

Kinetics of Direct Iron Ore Reduction with CO-H₂ Gas Mixtures

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Abstract— Though the reduction of iron oxide pellets by reducing gases is a well-studied phenomenon that has found a wide technological application, many poorly understood factors such as the effect of the water gas shift reaction on the reduction process and whether the reduction process is diffusion or interfacial chemical reaction controlled or mixed controlled still exist. The effect of diffusion and interfacial chemical reaction on the reduction of CVRD and KPRS pellets were investigated by varying the process temperature, and gas composition (H₂-CO mixture), and using diffusion and chemical reaction models to calculate the effective diffusion coefficient (D_e) and the chemical rate constant (K_r). The results from the study showed that the reduction process is both diffusion and interfacial reaction controlled. That is the initial stage of the reduction process is interfacial chemical reaction controlled while the later stage is diffusion controlled. By examining the phases present after the reduction process with optical microscope, it was observed that the phases present were mainly metallic Iron and Wustite since all the experiments recorded a reduction degree greater than 35%. The presence of cracks especially in the pellets reduced with H₂ was observed and it was attributed to the rapid diffusion of H₂ through the pellets during the reduction process.

Keywords—Iron ore pellets, Direct Reduced Iron, Diffusion, Chemical Reaction Controlled

I. INTRODUCTION

The global steel production has increased for more than 500 % over the last 5 decades. This can be attributed to the fast increasing steel production in China, currently the number one steel producer in the world [1]. The steel industry is faced with enormous environmental problems which are related to energy requirement, material usage and the by-product associated with the production process [2]. The conventional steel making process requires the use of coke. One major problem associated with the coke production is the emissions of hydrocarbons which are hazardous to the environment. A new technology which has emerged as result of the attempts being made to reduce the environmental problem associated with steel production is the direct reduced iron (DRI) technology.

A lot of research has been conducted so far as the DRI technology is concerned and as a result is currently being used in the steel production industry. DRI process does not require coke making and sintering, therefore it is more environmentally friendly and less capital intensive than the conventional steel production routes [3]. DRI technology involves the direct reduction of iron ore mainly hematite

(Fe₂O₃) in the form of pellets and lumps by a reducing gas which consist of Hydrogen (H₂) and Carbon Monoxide (CO).

As already mentioned, DRI technology which is an alternative route for iron making has been developed to overcome some of limitations of the conventional route. This process is mostly carried out in a shaft furnace with the reduction occurring in stages. The reduction process occurs above 570 °C and involves the following steps: the reduction of Hematite to Magnetite (Fe₃O₄), which is further reduced to wustite (FeO), and the reduction of wustite to Iron (Fe). Due to the instability of the wustite phase at temperatures below 570 °C, the magnetite is reduced directly to Iron at those temperatures [4].

There has been a rapid increase in the production of iron via the direct reduced process over the past 15 years. DRI technology is dominated by the MIDREX and HYL processes. In the MIDREX process, the iron oxide feed descends in a cylindrical shaft furnace and is heated and reduced by rising hot reducing gas. The reducing gas used in this case is nearly 95 % H₂ and CO with H₂ to CO ratio of 1.5-1.6 [4]. The basic HYL process employs a conventional natural gas-steam reformer for reducing gas generation. In this process, oxygen is removed from the iron ore by chemical reactions based on H₂ and CO from the gas-steam reformer. The reformed gas is typically 72 % H₂ and 17 % CO [4].

Most of the DRI technologies developed so far make use of CO as the major reducing gas. Reduction of iron ore pellets with CO leads to the generation of enormous amount of CO₂ which affects our environment negatively. The global anthropogenic emission of CO₂ is expected to increase to 37 Gt by 2020 [1,5,6]. It is well known that, the iron and steel industry is one of the largest producers of CO₂ in the metallurgical processing field, with a 3Mt blast furnace emitting as much as 4Mt of CO₂ per year. This value is comparable to CO₂ emitted by a 500MW coal fired power plant. In 1996, the iron and steel industry was responsible for 4.6 % of the total global CO₂ emission of 23.9Gt. With the increasing worldwide awareness of the effects of CO₂ emission on the global climate, the use of alternative ‘cleaner’ fuels and reductants in the iron and steel industry can be seen as an inevitable step [7].

