Fixed bed reduction of hematite under alternating reduction and oxidation cycles

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Abstract

The rate of the reduction reaction of a low cost natural hematite oxygen carrier for chemical looping combustion was investigated in a fixed bed reactor where hematite samples of about 1 kg were exposed to a flowing stream of methane and argon. The investigation aims to develop understanding of the factors that govern the rate of reduction with in larger reactors as compared to mostly TGA investigations in the literature. A comparison of the experimental data with a model indicated that reaction between the methane and the iron oxide shows multi-step reactions. The analysis also shows that the conversion occurs with a process that likely consumes all the oxygen close to the surface of the hematite particles and another process that is likely controlled by the diffusion of oxygen to the surface of the particles. Additional analysis shows that the thickness of the fast layer is on the order of 8 unit crystals. This is only about 0.4% of the hematite; however, it comprises about 20 to 25% of the conversion for the 10 min reduction cycle.

Key Words: Chemical Looping Combustion, Fixed Bed Reactor, Hematite Reduction

1. Introduction

Over the past couple of decades, anthropogenic CO₂ has been proposed as the reason for climate changes. Whether or not these CO₂ increases have led to climate change or are the result of climate change, it is important to investigate technology options that can reduce and control CO₂ emissions. The U.S. Department of Energy has set goals for carbon capture systems at 90% carbon dioxide (CO₂) capture with less than a 35% increase in cost of electricity [1]. There are four main categories of these technologies that can achieve these goals: pre-combustion, post-combustion, oxy-fuel and chemical looping [2]. The work presented in this paper looks into the reduction performance of a fixed bed chemical looping system.

Chemical looping is a new name to a relatively old concept that was utilized in the early 1900s for the coal gasification technology called the Steam-Iron Process and again in the late 1960s and 1970s for another gasification technology which was called the CO₂ Acceptor Process [3]. The terminology, chemical looping, was introduced in the 1990s to refer to a cyclic process in which an oxygen rich solid was contacted with a fuel such as natural gas to reduce the oxygen rich solid to form carbon dioxide and

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water (combustion products). The reduced solid could then be transferred to another vessel and re-oxidized. The cycling of the oxygen carrier between the reducer vessel and the oxidizer vessel is now termed chemical looping combustion. A conceptual process diagram is shown in Fig. 1. In this figure, a bed of the oxygen carrying solid particles is fluidized with a recycle stream of CO₂ and steam. Fuel (methane) is introduced to this reactor to produce CO₂ and water according to the chemical reaction noted below:

where MO represents the oxygen rich solid, usually a metal oxide and M represents the reduced carrier. The combustion products exit the process as shown while the reduced carrier is conveyed to the oxidizer through a loop seal to keep the gases apart. The reduced carrier is re-oxidized according to the chemical reaction

In the concept loop shown in Fig. 1, the re-oxidized carrier is separated from the oxygen depleted air (vitiated air) in the cyclone, passed through a loop seal and fed back to the reducer to complete the “loop”.

Chemical looping combustion is under investigation around the world for power production because the technology allows for fuel conversion with easy CO₂ separation [4-6]. The current investigation is aimed at evaluating hematite, a naturally occurring Fe₂O₃ mineral, as an oxygen carrier for natural gas fuels applications. Fe₂O₃ has been cited as a potential carrier in numerous research publications [7-24] with many of these focusing on the development of required kinetics from TGA experimental investigations for scale-up of this technology.

In an effort to jump start the chemical looping combustion technology, the Office of Research and Development at the US Department of Energy’s National Energy Technology Laboratory is focused on a two pronged (experimental and modeling) approach to introduce and develop chemical looping combustion. In one aspect of this work, NETL-ORD has been investigating natural gas chemical looping with hematite. The work presented herein has two purposes. The first is to provide model validation data such that large reactors can be designed using modern CFD approaches that NETL is pioneering. The second is to provide possible operational assessment on small batch systems for early technology adoption. In this second objective, it has been thought that in the current unconstrained carbon world that early adopters might be found for industrial applications that can utilize both the carbon dioxide and the process heat. One such application that has been considered is for a small cyclic batch unit at a green house, where the CO₂ can be used to accelerate the plant growth. Therefore, to accomplish both of these objectives, small scale cyclic tests were carried out in a batch unit. The experimental results are discussed below.

