>
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<td>$H$</td>
<td>Magnetic field intensity, A/m</td>
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<td>$B$</td>
<td>Magnetic field intensity, G</td>
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<td>$U_{mf}$</td>
<td>Minimum fluidization velocity</td>
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<tr>
<td>$M$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of reactive substrate</td>
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<tr>
<td>$d_p$</td>
<td>Particle size</td>
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<td>$dP^*$</td>
<td>Pressure drop (non-dimensional)</td>
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<tr>
<td>$k_o$</td>
<td>Pre-exponent</td>
</tr>
<tr>
<td>$\dot{r}$</td>
<td>Rate of reaction</td>
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<tr>
<td>$A$</td>
<td>Rate constant</td>
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<tr>
<td>$U_o$</td>
<td>Superficial velocity</td>
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<tr>
<td>$\dot{Q}$</td>
<td>Volumetric flow rate</td>
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<tr>
<td>$V$</td>
<td>Volume of the bed</td>
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Coal has been major source of energy since age of industrial revolution. In recent years, increase in pollution has forced the researchers to invent technologies to convert chemical energy of coal into clean fuels. Thermochemical looping of metals to generate hydrogen by two-step splitting of water is one of such prominent technologies. Current work focuses on study of reaction kinetics of redox reaction in two-step water splitting process. A novel concept of iron silica Magnetically Stabilized Porous Structure is introduced to enhance hydrogen production over consecutive cycles. A one-dimensional isothermal kinetic model is proposed to analyze reaction kinetics of oxidation step and key kinetic parameters including activation energy, pre exponent and order of reaction are determined. A reduction step is studied with different reducing agent including carbon monoxide, hydrogen and syngas. Similar to oxidation step, a kinetic model is proposed to explain reaction kinetics of reduction step with hydrogen as a reducing agent. Reduction step is characterized by coexistence of different reactions. Kinetic model is calibrated with experimental data to determine activation energy, pre exponent and order of reaction for each reaction. A reaction mechanism is identified for each reaction and transition in mechanism is observed. The technology developed at
laboratory scale is tested at scaled up reactor. The experimental results are in agreement with the inferences drawn in laboratory scale analysis and indicate that the technology can be scaled up successfully. An attempt is made to synthesize high surface area reactive material via deposition of iron on alumina particles, to enhance the hydrogen production. Although there is a scope for improvement, this technology has shown excellent performance based on rate of hydrogen generation per unit mass of iron.
CHAPTER 1
INTRODUCTION

Coal has been prime source of energy in ‘post- industrial revolution’ era. Even after onset of crude oil in last century, coal has retained its significance in modern world. The role of coal in today’s energy scenario can be underlined by the mere fact, that in year 2010, coal contributed to 21% of primary energy sources in US, most of which was used for electricity generation. In same year, almost 48% of electricity was generated using coal as a fuel. Abundance of coal reserves compared to crude oil has made it an economically favorable energy source. This prime energy source is now being considered as prime source of environmental pollution as well. The abundant use of coal releases large amounts of CO$_2$ in the atmosphere which has lead to the problem of global warming and climate change. It is now a challenge to maintain the status of coal as a prime source of energy for its inherent benefits mentioned earlier and at the same time keep a check on environmental pollution. Thus emphasis is being given on using the chemical energy in the coal in alternative ways rather than directly burning it; coal conversion to hydrogen is one of the steps being taken in that direction.

In recent years, hydrogen has attracted attention of researchers as a potential alternative to existing fuels for its high heating value and clean combustion. Hydrogen can be directly used as fuel for combustion or can be used in fuel cells to convert chemical energy into electricity. It can be combined with carbon monoxide to convert into hydrocarbon fuels (alcohols) using a Fischer-Tropsch reaction. The focus of this work is two-step water splitting process in which water is split using a reactive substrate to generate high purity hydrogen in the oxidation step, followed by the reduction of the oxidized substrate using a reducing agent including carbon monoxide and hydrogen.
Attempts are being made to use various metal oxides (-iron oxide being most favored for its abundance in nature) as reactive substrate in this looping process.

A major challenge is to maintain the reactivity of the reactive material and exhibit consistent production of hydrogen at a rate which will be economically viable. The metal oxides have tendency to undergo sintering when subjected to repeated redox (reduction – oxidation) cycles which reduces surface area available for the reaction. Various solutions were suggested to counter this problem; such solutions include the use of ceramic particles including silica and alumina as secondary material, addition of single – double metal additives like Mo, Zr, Al, Mo-Zr, operating in fluidized state thereby breaking the bond established during sintering. Although these methods can be a potential solution to a problem of sintering; they were examined in the temperature range of 300-600 °C and no knowledge is available about their feasibility at higher temperature. Thus the challenge is to develop a technology that can facilitate hydrogen production at higher temperature (~800 °C) over consecutive cycles without affecting the active surface area available for chemical reaction.

A novel concept is introduced to synthesize, magnetically stabilized iron silica porous structure. The ferromagnetic property of iron is capitalized wherein iron particles are aligned in a pattern forming chains along the applied magnetic field; silica particles acting as a buffer between neighboring iron chains. It minimizes sintering between iron particles availing large surface area for chemical reaction to take place. Before materializing this concept it is necessary to study the behavior of the iron silica mixture in the presence of a magnetic field. The experiments are performed for samples with different mass fraction of iron in the binary mixture (iron silica mixture) under different
magnetic field. The effect of magnetic field and mass content of iron in the mixture on minimum fluidization velocity, pressure drop, segregation and bed expansion are studied. This characterization study provided vital information about the conditions under which beds need to be stabilized as well as the operating conditions to be observed during first few redox cycles to keep the bed intact.

The iron silica magnetically stabilized porous structure is subjected to consecutive cycles at 800 °C. It exhibited consistent performance in terms of peak rate of hydrogen generation and total hydrogen yield. A 1D plug flow isothermal model is developed to determine key kinetic parameters including activation energy, pre-exponent and the order of reaction. Experiments are conducted at different operating conditions including reaction temperature, steam inlet molar concentration and steam inlet flow rate. It is proposed that the reaction follows contracting sphere model in the beginning of the oxidation reaction and then transition to the diffusion control model (Jander 3D model), a hybrid model is introduced to encompass the effect of both reaction mechanisms.

The reduction step is an important step in looping process. It reduces the iron oxide back to iron which is made available for consequent oxidation step. Thus effective reduction step is essential for better hydrogen yield. A choice of reducing agent is key for the reduction step and different reducing agent including carbon monoxide, syngas and hydrogen are analyzed for their feasibility as a reducing agent. Initially, carbon monoxide is used as reducing agent. Reduction step using carbon monoxide as a reducing agent is accompanied by coking and formation of iron carbide. These phenomenon are undesirable as they reduce the surface area available for the chemical
reaction, reduce the porosity of the bed which deteriorates the structure and the residual carbon may react with steam in subsequent oxidation step; forming CO/CO$_2$ along with $\text{H}_2$ reducing the purity of the $\text{H}_2$. The coking can be restricted either by increasing the temperature or by adding inert gas to carbon monoxide to reduce its molar concentration; both options are not viable for practical purpose. It is proposed to add another reducing agent to carbon monoxide to reduce coking without affecting rate of reaction; hydrogen being obvious choice. Experiments are conducted to compare carbon monoxide and syngas based on degree of reduction. The performance of reducing agent enhanced with higher hydrogen content; hydrogen exhibited the best performance. It is proposed to use impure hydrogen as a reducing agent in reduction step to generate high purity hydrogen in oxidation step. It is thus imperative to conduct parametric analysis of reduction step using hydrogen as a reducing agent. Experiments are conducted at different operating conditions including reaction temperature, hydrogen inlet molar concentration and hydrogen inlet flow rate. A one dimensional plug flow isothermal kinetic model is developed to determine key kinetic parameters. A reduction step is characterized by coexistence of two reactions; magnetite to wustite conversion and wustite to iron conversion. The reaction mechanism for both reactions is identified and a transition in reaction mechanism is captured with different models. The kinetic model shows good agreement with experimental measurements.

An investigation is conducted to analyze the feasibility of laboratory scale technology to generate hydrogen at industrial scale. The feasibility analysis is performed based on key parameters including the rate of hydrogen generation, overall hydrogen production and repeatability in performance over consecutive cycles. The
development of a larger scale reactor provided one step closer to this final goal. The iron silica magnetically stabilized porous structure exhibits excellent results at large scale reactor. Moreover, experiments are conducted to analyze the effect of different reducing agents on degree of reduction and hydrogen yield; reducing agent analyzed vary from pure hydrogen to syngas with varying composition. The results are in congruence with the laboratory scale analysis.

A novel method is introduced to enhance the surface area of reactive substrate via deposition of iron on alumina particles. The procedure to synthesize high surface area reactive material is explained in detail. The reactive substrate is subjected to consecutive redox cycles at different reaction temperatures; 800 °C, 900 °C and 1000 °C. The peak rate of hydrogen generation and rate of reaction is excellent and the material shows repeatability in performance indicating that the material has successfully inhibited sintering even at higher temperatures. The performance comparison is conducted between high surface area reactive material and iron –silica MSPS; former performs better in terms of peak rate and total yield of hydrogen.
CHAPTER 2
FLUIDIZATION CHARACTERISTICS OF IRON-SILICA BED UNDER MAGNETIC FIELD

The first step towards synthesis of magnetically stabilized iron silica structure is to study bed characteristics under different operating conditions including content of ferromagnetic material (will be alternately called iron in the scope of current study) and applied magnetic field. The bed characteristics are analyzed based on minimum fluidization velocity, pressure drop, bed expansion, and segregation. It is necessary to avoid segregation, formation of cracks and channeling or slugs in the bed as it would adversely affect the hydrogen generation. The pressure drop in the bed increases the operational cost and hence it is interesting to see effect of magnetic field on pressure drop across the bed. The bed characterization provides vital information regarding the operating conditions to be observed during magnetically stabilizing the iron silica structure for desired performance in terms of hydrogen generation.

The fluidization characteristics of a particle bed have been extensively studied by researchers. Minimum fluidization velocity is a demarcation between a fixed bed and a fluidized bed. Leva et al. [1], Rowe and Henwood [2], along with many other researchers have attempted to correlate the minimum fluidization velocity with particle size, density and fluid properties. The basis for modeling is either based on fixed bed pressure drop models or purely empirical correlations. Similar attempts were made by Goossens et al. [3], Cheung et al. [4] for binary mixtures which have more relevance in the present study. Thonglimp [5] made an attempt to validate some of the correlations by comparing them with experimental data; the deviation was evaluated. Pressure drop
across the bed for $U_o < U_{mf}$ (fixed bed) can be explained by the correlation suggested by Ergun [6].

Properties of the particles have significant impact on fluidization characteristics of the bed. Geldart [7] made a general classification of the particles based on their size ($d_p$) and density difference ($\rho_p - \rho_f$), into four different categories. Even though it is premature to assume that particles in the same category would exhibit similar fluidization characteristics, Geldart’s classification provides basic guidelines for the selection of the particle size.

Alina-Violeta et al. [8] studied the effect of magnetic field on the stability of mono-component bed comprising of ferromagnetic particles. The authors proposed that the magnetic field postponed the slug formation and outbreak intensity was low. A stability diagram was formulated which could assist in a design of fluidized reactor. A similar study was performed by Thivel P.X. et al. [9] for the mixture of magnetic and non-magnetic particles under a transverse magnetic field. The magnetic field was found to impact bed stabilization, bed expansion as well as stability. Rosensweig [10] found that the increase in content of nonmagnetic particles in the mixture decreases $U_T$ (transition velocity, close to $U_{mf}$, termed introduced by Rosensweig). Rosensweig [10] and Fillippov[11] studied the fluidization characteristics under the axial magnetic field. Fillippov [11] studied the phase diagram (magnetic intensity v/s flow velocity) and claimed that in case of ‘magnetization first’, the minimum fluidization velocity is independent of magnetic field intensity. The claim was then corroborated by Rosensweig [10]. As compared to the vast information available about the fluidization characteristics, there is a scarcity of studies that deal with the magnetic stabilization of
binary mixtures of magnetic and non-magnetic particles under a transverse magnetic field. The attempt is made to focus upon this area of interest.

2.1 Experimental Setup

Figure 2-1 shows the experimental setup. The quartz tube, 4.6 cm in diameter, 45 cm in length with inbuilt frit serves as a fluidization chamber. The gland is sealed with silicon O-ring fitted at the bottom of the tube. Air is used as a working fluid. An air dryer is fitted in the gas line so as to avoid any moisture entering the bed and settling there, thereby affecting the fluidization characteristics in an undesirable manner. A needle valve controls the flow of the air entering the chamber. Alicat-20 SLPM flow-meter is installed in line with the needle valve to measure the flow rate of the air. An inclined manometer is installed to measure pressure drop across the bed.

Figure 2-1. Experimental Setup: Fluidization Characteristics of iron silica mixtures under magnetic field
The magnetic field is applied by using permanent magnets. The graduated rail is installed on either side of the chamber. The magnets are installed on the rail in a manner in which they can slide symmetrically in the transverse direction and thereby generating a magnetic field with different field strength across the bed. A Gauss meter (Model GM-2, AlphaLab, Inc.) is used to measure the field strength of the magnetic field at the center plane of two magnets situated at different distances.

Another small magnet is placed near the exit of the chamber in order to trap the escaping iron particles, if any.

2.2 Material

Iron (Hoeganaes Corporation, Ancor MH-100) is used as ferromagnetic material while silica particles are used as supporting material. The sample is a mixture of iron and silica at different volume fractions. The size range of iron and silica particles is chosen in a manner as to have their minimum fluidization velocity close to each other. The size of iron particles ranges from 63 to 75 μm while that of silica particles ranges between 106 to 125 μm.

<table>
<thead>
<tr>
<th>Table 2-1. Properties of magnetic and non-magnetic material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Silica</td>
</tr>
</tbody>
</table>

2.3 Experimental Procedure

The material is loaded on the frit carefully without introducing any external disturbances as it would change porosity of the bed. The initial height of the bed is
recorded. The magnets are then installed on the rails at specific distance so as to have desired magnetic field across the bed. The chamber is always at the center plane with respect to the magnets. The air is passed through the bed at a desired flow rate. For each flow rate, corresponding pressure drop across the bed as well as expansion of the bed is recorded. The bed exhibits different phenomenon such as bubbling, channel formation, segregation and formation of slugs. These phenomena are recorded for the particular flow rate and magnetic field strength. The particular sample is subjected to different magnetic field strength, and similar observations are recorded. The procedure is repeated for six different mixtures of iron and silica.

Table 2-2. Binary Mixtures with varying apparent volume fraction of iron

<table>
<thead>
<tr>
<th>Binary Mixture</th>
<th>Apparent Volume fraction of Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (Pure Silica)</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.667</td>
</tr>
<tr>
<td>6</td>
<td>1.0 (Pure Iron)</td>
</tr>
</tbody>
</table>

2.4 Results and Discussion

2.4.1 Pressure drop

The experiments are conducted with six different mixtures of iron and silica with different apparent volume fraction of iron, ranging from pure silica to pure iron (Table 2-
Each sample is subjected to different magnetic fields ranging from 0 to 75.13 Gauss (Table 2-3). The pressure drop was normalized by the weight of the bed and superficial velocity was normalized by minimum fluidization velocity of the mixture. The dimensionless pressure drop (dP*) across the bed was plotted against the dimensionless superficial velocity (U*). The pressure drop increases linearly with velocity as long as bed is fixed. Once minimum fluidization velocity (U_{mf}) reached the pressure drop varied with velocity as predicted by theoretical analysis.

Table 2-3. Different magnetic field intensity (B and H) applied across the binary mixture.