The use of H₂ alone as a reducing gas results in a higher reduction of the iron ore pellets to iron, however the whole reduction process is thermally disadvantageous. Therefore a proposed CO-H₂ otherwise known as syngas (synthetic gas) is

being investigated for use as a reducing gas for the DRI process. The use of iron ore pellets as the main ore for the DRI process requires the need to investigate the kinetics of the reduction process. As will be shown in the theory section, such a reduction process follows the shrinking core concept with reducing gases diffusing through the pellets and reacting with the iron ore with subsequent diffusing of product gases out of the pellets. It can therefore be postulated that two processes may be controlling the reduction process; that is the diffusion of the reducing gases into the pellets and the reaction of the reducing gases with the ore. That is a lot of questions need to be answered so far the DRI technology is concerned. Some of these are: is the reduction process diffusion controlled? Is it interfacial chemical reaction controlled? and is it mixed controlled?

The main objective of this work is therefore to carry out laboratory investigations of the effect of diffusion and interfacial chemical reaction on the DRI process using mixed gases and then carrying out optical microscopy analysis to determine the manner in which the reduction occurred and the phases formed after the reduction process.

II. KINETICS OF THE REDUCTION PROCESS

The reduction of iron ore passes through a number of stages. That is the hematite is reduced to magnetite, then the magnetite is reduced to wustite and the wustite is then reduced to Iron as represented in Figure 1.

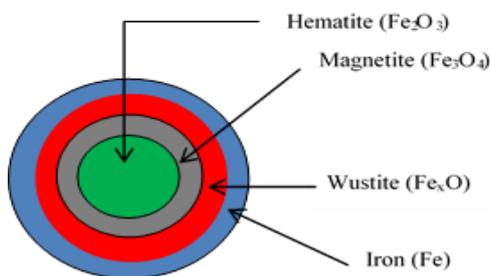


Figure 1 Shrinkage Core Concept

The complexity of the problem can be reduced by considering the reduction of wustite to iron.

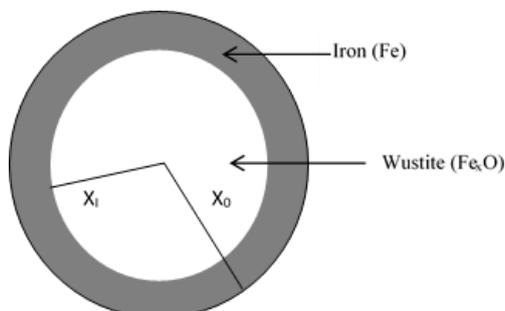


Figure 2 Shrinkage core concept for reduction of Wustite to iron

The removal of oxygen at the iron-wustite interface of a dense particle must proceed through the following 5 steps occurring during the reaction [8]:

- The Transport of gaseous reactant (hydrogen or carbon monoxide or both) from the bulk gas phase to outer surface of iron (Fe); (gas-film resistance)
- Diffusion of hydrogen or carbon monoxide through the porous iron layer to the surface of the un-reacted oxide core, in this case the iron-wustite interface; (shell-layer resistance)
- Chemical reaction of the gas with solid oxide (Wustite) to form gaseous product, water and or carbon dioxide; (interface resistance)
- Outward diffusion of the product gas through the iron layer; (shell-layer resistance).
- And transfer of product species from the outer surface of iron layer to the bulk gas (gas film resistance)

This model is generated based on the shrinking core concept that is the unreacted shrinking core model. However, this suffers from two major setbacks when it is specifically used for modelling gas-solid reactions in a porous pellet;

- The existence of a sharp boundary between the reacted and unreacted zones which contained both totally reduced and only partially reduced grains is not generally supported by experimental evidence.
- In this types of model, the role played by structural parameters (like porosity, grain size etc) in determining the overall reaction rate does not appear explicitly [9, 10].
- These steps offer resistance in series to the overall chemical reaction. If one is considerably slower than the others, it may be identified as “the rate controlling step”. The model for predicting the degree of reduction or oxidation can derived by considering the rate of gas film resistance, shell-layer resistance and the interfacial resistance [5, 9].