2. Literature Review of Fe₂O₃ Reduction

Numerous researchers are investigating various naturally occurring and manufactured iron oxide based carriers for reduction with methane [5-24]. These are summarized in Tab. 1. Of particular interest is the work of Abad et al. [9], as they have put forward the most advanced and complete model for the reduction of ilmenite. Ilmenite is a naturally occurring iron and titanium mineral in the form of FeTiO₃. The actual material tests by Abad et al. [9] consisted of 94.3% ilmenite with the balance being rutile (TiO₂) and hematite (Fe₂O₃). The material had an Fe to Ti ratio of approximately 1. Abad et al. [9] found the reactions of ilmenite with methane to follow the reaction scheme noted below:

82 Reduction with methane

85 Reduction with carbon monoxide

88 Reduction with hydrogen

91 After cycling numerous times, Abad et al. [9] found that the titanium migrated to the center as the
92 iron migrated to the shell of the particles and the following reactions best described the reduction process
93 of a Fe_2O_3 reactive particle having an inert core.

94 Reduction with methane

96 Reduction with carbon monoxide

98 Reduction with hydrogen

100

101 **Tab. 1. Fe₂O₃ reduction work with methane**

Author	Reactor Type	Sample Size (mg)	Particle Size (μm)	BET Surface Area (m ² /g)	Sample Frequency (Hz)	Reduction Gas	Reaction Control	Carrie Form
Abad et al. (2007) [8]	Circulating bed	110,000	90 to 212	-	-	Natural gas (88% CH ₄)	-	60% Fe ₂ O ₃ and Al ₂ O ₃
Abad et al. (2011) [9]	TGA	50	150 to 300	.8	-	CH ₄ and steam	Shrinking grain	FeTiO ₃ (Ilmenite)
Adanez et al. (2005) [10]	Bubbling fluidized bed	2 x 10 ⁵	100 to 300	-	-	CH ₄ saturated with H ₂ O vapor	-	60% Fe ₂ O ₃ and Al ₂ O ₃
Cho et al. (2002)[11]	Bubbling fluidized bed	15,000 to 60,000	125 to 250	-	-	CH ₄	-	Fe ₂ O ₃ and Al ₂ O ₃
Gayán et al. (2012)[12]	Bubbling fluidized bed	2 x 10 ⁵	100 to 300	9.3	-	CH ₄ in N ₂	-	Fe ₂ O ₃ on Al ₂ O ₃
Go et al. (2008)[13]	TGA	7 to 8	125	9.055	0.033	CH ₄	Diffusion	Fe ₂ O ₃
He et al. (2007)[14]	Fixed Bed	60,000	1500 to 2000	-	-	Humidified CH ₄ in Ar	-	80% Fe ₂ O ₃ and Al ₂ O ₃
Johansson et al. (2004) [15]	Bubbling fluidized bed	10,000 and 15,000	125 to 180	-	-	CH ₄ and steam	Diffusion for materials that have seen high temperatures	Fe ₂ O ₃ on MgAl ₂ O ₄
Leion et al. (2008) [16]	Bubbling fluidized bed	15,000	125 to 180	-	-	CH ₄	-	FeTiO ₃ (Ilmenite)
Mattisson et al. (2004) [17]	Bubbling fluidized bed	10,000	125 to 180	-	-	CH ₄ and steam	Kinetic to Diffusion	60% Fe ₂ O ₃ and Al ₂ O ₃
Mendiara et al. (2012) [18]	Bubbling fluidized bed	3 x 10 ⁵	150 to 300	.9	-	CH ₄ and steam in N ₂	-	71% Fe ₂ O ₃ and Al ₂ O ₃
Moghtaderi et al. (2010) [19]	TGA	28 to 40	30 to 40	3.5	1	CH ₄ and steam	-	Fe ₂ O ₃
Monazam et	TGA	60		.1	1	CH ₄ in N ₂	Kinetic and	Fe ₂ O ₃

al. (2013) [20]							Diffusion (JMA)	
Son et al. (2006) [21]	Circulating bed	6×10^5	106 to 150	-	0.04	CH ₄	-	Fe ₂ O ₃ on TiO ₂ , Al ₂ O ₃ and bentonite
Zhang et al. (2012) [22]	TGA	-	-	4	-	CH ₄	-	75% Fe ₂ O ₃ and Al ₂ O ₃
Ku et al. (2014) [23]	Fixed bed	2.9×10^6	-	-		CH ₄ in N ₂	-	Fe ₂ O ₃ and Al ₂ O ₃
Y. Zhang et al. (2014) [24]	TGA	10 to 15	75 to 150	-	-	CH ₄ in N ₂	-	Fe ₂ O ₃ and Al ₂ O ₃
Current work	Fixed Bed	10^6	230	.1	1	CH ₄ in Ar	Discussed below	Fe ₂ O ₃