<table>
<thead>
<tr>
<th>No.</th>
<th>Magnetic Field Intensity, B (Gauss)</th>
<th>Magnetic Field Intensity, H (A/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10.33</td>
<td>822.06</td>
</tr>
<tr>
<td>3</td>
<td>23.85</td>
<td>2032.469</td>
</tr>
<tr>
<td>4</td>
<td>33.54</td>
<td>2693.777</td>
</tr>
<tr>
<td>5</td>
<td>75.13</td>
<td>5978.832</td>
</tr>
</tbody>
</table>

Figures 2-2, 2-3 and 2-4 indicate that, qualitatively, this behavior remained unaltered under different magnetic fields or with different mass fraction of ferromagnetic material (iron). Although experimental measurements of pressure drop at different superficial velocity follow the theoretical estimation; a close observation reveals a peculiar pattern for U> U_{mf}, with varying magnetic field and/or mass fraction of iron. For a given binary mixture, with increase in magnetic field strength from 0 to 75.13 Gauss, pressure drop shows oscillations. Similarly, for constant magnetic field, with increase in
mass fraction of the iron in the sample, the oscillations in the pressure are observed (Figures 2-5 & 2-6).

![Figure 2-2](image1.png)

**Figure 2-2.** Dimensionless pressure drop plotted against dimensionless superficial velocity for binary mixtures under magnetic field intensity, 0 G.

![Figure 2-3](image2.png)

**Figure 2-3.** Dimensionless pressure drop plotted against dimensionless superficial velocity for binary mixtures under magnetic field intensity, 23.85 G.
The behavior can be explained based on, particle – particle and particle-wall interactions with changing magnetic field and/or mass fraction of iron. In the presence of the magnetic field, the ferromagnetic particles experienced the force of attraction, resulting in better contact between the particles. Even though all the iron particles may not be aligned one after another in the bed, the force of attraction can be experienced through neighboring non-magnetic (silica) particles. Similarly, the iron particles at the wall experience the force of attraction and results in better particle – wall contact. On a broader spectrum this can be seen as a mesh of ferromagnetic particles with silica particles trapped in between. As air flows through this mesh, the drag force tries to unsettle it while magnetic force and frictional force on account better particle-particle, particle-wall interaction, opposes this drag force. At very low magnetic field (10.3 Gauss, 23.85 Gauss) the drag force is dominant and pressure drop is constant without any major fluctuations. But as the strength of the magnetic field increases (33.54 Gauss, 75.13 Gauss), the magnetic and friction force is dominant, that oppose the flow
of air through the bed. As flow rate is increased, the pressure drop increases until a point is reached where the flow creates a disturbance in the bed in the form of channel, crack, slug formation or temporary fluidization. As flow finds its way through the bed, pressure drop decreases. This phenomenon is repeated in a cyclic manner leading to oscillations in the pressure drop across the bed.

Figure 2-5. Dimensionless pressure drop (dP*) plotted against dimensionless superficial velocity (U*) for Fe\(\alpha_{Fe}\) = 1.0, under different magnetic field intensity.

Figure 2-6. Dimensionless pressure drop (dP*) plotted against dimensionless superficial velocity (U*) for Fe\(\alpha_{Fe}\) = 0.5, under different magnetic field intensity.
2.4.2 Segregation

Binary mixtures exhibit this phenomenon when subjected to fluidization, primarily due to variation in particle size and density. These parameters govern the minimum fluidization velocity of the particles and consequently have greater impact on the segregation. Typically, the smaller particle is segregated at top of the bed, referred to as floatsam, and larger particles settle at the bottom, referred to as jetsam. If the particles of different component experience variation in a density, heavier components settle at the bottom, jetsam and lighter particles are accumulated at top as floatsam. Al Dibouni and Garside [12] did a study on the effect of particle size distribution on segregation. It shows that for the ratio,

$$d_R = \frac{d_{\text{Largest Particle}}}{d_{\text{Smallest Particle}}} < 2.2$$  \hspace{1cm} (2-1)

the mixture is well mixed. The voidage too has impact on mixing and the maximum mixing occurs in the range 0.6 to 0.8. The ratio, $d_R$, proposed by Al Dibouni and Garside [12], for the mixture under consideration is,

$$d_R = \frac{125}{63} = 1.98 < 2.2 .$$

Thus based on particle size if iron and silica it can be speculated that there is minimum segregation in the iron silica mixture. But there is significant density variation between components of binary mixture, 7.874gr/m$^3$ for iron and 2.65gr/m$^3$ for silica. Thus there are chances of iron getting settled at the bottom of the bed (jetsam) and silica getting accumulated at the top of the bed (floatsam) leading to segregation.

With this background, it is interesting to analyze segregation for the binary mixture under consideration, given a fact that the magnetic field strength and mass
fraction of ferromagnetic material will have significant role in the segregation. The segregation for different magnetic field strength and for mixtures with different mass fraction of ferromagnetic particles was analyzed. For the particular binary mixture, as magnetic field increased the segregation was observed at higher flow rate. This behavior can be explained based on the fact that magnetic force acts on iron particles alone and does not impact silica particles. Thus for the air flow passing through the bed, it is easier to carry silica particles with it as opposed to the iron particles. But with increasing magnetic field strength, inter-particle forces increase and the mesh of ferromagnetic particles gets stronger. Though magnetic forces do not have any direct impact on silica particles, the silica particles find it difficult to get carried along with the flow because they are interstitially squeezed by magnetic particles. Thus with increasing magnetic field the segregation is observed at higher flow rate at which drag force associated with air flow is strong enough to carry lighter, non-ferromagnetic silica particles with it.

Similarly, for the same magnetic field strength, as silica content increases, the segregation is observed at lower flow rates. As silica content in the bed increases (mass fraction of ferromagnetic particles decreases) the inter-particle forces become weak making it easy for air to carry silica particles with it.

It is particularly observed that, segregation is assisted by the formation of the channels. Channels provide a pathway for the flow which primarily carries silica particles with it and deposits it on the surface of the bed. Likewise channeling, bubbling and fluidization enhanced segregation.
2.4.3 Minimum Fluidization Velocity

Minimum fluidization velocity is a velocity at which the weight of the bed is balanced by the drag force applied by the fluid. If the flow exceeds this velocity, the bed residing in ‘fixed bed’ state enters the state of fluidization. In reality, the entire bed is not set to a state of fluidization. Even at \( U > U_{mf} \), the part of the bed will be in a state of fluidization while a portion of bed remain in fixed bed state. As it is a demarcation between fixed bed and fluidized bed, the measurement of \( U_{mf} \), is possible from the dP-U plot (Figure 2-7).

![Graph](image)

Figure 2-7. Theoretical plot of pressure drop against superficial velocity.

The minimum fluidization velocity for all the samples was measured under different magnetic field strength. The variation of \( U_{mf} \) with magnetic field strength (H) was plotted for all the samples. The minimum fluidization velocity is fairly constant under different magnetic field strength and does not show any significant dependence; similar observation was made by Filippov [11]. The minimum fluidization velocity shows some variation with change in mass fraction of ferromagnetic material (Figure 2-8). As the mass fraction of ferromagnetic material decreases, the minimum fluidization velocity decreases. The reduction can be attributed to the increase in silica content which has lower density as compared to iron. Similar observation was made by Rosensweig [10].
An attempt was made to compare the experimental measurement with the analytical models. For current study, models proposed by Goossens et al. [3] and Cheung et al. [4] are chosen.

Figure 2-8. Minimum fluidization velocity plotted against magnetic field intensity for binary mixtures with different $\alpha_{Fe}$.

**Goossens model**

$$U_{mf} = \frac{\mu}{\rho_g d_p} \{ (33.7^2 + 0.0408\rho_g \alpha_{Fe})^{0.5} - 33.7 \}$$  \hspace{1cm} (2-2)

As iron silica mixture contains particles with varying size range and density, average particle size and density are used based on the formula suggested by Gossens et.al [3]. The average particle size is given as,

$$\bar{d}_p = \frac{R \rho_f (d_p)_F (d_p)_j}{\rho_f}$$  \hspace{1cm} (2-3)

where,

$$R = (1 - \bar{X}_F)\rho_f (d_p)_F + \bar{X}_F \rho_j (d_p)_j$$  \hspace{1cm} (2-4)

$$R_\rho = (1 - \bar{X}_F)\rho_f + \bar{X}_F \rho_j$$  \hspace{1cm} (2-5)
And, the average particle density is,

\[
\frac{1}{\rho_P} = \frac{X_F}{\rho_F} + \frac{1 - X_F}{\rho_j}
\]  

(2-6)

**Cheung model**

Cheung suggested the expression for minimum fluidization velocity of the mixture based on minimum fluidization velocity of individual components. The expression is represented as:

\[
U_{mf} = [U_{mf}^F \left( \frac{U_{mf}^P}{U_{mf}^F} \right)]^{X_P^2}
\]  

(2-7)

\(U_{mf}^F\) is minimum fluidization velocity of particles that fluidize at lower velocity; \(U_{mf}^P\) is minimum fluidization velocity of particles that fluidize at higher velocity; \(X_P\) is the mass fraction. Figure 2-9 shows comparison between the analytical models and experimental measurements. Goossens model significantly under-predicts minimum fluidization velocity; whereas Cheung model shows good agreement.

![Figure 2-9. Comparison between experimental data and analytical models for minimum fluidization velocity](image-url)
2.4.4 Bed Expansion

Figure 2-10 shows bed expansion (h/h_o), plotted v/s dimensionless superficial velocity (U^*), for different magnetic field intensity. In fluidized bed region, the bed expands linearly with velocity. The plot indicates that the expansion starts at the same velocity for different magnetic field.

Figure 2-10. Bed expansion (h/h_o) plotted against U^* for binary mixture with \( \alpha_{Fe} = 0.333 \) under varying magnetic field intensity.

The bed expansion is affected by the magnetic field intensity and mass fraction of iron particles. Especially higher mass fraction of iron has greater impact assisted by magnetic field intensity.

It will be interesting to observe two cases in this context; samples with \( \alpha_{Fe} = 0.667 \) and \( \alpha_{Fe} = 1.0 \) (Figure 2-11 and 2-12). Typically, the structure developed cracks with increase in the flow rate and the tendency increased with increase in magnetic field. At magnetic field intensity of 75.13 G, the crack widened leading to slug formation. The slug was carried by the flow; and then dropped back on the lower part of
the structure (or the fret in case entire bed is lifted by the flow). The behavior can be observed on the bed expansion vs. velocity plot.

Figure 2-11 Bed expansion ($h/l_o$) and dimensionless pressure drop ($dP^*$) v/s $U^*$ for binary mixture with $\alpha_{Fe}=0.667$ under magnetic field intensity of 75.13 G.

The formation of slugs was not observed as iron content decreased. Moreover, at lower $\alpha_{Fe}$ values, there was no significant change in bed expansion characteristics with changing magnetic field changes, indicating stronger impact of non-magnetic particles. Although the bed expansion increases linearly with superficial velocity; the close observation of the plot reveals another interesting characteristic of bed expansion. The expansion of the bed takes place in a stepwise manner.
Figure 2-12 Bed expansion ($h/h_o$) and dimensionless pressure drop ($dP^*$) v/s $U^*$ for binary mixture with $\alpha_{Fe}=1.0$ under magnetic field intensity of 75.13 G.

This behavior has close association with pressure drop characteristics. As mentioned in the previous section, for $U_o > U_{mf}$, the pressure drop shows cyclic fluctuations with superficial velocity and the bed expansion synchronizes with these fluctuations as shown in figure 2-13. It was observed that as the pressure drop increased, there was little or no bed expansion. At particular superficial velocity, bed was unsettled via cracking, channel formation or temporary fluidization, and the bed adjusted itself to more stable state. During this process, a reduction in pressure drop accompanied by simultaneous bed expansion took place. This relation between pressure drop fluctuations and bed expansion was prominent at higher magnetic field intensity for mixtures with higher $\alpha_{Fe}$. 
Effect of wall roughness

In earlier sections, effect of inter-particle and particle-wall interaction, under varying magnetic field and mass fraction of iron, on bed characteristics including pressure drop and bed expansion has been analyzed. An attempt was made to analyze further, the effect of particle–wall interaction on pressure drop across the bed by varying the wall roughness.

A thin layer of adhesive was applied on the inner wall of the quartz tube and silica was sprinkled on it to increase the roughness of the wall. The quartz tube was then loaded with sample containing iron only. The experimental procedure mentioned earlier was repeated. Figure 2-14, compares pressure drop in the bed for a smooth wall and rough wall under two different magnetic field intensity values, 33.54 G and 75.13. It can be observed that for same magnetic field, the pressure drop for rough wall is significantly higher compared to the smooth wall, under a magnetic field intensity of 75.13 G. It shows significant contribution of wall roughness on pressure drop.
2.6 Summary

The characteristics of fluidized beds are studied under different magnetic field strengths ranging from 0 to 75.13 G and varying $\alpha_{Fe}$ in a binary mixture. Pressure drop across the bed shows cyclic fluctuations in the fluidized bed region. The tendency of cyclic fluctuations increases with an increase in the magnetic field and $\alpha_{Fe}$. The segregation is affected by the presence of the magnetic field. The segregation is shifted to higher flow rates as the magnetic field strength and/or $\alpha_{Fe}$ is increased. The behavior exhibited by pressure drop and segregation is explained based on formation of structure of ferromagnetic material which gets stronger with increasing magnetic field and $\alpha_{Fe}$. Minimum fluidization velocity does not show any significant change at different magnetic field but shows a marginal decrease with decreasing $\alpha_{Fe}$. Bed expansion shows linear increase with superficial velocity for $U_o > U_{mf}$. Formation of slug is observed for binary mixtures 5 and 6 under 75.13 G. Bed expansion is observed to follow a pattern in synchronization with cyclic fluctuations exhibited by pressure drop especially at higher...
magnetic field strength and/or $\alpha_{Fe}$. Increase in wall roughness has a significant impact on pressure drop across the bed and corroborated its role in bed characteristics.
CHAPTER 3
STUDY THE ENHANCEMENT IN HYDROGEN PRODUCTION IN IRON-SILICA MAGNETICALLY STABILIZED POROUS STRUCTURE

In recent years, hydrogen is gaining a significant importance as a promising alternative to conventional fuels for different reasons including high calorific value, clean combustion and its suitability in different technologies including fuel Cell and Fischer – Tropsch reaction. The two-step water splitting process has emerged as a promising technology to generate high purity hydrogen via looping process. Different metals and their oxides are used as a reactive substrate in looping process; iron is most commonly used. The researchers have studied thermochemical looping of iron and key parameters including the rate of hydrogen generation and repeatability over consecutive cycles have been investigated. Attempts were made to study reaction kinetics of oxidation step and evaluate kinetic parameters including activation energy, pre exponent and order of reaction. The two-step water splitting reaction is represented as,

Oxidation Step

\[ 3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \]  \hspace{1cm} (3-1)

Reduction Step

\[ \text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2 \]  \hspace{1cm} (3-2)

Fukase et al. [13] studied hydrogen generation via steam iron reaction. They found a decline in the reactivity of iron oxide in consecutive cycle due to the sintering. Otsuka et al. [14] examined various metal additives and found Al, Mo, Ce to be favorable in preserving the reactivity of iron oxide. Addition of Ir and Rh enhanced the rate of water splitting process, but the sintering could not be avoided. Thaler et al. [15] investigated the life time of iron pallets subjected to repeated redox cycle and observed
the quick decline in the reactivity due to sintering. Use of additives like SiO$_2$ prevented sintering over 20 cycles. Xiaojie et al. [16] studied the effect of single and double metal additives in the iron oxides on the reactivity and ability to prevent the sintering. Fe$_2$O$_3$ – Mo – Zn combination was the most effective as far as hydrogen generation is concerned even though the sample suffered severe sintering. Urasaki et al. [17] compared unmodified iron oxides with palladium and zirconium modified iron oxides. The addition of palladium and zirconia enhanced the hydrogen production and suppressed the sintering. Wen et al. [18] studied the effect of addition of different weight percent of Mo in Fe$_2$O$_3$; Fe$_2$O$_3$-8%Mo proved to be most effective combination. The conventional model and Jander model well fitted the experimental data. Activation energy for unmodified Fe$_2$O$_3$ was 55.53-65.30 kJ/mol and for Fe$_2$O$_3$-8%Mo was 36.17-45.19 kJ/mol. Go et al. [19] compared Fe$_2$O$_3$ with Mn-ferrite and Zn-ferrite in the temperature range of 773K-1173K. The activation energy for oxidation reaction of metal oxides was 57-110 kJ/mol. The diffusion controlled model explains reaction kinetics except for Zn-ferrite.