III. CHARACTERISING THE KINETICS OF THE REDUCTION PROCESS

Based on previous studies, it can be concluded that, the reduction of the pellets proceeded topochemically. This kind of reaction includes the process of diffusion of gaseous species and that of intrinsic chemical reaction. The total reduction time is expressed in Eq (1), and is valid under conditions of solid sphere being reacted with a gas phase, the effect of gas phase mass transfer being negligible and the reaction rate controlled by interfacial chemical reaction and the diffusion of reactant and product gas species through the solid product layer.

$$t = \frac{r_o \rho_o}{k(C_o - C_q)} \left[1 - (1-R)^{1/3} \right] + \frac{r_o^2 \rho_o}{D_e(C_o - C_q)} \left[\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2} \right] \dots \dots \dots (1)$$

Where t is reduction time (min), C_o and C_q are reduction gas concentration at granule surface and in equilibrium respectively (mol/cm^3), r_o is characteristic initial radius of the pellet (cm), ρ_o is initial oxygen concentration in the pellet (mol/cm^3), k is the reaction rate constant (cm/min), D_e is the effective diffusion coefficient (cm^2/min) and R is the reduction degree. The first part of the equation represents the reaction controlled part of the process and the second part represents the diffusion controlled part of the process [11].

IV. MATERIALS AND METHODS

A. Iron ores investigated

The two ores investigated in this experiment were KPRS pellets from LKAB and CVRD pellets from Arcelor-Mittal. In terms of the pellets sizes, the KPRS pellets are quite smaller than the CVRD pellets.

B. Reducing the Iron ore pellets in TGA equipment

The reduction of the pellets was carried out in a TGA furnace and the detailed description of the process is reported in our previous article [12]. Briefly, different samples of the pellets (KPRS and CVRS) weighing about $\sim 250\text{g}$ was used for the analysis. Half of the samples were first placed in the crucible, the thermocouple detecting the temperature of the samples was placed in the middle of the sample and the remaining pellets were added. This was done to improve the accuracy of the temperature taken by the thermocouple. The crucible was then connected and placed in the furnace. The various process parameters were programmed into the LabVIEW software so that, the degree of reduction, and sample temperatures could be examined.

C. CO-H₂ gas mixture Composition variation

The sample (KPRS) pellets were heated to a temperature of $\sim 812^\circ\text{C}$ in the furnace within a time interval of 45 minutes in Ar. The temperature was held at $\sim 812^\circ\text{C}$ for two hours during which the sample was subjected to different gas composition and the degree of reduction monitored. The different gas compositions examined at this temperature include: 100 % CO, 100 % H₂, 20 % CO and 80 % H₂, 40 % CO and 60 % H₂, 60 % CO and 40 % H₂ and 80 % CO and 20 % H₂ with 100 % corresponding to 5 l/min flow rate of the reducing gas. Before and after the experiment, the furnace was purged with Ar for 15 minutes. This was done to ensure that, no traces of the other gases are left in the gas tubes. The first experiment was carried out at the said temperature ($\sim 812^\circ\text{C}$) because the equilibrium constant for the water gas shift reaction (WGSR) is Approximately 1 at this temperature.

D. Temperature variation

The effect of temperature was investigated by carrying out the reduction process for a fixed composition of the KPRS pellets at different temperatures; that is 812 and 822 $^\circ\text{C}$.

E. Optical microscopy analysis

The reduced CVRD and KPRS pellets were analysed with an optical microscope to examine the manner and degree of reduction since the shrinking core concept for the reduction of the iron ore pellets to iron can easily be seen under an optical microscope. The pellets from the TGA equipment were imbedded in EpoFix resin and were left for eight hours to harden. The pellets imbedded were removed and divided into two halves. The cut samples were grinded with SiC paper on a rotor and images of the surface taken.

F. Etching

In order to see clearly the different phases in the polished pellets, the samples were etched in 5 % HF. This was achieved by putting the polished pellets in 5 % HF solution for 20 seconds. After which they were washed thoroughly using distilled water to remove traces of the etchant from the polished sample. Images of the etched dried samples were taken after which the microstructure of the various revealed phases were observed in optical microscope and pictures of the various microstructures taken

V. RESULTS AND DISCUSSION

A. Microstructural analysis of the reduced pellets

From Figure 3 it can be seen that the reduction of the iron ore pellets followed the shrinking core concept. That is the reduction of the iron oxide (hematite) occurred in concentric layers or rings. The outer ring is likely to be made up of mainly reduced iron while the inner ring is made up of unreduced hematite, magnetite and wustite. Hence the nature of the reduction process can be well explained with the shrinking core model.