Based upon this finding, it was initially hypothesized that the hematite would behave similar to the cycled ilmenite – an assumption that will be shown not to hold in the analysis provided below. Abad et al. [9] found that the ilmenite methane reaction was kinetically controlled and followed the following equation

$$\frac{t}{\tau_i} = 1 - (1 - X)^{1/3} \quad (12)$$

In the above equation, X is the conversion of Fe₂O₃ and τ_i is the time for complete conversion which is given by

$$\tau_i = \frac{\rho_m r_g}{b k_{si} C_i} \quad (13)$$

where ρ_m is the molar density of Fe₂O₃, r_g is the grain radius, b is the stoichiometric coefficient, k_{si} is the reaction rate, C_i is the reacting gas concentration and the index i stands for CH₄, CO or H₂.

Monazam et al. [20], working at the US Department of Energy, National Energy Technology Laboratory (NETL), have been exploring the kinetics of North American iron containing ores, primarily hematite from Canada [20, 25-26]. Monazam et al. [20] found the reaction of methane with the Canadian hematite to occur with a two reaction process. (R_1 and R_2) according to equations 14 and 15 as opposed to the single step process obtained by Abad.

Based upon TGA experiments, Monazam et al. [20] showed that the kinetics for the first reaction (R_1) to be kinetic controlled and to follow the rate equations

$$\frac{dX_1}{dt} = k_1 (w_1 X_\infty - X_1) \quad (16)$$

$$k_1 = 4.759 y_{CH_4}^{0.636} e^{\frac{-4134.2}{T}} \quad (17)$$

where k_1 = rate constant for the first mechanism (min.^{-1}), w_1 = weight factor for the first mechanism, X_1 = conversion of Fe_2O_3 by R_1 at any time t , X_∞ = equilibrium conversion, t = time (min), y_{CH_4} is the methane mole fraction and T is the temperature (K).

In the same work, Monazam et al. [20] showed that the second reaction (R_2) to be controlled according to a nucleation and growth mechanism that behaved according to the equations

$$\frac{dX_2}{dt} = k_2 (w_2 X_\infty - X_2) \left(-\ln \left(1 - \frac{X_2}{w_2 X_\infty} \right) \right)^{1/2} \quad (18)$$

$$k_2 = 133 y_{CH_4}^{1.06} e^{\frac{-4731.2}{T}} \quad (19)$$

where k_2 = rate constant for the first mechanism (min.^{-1}), w_2 =weight factor for the second mechanism, and X_2 = conversion of Fe_2O_3 by R_2 at any time t . Three other relationships are needed for w_1 , w_2 and X_∞ .

$$w_1 + w_2 = 1 \quad (20)$$

$$w_2 = 0.7953 - 0.000644T(^{\circ}\text{C}) + 0.5443y_{CH_4} \quad (21)$$

$$X_\infty = -1.374 + 0.00237T(^{\circ}\text{C}) + 0.6624y_{CH_4} \quad (22)$$

The other authors [11-19, 21-22] worked primarily with supported Fe_2O_3 or mixtures prepared with various binders such as Al_2O_3 or SiO_2 . Furthermore, most use steam or at least humidified CH_4 to inhibit coke formation due to the CH_4 cracking. In general, the rate improved in these studies as the initial fabricated particle became conditioned after several cycles. This is in the opposite direction with the current study which is discussed below for the naturally occurring Canadian hematite reactions in a fixed bed.

Also, with regard to Tab. 1, there are some additional points of interest. The first of these is that Go et al. [13] found the reaction with Fe_2O_3 and methane to be diffusion controlled. That work used the smallest sample size reported. Also, Johansson et al. [15] found that materials that had seen high temperatures were diffusion controlled.