The major challenge in two-step water splitting process is to counter the sintering of metal powder at high temperature that reduces the active surface area and adversely affects the rate of reaction. Although, use of single and double metal additives and ceramics including silica and alumina did solve this problem to a greater extent; these techniques were tested in the temperature range of 300 – 600 °C and no knowledge is available about their feasibility at higher temperatures (~800 °C). The rate of reaction increases exponentially with temperature; thus it is essential to operate the looping process at high temperature to make it economically viable. Thus, a technology must be
developed to facilitate high purity hydrogen generation at higher temperatures over consecutive cycles.

A novel concept is proposed to synthesize iron silica porous structure via magnetic stabilization. An external magnetic field is applied to align the iron particles in the direction of the magnetic field forming chains. Neighboring chains repel each other due to similar magnetic polarity and the silica particles act as a buffer between them. It allows minimum contact between iron particles and retains active surface area available for chemical reaction. The experimental set up and procedure to synthesize iron silica magnetically stabilize porous structure is explained in the section to follow.

3.1 Experimental Setup

Figure 3-1 shows the experimental configuration for the hydrogen reduction investigation. A 4.6 cm ID quartz tube serves as the reactor. The reactor tube is 45 cm in length and is fitted with an integrated frit that acts as a support for the iron-silica MSPS. The tube can sustain temperatures as high as 1200 °C. It is supported by gland seals at both ends and silicon O-rings are used for sealing. The O-ring can sustain temperatures up to 250 °C and are thus placed far from the heated section. Radiative ceramic heater serves as the primary heater that can raise the bed temperature up to 1100 °C. It is necessary to keep the gas line carrying hydrogen and helium, steam line and reactor itself at sufficiently high temperature to avoid condensation of steam, and drop in bed temperature due in inflow of relatively cold gas. Two rectangular magnets are installed on either side of reactor to help prepare the magnetically stabilized iron-silica structure. A steam line connects the steam generator to the inlet of the reactor. An inline steam generator coupled with a syringe pump generates the steam. The steam
line is heated with a rope heater to maintain steam temperature above condensation point.

A gas line carries various gases to the reactor, including, Ar, H₂ and He. Individual gas lines equipped with a gas flow controller supply a manifold. The manifold is connected to the reactor inlet. A pre-heater is installed on the gas line to maintain it at temperatures in the range of 150-200 °C.

3.1.2 Separation of Product Gases

The gaseous products of the oxidation reaction are comprised of steam and H₂. In order to ensure accurate measurement of H₂ and protect the electronic instruments, steam needs to be condensed and separated from H₂. A shell and tube type condenser is installed which condenses the steam while allowing only H₂ to reach the flow-meter reactor outlet flow meter.

3.1.3 Measurement Devices and Data Acquisition System

A gas flow meter (Alicat) is used to record the flow rate of hydrogen. The output gases are analyzed using a mass spectrometer (Hiden Analytical). The mass spectrometer is calibrated with known flow rates of different gases and serves as alternative device for measuring the H₂ flow rate. A K-type thermocouple is installed to measure the bed temperature. The thermocouple is connected to the PID controller, which controls the bed temperature. A Data acquisition system, comprised of an NI 6211DAQ board coupled with LabVIEW, is used to control various parameters, including temperature and flow rate. The hydrogen flow rate at the reactor outlet is captured as well.
3.2. Experimental Procedure

A 100 gram sample of iron powder (size: 63-75 μ) was mixed with silica powder (size: 75-106 μ) in a 2:1 ratio (silica: iron) by volume. The thermocouple position was fixed at the desired bed location prior to loading the powder into the reactor. Once the powder sample was loaded, the bed was fluidized by passing the inert gas (Ar) through the bed. A well fluidized bed was then subjected to a stationary magnetic field, and the flow of argon was simultaneously cut off. The iron particles aligned themselves in the direction of the magnetic field. The neighboring iron chains repelled each other due to similar polarity, and silica particles settled between neighboring iron chains to act as a buffer.

Figure 3-1. Experimental Setup: Redox reaction in magnetically stabilized iron silica porous structure
As the Curie temperature of iron is 770 °C, it was necessary to keep the bed temperature below this temperature. Moreover, the flow of steam should be low enough to keep bed intact. First oxidation was performed at 600 °C and steam was supplied at a rate 1g/min. After the bed was stabilized, the flow rate as well as the bed temperature was raised to higher value. Then oxidation continued at 800 °C with a steam flow rate of 3g/min.

3.3 Results and Discussion

The iron silica magnetically stabilized porous structure was subjected to 10 consecutive redox cycles at 800 °C. A drop in the rate of reaction was observed for first few cycles; it was attributed to loss of surface area. An un-reacted iron particle has micro-pores and provides high surface area for chemical reaction (Figure 3-2). Over first few cycles, these pores got closed and particles suffered a loss of surface area. Furthermore, the neighboring iron particles in the chains formed along magnetic field sinter to some extent and lead to a loss of chemically active surface area. The structure was stabilized after three cycles and no significant loss in reactivity was observed later on.

Figure 3-3 shows the SEM image of the structure, after 10 redox cycles at 800 °C. The iron chains are aligned along the magnetic field and silica particles act as a buffer between neighboring iron chains; as proposed. In a detail view, it is observed that iron particles are sintered at the contact point but the particles are not completely fused in each other retaining chemically active surface area.

The oxidation was performed at 800 °C with steam inlet flow rate of 3 g/min. The duration for oxidation step varied between 60 – 90 minutes. The reaction was stopped once the hydrogen production dropped to substantially low rate (~0.05 SLPM).
Figure 3-2. SEM image of iron particle before reaction.

Figure 3-3. SEM images of magnetically stabilized iron silica structure after 10 oxidation reduction cycles operated at 800 °C
The oxidation step was followed by the reduction step with carbon monoxide (CO) as a reducing agent. As carbon monoxide has tendency to undergo coking, its flow rate was kept sufficiently low (~0.15 SLPM). Typically, reduction reaction with CO is a slow reaction especially at given flow rate and operating temperature; thus reduction reaction continues for five hours. The mass spectrometer was used to determine amount of CO₂ generated.

Figure 3-4 shows rate of hydrogen generation for cycle 4 to 11. There is no remarkable change in the rate of reaction across the cycles and the structure exhibits excellent repeatability. It corroborates the hypothesis that the magnetic stabilization of iron silica mixture inhibits sintering and retains the active surface area. The variation in the peak is attributed to the variation in carbon monoxide inlet flow rate due to lack of precisely control. This variation in carbon monoxide inlet flow rate alters the degree of reduction that eventually changes the iron available for subsequent oxidation step.

Figure 3-5 shows Degree of Oxidation (DO) for cycles 4 to 11. The degree of oxidation is represented as:

\[
\text{Degree of Oxidation} = \frac{\text{Amount of Hydrogen Generated till Time (t)}}{\text{Stoichiometric Amount of Hydrogen Generated (56.85 lit)}}
\] (3-3)

The Degree of Oxidation resides between 30 to 60% depending upon the degree of reduction in the previous cycle. Although, the duration of the oxidation step varies between 60 - 90 min, most of the oxidation takes place within first 20 minutes. The hydrogen generation drops to significantly low rate after 20 min and Degree of Oxidation starts approaching asymptote. It provides vital information about the duration for which oxidation step should continue before switching to reduction step.
Figure 3-4. Rate of hydrogen generation (SLPM) against time for cycles 4 to 11 at 800 °C with steam flow rate of 3 gr/min.

### 3.5 Performance Comparison

It is now prudent to conduct comparative analysis between the results available in open literature and the one exhibited by iron-silica magnetically stabilized porous structure. A brief overview of some of the important results is as follows.
Wen et al. [18] studied effect of addition of Mo in hematite (Fe$_2$O$_3$) on the catalytic activity and cyclic stability. The Mo content was varied from unmodified Fe$_2$O$_3$ to Fe$_2$O$_3$-5%Mo, Fe$_2$O$_3$-8%Mo and Fe$_2$O$_3$-10%Mo; Fe$_2$O$_3$-8%Mo showed the best performance. The activation energy for oxidation step with unmodified Fe$_2$O$_3$ was 55.53 – 65.30 kJ/mol and for Fe$_2$O$_3$-8%Mo, 36.17 – 45.19 KJ/mol. Maximum operating temperature was 380 °C.

Xiaojie et al. [16] studied the effect of single and double metal additives to Fe$_2$O$_3$. Various metals including Cr, Ni, Zr, Ag and Mo (single additives) and Mo-Cr, Mo-Ni, Mo-Zr and Mo-Ag (double additives) were added by method of impregnation. Mo amongst the single metal additives and Mo-Zr double additives exhibited best performance in terms of enhancement of hydrogen production. The maximum production was observed at 338 °C for Fe$_2$O$_3$- Mo-Zr. Interestingly, this sample experienced severe sintering.
Otsuka et al. [14] examined 26 metal additives to study their effect on reactivity of oxidation step as well as ability to inhibit the sintering. Al, Mo and Ce proved to be effective in preserving the reactivity of the material over the repeated cycles, Mo being the most effective additive. Rh and Ir enhanced the rate of water splitting but could not prevent the sintering.

The best performances reported in the literature are compared with the results of the current work in terms of peak hydrogen generation rate (NCm$^3$/min., gram of Fe). Figure 3-6 shows comparative analysis. The peak values reported by Otsuka et al. [14] are significantly low as compared to current work and repeatability was shown up to 5 cycles only. Although the peak rate of hydrogen generation shown by Wen et al. [18] is comparable with current work; results beyond 4th cycle are not presented. Xiaojie et al. [16] have reported the results for 10 cycles but the peak values are lower and for cycles 8, 9 and 10 peak value dropped significantly while current work exhibited consistent performance.

![Figure 3-6](image-url)

Figure 3-6. Comparison between peak values reported in the literature with the current work for repeated cycles.
3.6 Kinetic Modeling

Experimental analysis of oxidation reaction showed that iron silica MSPS is a promising technology to generate hydrogen over consecutive cycles. It was imperative to conduct a parametric study of oxidation reaction and develop a kinetic model that can serve as an analytical tool to design the reactors for industrial applications. Experiments were conducted at different operating conditions including reaction temperature, steam inlet flow rate and steam inlet molar concentration. They play an important role in determining the rate of reaction and it is prudent to study their impact.

3.6.1 Effect of steam inlet flow rate

An increase in steam inlet flow rate increases the velocity of the species through the structure and reduces the residence time. Thus, an average molar concentration of the steam across the structure increases with increase in steam inlet flow rate, which results in higher rate of reaction. Figure 3-7 shows the rate of hydrogen generation for different steam inlet flow rate at 800 °C. The peak rate of reaction shows substantial increase with steam inlet flow rate.

![Figure 3-7. Rate of hydrogen generation v/s time for different steam inlet flow rate at 800 °C.](image)
It can be observed that the increase in peak rate and overall rate of reaction is significant as steam inlet flow rate is increased from 1 to 3 g/min but there is no substantial increase as steam inlet flow rate is increased from 3 g/min to 4 g/min. As discussed earlier, increase in steam inlet flow rate increases average concentration of steam across the structure and at particular flow rate the structure gets saturated with steam. Any further increase in the steam flow rate has no impact on the rate of hydrogen generation. It is very important to determine this limit for optimal utilization of the steam.

### 3.6.2 Effect of temperature

Reaction temperature has exponential effect on the rate of reaction. Figure 3-8 shows rate of hydrogen generation for different reaction temperature in the range 600-800 °C for steam inlet flow rate of 3 g/min. The peak hydrogen production and rate of reaction shows substantial increase with temperature. The experimental measurement of rate of reaction at different reaction temperature facilitates kinetic
model to determine key kinetic parameters including activation energy and pre-exponent.

### 3.6.3 Effect of steam inlet molar concentration

Experiments are conducted at different steam inlet molar concentration to study its effect on rate of reaction. Figure 3-9 shows rate of hydrogen generation at different steam inlet molar concentration at 800 °C. The molar concentration of steam is varied by mixing helium with steam at the inlet of the reactor; steam molar fraction ranges from 1 to 0.4. The inlet flow rate of the mixture is kept constant for all the experiments. Figure 3-9 indicates that the rate of hydrogen generation varies significantly with steam molar concentration indicating that later has crucial role to play in determining the rate of reaction. The experimental measurements of rate of reaction at different inlet steam molar concentrations facilitates in determination of order of reaction.

![Figure 3-9. Rate of hydrogen generation v/s time at different steam inlet molar concentration at 800 °C](image)

Table 3-1 summarizes the operating conditions observed during experimental measurement of rate of hydrogen generation.
Mehdizadeh et al. [20] developed a one dimensional isothermal plug flow kinetic model for the oxidation step. The kinetic model was implemented to determine key kinetic parameters including activation energy, pre-exponent and order of reaction. They are listed in Table 3-2.

Table 3-1. Summary of the operating conditions observed during the experimental measurement of rate of reaction over consecutive cycles.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Reaction Temperature (°C)</th>
<th>Steam inlet flow rate (g/min)</th>
<th>Steam inlet molar fraction</th>
<th>Parameter of interest</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>3.0</td>
<td>1.0</td>
<td>Activation energy, pre-exponent</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>3.0</td>
<td>1.0</td>
<td>Activation energy, pre-exponent</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>3.0</td>
<td>1.0</td>
<td>Activation energy, pre-exponent</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>1.0</td>
<td>1.0</td>
<td>Residence time</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>3.0</td>
<td>1.0</td>
<td>Residence time</td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>4.0</td>
<td>1.0</td>
<td>Residence time</td>
</tr>
<tr>
<td>7</td>
<td>800</td>
<td>3.0</td>
<td>1.0</td>
<td>Order of reaction</td>
</tr>
<tr>
<td>8</td>
<td>800</td>
<td>2.39</td>
<td>0.8</td>
<td>Order of reaction</td>
</tr>
<tr>
<td>9</td>
<td>800</td>
<td>1.79</td>
<td>0.6</td>
<td>Order of reaction</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>1.19</td>
<td>0.4</td>
<td>Order of reaction</td>
</tr>
</tbody>
</table>

3.7 Summary

A novel, iron silica magnetically stabilized porous structure is a promising technology to generate high purity hydrogen via thermochemical looping of iron oxide over consecutive cycles.
Table 3-2. Reaction constants of kinetic model applied to oxidation step of two-step water splitting process.

<table>
<thead>
<tr>
<th>Activation Energy, Ea (KJ/mol)</th>
<th>Pre-exponent, $k_0$ (s$^{-1}$)</th>
<th>Order of Reaction (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.29</td>
<td>54843</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The procedure to synthesize the porous structure is simple, inexpensive and does not require particular expertise, complex processes or facilities. The material used, iron and silica, is available in abundance which makes it commercially viable technology. The structure has exhibited excellent rate of hydrogen generation and repeatability over consecutive cycles at 800 °C.

The comparative analysis between the results reported in the literature and current work indicates that the performance of the magnetically stabilized iron silica structure is far better in terms of peak rate and repeatability. A 1-D kinetic model developed for the oxidation step is in agreement with the experimental measurements under different operating conditions including reaction temperature, steam inlet molar concentration and steam inlet flow rates. The activation energy, pre-exponent and order of reaction calculated using the kinetic model is 88.29kJ/mol, 54843s$^{-1}$ and 1.2 respectively. The kinetic model is robust and is an excellent analytical tool to design reactors at industrial scale.
CHAPTER 4
STUDY OF REDUCTION STEP TO INVESTIGATE THE PERFORMANCE OF CARBON MONOXIDE, SYNGAS AND HYDROGEN AS A REDUCING AGENT

Reduction of iron oxide is an important step in the two-step water splitting process. In reduction step, iron oxide formed during preceding oxidation step is reduced back to iron. It is then oxidized in subsequent oxidation step to generate high purity hydrogen. Thus effective reduction step must be sought to ensure satisfactory hydrogen yield. There is a wide range of reducing agents including carbon monoxide, hydrogen and syngas. Several studies have been conducted to analyze reduction of iron oxides (magnetite as well as hematite) using these reducing agents. Wagner et al. [21] studied the reduction of hematite using H₂ and proposed the stepwise reduction of hematite to elemental iron through magnetite and wustite. The structural changes due to whisker formation were reported. Pineau et al. [22, 23] studied reduction of hematite and magnetite using hydrogen at different temperatures. The activation energy was reported and the reaction mechanism showed variation above and below the transition temperature. They also compared hydrogen and carbon monoxide and found the former to be a better reducing agent based on reduction rate. The reduction with carbon monoxide was characterized by formation of iron carbide. The presence of intermediate iron oxides was reported. Hsin-Yu Lin et al. [24] studied Temperature Programmed Reduction (TPR) of hematite and suggested the presence two reactions; hematite to magnetite and magnetite to elemental iron. The reactions followed the unimolecular and Avrami - Erofeev models, respectively. Mondal et al. [25] studied reduction of hematite using carbon monoxide in the temperature range 800-900 °C. The presence of carbon and iron carbide was reported. Activation energies reported were in the range 9.97 - 14.65 kJ/mol for the different reactions involved. Bonalde et al. [26] studied the
reduction of hematite using hydrogen, carbon monoxide and a mixture of both gases as a reducing agent. A kinetic model was proposed for a reduction reaction involving each reducing agent. These studies showed that iron oxide was reduced to iron in a stepwise manner indicating coexistence of multiple reactions. Hydrogen was claimed to outperform carbon monoxide and syngas in terms of the rate of reduction.