Figure 3 Picture of the cut etched sample reduced in 5 l/min H₂ for CVRD pellets

The iron ore pellets made up of mainly hematite was reduced to magnetite, which was then, reduced to wustite and the wustite was reduced to metallic Iron. From the images in Figure 3, three layers can be observed: the first outermost layer can be speculated to be mostly metallic Iron. This is due to the fact that, a microscopic observation revealed shiny grain structure which is a representation of metallic Iron. The next layer (intermediate) is mostly a combination of the metallic Iron and an unreduced oxide (hematite, magnetite and

wustite). The reduction of hematite to magnetite and from magnetite to wustite has a reduction degree of 11.1% and 35 % respectively [7]. Since the total reduction degree recorded for all the experiments in this study as reported in our previous article exceeded 35 %, the unreduced oxide was mainly wustite. The third layer, which is mainly in the center of the reduced pellets, is made up of unreduced wustite.

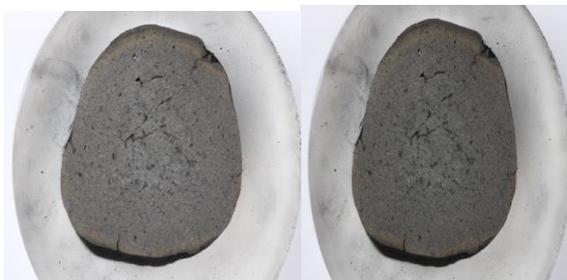


Figure 4 A picture of a cut etched CVRD pellet reduced in 5 l/min CO

Different crack sizes and lengths were observed in the reduced pellets upon examination. Larger and visible cracks were observed in the pellets reduced with 100 % H₂ (Figure 3) compared with those reduced with 100 % CO (Figure 4). The cracks may be related to a large degree in swelling associated with pellets reduced in H₂. Pellets reduced in H₂, swells easily due to the rapid phase transformation (Hematite-Magnetite-Wustite-Iron), which is associated with the higher reduction degree observed with H₂. It can also be attributed to the faster rate of H₂ diffusion through the reactants and product layers in the pellets [12].

Comparing the images in Figures 3 and 4, it can be deduced that, the nature of the shrinking core differs with respect to the kind and composition of the reducing gas used. A vivid observation of the various images depicts that, the pellets reduced from a gas composition of 100 % H₂ has a very visible reduced concentric layers. This can be associated with the higher rate of reduction associated with using H₂ as a reducing gas. However an almost invisible concentric rings were observed in the case where pure CO was used as the reducing gas. By varying the composition of CO-H₂ gas mixture, it was observed that, the gas mixture with higher H₂ content recorded a much visible ring compared to those with higher CO content. The observed trend is due to the faster diffusion rate of H₂ compared to CO and the fact that oxygen removal rate by H₂ is higher than CO as we reported earlier [12].

The etched samples were mounted on a light microscope and images of various sections taken to examine the morphology of the reduced pellets. The images were taken from the centre and edge of the cut samples using a magnification of 50X. Both the CVRD and KPRS pellets were used in this analysis.

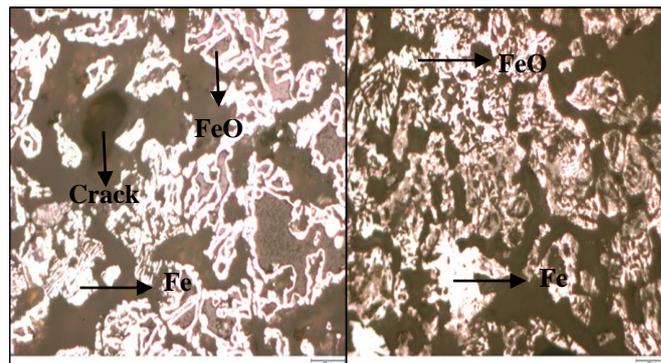


Figure 5 Optical microscope images of the; (Left) centre and (Right) edge of a CVRD pellets reduced in 5 l/min H₂.