3. Experimental Facility and Test Procedure.

The test facility consists of a reactor which is fed from gas tanks (methane, argon, and oxygen) through the mass flow controllers which allow precise control of the gases. The reactor has an overall height 62.3 cm, an internal diameter of 6.0 cm in the lower reactor zone which is 34.8 cm high and 10.1 cm freeboard region. The reactor feed gases are fed to the reactor through a sintered quartz distributor plate. The temperature is measured at the bottom, middle and top of the 6.0 cm reacting zone. The product gases exit the reactor at the top through a 0.05 cm ID outlet tube. It is surrounded by heaters to control the reaction temperature. The feed gas reacts with the hematite inside the vessel and the product gases are directed through a mass spectrophotometer gas analyzer before it exits the system.

As noted above, experiments are being conducted for two purposes: to provide experimental validation of the TGA data and to provide an assessment of a small cyclic batch chemical looping unit for

early proof of concept adoption in a commercial setting where both the heat and CO₂ can be utilized. This latter objective put some constraints on the test conditions. Tests need to be carried out in a low methane flow rate to avoid coke formation. Steam, the expected diluent in larger conceptual units, gasifies the deposited carbon. In this smaller application steam is not available and methane concentrations need to be kept quite small, less than 10%. Therefore, in this initial assessment, two series of tests were conducted at 800°C, one at approximately 7.23% CH₄ by volume and the other at approximately 5% CH₄ by volume with the balance being argon. The tests conducted at 7.23% CH₄ were conducted at feed flow rate corresponding to a superficial velocity of 2.7 cm/s while the other test series was run at a corresponding velocity of 7.3 cm/s. The operating data for the two test series is summarized in Tab. 2. Tests in each series were conducted over a two day period and conditions varied slightly during each series between the days. The material was added to the reactor (nominally 1050 g) and the reactor closed up and the tests begun. The material properties are presented in Tab. 3.

Tab.2. Operating Conditions, Fixed T_{in} (800 °C) and Pressure (170 kPa)

	Series 1		Series 2	
	Day 1	Day 2	Day 1	Day 2
Flow rate, kg/s	6.45E-05	4.68E-05	1.51E-04	1.51E-04
Superficial Velocity, m/s	0.0318	0.0231	0.0735	0.0734
CH ₄ mass fraction	0.030	0.030	0.021	0.020
Cycles	1 - 4	5 - 9	1 - 5	6 - 10

Tab. 3. Material Properties.

	Units	Value
Composition		
Fe ₂ O ₃	%	95
Inert	%	5
Particle Size	um	200
Particle Density	kg/m ³	4770
Langmuir Surface Area		
800 °C	m ² /g	0.41
900 °C	m ² /g	0.09

The general experimental facility operation is summarized in Fig. 2. In this figure the temperature, gas flow rate and gas species mass fractions are shown. The temperature is ramped up to the operating temperature under an argon gas flow. Once the reactor temperature has stabilized at the set condition (800 °C), the fuel (reduction) gas flow is initiated and maintained for 10 minutes. This can be seen in Fig. 2 by the dip in the argon mass fraction and an increase in the CO₂ and CH₄ mass fraction values. At this time, the fuel gas is switched off and the argon flow increased to purge the reactor of combustible gas for approximately 25 minutes prior to regenerating the hematite with air. The carrier is regenerated for 20 minutes after which the air flow is stopped and the reactor purged of oxygen prior to starting the next reduction cycle. The temperature for the process is essentially constant at 800 °C as seen by the temperature trace with the exception of a small rise (15 °C) in the gas temperature when air is introduced during regeneration. This temperature rise will be shown to affect the cyclic stability of the carrier in batch operation.

4. Results

The gas composition data for methane, carbon monoxide and carbon dioxide are shown in Fig. 3 and 4 for tests series 1 and 2, respectively. In Fig. 3 and 4, the data for cycle 1 is significantly different than that for the other cycles in the test series. Looking at the CH₄ mass fraction data for cycles 1, 2 and 3 in Fig. 3, it can be seen that the exit concentration of methane for cycle 1 is significantly different from the values of cycles 2 and 3. Note, that a gas valve switching error occurred during the Series 1, cycle 4 test rendering the data unusable and subsequently omitted from Fig. 3. An ANOVA analysis conducted at a 95% confidence level showed that the mean values in cycles 1, 2 and 3 were not the same but that the means for cycles 2 and 3 were the same. The same finding was obtained for cycles 1 through 5 and 2 through 5 for methane in Fig. 4. Other interesting features in the data can be seen by comparing Fig. 3 to Fig. 4. In this comparison, it can be seen most clearly in the methane curves that there is a sudden decrease in the exit mass fraction for cycles 4 through 10. Incidentally, 40 more cycles have been conducted on the Series 2 conditions showing the same phenomena. This decrease in the methane composition is simultaneously accompanied by an increase in the carbon monoxide concentration and in the hydrogen concentration as seen by examining Fig. 5.