The choice of a reducing agent plays a crucial role in the success of the reduction step. It not only depends on the rate of reaction and degree of reduction but also pragmatic parameters including availability and cost of a reducing agent. Carbon monoxide, syngas and hydrogen are examined based on these parameters.

4.1 Carbon Monoxide as a Reducing Agent

The reduction of magnetite using carbon monoxide as a reducing agent is represented as:

$$\text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2$$  \hspace{1cm} (4-1)

Carbon monoxide has a tendency to undergo different reaction apart from reduction of magnetite.

$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$$  \hspace{1cm} (4-2)

$$\text{CO} \rightarrow \frac{1}{2}\text{O}_2 + \text{C}$$  \hspace{1cm} (4-3)

$$\text{Fe}_3\text{O}_4 + 6\text{CO} \rightarrow \text{Fe}_3\text{C} + 5\text{CO}_2$$  \hspace{1cm} (4-4)

Equation 4.2 and 4.3 indicate Boudouard reaction (typically known as coking) wherein elemental carbon is deposited on the surface of reactive substrate and reduces the porosity of the structure. It leads to increase in the pressure drop across the
structure and at higher flow rates, structure may get damaged. Equation 4.4 represents the chemical reaction between carbon monoxide and magnetite to form iron carbide.

Equation 4.4 represents the chemical reaction between carbon monoxide and magnetite to form iron carbide.

Figure 4-1 shows the open system solid composition for the reduction of magnetite at 1 bar pressure for varying amount of carbon monoxide: stoichiometric amount (left), 2 times stoichiometric amount (center) and 4 times stoichiometric amount.

Figure 4-1 shows the open system solid composition for reduction of magnetite at 1 bar for different stoichiometric amount of carbon monoxide. It is evident that as stoichiometric amount of carbon monoxide increases, tendency of Boudouard reaction and iron carbide formation increases. Moreover, as reaction temperature increases, the amount of carbon deposited in the structure decreases and no trace of elemental carbon is available at temperatures above 850 °C. Although Boudouard reaction is suppressed with increase in temperature, iron carbide is formed above 750 °C. In succeeding oxidation step, this iron carbide reacts with steam to form gaseous products including carbon monoxide, carbon dioxide and methane. These gaseous product contaminate the hydrogen generated in the oxidation step making it unsuitable for its application in fuel cell technology. Figure 4-2 shows the composition of gaseous products for the steam oxidation of reactive substrate that contain maximum amount of iron carbide. It is
evident that along with hydrogen other gaseous products are generated in oxidation step that reduce the purity of hydrogen, as proposed earlier.

Figure 4-2. Open system gaseous products of steam oxidation of the reactive material with maximum amount of iron carbide at 1 bar for varying amount of steam: stoichiometric (left), 2 times stoichiometric (center) and 4 times stoichiometric.

Experiments are conducted at temperatures 900 °C with carbon monoxide inlet flow rate of 1 SLPM to analyze the effect of coking and carbide formation on the degree of reduction. Figures 4-3 shows the rate of CO₂ generation for cycle 3 to 8 reaction. (All cycles are not included for brevity).

Figure 4-3. Rate of CO₂ generation at 900o C for carbon monoxide inlet flow rate of 1 SLPM.
The peak rate of reaction decreases substantially and a decrease in rate of reduction reaction is observed. This poor performance can be attributed to coking and iron carbide formation. A qualitative analysis was conducted for the sample after 8 consecutive redox cycles to detect the presence of carbon. Figure 4-4 shows the line-scan on the surface of the reactive sample; corresponding signals for different elements including carbon, oxygen, silica and iron are shown in Figure 4-5. It can be observed that there is sharp increase in carbon signal between 5 to 8 μm that corresponds to a line-scan over a grey patch in Figure 4-4. It clearly indicates the presence of the carbon in the reactive sample.

![Line-scan on the surface of the sample to identify presence of different elements.](image)

Figure 4-4. Line-scan on the surface of the sample to identify presence of different elements.
Thermodynamic analysis (Figure 4-1 and 4-2) indicates that coking and formation of iron carbide can be eliminated/reduced either by increase in the reaction temperature or decrease in inlet flow rate and/or inlet molar concentration of carbon monoxide. There is an upper limit imposed on reaction temperature by the reactor design. Moreover, decrease in carbon monoxide inlet flow rate and/or inlet molar concentration would lead to decrease in rate of reaction. A pragmatic solution is to mix another reducing agent with carbon monoxide; thus inhibiting coking without affecting the rate of reduction reaction. The obvious choice of such reducing agent is hydrogen gas. A mixture of carbon monoxide and hydrogen; commonly known as syngas; is a product of coal gasification process. It is industrially standardized, well established process that can serve as reliable source of syngas.

4.2 Performance Comparison between Different Reducing Agents

The composition of a syngas is not fixed but depends upon various parameters including the quality of the coal, operating temperature of gasification process, steam to carbon ratio and steam to air ratio. It is imperative to conduct a preliminary analysis to
understand the effect of varying composition of syngas on reduction step. Experiments were conducted to study the effect of composition of a reducing agent and the total flow rate; at 1000 °C and comparative analysis was performed based on the degree of reduction. Table 4-1 enlists reducing agents with varying composition including carbon monoxide, hydrogen and syngas with two gas compositions; H\(_2\): CO=1:1 and H\(_2\): CO=1:1, by volume.

Table 4-1. A composition of different reducing agents studied for comparative analysis based on the degree of reduction.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>CO (SLPM)</th>
<th>H(_2) (SLPM)</th>
<th>CO(_2) (SLPM)</th>
<th>He (SLPM)</th>
<th>Total Flow Rate (SLPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.45</td>
<td>0.1</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.1</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>6</td>
<td>0.9</td>
<td>0.9</td>
<td>0.2</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>0.9</td>
<td>0.0</td>
<td>0.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 4-6 shows a comparison between different reducing agents (Exp. No. 1-4) based on the degree of reduction. The degree of reduction is defined as,

\[
\text{degree of reduction} = \frac{\text{Amount of product gases generated (lit)}}{\text{Stoichiometric amount of gases generated (lit)}}
\]  

(4-4)

It is evident that, as the hydrogen content in syngas composition increases, the degree of reduction increases significantly. The degree of reduction achieved with
carbon monoxide alone as a reducing agent is 20%. As the hydrogen content in a reducing agent is increased, the degree of reduction increases significantly and reaches to 55% for reduction with hydrogen as a reducing agent. This trend is prominent at higher flow rates (Exp. No. 5-8); degree of reduction with hydrogen is reaching to 85%; and that for carbon monoxide is restricted to 25%. (Figure 4-7).

![Graph showing degree of reduction for different flow rates at 1273 K.]

Figure 4-6. Comparison of \( \text{H}_2 \), CO and syngas (Exp. No. 1-4) based on Degree of Reduction (\%) for different flow rates at 1273 K.

It is counterintuitive to expect hydrogen mixed with equal amount of helium to outperform syngas based on degree of reduction. Helium is an inert gas and does not participate in reduction reaction. The syngas, on other hand, is composed of two reducing agents and expected to exhibit better performance than hydrogen diluted with helium. It can be observed that this premise holds true for initial duration of the reduction reaction during which the degree of reduction with syngas is higher than that of hydrogen; although the difference is not significant. As reaction progresses, syngas failed to perform as expected; hydrogen exhibited much better performance.
This phenomenon can be attributed to coking and iron carbide formation. It is speculated that the carbon monoxide undergoes Boudouard reaction as well as iron carbide formation. It may have affected the ability of syngas to effectively reduce the iron oxide and thus did not perform better than hydrogen. It is a preliminary analysis and detail investigation is required.

It is evident that the hydrogen enriched reducing agent will effectively reduce iron oxide to iron and ensure satisfactory yield of high purity hydrogen in subsequent oxidation step. (It is counterintuitive to use hydrogen as an input the process which is being developed to generate hydrogen itself. The key is the purity of the hydrogen being used as a reducing agent and the purity of hydrogen generated in oxidation step. This aspect is discussed in details in Chapter 8.) Thus it is important to study reduction of iron oxide using hydrogen as a reducing agent.
CHAPTER 5
SOLID STATE REACTION KINETICS OF IRON OXIDE USING HYDROGEN AS A REDUCING AGENT

The investigation of reducing agents including carbon monoxide, hydrogen and syngas indicated that the performance of reduction step is enhanced as hydrogen content in the reducing agent increases. The degree of reduction achieved using pure hydrogen is substantially higher than that with carbon monoxide and syngas under identical operating condition. It is thus imperative to conduct kinetic study of reduction step in iron silica MSPS, using hydrogen as a reducing agent. Experiments are conducted for different operating conditions including reaction temperature, hydrogen inlet molar concentration and hydrogen inlet flow rate. The reduction reaction is characterized by stepwise conversion of magnetite to iron via wustite. Thus reaction kinetics is governed by coexistence of two reactions; magnetite to wustite conversion and wustite to iron conversion. A one-dimensional plug flow isothermal kinetic model is proposed, and a numerical scheme is developed to solve the species transport and substrate conversion equations. The numerical scheme is used as a tool to calibrate the kinetic model, and the critical kinetic parameters, including activation energy, pre-exponent and order of reaction, are determined for both reactions. The reaction mechanism for both reactions is identified, and a transition in the reaction mechanism is captured with different models. The kinetic model shows good agreement with the experimental data for different operating conditions. This study provides an excellent basis for scaling hydrogen reduction reactors to an industrial scale.

The details of the experimental set-up are discussed in section 3.1.
5.1 Experimental Procedure

A 100 gram sample of iron powder (size: 63-75 μ) is mixed with silica powder (size: 75-106 μ) in a 2:1 ratio (silica: iron) by volume. The thermocouple position is fixed at the desired bed location prior to loading the powder into the reactor. Once the powder sample is loaded, the bed is fluidized by passing the inert gas (Ar) through the bed. A well fluidized bed is then subjected to a stationary magnetic field, and the flow of argon is simultaneously cut off. The iron particles align themselves in the direction of the magnetic field. The neighboring iron chains repel each other due to similar polarity, and silica particles get settled between neighboring iron chains to act as a buffer. This inhibits sintering and greater surface area is made available for chemical reaction to take place. Since the Curie temperature of iron is 770 °C, it is necessary to keep the bed temperature below this temperature. Moreover, the flow of steam should be low enough to keep bed intact. First oxidation step is performed at 600 °C and steam is supplied at a rate 0.5 g/min. After the bed is stabilized, the flow rate as well as the bed temperature is raised to higher value. Then oxidation continues at 800 °C with a steam flow rate of 2 g/min. The experiments are conducted at different operating conditions including reaction temperature, hydrogen inlet flow rate and hydrogen inlet molar concentration. Helium is mixed with hydrogen at the inlet of the reactor to change the molar concentration. Table 5-1 lists the operating conditions for the hydrogen reduction reactions.

5.2 Results and Discussion

5.2.1 Effect of Hydrogen Inlet Flow Rate

The hydrogen inlet flow rate increases the convection velocity of the species passing through the structure and reduces the resident time. It leads to increase in the
average concentration of the hydrogen in the structure resulting in increase in rate of reaction. Figure 5-1 shows the rate of steam generation for hydrogen inlet flow rate of 1.5 SLPM and 2 SLPM, at 800 °C. It is observed that the peak rate of steam generation is increased and there is enhancement in rate of reaction with increase in hydrogen inlet flow rate.

![Graph showing rate of steam generation for different hydrogen inlet flow rate.](image)

Figure 5-1. Rate of steam generation for different hydrogen inlet flow rate of hydrogen at 800 °C.

### 5.2.2 Effect of Reaction Temperature

The reaction temperature has significant effect on rate of reaction. The rate of reduction reaction increases exponentially with reaction temperature. The experiments are conducted at different reaction temperatures in the range 800-1000 °C; Figure 5-2 shows the rate of reduction reaction. An enhancement in the rate of reaction is observed with increase in reaction temperature. The experimental measurements at different reaction temperature facilitate measurement of activation energy and pre-exponent.
5.2.3 Effect of Hydrogen Inlet Molar Concentration

Inlet molar concentration of reacting species is another important parameter that governs the rate of reaction. The inlet molar concentration represents the number of moles of the reacting species made available for the reaction; thus rate of reaction increases with increase in hydrogen inlet molar concentration. Figure 5-3 shows the rate of reduction reaction for different hydrogen inlet molar concentration at 800 °C. Molar concentration of hydrogen is varied by adding helium at the inlet of the reactor; the total inlet flow rate is kept constant to avoid variation in resident time. It is observed that the inlet molar concentration significantly affects the reduction reaction in terms of peak rate of steam generation and rate of reduction reaction. These experimental measurements are used to determine the order of reaction.

The analysis of the experimental measurements indicates a sudden change in the slope of the rate of reduction at a particular time. Similar phenomenon was observed by Wagner et al. [21] in the reduction of hematite using hydrogen as a
reducing agent. The change in the slope of rate of reduction was attributed to complete conversion of higher oxide to lower oxides. A detail discussion and its impact on kinetic modelling is discussed in detail in next section.

Figure 5-3. The rate of steam generation for different hydrogen inlet molar concentration at 800 °C.

5.3 Kinetic modelling

Kinetic modeling is important to predict the rate at which the reaction proceeds based on local thermodynamic conditions. It not only provides physical insight into the reaction but also serves as an important tool that can be used for reactor design. The reduction of magnetite using hydrogen as a reducing agent can be represented as,

\[ \text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O} \]  \hspace{1cm} (5-1)

A single step conversion of magnetite to elemental iron is too simplistic to capture the correct kinetics since the reduction of magnetite likely takes place through intermediate steps. As mentioned earlier, researchers identified the presence of wustite during the reduction of magnetite. Thus the reaction sequence for the reduction of magnetite is characterized by the presence of two reactions,
Magnetite-wustite conversion

\[ \text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{FeO} + \text{H}_2\text{O} \]  
(5-2)

Wustite-Fe conversion

\[ \text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \]  
(5-3)

Table 5-1. Summary of operating conditions of reduction reaction in looping cycles.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Reaction temperature (°C)</th>
<th>Inlet flow rate ( \text{H}_2, \text{He} ) (SLPM)</th>
<th>Inlet molar concentration (moles/m(^3))</th>
<th>Parameter of interest</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>1.5, 0</td>
<td>11.36</td>
<td>Flow rate</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>2.0, 0.0</td>
<td>11.36</td>
<td>Flow rate, Inlet molar concentration, Temperature</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>1.5, 0.5</td>
<td>8.56</td>
<td>Inlet molar concentration</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>1.0, 1.0</td>
<td>5.68</td>
<td>Inlet molar concentration</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>0.5, 1.5</td>
<td>2.84</td>
<td>Inlet molar concentration</td>
</tr>
<tr>
<td>6</td>
<td>900</td>
<td>2.0, 0.0</td>
<td>11.36</td>
<td>Reaction temperature</td>
</tr>
<tr>
<td>7</td>
<td>1000</td>
<td>2.0, 0.0</td>
<td>11.36</td>
<td>Reaction temperature</td>
</tr>
</tbody>
</table>

These two reactions occur simultaneously, but their extent and rate of reaction may be different and dynamic in nature. Experimental measurements on hydrogen flow rate reflect the combined effect of both reactions, and it is necessary to develop an appropriate kinetic model that captures the kinetics of both.