Different microstructural phases were observed from the reduced pellets as can be seen in Figure 5. The optical microscopic images of metallic iron showed a shiny metallic surface, which can be speculated to be metallic iron. The light grey strips can be associated with the unreduced oxide. As already stated, considering the overall degree of reduction, the unreduced iron was wustite since all the hematite and magnetite has been reduced. The reduced phases were pronounced at the edges of the pellets than the inner region. This is not surprising since the pellet edges were exposed to the reducing gases at the entire duration of the reduction process. There exist some pores (cracks) in the pellets after the reduction process. The phases present in Figure 5 would have been best identified by using Electron Micro-Probe Analyzer (EMPA), but it was not used due to its unavailability.

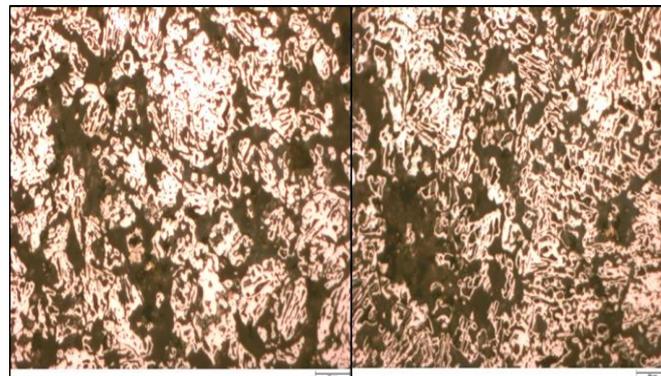


Figure 6 Microstructural images of the; (left) centre and (right) edges of the reduced pellets in 3 l/min H₂-2 l/min CO gas mixture

A similar morphology of the reduced pellets was observed by combining the reducing gases in different ratios. Referring to Figure 6, it was observed that, the edge of the sample was mainly made up of a shiny structure which is metallic Iron while the centre of the pellets was made up of light greyish grains which can be attributed to the unreduced oxide (wustite) with some shiny metallic iron. Some of the phases identified resulted from the EpoFix used in the imbedding. There were also some cracks that resulted from the rapid diffusion of the reducing gasses through the pellets.

B. Kinetics of the reduction process

From Eq (1), two different graphs can be drawn to investigate whether the process is chemical reaction

controlled, diffusion controlled or mixed controlled. For the reaction controlled part, a plot of

$$\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2}$$
 against reducing time (min)

gave a straight line whose slope is $\frac{D_e(C_o - C_q)}{r_o^2 \rho_o}$

while for the diffusion controlled part, the slope of the

$$\frac{k(C_o - C_q)}{r_o \rho_o}$$

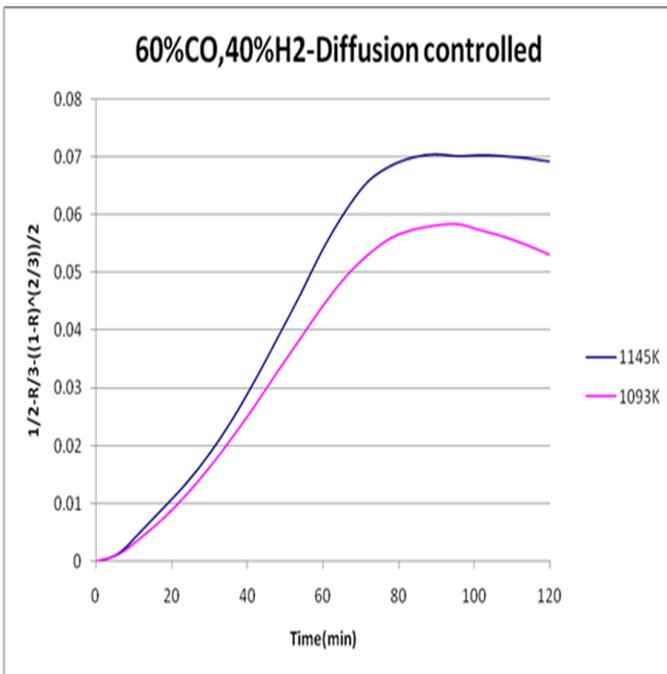


Figure 7 A plot of $\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2}$ vs time (min) for the reduction of KPRS pellets by 60 % CO - 40 % H₂ gas mixture.

Different observations were made from the plots obtained with a reducing gas composition of 60 % CO and 40 % H₂. From Figure 7, it can be seen that the plot is not perfectly straight. The early stages of the plot curved slightly while the later part is fairly straight. The calculated slopes for the straight portion of the curves are summarized in Table 1. By considering the same gas composition in Figure 8, it was observed that the early stages of the curve was fairly straight while the later part of the plot started curving earlier than that of Figure 7 and 9. The slopes of the straight portion of the curves were calculated and summarized in Table 1.