One last observation of the experimental results can be seen by looking at the CO₂ curves in both Fig. 3 and 4 for Series 1 and 2 noticing the “bubble” of excess CO₂ in Cycle 1 as compared to Cycle 2. The size of this “bubble” will be shown to be a function of the conditions during oxidation of the reduced carrier, but for now, note that it appears in only the first cycle of each series. Furthermore, it is interesting to note that this same “bubble” appears in the fluidized bed data taken at the NETL/DOE in its single fluid bed (SFB) facility for the same hematite, however, this “bubble” appears in all cycles not just the first. Also, this “bubble” appears in literature data, although not discussed in those works. For example, in the work reported by Adanez et al. [10] for mechanically mixed Fe₂O₃ and Al₂O₃ a “bubble” of CO₂ can be seen in the data. A summary of the information presented in the Adanez et al. [10] work and that for the NETL SFB results is presented in Fig. 6. In this figure, the normalized values of the CO₂ concentration are plotted against normalized value of time to fit the two data sets on the same graph. A “dashed” line is shown in both data sets to show the “bubble” of CO₂ that is present in both data sets. This implies that there is similar behavior for mixtures of iron oxide and iron oxide ore, at least in the early stages of the reaction.

5. Analysis and Discussion

Recent modifications to the Barracuda CFD software have resulted in speed improvements significant enough that it can now be used as an expedient tool for data analysis. Therefore, a model of the MIR reactor was built using the Abad et al. [9] mechanism and kinetics. The details of the model parameters are presented in Tab. 4. A summary of the code and its sub-models can be found Breault and Huckaby [27]. The Abad et al.[9] kinetics for ilmenite greatly over predicted the CO₂ product such that the amount of reactive Fe₂O₃ needed to be significantly reduced to produce comparable results. These are shown in Fig. 7. In Fig. 7, the experimental data for the first cycle is shown with the solid squares and that for the second cycle with solids circles. Note that the active Fe₂O₃ (33% in Abad’s mechanism) needed to be reduced to about 10% to reasonably model the first 40s of the first cycle prior to over predicting the conversion to CO₂ at times greater than 40s as shown by the simulation data marked by the open diamonds. Looking at the simulation curve with 5% reactive Fe₂O₃ (open circles), it can be seen that the predicted CO₂ at times less than about 150s shows significant differences when compared to the experimental data of the first cycle. However at times greater than 150s, the agreement is quite good. Looking at the second cycle, the predicted results (for 3% reactive Fe₂O₃) are quite similar with the experimental data, although it can be seen that the fit is not quite right and reducing the reactive content would give a better fit for the early times but misses the latter times as one can see that the slope of the model predictions (open triangles) is greater than the experimental data at large times. In summary, this plot gives two important clues to understanding the reaction with naturally occurring hematite and methane: (1) conversion to CO₂ consists of multiple reactions with a fast reaction and a much slower reaction and (2) hematite and ilmenite do not react similarly even though the ilmenite kinetics are based upon an Fe₂O₃ shell and a TiO₂ core.

239 Tab. 4. Barracuda Model Parameters

Parameter	Value or Minimum	Maximum
Δx	4.13 mm	5.99 mm
Δy	4.13 mm	5.99 mm
Δz	4.52 mm	5.19 mm
Δt	0.006 s	0.15 s
No. Clouds	216,160	
No. Particles	34,280,798	
No. Cells (Total)	50,400	
No. Cells (Real)	22,712	
Grid Technique	Cut Cell	
Model	E-L Hybrid (PIC)	
Frictional Shear Viscosity	Harris-Crichton $P_s = 1, B = 3, \epsilon = 10^{-8}$	
Turbulent Stress	N/A	
Particle-Wall BC	Smagorinsky $C_s = 0.01$	
Gas Boundary Condition	No slip	
Equation of State	Ideal Gas	
Energy Equations	Compressible no viscous heating	
Drag	Ergun/Wen-Yu agglomeration w/ 18 um cutoff	