5.3.1 Governing equations

The rate of reaction, \( \dot{r} \) (moles/s,m\(^3\)), is the rate of generation or consumption of species, \( k_o \) (s\(^{-1}\)) is a pre-exponent and \( \text{Ea} \) (J/mole) is the activation energy. \( f(x) \) is a dimensionless function that characterizes available surface area and depends on the reaction mechanism, \( x \) is fractional conversion of reactive material, \( C \) (moles/m\(^3\)) is the molar concentration. The subscript \( j \) denotes the species, \( j=1 \) for hydrogen and \( j=2 \) for
steam. The superscript \( n \) denotes the order of reaction. The subscript \( i \) denotes the phase of the oxide substrate, \( i=1 \) for magnetite and \( i=2 \) for wustite.

For an open system, the species transport equation is solved to find concentration of the species along the bed at every instance. Here only gradients along the length of the reactor are considered, which is essentially a plug flow assumption.

\[
\frac{\partial C_i}{\partial t} + U \frac{\partial C_i}{\partial Z} = \dot{r}_i \tag{5-4}
\]

The sink/source term \( \dot{r}_i \), inherently has dependence on the reaction extent, and the substrate conservation of mass is solved to determine \( x \),

\[
\frac{dx}{dt} = \beta_i k_0 \exp(-Ea/RT)f(x_i)C_j^n \tag{5-5}
\]

where \( \beta_i \), is a conversion factor for the oxide substrate, magnetite or wustite,

\[
\beta_i = \left( \frac{1.0}{1.0} \right) \left( \frac{M_i V_{bed}}{m_i} \right) \tag{5-6}
\]

The governing equations are implicitly interdependent and require an appropriate numerical scheme to obtain a solution. The solution requires realistic initial and boundary conditions, and these must be dealt with appropriately.

There are two different considerations for iron oxide distribution that require attention: \textit{macroscopic} and \textit{microscopic} distribution. Macroscopic distribution represents the distribution of mass across the bed as function of bed length. Microscopic distribution is associated with the distribution of iron oxide within a single particle.
5.3.2 Macroscopic distribution of mass

The oxidation step plays an important role in the macroscopic distribution of mass within the reactor bed. During oxidation, the inlet of the bed receives steam with maximum molar concentration and progressively the steam concentration is diluted along the bed length by the production of hydrogen. Thus, during the oxidation step it is more likely that elemental iron near the bed inlet receiving fresh steam is completely converted to magnetite and conversion extent will progressively decline along the bed length due to a decrease in steam concentration. Thus there is a need to estimate the distribution of both magnetite and wustite along the bed following oxidation in order to provide a realistic initial condition needed to solve (5-4 to 5-6). A framework is established to determine a macroscopic distribution of iron oxide in terms of its apparent density ($\rho$). A polynomial is proposed to define the apparent density as a function of length of the bed. Specified conditions (Table 5-2) are identified based on fundamental physics and applied to this polynomial function to determine the unknown coefficients. Ideally, this analysis must be conducted to determine the macroscopic distribution magnetite and wustite in the structure. The experimental measurement of hydrogen generation in oxidation step does not provide any information regarding mass of individual oxide obtained at the end of oxidation step. A thermodynamic analysis of the oxidation step does provide information regarding the probable presence of different iron oxides at the end of reaction, but it is not sufficient to determine mass of individual oxide. Thus a pragmatic approached is adopted to assume presence of single oxide, magnetite at the end of oxidation step.

In dimensionless form the function is represented as,
\[
\rho^* = a\eta^3 + b\eta^2 + c\eta + d
\]  

(5-7)

\(\rho^*\) is dimensionless apparent density and \(\eta (z/L)\) is non-dimensional length of bed. \(\rho^*\) is obtained by normalizing apparent density by \(\rho_{max}\); a maximum apparent density of magnetite attained after complete conversion of iron into magnetite.

**Specified conditions**

1. In oxidation step, the inlet of the structure receives fresh steam with maximum molar concentration. Thus it is proposed that the iron at the inlet is completely converted into magnetite. Thus the apparent density at inlet of the structure is maximum

\[
\rho^*|_{\eta=0} = 1
\]  

(5-8)

2. At the inlet of the structure, \(\eta = 0\) operating conditions of molar concentration and reaction temperature, do not vary significantly.

\[
\frac{d\rho^*}{d\eta} (\eta = 0) = 0
\]  

(5-9)

3. Similarly, at the outlet of the structure

\[
\frac{d\rho^*}{d\eta} (\eta = 1) = 0
\]  

(5-10)

4. Conservation of mass

The initial mass of the magnetite \((m)\) at the beginning of the reduction step is represented as

\[
\int_V \rho \, dV = m
\]  

(5-11)

\(V\) is the volume of the structure which can be represented in terms of area of cross section \((A_c)\) and length of the bed \((L)\)
\[ V = A_c L \]  
(5-12)

Thus,
\[ \int_{z=0}^{z=L} \rho A_c \, dz = m \]  
(5-13)

Initial mass of the magnetite is normalized by the maximum mass of the magnetite \( m_{\text{max}} \) that would be available after complete conversion of iron into magnetite. This maximum mass of the magnetite can be represented in terms of maximum apparent density.

\[ m_{\text{max}} = \rho_{\text{max}} V = \rho_{\text{max}} A_c L \]  
(5-14)

Dividing both sides of above equation by \( m_{\text{max}} \),
\[ \int_{z=0}^{z=L} \frac{\rho A_c \, dz}{\rho_{\text{max}} A_c L} = \frac{m}{m_{\text{max}}} \]  
(5-15)

In dimensionless form,
\[ \int_{\eta=0}^{\eta=1} \rho^* \, d\eta = \frac{m}{m_{\text{max}}} \]  
(5-16)

Table 5-2. Specified conditions to solve unknown constants of the cumulative mass fraction for magnetite.

<table>
<thead>
<tr>
<th>No</th>
<th>Magnetite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \rho^*</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{d\rho^*}{d\eta} (\eta = 0) = 0 )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{d\rho^*}{d\eta} (\eta = 1) = 0 )</td>
</tr>
<tr>
<td>4</td>
<td>( \int_{\eta=0}^{\eta=1} \rho^* , d\eta = \frac{m}{m_{\text{max}}} )</td>
</tr>
</tbody>
</table>

This analysis is conducted for each cycle to define the apparent density distribution function determining the macroscopic distribution of the magnetite at the
beginning of reduction step (Table 5-3). Figure 5-4 shows apparent density distribution
function for cycle 1.

Table 5-3. Apparent density distribution function for each cycle.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Dimensionless, initial mass of magnetite (( \frac{m}{m_{\text{max}}} ))</th>
<th>Apparent density distribution function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.76</td>
<td>( \rho^* = 0.9796\eta^3 - 1.4694\eta^2 + 1 )</td>
</tr>
<tr>
<td>2</td>
<td>0.77</td>
<td>( \rho^* = 0.9388\eta^3 - 1.4082\eta^2 + 1 )</td>
</tr>
<tr>
<td>3</td>
<td>0.79</td>
<td>( \rho^* = 0.8571\eta^3 - 1.2857\eta^2 + 1 )</td>
</tr>
<tr>
<td>4</td>
<td>0.77</td>
<td>( \rho^* = 0.9388\eta^3 - 1.4082\eta^2 + 1 )</td>
</tr>
<tr>
<td>5</td>
<td>0.82</td>
<td>( \rho^* = 0.7347\eta^3 - 1.102\eta^2 + 1 )</td>
</tr>
<tr>
<td>6</td>
<td>0.85</td>
<td>( \rho^* = 0.6122\eta^3 - 0.9184\eta^2 + 1 )</td>
</tr>
<tr>
<td>7</td>
<td>0.84</td>
<td>( \rho^* = 0.6531\eta^3 - 0.9796\eta^2 + 1 )</td>
</tr>
</tbody>
</table>

Figure 5-4. Apparent density of magnetite as function of length of the structure in the beginning of reduction step of cycle 1.

5.3.3 Microscopic Distribution

Analysis of the experimental reduction data shows an abrupt change in the slope of the rate of reaction at a particular time, denoted as the ‘transition point’. This
transition is indicative of different physical phenomenon driving the reaction before and after. This can be explained on the basis of microscopic distribution of iron oxide in the particle and a change in the reaction mechanism across at the transition point.

To understand the effect of microscopic distribution of the iron oxide, consider a spherical iron particle subjected to oxidation with steam as shown in Figure 5-5. Mehdizadeh et al. [20] showed that the reaction mechanism initially follows a surface controlled reaction and then transitions into a diffusion controlled reaction. Thus the outer region of the sphere is likely oxidized completely to magnetite, while the core of the iron particle only is partially oxidized to wustite as depicted in Figure 5-5.

![Figure 5-5. Postulated ideal distribution of magnetite and wustite within a single particle.](image)

When such an ideal particle is subjected to chemical reduction, magnetite in the outer region is converted to iron via wustite. Thus reaction kinetics is governed by the presence of two reactions, magnetite -wustite and wustite- Fe. Once magnetite is converted to wustite (the reaction front reaches the interface), the only oxide phase distributed within the particle is wustite, and henceforth the reaction kinetics is governed by a single reaction, wustite- Fe. Ideally, this shift takes place at the transition point.
5.3.4 Reaction mechanism, f(x):

Reaction mechanisms for solid state chemical reactions have been extensively studied and several models were reported. Go et al. [19] divided important reaction mechanisms in three categories; diffusion controlled, boundary controlled and random nucleation. As mentioned earlier, experimentally measured rate of reduction reaction shows an abrupt change in slope at the transition point. It is speculated that there is likely a shift in the reaction mechanism for both reactions at the transition point. The iron oxide particle can be approximated as spherical in shape. It is proposed that both reactions, magnetite-wustite and wustite to iron conversions follow a contracting sphere reaction mechanism until the transition point. At the transition point, the reaction mechanism for magnetite-wustite conversion transitions into unimolecular decay and the reaction mechanism for wustite-iron conversion transitions into contracting a cylinder mechanism. It must be acknowledged that this is an attempt to interpret highly complex chemical reactions using simplistic and idealized models. The goodness of fit to the experimental data was used as a criterion for choosing the appropriate solid state reaction mechanism. Tables 5-4 & 5-5 list the proposed reaction mechanisms before and after transition point, respectively.

Table 5-4. Proposed reaction mechanisms for chemical reduction before the transition point.

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Reaction Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite –wustite</td>
<td>((1-x)^{2/3}) (contracting sphere)</td>
</tr>
<tr>
<td>Wustite- Fe</td>
<td>((1-x)^{2/3}) (contracting sphere)</td>
</tr>
</tbody>
</table>
Table 5-5. Proposed reaction mechanism for chemical reduction after the transition point.

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Reaction Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite –wustite</td>
<td>(1-x) (Unimolecular decay law)</td>
</tr>
<tr>
<td>Wustite- Fe</td>
<td>(1-x)^{1/2} (contracting cylinder)</td>
</tr>
</tbody>
</table>

5.3.5 Numerical Scheme

The species transport equation is a first order PDE in time and space. The equation is solved by an explicit finite difference scheme, forward in time and upwind in space. The bed is discretized into 40 cells (N=40) and each time step is of 0.01s. A sufficiently small time step is chosen in order to avoid any instability due to the use of the explicit method. The substrate conservation of mass equation is a first order ODE in time and solved by an explicit method.

Species concentration and fractional conversion of reactive substrate are solved for all the cells in each time step. The steam concentration in the Nth cell represents the cumulative generation of steam in that time step. It is transformed into rate of steam generation (g/min) for comparison with experimental measurement.

Species concentration:

Bed inlet (z=0), always receives hydrogen with maximum inlet molar concentration

\[ C_1(t, z = 0) = C_o \]  \hspace{1cm} (5-17)

At bed inlet (z=0), only hydrogen is present and no reaction takes place

\[ C_2(t, z = 0) = 0.0 \]  \hspace{1cm} (5-18)

Initial condition:
- Species concentration,
At \( t=0 \), no reaction is taking place.
\[
C_1(t = 0, z) = 0.0 \quad (5-19)
\]
\[
C_2(t = 0, z) = 0.0 \quad (5-20)
\]

- Fractional conversion of reactive substrate:
  
  At \( t=0 \), reaction has not started and thus iron oxide is not reduced.
  
  \[
  X_1(t = 0, Z) = 0.0 \quad (5-21)
  \]
  \[
  X_2(t = 0, Z) = 0.0 \quad (5-22)
  \]

### 5.3.6 Determination of kinetic parameters

#### 5.3.6.1 Order of reaction

The order of reaction, \( n \) determines the degree of influence molar concentration of species has on the rate of reaction. Experimental measurements on the peak rate of reaction can be used for an initial estimation of the reaction order. After, initial estimation, the reaction order can be further refined through a kinetic model.

The peak rate of reaction was observed at the very beginning of the reduction step. At this moment, the molar concentration of hydrogen in the reactor is the hydrogen inlet molar concentration. Thus for constant temperature operation, the peak rate of reaction can be expressed as

\[
\ln(\dot{r}_{\text{peak}}) = \text{constant} + n \ln(C_o) \quad (5-23)
\]

Figure 5-6 shows the natural log of the peak reaction rate, \( \ln(\dot{r}_{\text{peak}}) \) against the natural log of the hydrogen inlet molar concentration \( \ln C_o \). It is observed that the reaction order is unity.
Figure 5-6. Peak rate of reaction plotted against hydrogen inlet molar concentration.

5.3.6.2 Activation Energy and pre exponent

Activation energy and pre exponent are key parameters of the kinetic model. According to Arrhenius equation, a rate constant for a chemical reaction is given as

$$A = k_o \exp\left(-\frac{E_a}{RT}\right)$$

(5-24)

It can be easily realized that equation for rate of reaction can be represented in terms of Arrhenius equation as follows,

$$\dot{r}_j = A f_j(x_i) C_j^n$$

(5-25)

A kinetic model is applied to experimental data at different reaction temperature and rate constant A is determined for reactions, magnetite-wustite and wustite-Fe. A linear plot of Arrhenius equation is plotted to determine activation energy and pre-exponent (Figure 5-7 and 5-8).

5.3.6.3 Transition point

The transition point is characterized by the transition in chemical reactions and reaction mechanisms. As transition point represents complete conversion of magnetite
Figure 5-7. Linear plot of Arrhenius equation: Rate constant plotted against temperature for magnetite to wustite conversion.

Figure 5-8. Linear plot of Arrhenius equation: Rate constant plotted against temperature for wustite to elemental iron conversion.

to wustite; $X_1$ (extent of reaction for magnetite) was tracked to determine its onset. Ideally at ‘transition point’. $X_1=1$ but a shift from this value was observed. A kinetic model was used to calibrate the value of ‘transition point’, to $X_1=0.8$ for best fit to experimental measurements at all operating conditions.
5.4 Comparison between experimental data and kinetic model

The kinetic parameters determined so far are primarily based on the comparison of kinetic model with experimental measurement for different reaction temperature. It is necessary to compare the kinetic model with experimental measurements for different operating conditions including hydrogen inlet molar concentration and hydrogen inlet flow rate, to validate the kinetic parameters. The kinetic parameters are tuned to minimize the error between experimental measurements and kinetic model; a maximum threshold value for error was set as 0.03. Moreover, a standard deviation was calculated to determine the distribution of an error over entire data set (Table 5-7). Kinetic model achieved good agreement with experimental data (Figures 5-9 to 5-17), under all operating conditions listed in Table 5-1. Table 5-6 summarizes all the key kinetic parameters for both reduction reactions.

Table 5-6. Summary of kinetic parameters for reduction reactions.