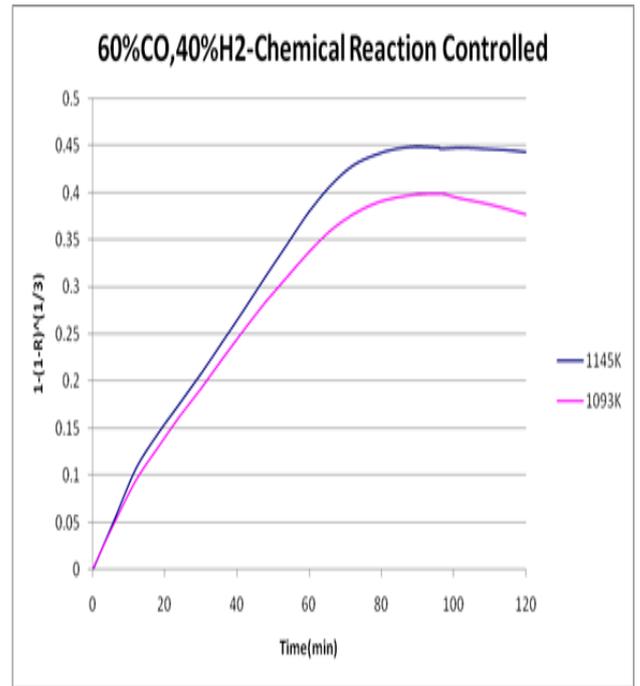


Figure 8 A plot of $1 - (1-R)^{1/3}$ vs time (min) for the reduction of KPRS pellets by 60 % CO -40 % H₂ gas mixture.

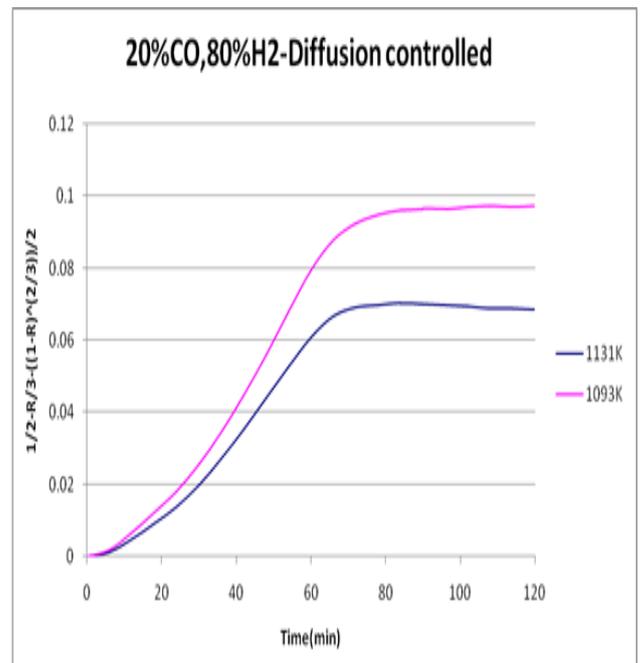


Figure 9 A plot of $\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2}$ vs time for the reduction of KPRS pellets by 20 % CO -80 % H₂ gas mixture.