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241 The above findings are further supported from a side by side comparison of TGA results for
242 ilmenite (Abad et al [9] and TGA results for hematite Monazam et al. [20] as shown in Fig. 8. In Fig. 8,
243 the solid carrier conversion (defined as $(\text{mass}_{\text{initial}} - \text{mass}_{\text{final}}) / (\text{mass}_{\text{initial}} - \text{mass}_{\text{FeO}})$) is plotted against time
244 for the results by Abad et al. [9] for ilmenite and by Monazam et al. [20] for the Canadian hematite used
245 in the present work. The differences in how the two ores react are quite apparent when the curves are
246 placed side by side. The ilmenite data show a more or less typical first order rate law conversion versus
247 time plot. A non- zero initial rate that is constant for about one third of the reaction time and then
248 decaying to zero as the full conversion of the carrier is asymptotically approached. This behavior
249 contrasts significantly with that for the hematite, which shows a period with a near zero initial rate that
250 lasts approximately 2 minutes in duration. The reaction then ignites at a rate corresponding to that seen
251 for the ilmenite material. Finally, the rapid reaction is somewhat extinguished leading to a period with a
252 much slower reaction rate. Monazam et al. [20] found that the conversion of hematite occurred through
253 two reactions as shown above; one rate having an initial non-zero value which occurred overall the times
254 investigated and a second reaction that had an initial rate near or equal to zero during an induction period
255 a high rate period that extinguished after a short period. This is consistent with the results herein as will
256 be shown.

257 An example of the methane reaction rate data as a function of time for one of the tests is shown in
258 Fig. 9. The shape of this curve as well as the shape of the CO_2 product curves, particularly for cycle 1 in
259 both sets of experiments, leads the author to believe that the rate is a combination of two reactions in
260 parallel as was found by Monazam et al [20]. The time series reaction rate data was then approximated

with the sum of two exponential functions as shown in Fig. 9. The overall fit for the sum of the two exponential curves and the experimental data has an R^2 value greater than 0.99. The area under the surface curve represents in the methane consumed in that reaction and is proportional to the mass loss of oxygen from the solid carrier particles. This ranges from about 0.1 to 0.5% of the carrier weight in the bed but as much as 25% of the conversion of the solid carrier over the 600 s of the reduction process. The area under the slow reaction curve, when extrapolated to zero corresponds to a carrier weight loss of

Now, knowing that the particle reacts rapidly with a thin shell at the surface and much slower with the bulk of the material, a reaction model can be identified. Therefore, a reaction model is proposed as follows, the overall reaction rate, R_T , is the sum of the surface reaction, R_s , and the core reaction, R_c .

$$R_T = R_s + R_c \quad (23)$$

Where these rates can be expressed as

$$R_s = k_s(u, S_A, T, y_g) X_s^{n_s} \quad (24)$$

and

$$R_c = k_c(u, S_A, T, y_g) X_c^{n_c} \quad (25)$$

Where the subscript, s , refers to the surface reaction and the subscript, c , to the core reaction. The rate constant, k , is a function of the gas velocity, u ; the particle surface area, S_A ; the temperature, T ; and the gas concentration or mole fraction, y_g . Also, the solids conversion is represented by, X and the superscript, n , represents the solids reaction order.

This model is applied to all the data for each series and each cycle. A typical plot of the results is shown in Fig. 10 for series 1, cycle 1. The sum of the surface and core models are compared to the experiment with an R^2 value greater than 99%. There is a slight deviation at the larger time values. This is, however, a relatively small error given the likely solids residence times (5 to 10 min) in a fuel reactor. The reaction order with respect to the solids was obtained from the model fit. The order for the core reaction, n_s , was found to be equal to 2. This is consistent with the stoichiometry proposed by Monazam et al. [20] which suggests this order ought to be near 2.6 which this appears to be. On the other hand, the reaction order for the surface reaction, n_f , was found to range from 4 to 12 with an average of 9. This is also consistent with the stoichiometry proposed by Monazam et al. [20] for the surface reaction which suggests that the reaction order should approximately 7 which it appears to be. A similar level of agreement was found for all the other cycles, with R^2 values for all cycles exceeding 0.99. The area under the surface model in Fig. 10 is represents the methane consumed in this process step. This mass is represents a penetration depth on the order of 50 to 60 °A. Given that a unit cell for Fe₂O₃ is on the order of 6.5 °A, the surface reaction occurs over a depth of about 8 unit cells. Since the grains are none porous (see Tab. 3) given the low surface area, for reactions to occur beyond this limit set by the surface reaction process oxygen must migrate to the surface through vacancy diffusion [28].