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Magnetite-wustite</th>
<th>Wustite-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy (kJ/mol)</td>
<td>47.09</td>
<td>32.7</td>
</tr>
<tr>
<td>Pre-exponent (s(^{-1}))</td>
<td>55.74</td>
<td>7.08</td>
</tr>
<tr>
<td>Order of reaction</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Transition point (X_t)</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Table 5-7. Average error and standard deviation of the error for the comparison of kinetic model with experimental measurements.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Mean error</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0268</td>
<td>0.0123</td>
</tr>
<tr>
<td>2</td>
<td>0.0222</td>
<td>0.0088</td>
</tr>
<tr>
<td>3</td>
<td>0.014</td>
<td>0.0082</td>
</tr>
<tr>
<td>4</td>
<td>0.0191</td>
<td>0.0092</td>
</tr>
<tr>
<td>5</td>
<td>0.0138</td>
<td>0.005</td>
</tr>
<tr>
<td>6</td>
<td>0.0097</td>
<td>0.0089</td>
</tr>
<tr>
<td>7</td>
<td>0.0219</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Following are the figures showing comparison between experimental measurements and kinetic model for different operating conditions.  

**Reaction Temperature:**

![Comparison between experimental data and kinetic model at reaction temperature of 800 °C.](image)

Figure 5-9. Comparison between experimental data and kinetic model at reaction temperature of 800 °C.
Figure 5-10. Comparison between experimental data and kinetic model at reaction temperature of 900 °C.

Figure 5-11. Comparison between experimental data and kinetic model at reaction temperature of 1000 °C.
Hydrogen inlet molar concentration

Figure 5-12. Comparison between experimental data and kinetic model at hydrogen inlet molar concentration of 2.84 moles/m$^3$.

Figure 5-13. Comparison between experimental data and kinetic model at hydrogen inlet molar concentration of 5.68 moles/m$^3$. 
Figure 5-14. Comparison between experimental data and kinetic model at hydrogen inlet molar concentration of 8.52 moles/m$^3$.

Figure 5-15. Comparison between experimental data and kinetic model at hydrogen inlet molar concentration of 11.36 moles/m$^3$. 

Figure 5-16. Comparison between experimental data and kinetic model at hydrogen inlet flow rate of 1.5 SLPM.

Figure 5-17. Comparison between experimental data and kinetic model at hydrogen inlet flow rate of 2 SLPM.

5.5 Summary

Reaction kinetics of solid state reduction of iron oxide in iron-silica magnetically stabilized porous structure is investigated in laboratory scale reactor. Effect of reaction temperature, hydrogen inlet molar concentration and hydrogen inlet flow rate is studied
experimentally. One dimensional plug flow isothermal kinetic model is developed to
determine important kinetic parameters including activation energy, pre-exponent and
order of reaction. The reduction of iron oxide is characterized by presence of two
reactions, conversion of magnetite to wustite and wustite to iron; the kinetic model is
used to determine key parameters for both reactions independently. The key
parameters calculated for magnetite to wustite and wustite to iron are; activation energy
47.09kJ/mol & 32.7kJ/mol; pre-exponent 55.74s\(^{-1}\) & 7.08s\(^{-1}\) respectively; order of
reaction is unity for both reactions. A sudden change in slope of rate of reduction is
attributed to transition in chemical reactions and reaction mechanisms followed by these
reactions. A transition point is defined in terms of \(X_1\) (fractional conversion of magnetite)
and its value is determined to be 0.8 using kinetic model. A good agreement is achieved
between kinetic model and experimental measurement for different operating
conditions. The kinetic model is robust and excellent analytical tool that can be used to
design industrial reactors.
CHAPTER 6
LARGE SCALE REACTOR

The oxidation and reduction step of two-step water splitting process to generate high purity hydrogen in iron silica magnetically stabilized porous structure (MSPS) has been extensively studied in a laboratory scale reactor. A kinetic model is proposed for both steps and key kinetic parameters are determined. It is important to investigate the feasibility of the technology, developed at laboratory scale, for industrial applications, based on the critical parameters including the rate of hydrogen generation, total hydrogen yield, efficiency of the process, and the cost of the fuel (hydrogen). The large scale reactor is one step closer to the commercial application as the final goal. It is important to ensure the repeatability of the rate of reaction and total hydrogen production in consecutive redox cycles at high operating temperature (~800 °C).

Moreover, the reduction reaction using syngas in lieu of CO as reducing agent is quite relevant to commercial applications. The proportion of CO and H₂ in Syngas is varied and its effect on the degree of reduction is investigated.

6.1 Experimental Set-up

The experimental set up of large scale reactor (Figure 6-1), in nature, resembles that of laboratory scale reactor. The stainless steel tube, 6 inches in I.D. and 18 inches in length, serves as a reactor. The reactor can be operated at high temperature (up to 1000 °C) and high pressure (up to 150 psi gauge). The ends of the reactor are welded to flanges. The steel plates are bolted to the flanges with graphite gaskets positioned in between. The graphite gaskets get compressed between flange and end plate and seal the reactor. The reactor has no inbuilt frit to support the iron-silica MSPS. The ceramic plate supported by steel structure is placed inside the reactor and two inch thick layer of
glass-wool insulation is placed on the ceramic plate. The entire assembly served as a frit. The frit not only supports the structure but also raises the temperature of the gases/steam to the temperature of the bed. The 'radiative ceramic split heater' (220 V, 7200 Watt) is a primary heater.

The stainless steel being a good heat conductor, the end plates could reach to the higher temperature. Since graphite gasket could not sustain temperature above 400°C, it is necessary to implement active cooling system at the end plates. Cooling fans are installed on either side of the end plates which provided necessary cooling. The iron-silica MSPS is insulated with glass wool at either ends to reduce the radiative heat loss from structure to the end plates.

The half inch stainless steel tube heated with the rope heater serves as an inline steam generator that can generate the steam at the rate of 20 g/min. The stainless steel tube is filled with ceramic pallets that not only increase surface area for heating but also minimize the chances of water slogs formation, ensuring uninterrupted supply of the steam. The steam generator is equipped with the syringe pump to supply the water at required flow rate. The steam line connects inline boiler to the inlet of the reactor. The steam line is heated using rope heater to keep it at temperature above 100°C to avoid condensation of the steam.

The product gas leaving the reactor during oxidation step is a mixture of the hydrogen and the steam. The ‘tube in shell’ condenser is installed in-line with the exit of the reactor. The condensed steam (water) was stored in the water trap. The flow-meter was used to measure the flow of H₂.
It is speculated that Iron silica structure in large scale reactor will experience non-uniformity in the temperature distribution. Three K-type thermocouples are installed in the structure to capture the distribution of the temperature. Two thermocouples, one at each end plate, are installed to monitor the temperature of the graphite gaskets.

Data Acquisition system is installed to retrieve the temperature and flow rate data as well as to control flow-controllers. The system comprises of NI-6211 DAQ board which communicates with LABVIEW. LABVIEW retrieves vital data and stores in computer as well as gives instructions to DAQ board to control devices including flow-controller.

Figure 6-1. Image of Experimental Set-up.

6.2 Experimental Procedure

The experimental procedure follows the guidelines established during laboratory scale analysis. The 1064 g of iron powder was mixed with silica powder in 2:1 (silica:
iron) volume ratio. The sample was loaded in the reactor and the inert gas (Argon) was passed through the reactor to set the iron-silica mixture in fluidized state. Once the bed was completely fluidized, a strong magnetic field was applied and the flow of Argon was cut off, at the same time. The temperature of reactor was raised to 600 °C (less than Curie temperature of the iron) and steam was introduced in the reactor at the rate of 8 g/min. The oxidation step continued for 60 minutes after which looping process was switched to reduction step. The temperature of the reactor was raised to 800 °C and hydrogen was introduced in the reactor at the rate of 5 SLPM; that served as a reducing agent. For the subsequent cycles, flow rate of reacting gases was increased for both, oxidation as well as reduction step. Moreover, in subsequent cycles, different reducing agents were introduced to analyze their effect on hydrogen generation. Table 6-1 shows the summary of the operating conditions of various cycles.

Table 6-1. Summary of Cycles.

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Operating Temperature (°C) (avg)</th>
<th>Steam flow rate (g/min)</th>
<th>Composition of Reducing Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>825</td>
<td>14 Hydrogen</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>825</td>
<td>14 Hydrogen</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>825</td>
<td>14 Hydrogen</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>825</td>
<td>14 Syngas(60%H₂,30%CO,10%CO₂)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>825</td>
<td>14 Syngas(45%H₂,45%CO,10%CO₂)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>825</td>
<td>14 Syngas(30%H₂,60%CO,10%CO₂)</td>
<td></td>
</tr>
</tbody>
</table>

6.3 Result and Discussion

Figure 6-2 shows the rate of hydrogen generation for cycle 4 to 8. The laboratory scale analysis showed that the structure is stabilized in first three cycles; thus cycles 4 and onwards are considered for the analysis. The rate of hydrogen generation for cycles
3, 4 and 5 exhibit excellent repeatability. It is very vital information which indicates the feasibility to implement the technology developed to synthesize the iron silica magnetically stabilized porous structure to inhibit the sintering and retain active surface area, in large scale reactors. Figure 6-3 shows the Degree of Oxidation for cycles 4 to 8. For cycles 4, 5 and 6, degree of oxidation (DO) is 60%. Although, the total reaction time is 110 min, degree of oxidation reached to 50% in first 60 min after which rate of reaction declines. It gives a better estimation of the duration of the oxidation step after which looping process should be switched to reduction stage.

The rate of hydrogen generation as well as degree of oxidation for cycles 7 and 8 indicates significant deviation from previous cycles. The peak rate of reaction is comparable to that of cycles 4-6 but thereafter sharp decline in rate of reaction is observed. The degree of oxidation settles at 30-35% at the end of the oxidation step; almost half, compared to cycles 4-6. The cause of this poor performance is found in the choice of a reducing agent for the preceding reduction step.

The degree of reduction in a reduction step of a particular cycle governs the amount of iron available in oxidation step of next cycle. Till cycle 5, pure hydrogen is used as reducing agent. As discussed earlier, hydrogen is an effective reducing agent in terms of the rate of reaction and total yield; thus results in availability of substantial mass of iron in next oxidation step. In cycles 6 to 8, instead of pure hydrogen, syngas with increasing volume percentage of carbon monoxide is used (Table 6-1). The carbon monoxide is a poor reducing agent compared to hydrogen and adversely affects the degree of reduction. Thus less amount of iron is available for the subsequent oxidation step affecting its rate of hydrogen generation and yield of hydrogen.
Although syngas adversely affects the total hydrogen production in subsequent oxidation step, it is interesting to observe that the peak rate of hydrogen generation, as well as degree of oxidation for first 15-17 minutes is comparable across cycles 4-8. The kinetic model by Mehdizadeh et al. [20] proposed that the peak rate of hydrogen generation and the rate of reaction during initial period (for $X_{\text{iron}}<0.3$) of oxidation step is governed by the surface controlled (contracting sphere) reaction mechanism. Thus, at microscopic level, availability of iron in the outer layer of the iron particle has a significant impact on these parameters. It is speculated that, although syngas is a poor reducing agent compared to hydrogen on the basis of rate of reduction and degree of reduction; it might be capable enough to reduce, at least outer layer of iron oxide particles, to the same extent as that is reduced by pure hydrogen. For remaining duration ($X>0.3$), diffusion control mechanism governs the rate of reaction and hydrogen may have exhibited a better performance compared to syngas which resulted in deviation observed in rate of reaction and the degree of oxidation.

Figure 6-2. Rate of hydrogen generation at 825 °C (avg) for cycles 4 to 8.
The laboratory scale analysis inferred that the reducing agent with higher hydrogen content performs better. The syngas with two different compositions, (CO: H₂ = 2:1) and (CO: H₂=1:1), hydrogen and carbon monoxide were examined as a reducing agent in laboratory scale investigation. It is necessary to achieve qualitatively similar results in large scale reactor analysis. A composition of a reducing agent was varied from pure hydrogen to syngas with increasing carbon monoxide content, through cycles 5 to 8. Figure 6-4 shows the degree of reduction for each cycle. It is observed that, as the carbon monoxide content in syngas increases, the degree of reduction reduces from 52% to 40%, from cycle 5 to cycle 8; thus underlines the effect of composition of reducing agent on reduction step. These observations are in accordance with the investigation conducted at laboratory scale.

6.4 Summary

The iron silica magnetically stabilized porous structure exhibited consistent rate of hydrogen generation indicating successful inhibition of the sintering and retention of the chemically active surface area. The degree of oxidation for cycles 4 to 6 reached to
60% while for cycles 7 and 8 it dropped to 30-35%. The drop in the performance is attributed to the choice of reducing agent in reduction step prior to the oxidation step under consideration.

![Degree of Reduction v/s time for cycles 5 to 8.](image)

Figure 6-4. Degree of Reduction v/s time for cycles 5 to 8.

The composition of a reducing agent has a significant impact on the degree of reduction. The composition is varied from pure hydrogen to syngas with increasing carbon monoxide content with each cycle. Carbon monoxide being a poor reducing agent compared to hydrogen, degree of reduction dropped significantly with increasing carbon monoxide content. Consequently, it affected the amount of iron available for next oxidation step and thus drop in rate of hydrogen generation is observed. The results of oxidation and reduction step are in accordance with the laboratory scale analysis. It can be inferred that the technology developed at laboratory scale to generate high purity hydrogen via thermochemical looping of iron oxide in iron silica magnetically stabilized can be successfully implemented at industrial scale.
CHAPTER 7
SYNTHESIS OF HIGH SURFACE AREA REACTIVE MATERIAL VIA DEPOSITION OF IRON ON ALUMINA PARTICLES TO ENHANCE THE HYDROGEN GENERATION IN TWO-STEP WATER SPLITTING PROCESS

The investigation of two-step water splitting process indicated that, a novel concept of iron-silica magnetically stabilized porous structure (MSPS), is a promising technology to generate high purity hydrogen at industrial scale. Despite its excellent performance, this technology suffers drawbacks that need to be addressed. The synthesis of MSPS involves stabilization of fluidized bed. Typically, particles below 40 μ cannot be well fluidized; thus iron particles below this size cannot be used to synthesize iron-silica MSPS. It inherently restricts maximum active surface area available in MSPS, as total surface area of reactive material increases with decrease in particle size. Secondly, as reactor size increases, it is difficult to apply magnetic field in transverse direction and maintain uniform magnetic field throughout the reactor. Moreover, experimental measurements indicate significant drop in rate of conversion once total hydrogen yield reaches 40% of stoichiometric production, compelling to switch to reduction step as it is not economical to continue with oxidation. Thus substantial mass of reactive material is left unreacted costing valuable reactor space and energy. Current work focuses on addressing these issues. An attempt is made to synthesize a reactive material that can render higher surface area, facilitate maximum utilization of reactive substrate and inhibit sintering. Experiments are conducted in laboratory scale reactor at different operating temperatures; 800 °C, 900 °C and 100 °C. The performance of the reactive material is investigated based on rate of hydrogen generation, degree of oxidation and repeatability over consecutive cycles. Performance of the high surface
area reactive material is compared with iron silica MSPS; former exhibits better performance in terms of rate of hydrogen generation per unit mass of iron.

7.1 Experimental Set-up

There are two independent experimental configurations; for synthesis of the high surface area reactive material and to investigate the two-step water splitting process to generate high purity hydrogen. Refer section 3.1 for the experimental configuration for two-step water splitting process. The experimental configuration for synthesis of high surface area reactive material is explained in this section.

Figure 7-1 shows the experimental configuration for synthesis of high surface area reactive material. The alumina tube serves as a reactor. The reactor is 2 inches in I.D. and 24 inches in length, and can withstand temperatures up to 1600 °C. The reactor is supported by gland seals at both ends. A high temperature tube furnace (Sentro Corp) serves as a primary heater and it can raise the temperature of the reactor up to 1500 °C. The furnace is equipped with the controller to monitor the temperature of the reactor. There are two independent gas lines to carry inert gas (Argon) and hydrogen. The gas lines supply a manifold which is connected to the inlet of the reactor. Gas lines are equipped with flow controllers (Alicat) to monitor the gas flow rate. The outlet of the reactor is connected to exhaust for safe discharge of the gases.

7.2 Experimental procedure

A 72 gram sample of alumina powder is mixed with 24 grams of magnetite powder (< 40 microns). A mixture is loaded in the reactor and the reactor is positioned in high temperature tube furnace; reactor is supported at both ends by gland seals. The temperature controller of the tube furnace is programmed to achieve desired
temperature (1500 °C) at appropriate ramp rate to avoid possible thermal shocks in the reactor tube.