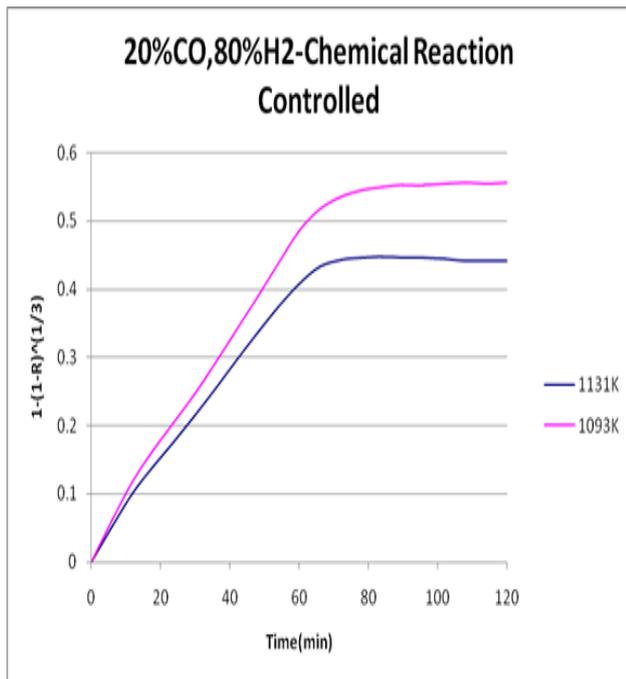


Figure 10 A plot of $1 - (1 - R)^{1/3}$ vs time for the reduction of KPRS pellets by 20 % CO -80 % H₂ mixture.

The features of Figures 9 and 10 were the same as those of Figures 7 and 8, respectively. Their slopes were summarized in Table 1.

Table 1 Slope of the straight portions in Figures 7-10

Figure	Temperature (K)	Slope (min ⁻¹)
7	1145	0.0013
	1093	0.00093
8	1145	0.0058
	1093	0.0051
9	1131	0.002
	1093	0.0014
10	1131	0.0072
	1093	0.0067

The kinetics of the reduction process can best be analysed by taken into consideration the factors that control the reduction process as stated in the theory. In order to achieve this, different plots were made with equation 1 and analysed. Examining Figures 7 to 10, it can be seen that, the chemical reaction controlled curves show straight line in the initial stages of the curve while those of the diffusion controlled show straight line at the later part of the curve. This implies that, the initial stages of the reduction process were interfacial chemical reaction controlled while the later part of the process was diffusion controlled. The initial stages of the reduction process were characterized with the diffusion of reducing gas

through the pellet; therefore there was enough concentration build up in the pellet to allow for the diffusion process to occur. The only process which can slow down the reduction process is the reaction between the reducing gasses and the iron ore pellets. That is the rate limiting step is the interfacial chemical reaction between the reducing gasses and the iron ore. At the later stages of the reduction process, the rate limiting step is the diffusion of the reducing gasses through the product and reactants layers. The rate of diffusion is reduced as a result of the decreased driving force, which is associated with reduction in concentration difference between the reducing gasses at the surface and at the centre of the pellets. The rate of diffusion is further reduced with the formation of more metallic irons. As a result, the later stages of the reduction process were diffusion controlled. From the above analysis, it can be deduced that, the reduction process of the Iron pellets is both diffusion and chemical reaction controlled, that is the process is mixed controlled. The calculated reaction rate constants (Kr) and Effective diffusion coefficient (De) are summarized in Table 2

Table 2 Calculated kinetic parameters

Gas composition	Temperature (°C)		High temperature		Low temperature	
	High	Low	De (cm ² /min)	K (cm/min)	De (cm ² /min)	Kr (cm/min)
100 % H ₂	850	815	1195	9842	824	7548
80 % H ₂ , 20 % CO	858	820	920	6776	632	5960
60 % H ₂ , 40 % CO	867	814	612	5712	461	4458
40 % H ₂ , 60 % CO	870	820	556	5044	317	3479
20 % H ₂ , 80 % CO	870	816	334	3666	231	2693
100 % CO	878	825	322	3612	188	2456

Since the reduction process is both diffusion and chemical reaction controlled, the kinetics of the reaction can best be studied by calculating the effective diffusion coefficient (De) and the rate constant (Kr) for the different experiments carried out. The effect of the various gas compositions on the reduction process can be analyzed by calculating De and Kr. From Table 2, the effect of the various gas composition can be clearly seen by taken a closer look at the De and Kr values. It was observed that, as the H₂ composition increased, Kr and De became larger. However a significant reduction in De and Kr occurred when the CO composition was increased. This can be connected with the easy diffusion of H₂ through the pellets than CO as already mentioned in the early part of the discussion. The reduction process was therefore characterized with higher reduction degree when H₂ was used as the reducing gas and also when the H₂ content in the reducing CO-H₂ gas composition was increased.

VI. CONCLUSIONS

The results from the study showed a pronounced reduction of iron ore pellets to metallic iron at the edges of the pellet and the unreduced iron ore was mainly wustite. From the kinetics analysis, we concluded that the entire reduction process was mixed controlled since the initial and later stages were interfacial chemical reaction and diffusion controlled, respectively.

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