The rate constant for the surface reaction, k_s , for all the data is plotted versus cycle number in Fig. 11. General observations are that there is a slight decay (20 to 25%) in the rate with cycle number and that the rate constant for the high velocity series (Series 2) is about 3 to 4 times greater than that for the low velocity data.

Noting that in the proposed reaction rate model and that these experiments were conducted at a single temperature, the reaction rate constant reduces to a function of the gas concentration, the particle surface area and the gas velocity;

$$k_s = k_s(u, S_A, y_g) \quad (26)$$

The velocity effect is accounted for using the particle Sherwood Number. According to Kunii and Levenspiel [29] the Sherwood Number in fixed beds is a power function of the Reynolds Number. A fit of the data presented in Kunii and Levenspiel [29] gives the following relationship

$$Sh = 0.1061Re^{1.6} \quad (27)$$

Therefore, normalizing the reaction rate constant by the ratio of (u/u_i) raised to the 1.6 power where (u) is either the high velocity for the Series 2 data set or the low velocity for the Series 1 data should correct for the velocity.

The effect of methane concentration was analyzed by normalizing both sets of data by the inlet mass fraction of methane. It was postulated that since the fast reaction being discussed here is controlled by how fast that methane can get to the surface that the reaction front in the fixed bed would be quite sharp. This implies that the inlet gas concentration should give a better relationship between the rate constant and the functionality with concentration than using the mean value of the feed and exit concentrations during the reaction period. The results of this assumption can be seen in Fig. 12 in which the velocity normalized rate constant is divided by the inlet mass fraction. The comparison is quite good for the last five cycles or so. The reaction order was explored by assessing improvements to the agreement in the later cycles by changing the power that the methane mass fraction was raised. The best fit was for a reaction order of one.

Finally, the fast reaction rate constant was corrected for the changing surface area with cycle number (see material in Supplemental Data for this relationship). Applying this functionality by normalizing all the data in both sets by the ratio of the surface area at each cycle by the surface area for the first cycle (SA_i/SA_1) where 'i' is the cycle being analyzed. This brought all the data for both cycles to reaction rate constant corrected for velocity, surface area and methane concentration to a value of 0.028 at a 95% confidence interval as found through an ANOVA analysis of the Series means as is seen in Fig. 12.

A similar analysis was conducted for the core reaction where the reaction rate constant is presented in Fig. 13 as was done for the surface reaction. The most obvious trend is the decay in the rate constant with increasing cycle number. After correcting for the gas velocity, the particle surface area and the methane concentration the rate constants for the two series converged to an average of 29.2 with a 95% confidence level as determined by an ANOVA analysis of the two series means. This data is presented in Fig. 14.

The above findings have numerous implications in the design of commercial chemical looping combustion systems. The first, and likely the most important, finding is that regardless of the carrier type, heat generated within the particle during its oxidation in the air reactor has the potential to make permanent and adverse changes to the particle morphology as indicated by the strong effect seen above and reported by Johansson et al. [15]. In conventional, heterogeneous carbonaceous fuel combustion, the reaction products are gaseous and convect the heat of reaction out of the particle. This is not the case with the oxidation of chemical looping carriers. In this situation, the products are solid, keeping the heat of reaction within the particle. This causes locally high temperatures near the reaction sites and morphological changes of the carrier. The more dense the carrier, the more pronounced the morphological changes. By observing that fluidized bed operation at NETL/DOE and reported in the literature do not appear to have a significant decay in the performance with the limited number of cycles, indicates that if the particle temperature can be controlled by high heat transfer rates the carrier performance will be longer lasting.

Another finding is that both natural hematite and manufactured carriers (Johansson et al. [15]) both have a very fast surface reaction with methane followed by slower reaction(s) that progress by oxygen transport from the bulk of the lattice to the surface. The smaller the grains, the faster this process will occur. Grain size in naturally occurring ores cannot be controlled. This is the most likely reason why some hematite ores have poor reactivity and others do not. It also implies that manufactured carriers that are made with smaller particles should have better performance than carriers made with relatively large particles.