Figure 7-1. Experimental set up for synthesis of high surface area reactive material.

The mixture is kept under inert environment by flowing Argon through the reactor. The flow rate of Argon is increased with the temperature to keep the reactive material in fluidized state to avoid sintering. As the temperature reaches 1500 °C, the reactor is maintained at this temperature for 20 minutes. During this dwell period, the hydrogen is introduced at the inlet flow rate of 20 SCCM. The hydrogen flow rate is cut off at the end of dwell period and reactor temperature is reduced at pre-programmed rate. The flow of Argon is stopped as the reactor is cooled to a sufficiently low temperature (<500 °C). At room temperature, sample is removed from the reactor tube. SEM analysis is performed.
to ensure successful deposition of iron on alumina particles. Then the reactive material is loaded in another reactor to perform two-step water splitting process.

7.3 Results and Discussion

The motivation behind synthesis of high surface area reactive material is an efficient utilization of the reactive substrate to make the thermochemical looping process, economically viable. Figures 3-4 & 3-5 show the rate of hydrogen generation and degree of oxidation of iron-silica MSPS. The hydrogen generation drops to a substantially low rate (1.5 -3 cm$^3$/(min.gr$_{Fe}$), approximately 20 minutes into the reaction. It is not economical to continue oxidation at this rate of hydrogen generation and it is prudent to switch the looping process to reduction step. At this point, degree of oxidation is 40-50%; thus substantial amount of reactive substrate (iron) is left unused. An inactive mass of substrate occupies valuable reactor space and consumes energy (heat) to be maintained at high temperature. It adversely affects the efficiency of the process. Thus, it is of important to achieve better distribution of reactive substrate for higher rate of reaction throughout the reaction time.

The procedure to synthesize high surface area reactive material is designed to achieve this goal. It is proposed to deposit the reactive material, in molten state, on the highly stable ceramic particles like alumina. As explained earlier; the mixture of alumina powder and magnetite powder was heated up to 1500 °C in fluidized state, under inert atmosphere and hydrogen was introduced in the reactor. In stepwise reduction, magnetite was initially reduced to wustite. Wustite has a melting point of 1377°C; well below reactor temperature. It is speculated that at 1500 °C, wustite melted and formed a coating on alumina particles. The surface tension between molten wustite and alumina particles forced wustite to get coated in the form globules instead of a continuous layer.
The wustite was further reduced to iron. Figure 7-2 and 7-3 shows the SEM image of alumina particle coated with iron. Deposition of iron in the form of nano-scale globules enhanced the active surface area available. A qualitative analysis of the surface of the alumina particle was conducted to determine its composition. Figure 7-4 shows the signals representing presence of different elements along the line-scan conducted on the surface of an alumina particle. A strong signal for iron indicates its significant presence on the surface of alumina particle. The SEM images and qualitative analysis of the alumina surface clearly indicates successful deposition of the reactive substrate on the alumina particles. It is now necessary to investigate the performance this reactive material on the basis of rate of reaction, total yield and repeatability of over consecutive cycles. The experiments were conducted reaction temperatures 800 °C, 900 °C and 1000 °C; steam inlet flow rate in oxidation step was 1g/min; hydrogen inlet flow rate in reduction step was 1 SLPM.

Figure 7-2. SEM image of alumina particle coated with iron.
Figure 7-3. SEM image showing nano-scale iron particles deposited on alumina particle

![SEM image](image)

Figure 7-4. The signal indicating presence of different elements on the surface of an alumina particle in Figure 7-2.

7.3.1. Hydrogen generation

Figure 7-5 shows the rate of hydrogen generation at 800 °C. The peak rate of reaction is substantially high; 0.95-1 SLPM. The reactive material exhibits excellent repeatability in terms of the peak rate as well as overall rate of reaction. The reactive
material exhibits similar performance at higher temperatures, 900 °C and 1000 °C (Figure 7-6 and 7-7). It indicates that the sample has successfully inhibited the sintering and preserved the active surface area, at significantly higher temperatures, in the range 800 -1000 °C.

Figure 7-5. Rate of hydrogen generation v/s time plotted for cycles 4-12; reaction temperature, 800 °C.

Figure 7-6. Rate of hydrogen generation v/s time plotted for cycles 13-16; reaction temperature, 900 °C.
The comparison between experimental measurements of the rate of hydrogen generation at different temperatures underlines a very interesting phenomenon (Figure 7-8). The peak rate of hydrogen generation is expected to increase with reaction temperature. Figure 7-8 indicates that the peak rate of reaction is same for all the reaction temperatures. Moreover, the peak rate sustains for longer duration as the reaction temperature is increased. The oxidation of iron by steam to generate hydrogen is represented as:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2.$$

(7-1)

The stoichiometric analysis of this reaction shows that, for 1 g/min of steam inlet flow rate, maximum rate of hydrogen generation is, 1.36 SLPM. It must be acknowledged that there are kinetic and thermodynamic constrains that limits the actual peak rate, at a value lower than stoichiometric limit. Despite these constrains, the peak rate of hydrogen generation attained is 69-73% of stoichiometric limit which is significant and must be attributed to high surface area available for chemical reaction.
7.3.2 Performance comparison with iron silica MSPS

The performance of iron-silica MSPS is among the excellent results available in open literature and thus considered as a benchmark for performance comparison. Mehdizadeh et al. [20] developed a kinetic model for oxidation step in iron silica MSPS. This kinetic model is used as an analytical tool to predict the rate of hydrogen generation in iron silica MSPS under similar operating conditions as that of current work. Figure 7-9 compares kinetic model for MSPS with the experimental measurements of high surface area reactive material based on the rate of hydrogen generation per unit mass of iron, in the temperature range 800-1000 °C. At 800 °C, peak rate of hydrogen generation is substantially higher than predicted by the kinetic model. At higher temperatures, 900 & 1000 °C, the peak rate predicted by the model for iron-silica MSPS is comparable with experimental peak rate for high surface area reactive material; though peak rate for later sustains for longer duration exhibiting better performance.

Figure 7-8. Rate of hydrogen generation v/s time plotted for different reaction temperatures, 800-1000 °C.
Figure 7-10 compares the cumulative hydrogen yield for iron silica MSPS and experimental measurements of the current work. The cumulative hydrogen yield for high surface area reactive material is substantially higher than that of iron-silica MSPS. The comparative analysis indicates that, equal hydrogen yield can be achieved in shorter duration with high surface area material leading to improved efficiency.

Figure 7-9. Comparison between MSPS and high surface area reactive material, based on rate of hydrogen generation at different reaction temperatures.

Figure 7-10. Comparison between MSPS and high surface area reactive material, based on total yield, at different reaction temperatures.
High surface area reactive material is compared with iron-silica MSPS based on the hydrogen generation per unit mass of iron. Another critical parameter for the performance analysis is the reactor space utilized for the hydrogen generation. Figure 7-11 shows the performance comparison between iron-silica MSPS and high surface area reactive material based on rate of hydrogen generation per unit volume of the reactor. It can be observed that the iron-silica MSPS exhibits significantly better performance than high surface area reactive material indicating that the former achieved optimum utilization of the reactor space than later.

![Figure 7-11](image)

Figure 7-11. Performance comparison between iron-silica MSPS and high surface area reactive material based on hydrogen generation per unit volume.

This significant difference in the performances can be attributed to the amount of the non-reactive material present in reactor. In iron-silica MSPS, iron and silica are mixed in 1:2 volume ratio, thus 66.67% of reactor space is occupied by non-reactive material (silica). In high surface area reactive material, iron to alumina ratio is 1:4 by mass, indicating that 80% of the total mass of in the reactor is non-reactive (alumina). It can be realized that, high surface area reactive material contains significantly higher
amount of non-reactive material compared to iron-silica MSPS. Experimental measurements indicated that for the same mass of the iron in the reactor, high surface area reactive material occupied four times more reactor space compared iron-silica MSPS leading to poor utilization of the reactor space.

The performance of high surface area reactive material can be improved by optimizing the size of alumina particles that act as a support for reactive material. For the given mass of alumina, particles with smaller size would facilitate higher surface area available for the loading of reactive material, thus achieving better utilization of the reactor space. Experiments must be conducted to determine the optimum size of the alumina particles as well as the %loading by mass of the iron to achieve higher rate of reaction and inhibit the sintering.

7.4 Summary

A novel method to synthesize high surface area reactive material via deposition of iron on ceramic (alumina) particles was developed. The SEM analysis showed that nano-scale iron particles uniformly deposited on the surface of alumina particles availing high surface area for chemical reaction to take place. The peak rate of hydrogen generation was 73% of stoichiometric limit and sustained for longer duration as reaction temperature was increased, indicating excellent utilization of steam and the reactive material. The reactive material exhibited excellent consistency in peak rate of hydrogen generation and rate of reaction in the temperature range, 800-1000 °C; thus successfully inhibited sintering and retained active surface area. A comparative analysis showed that the high surface area reactive material exhibited better performance than iron-silica magnetically stabilized porous structure, based on peak rate of reaction per unit mass of iron and total hydrogen yield. High rate of reaction leads to rapid
conversion of reactive substrate; thus increases the frequency of the looping process. Although new technology exhibited excellent results based on rate of hydrogen generation per unit mass of iron, the reactor space utilization is significantly poor compared to iron-silica MSPS. Attempts must be made to increase the loading of iron on alumina particles leading to better utilization of the reactor space.
CHAPTER 8
FUTURE WORK

The focus of the current study has been profound analysis of two-step water splitting reaction to generate high purity hydrogen. A novel concept of iron silica magnetically stabilized porous structure is studied for enhancement of hydrogen generation. A variety of reducing agents are investigated to determine appropriate a reducing agent. The kinetics of oxidation and reduction step is extensively studied and analytical models are proposed. The feasibility of the technology to implement it at industrial scale is examined. Moreover, an attempt is made to synthesize high surface area reactive material for better hydrogen generation. This study has laid a foundation for the generation of high purity hydrogen at industrial scale.

Despite profound investigation, there exist important processes associated with coal conversion to hydrogen technology; that are not addressed in the current study. They have a potential to be an independent research project and a in depth study must be conducted. A successful implementation of these processes will enhance the commercial viability of coal conversion to hydrogen technology. They are discussed in brief in this chapter.

8.1 Investigate the Feasibility of WGS Reaction to Enhance Hydrogen Content in a Reducing Agent

The analysis of reduction step proposed that, effective reduction of iron oxide can be achieved with hydrogen enriched reducing agent. The coal gasification process is generates syngas that can be used as a reducing agent. The composition of syngas varies significantly depending upon various parameters including quality of the coal, reaction temperature and steam to carbon ratio. It is necessary to process this syngas
to increase its hydrogen content and use it as an effective reducing agent; a water gas shift reaction is a promising technology to achieve this goal. It is can be represented as:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \]  

(8-1)

It may be counterintuitive to use hydrogen as a reducing agent in the scenario where hydrogen generation is a prime goal of this technology. The key is the purity of the hydrogen. Coal contains trace amount of sulfur which leads to a formation of sulfur agents including \( \text{COS} \) and \( \text{H}_2\text{S} \), during coal gasification. These sulfur agents pose a danger of contamination of hydrogen. Sulfur can damage the catalysts used in the fuel cells; hence hydrogen contaminated by \( \text{COS} \) and \( \text{H}_2\text{S} \) cannot be used in fuel cell technology. Instead, it can be used as reducing agent in reduction step of two-step water splitting process and the high purity hydrogen generated in oxidation step can be used in fuel cell technology.

WGS is broadly classified into two categories based on operating temperature as High Temperature Shift Reaction (HTSR) operated between 350 – 500 °C and Low Temperature Shift Reaction (LTSR) operated between 150 – 250 °C. The WGS reaction is slightly exothermic; hence thermodynamically it is not favored at high temperatures. Various studies have reported the effect of the temperature on the WGS reactions. Chen et al. [27] observed that HTSR was favored at high temperature and CO conversion increased with temperature, contrary to the thermodynamic equilibrium analysis. It indicates the dominance of reaction kinetics over thermodynamic equilibrium in prescribed temperature range. However, LTSR is not favored as temperature was increased from 200 to 400 °C consistent with thermodynamic analysis. Chen et al. [27] studied the effect of steam/CO ratio in syngas on WGS shift reaction and found that CO
conversion increases at higher steam/CO ratio. At favorable operating conditions, both HTSR and LTSR exhibited excellent CO conversion (> 90%). The gas at the exit of WGS reaction mainly comprise of CO$_2$ and H$_2$ with trace amount of other gases.

Although primary analysis of WGS reaction indicates that its implementation would lead to an effective reduction step and eventually enhance the hydrogen production; there arise key concerns that need attention.

Syngas is a product of coal gasification reaction. The gasification process is favored at high temperature and typically syngas exits the gasifier at high temperatures (> 750-900 °C). The thermodynamic equilibrium analysis of WGS reaction shows the reaction is favored at low temperature. Although HTSR has shown excellent results at high temperature, no experimental data is available about its performance above 500°C. Experimental analysis is necessary to study the performance of the WGS shift reaction above 500°C. It would give better estimate of an upper limit of the temperature ($T_{\text{critical}}$) above which HTSR is not favored. If $T_{\text{critical}}$ is well below syngas exit temperature, there will be a penalty associated with the cooling of high temperature syngas. Moreover, introduction of cooling system would increase initial and operating cost of the plant. It is essential to conduct a thorough analysis to weigh the gain in terms of increase in the hydrogen generation (in oxidation step) with the energy lost in cooling and increase in plant cost.

Secondly, the sulfur agents including H$_2$S and COS can poison catalysts of various processes. Hla et al. [28] investigated effect of H$_2$S on iron chromium based catalyst in HTSR. There is no substantial drop in catalytic activity at low concentration (till 50 ppm). As H$_2$S concentration is increased, the catalytic activity drops drastically.
leading to failure of WGS shift reaction. Similar observation was reported by Schaidle et al. [29] for Mo$_2$C and Pt/Mo$_2$C for H$_2$S concentration as low as 5ppm. Sulfur agents may have such hazardous effects on the reactive substrate of two-step water splitting process. This enforces a need for profound investigation to analyze the effect of sulfur.

8.2 Potential for CO$_2$ Capture

Carbon dioxide is one of the prominent greenhouse gases that contribute significantly towards the air pollution. Moreover, carbon dioxide is used in different industries and thus it is commercially important gas. Thus it is imperative to study a potential to capture CO$_2$. Researchers [30-32] have studied different processes including PSA (Pressure Swing Adsorption) and Thermal Swing Sorption Enhanced Reaction (TSSER) to capture carbon dioxide from mixture of gases including syngas and flue gases. The purity and recovery of carbon dioxide depends up on various parameters including operating pressure and CO$_2$ content in the feed gas. There are two important processes in coal conversion to hydrogen technology that need to be investigated for possible CO$_2$ capture

8.2.1 Water gas shift reaction

As studied in previous section, water gas shift reaction converts carbon monoxide and steam into hydrogen and carbon dioxide. It not only increases hydrogen content in product gas; which benefits reduction step; it also enhances carbon dioxide content. Thus, a possibility to sequester carbon dioxide from the product gases must be investigated. Moreover, effect of sulfur agents including COS and H$_2$S on sequestration process must be analyzed.
8.2.2 Reduction step with syngas as a reducing agent

The reduction of iron oxide using syngas as a reducing agent can be represented as,

\[
\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}
\]  
(8-2)

\[
\text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2
\]  
(8-3)

The product gases of reduction step are composed of steam, carbon dioxide, unreacted carbon monoxide and hydrogen; steam can be condensed. Figure 8-1 shows the carbon dioxide content (% by volume) in the product gases of reduction step using syngas as a reducing agent. There is substantial rise in the carbon dioxide content in product gas compared to input gas. A potential to capture carbon dioxide from these gases must be investigated.