Abad's [9] particle reaction scheme for ilmenite was presented above in Equation 13 for shrinking core particle. A more likely scheme for the hematite is presented conceptually in Fig. 15. In this case, the particle consists of grains that are dense nonporous Fe_2O_3 masses. Also, the grains have germs or nuclei where reactions are favored. After initially removing the oxygen in these regions, the reaction proceeds by oxygen transport through the lattice to the germ at the surface, a relatively slow process for deep reduction. Incidentally, the oxidation of a deeply reduced particle will also be relatively slow as oxygen diffuses back into the solid lattice.

6. Conclusion

Fixed bed reduction-oxidation cycles were conducted using Canadian hematite in a nominally 5 cm diameter reactor with approximately 1 kg of the hematite. The hematite, as well as manufactured carriers utilizing Fe_2O_3 as the oxygen source, have a very fast surface reaction that depletes the grain surface to a depth of about 8 unit cells and then proceeds by one or more reactions that involve oxygen diffusing out of the lattice to the surface. There is an adverse effect on the rate and capacity caused by particle exposure to high temperatures during the oxidation half of the cycle. Increased heat transfer during the oxidation cycle can reduce and effectively cancel this effect. Increased heat transfer as experienced in the high velocity fixed bed work here and in fluidized bed conditions also increase the mass transfer of oxygen through the gas film to the surface. If this mass transfer is faster than the rate of oxygen diffusing out of the lattice, coke formation will occur. Also, the chemical reactions proposed by Monazam et al. [20] appear to be consistent with the data. Additionally, based upon these findings, a small scale fixed bed unit does not appear to be practical for an early demonstration due to the decay in the rate in these fixed bed units.

381 **Nomenclature**

382 b - the stoichiometric coefficient in Abad model

383 C_i - the reacting gas concentration in Abad model where i - denotes gas species CH₄, CO or H₂

384 k - rate constant in current work

385 k_1 - rate constant for the first mechanism in Monazam et al. model

386 k_2 - rate constant for the first mechanism (min.⁻ⁿ₁) in Monazam et al. model

387 k_{si} - the reaction rate in Abad model

388 n - solids reaction order

389 r_g - the grain radius in Abad model

390 Re - Reynolds Number

391 R_T - overall reaction rate in current work

392 R_f - rate of the fast reaction in current work

393 R_s - rate of the slow reaction in current work

394 S_A - the particle surface area in current work

395 Sh - Sherwood Number

396 t - time

397 T - the temperature (K) in Monazam et al. model and in current work

398 u - gas velocity in current work

399 w_1 - weight factor for the first mechanism in Monazam et al. model

400 w_2 - weight factor for the second mechanism in Monazam et al. model

401 X - conversion of Fe₂O₃ in Abad model and current work

402 X_1 - conversion of Fe₂O₃ by R₁ at any time t in Monazam et al. model

403 X_2 - conversion of Fe₂O₃ by R₂ at any time t in Monazam et al. model

404 X_∞ - equilibrium conversion in Monazam et al. model

405 τ_i - time for complete conversion in Abad model

406 ρ_m - the molar density of Fe₂O₃ in Abad model

y_{CH_4} - the methane mole fraction in Monazam et al. model

y_g - gas mole fraction in current work

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Disclosure

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Fig. 1. Chemical Looping Concept Configuration.

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operating cycle for experiments

Fig. 2. Typical

Fig. 3. CH_4 , CO and CO_2 mass fractions for Series 1

Fig. 4. CH₄, CO and CO₂ mass fractions for Series 2

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Fig. 5. H₂ mass fractions for Series 2

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Fig. 6. Comparison of CO2 exit gas profiles in other reactors

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530 approximately 10 %, the weight loss associated with a final conversion of the Fe_2O_3 to FeO .

531
532 **Fig. 8. A comparison of the TGA results of the hematite used in the current work to TGA data for**
533 **Ilmenite (Abad [9]).**

534

Fig. 9. Partitioning of the data into a fast and slow set for analyzing the process

Fig. 10. Comparison of rate models with experimental data for Series 1, Cycle 1.

Fig. 11. Reaction rate constant for surface reaction

Fig. 12. Reaction rate constant for surface reaction corrected for gas velocity effects, inlet gas concentration and particle surface area

Fig. 13. Reaction rate constant for core reaction

Fig.14. Reaction rate constant for core reaction corrected for gas velocity effects, inlet gas concentration and particle surface area

Fig. 15. Particle grain model with oxygen diffusion from the lattice core