![Graph showing CO2 content over time](image)

Figure 8-1. Carbon dioxide content (% by volume) in product gases of reduction step using syngas as a reducing agent.
CHAPTER 9
CONCLUSION

The magnetically stabilized iron silica porous structure showed significant enhancement in the hydrogen production. It exhibited excellent performance in terms of peak rate of reaction and hydrogen yield; over consecutive redox cycles at 800 °C. The iron silica MSPS successfully inhibited sintering and retained active surface area. A one dimensional isothermal plug flow kinetic model was developed to for oxidation step. The activation energy (Ea), pre exponent (k₀) and the order of reaction is found to be 88.29 KJ/mol, 54843s⁻¹ and 1.2 respectively. The model showed good agreement with experimental measurements. The reduction reaction in magnetically stabilized iron silica structure was investigated using different reducing agents including carbon monoxide, syngas and hydrogen. The analysis indicated that the reducing agent with higher hydrogen content exhibits better performance in terms of degree of reduction. A one dimensional isothermal plug flow model was developed to study reduction kinetics with hydrogen as a reducing agent. The reduction step was characterized by presence of two reactions; magnetite to wustite conversion and wustite to iron conversion. The key parameters calculated for magnetite to wustite and wustite to iron were; activation energy 47.09kJ/mol & 32.7kJ/mol; pre-exponent 55.74s⁻¹ & 7.08s⁻¹ respectively; order of reaction was unity for both reactions. The reaction mechanism for both reactions was identified and transition in reaction mechanism was captured. A feasibility of laboratory scale technology to implement it at industrial scale was investigated with large scale reactor. The iron-silica porous structure exhibited consistent performance in terms of rate of reaction and total hydrogen yield at 800 °C. The reduction step was investigated using different reducing agents ranging from pure hydrogen to syngas with increasing
carbon content. The decline in degree of reduction and consequently drop in hydrogen generation was observed with increase in carbon monoxide content in reducing agent; consistent with laboratory scale analysis. Large scale reactor analysis indicated that iron-silica MSPS can be successfully implemented for industrial applications. An attempt was made to develop a method to increase the surface area of reactive material via deposition of iron on alumina particles. The high surface area reactive material exhibited significantly higher rate of reaction and total hydrogen yield in the temperature range, 800-1000 °C. The comparison with iron silica MSPS shows that the high surface area reactive material outperforms iron silica MSPS in terms of rate of hydrogen generation per unit mass of iron and hydrogen yield. Despite excellent performance, there is substantial scope for improvement in utilization of the reactor space. A feasibility of water gas shift reaction and potential for carbon dioxide capture was discussed.
APPENDIX
POST PROCESSING OF THE EXPERIMENTAL DATA

The investigation of two-step water splitting process via thermochemical looping of iron to generate high purity hydrogen involved experimental measurements of various parameters including flow rate of reactants and rate of oxidation and reduction reaction. A variety of devices including mass flow meter, mass flow controller and mass spectrometer were used for this purpose. The raw data generated by these devices must be processed before further analysis is performed. An attempt is made to take an overview of different methods adopted for the post processing of the experimental measurement and their significance.

A.1 Mass-spectrometer Calibration

The experimental set up is equipped with mass-spectrometer to analyze the composition of the product gases. Mass-spectrometer probe collects the sample of the product gas which is subjected to qualitative analysis. The presence of different gases in the product gas can be analyzed based on different parameters including molecular weight and partial pressure of the gas; partial pressure is selected in present study. In oxidation step, hydrogen is only product gas, thus mass spectrometer serves as an alternative device to measure flow rate of hydrogen. Moreover, in reduction step, product gas is a mixture of carbon dioxide and unreacted carbon monoxide; gas flow meter is not capable of measuring the flow rate of carbon dioxide alone. Thus in reduction step, mass spectrometer serves as a primary device to measure the flow rate of carbon dioxide. The mass spectrometer is designed for qualitative analysis of the composition of product gas but it is not capable of measurement of the flow rate,
explicitly. It is necessary to calibrate the partial pressure measured by the mass spectrometer to measure the flow rate of the individual gas.

**Calibration process:** The product gases were calibrated against a reference gas; Argon was chosen as a reference gas. The flow rate of Argon was maintained at 0.3 SLPM throughout the calibration process as well as experiments. Hydrogen, carbon monoxide and carbon dioxide are the primary gases for which calibration was conducted. A mass flow controller was used to monitor the flow rate of the gas. The range of the flow rate of the primary gas during the calibration process must accommodate the range of its flow rate during the experiment. The primary gas was supplied at a designed flow rate and corresponding partial pressure signal was recorded by the mass-spectrometer. A caution was taken to flow a primary gas for sufficiently long period of time to stabilize the partial pressure signal and sufficient data was available for the post-processing. The procedure was repeated for different flow rates of the primary gas. The flow rate data and partial pressure signal data for the primary gas was normalized by flow rate and partial pressure of reference gas, Argon. An empirical correlation was established that transformed normalized partial pressure of a primary gas to normalized flow rate of a primary gas. It was used as an analytical tool to post process partial pressure signal recorded by the mass-spectrometer during the experiment and measure the flow rate.

**Example:** Following is an example of a calibration of the carbon dioxide with Argon as a reference gas. The flow rate of the carbon dioxide is varied in the range of 0.05-0.5 SLPM with Argon flow rate maintained at 0.3 SLPM. The mass-spectrometer records partial pressure signal of carbon dioxide and argon for sufficiently long time (~10 min) to
allow the signal to stabilize and generate sufficiently large data points. A statistical average of the partial pressure corresponding to particular flow rate is calculated for both the gases. Table A-1 lists the details of the flow rate and the partial pressure signal. A normalized flow rate is plotted v/s normalized partial pressure (Figure A-1) to determine the correlation. This correlation is applied to a normalized partial pressure of carbon dioxide generated during the experiment and flow rate is determined. Figure A-2 shows the partial pressure and corresponding flow rate of carbon dioxide plotted with the time.

Table A-1. Flow rate of the primary gas and corresponding partial pressure data.

<table>
<thead>
<tr>
<th>Flow rate of CO₂</th>
<th>Normalized flow rate of CO₂ (Q’)</th>
<th>Average normalized partial pressure (P’)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.667</td>
<td>1.18</td>
</tr>
<tr>
<td>0.35</td>
<td>1.167</td>
<td>0.827</td>
</tr>
<tr>
<td>0.2</td>
<td>0.667</td>
<td>0.47</td>
</tr>
<tr>
<td>0.1</td>
<td>0.333</td>
<td>0.23</td>
</tr>
<tr>
<td>0.05</td>
<td>0.167</td>
<td>0.115</td>
</tr>
</tbody>
</table>

The mass-spectrometer serves as an alternative device to measure hydrogen flow rate; thus it is necessary to compare the mass-spectrometer with mass flow meter based on experimental measurement of hydrogen flow rate. Experimental measurements of rate of reduction using hydrogen as a reducing agent are selected as a sample to conduct a comparison. The rate at which hydrogen is used in the reaction is measured by both the devices independently and rate of steam generation is deduced by stoichiometric analysis. Figure A-3 shows the comparison of experimental
measurement of rate of steam generation measured by mass spectrometer and mass flow meter; a good agreement is observed between them.

![Graph showing normalized partial pressure vs normalized flow rate of carbon dioxide]

Figure A-1. Normalized partial pressure v/s normalized flow rate of carbon dioxide to determine the correlation.

![Graph showing rate of carbon dioxide generation vs time]

Figure A-2. Partial pressure and corresponding flow rate of carbon dioxide v/s time.

The mass-spectrometer detects the presence of different gases based charge to mass ratio of the ions of respective gases (Refer to the literature for detail information regarding the working of mass spectrometer). During the ionization process it is likely that a particular species dissociate to generate another species that is a component of
the mixture subjected to the analysis. Consider a mixture of carbon dioxide and carbon monoxide subjected to mass-spectrometer analysis. The signal recorded by mass spectrometer for molecular weight of 28 corresponds to carbon monoxide present in the original mixture and the carbon monoxide generated in the process of ionization of carbon dioxide.

![Figure A-3](image)

Figure A-3. The comparison between experimental measurements of rate of reduction reaction using mass-spectrometer and mass flow meter.

The manufacturer of mass-spectrometer (Hiden Analytical) has provided the contribution of each species in the partial pressure signal recorded by the mass-spectrometer. The contribution to the single partial pressure signal by two different species must be accounted during calibration and post processing of the mass-spectrometer data for accurate measurement. Table A-2 lists some of such occurrences.

**A.1.2 Mass flow meter calibration**

In current study, experimental were conducted to analyze an effect of the inlet molar concentration of reacting species on rate of reaction in oxidation and reduction
step. In oxidation and reduction step, helium was mixed with steam and hydrogen respectively, to alter the inlet molar concentration; thus the flow meter records the flow of the mixture of hydrogen and helium.

Table A-2. List of gases contributing to same signal in mass-spectrometer analysis

<table>
<thead>
<tr>
<th>No</th>
<th>Mixture of gases</th>
<th>Molecular weight</th>
<th>% contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO + CO₂</td>
<td>28</td>
<td>CO - 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ - 11.4</td>
</tr>
<tr>
<td>2</td>
<td>H₂ + H₂O</td>
<td>2</td>
<td>H₂ - 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O - 0.7</td>
</tr>
</tbody>
</table>

A scenario wherein a ‘gas’ setting of the mass flow meter is tuned to read the flow rate of a particular gas, and a different gas is passed through it, the recorded flow rate does not represent actual flow rate but its scaled value. In this particular case, helium is passed through the mass flow meter which is set to read hydrogen; thus the recorded flow rate of helium is a scaled value of real flow rate at which helium is introduced in the system. A calibration of the mass flow meter is conducted to find the correlation between actual and recorded value of helium; it is applied to the flow rate of the mixture to determine the flow rate of the hydrogen in the mixture.

Hydrogen is passed through the mass flow meter at constant flow rate of 0.6 SLPM. The flow rate of helium is varied from 0.2 to 1.0 SLPM. The mass flow rate of the mixture of both gases is recorded (Table A-3). The known flow rate of hydrogen is subtracted from the total flow rate to obtain the scaled flow rate of helium recorded by the flow meter which was used to determine the necessary correlation (Figure A-4).
Table A-3. Summary of the flow rates of hydrogen and helium observed in the process of mass flow meter calibration.

<table>
<thead>
<tr>
<th>No</th>
<th>Inlet H₂ flow rate (SLPM)</th>
<th>Inlet He flow rate (SLPM)</th>
<th>Flow rate of mixture (SLPM)</th>
<th>Flow rate of He (SLPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>0.2</td>
<td>1.03</td>
<td>0.43</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>0.4</td>
<td>1.48</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.6</td>
<td>1.93</td>
<td>1.33</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>0.8</td>
<td>2.39</td>
<td>1.79</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>1.0</td>
<td>2.84</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Figure A-4. The calibration curve for the mass flow meter to correlate the flow rate of helium measured by the flow meter and actual flow rate of helium.

**A.2. Determining the Starting Point of Oxidation Step**

In the current study, to facilitate accurate experimental measurement, a deliberate attempt was made to isolate the consecutive oxidation and reduction process by purging of the product gases with the inert gas like Argon. Thus, at the beginning of any process, oxidation or reduction, reactor contained inert gas only and it was purged.
by the product gas during initial time period of the reaction. In oxidation step, flow meter records flow rate of inert gas during purging process before it starts recording the flow rate of hydrogen. Thus it is critical to determine the time instance at which inert gas is completely purged out of the system and experimental measurements correspond to flow rate of hydrogen alone. During this study, independent techniques were adopted to determine the starting point of the oxidation reaction.

A.2.1 Mass-spectrometer signal analysis

In the previous section, role of mass-spectrometer was discussed in brief to identify the composition of the product gas. In oxidation step, mass-spectrometer serves as an alternative device to measure the flow rate of hydrogen. Moreover, it can be employed to determine the starting point of the oxidation step. As discussed earlier, in oxidation step, hydrogen generated during initial period of the process purges argon from the reactor and mass-spectrometer reads argon signal only. As argon is purged out completely its signal drops and hydrogen signals shoots up, indicating start of the oxidation step.

A.2.2 Analysis of the flow meter data

The mass flow-meter is not capable of distinguishing the composition of the gas flowing through it and there is no explicit method to identify the instance at which oxidation step begins. The flow rate data recorded by the flow meter indicates the demarcation point at which argon is completely purged out and hydrogen alone flows through the mass flow-meter. Figure A-5 shows the data recorded by the flow meter for oxidation step including purging of argon.
It can be observed that, as steam is introduced in the reactor, the flow rate of the gas rises quickly to 6 SLPM (approximately) and then drops to 2 SLPM. At this point, there is sudden change in slope of the rate of reaction which is attributed to the shift from purging of argon to oxidation reaction. This demarcation point is considered as a starting point of the oxidation step. It is validated by the starting point determined using mass-spectrometer signal.

**A.3. Smoothing the data**

The flow rate data recorded during oxidation and reduction step can be noisy; the reasons include,

1. The steam inlet flow rate observed during the experiments is in the range of 3-5g/min. The water supplied to the boiler at such a low flow rate is introduced in the form of drops rather than a continuous stream. Thus steam is generated in pulsating manner introducing fluctuations in hydrogen flow rate.
2. In the condenser, steam is getting condensed into water leading to two phase flow of hydrogen and water. Thus hydrogen flowing through the liquid water may lead to bubbling and introduce fluctuations in the flow rate measurements.

3. There is substantial temperature variation from outlet of the reactor to the point of data acquisition. Thus the density of the product gas varies significantly which may lead to fluctuations in the flow rate.

It is essential to smooth the raw data obtained from the measuring devices before conducting any analysis to avoid the propagation of the errors. A moving average of the flow rate data is calculated using MATLAB function ‘tsmovavg’. Figure A-6 compares the raw data obtained from the mass flow meter and the moving average calculated using MATLAB function. The post processing of the raw data effectively filtered the noise leading to smooth flow rate data that can be used for further analysis.

![Graph comparing unprocessed and smoothed data](image)

Figure A-6. A comparison between unprocessed data and smoothed data obtained by the moving average of the unprocessed data.
LIST OF REFERENCES


22. Pineau A, Kanari N, Gaballah I. Kinetics of reduction of iron oxides by H2


23. Pineau A, Kanari N, Gaballah I. Kinetics of reduction of iron oxides by H2


BIOGRAPHIC SKETCH

Amey Barde was born in year 1987 at Karad in state Maharashtra, India. He was born in educated, middle class family. His father was senior lecturer at College of Pharmacy, Karad and mother is a senior officer in Bank of India. He has an elder sister pursuing her career in German language and settled in her life. His mother shouldered responsibility of the family after sad demise of his father and has been a great support for him.

Amey finished his high school education at Karad and moved to Pune to pursue undergraduate degree in Mechanical Engineering. Pune is the educational hub in India and University of Pune is often referred as Oxford of East. He was admitted to PVG’s college of Engineering and Technology affiliated to University of Pune. During his undergraduate studies, he developed special interest for the subjects related to thermal science and fluid mechanics. He played a key role in the development of the novel design of the Stirling engine for his final year project. It was awarded by the first prize in at National Level Technical Competition conducted at NIT, Hamirpur, India. After completing his undergraduate study, Amey was joined Geometric Software Solution. The company is in the field of development of software tools that are important in the field of Mechanical Engineering. He was recruited as a software engineer in 3D PLM, a joint venture between Dassualt System, France and Geometrics Software Solutions, India. He was a member of a team that was in charge of development of the linear stress analysis module of design software, CATIA. He got an exposure to various software tools including C, C++ and CAA. Amey earned valuable industrial experience for two years before he decided to move back to academics and applied to pursue MS in Mechanical Engineering. He was keen to get involved in the research related to field
of thermal science and fluid mechanics; he soon joined Prof. Klausner’s research group to work on the investigation of two-step water splitting process via thermochemical looping of iron to generate high purity hydrogen. It has been a great opportunity for him to work on cutting edge technology that has potential to change the energy scenario in years to come. He was involved in the development of laboratory scale reactor facility for the analysis of the two-step water splitting reaction. Amey played a critical role in scaling of the laboratory scale technology to analyze its feasibility at industrial level. He took a special interest in the development of kinetic model of the reduction reaction to develop an analytical tool that can be used to design the reactors. Amey is co-author of two research papers published in the international journals. This experience has laid a foundation stone of his career.