Mechanism of Iron Oxide Reduction with Hydrogen/Carbon Monoxide Mixtures*

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Synopsis

Pure iron oxide briquettes, having different grain size and porosity, indurated at different temperatures, were reduced with H_2 , CO and mixtures of both gases which are representing reformed natural gas, over the temperature range of 800° to 1100°C. The reduction mechanism deduced from activation energy calculations, microscopic examination, chemical and X-ray analysis, was found to depend mainly on the original structure of the briquette and the reducing gas composition.

Reduction of dense briquettes with H_2 is controlled by the chemical reaction and becomes mixed controlled by both the chemical reaction and gaseous diffusion for reduction with either CO or CO/H_2 mixtures, with more contribution of the gaseous diffusion part as the CO ratio in the gas increases. Reduction of porous briquettes is diffusion controlled for all gases. Rate minima for porous briquettes were detected at 975°C for CO reduction and at 1025°C for CO/H_2 mixtures. The overall reduction rate exponentially varied with gas composition.

I. Introduction

In view of the abundant and cheap reserves of natural gas in many parts of the world and due to its economical and technical advantages in reducing iron ores, many gaseous direct reduction processes are now well developed on industrial scale. On the other hand, the continuous decrease in the world reserves of suitable metallurgical coke and the increase in its prices add problems to the use of the traditional blast furnace, especially in countries lacking in coking coals.

The present investigation is a trial for understanding the reduction mechanism of fired hematite briquettes, of low and high porosity, during reduction with H_2 /CO mixtures which are the constituents of reformed natural gas.

The complexity of the reduction process combined with the fact that under different experimental conditions the controlling stage of the reduction process may not be necessarily the same, has led workers in this field to a wide diversity of opinions regarding the reduction mechanism. Some authors studied gas diffusion controlled reactions,¹⁻⁹ solid-state diffusion controlled reactions¹⁰⁻¹² and chemically controlled reactions.¹³ Many others derived mathematical models describing the reduction process,¹⁴⁻²⁰ but most of them are limited for certain conditions. Reduction with H_2 ,⁵⁻¹³ CO,²¹⁻²⁴ mixtures of both gases²⁵⁻²⁸ and natural gas^{29,30} were also studied.

II. Experimental

Chemically pure iron oxide was used to avoid side effects arising from other ingredients in the ore. The method of preparation of briquettes, their firing and

porosity measurements were given in a previous paper.³¹ Characteristics of the briquettes are shown in Table 1.

A weight-loss method was used for accurate determination of the course of reduction. The reduction system was as described previously,³¹ except for the addition of a purification system for CO. The total gas flow rate for pure gases or for mixtures is 1 l/min. Analysis of carbon in reduced briquettes was carried out by the ignition method (using Carbon & Sulphur Apparatus, Strölein, W. Germany).

III. Results and Discussion

Two types of briquettes were used in the present investigation, the dense, having 7% porosity and constitutes of about 200 μ particles sintered together; the other is porous, 35% porosity and 100 μ particles. These two materials were reduced with CO or 25, 50 and 75% mixtures of CO/H_2 . Reduction with H_2 was extensively studied in a previous paper,³¹ and will be considered here for comparison.

1. Reduction of Dense Briquettes

1. Rate of Reduction

Figure 1 represents the reduction curves of dense Fe_2O_3 briquettes with CO. It shows that reduction stops at about 40% at 700°C and at 85% at 800°C, but is complete at higher temperatures. Incomplete reduction at low temperatures is ascribed to the great amounts of carbon deposited on the surface of the briquettes, which seal up the porosity preventing diffusion of the gas.

By adding H_2 to CO the reduction rate was improved as indicated by Fig. 2, which is a plot of initial reduction rates against gas composition. An example for the reduction curves obtained for gas mixtures is given in Fig. 3. Incomplete reduction is also observed at 700° and 800°C but at higher reduction extents as compared with CO reduction.

Table 1. Characteristics of Fe_2O_3 briquettes

Sample	Firing Temp. (°C)	Diameter (mm)	Height (mm)	Total porosity (%)	Mean grain diameter (mm)
Green	110	12.3	13.4	50	0.33
Porous	850	10.8	12.2	35	1.04
Dense	1000	9.8	11.1	7	2.10

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Fig. 1. Reduction curves of dense briquettes with CO

Fig. 2. Effect of gas composition on the rate of reduction of dense briquettes at 1000°C

Comparing with H_2 reduction,³¹⁾ it is clear that H_2 gives faster reduction rates than CO, and by mixing the two gases the rates are intermediate. Thermodynamically, H_2 reduces Fe_2O_3 more easily than CO as revealed by the free energy changes calculated for both cases (Table 2).³²⁾

For reduction with gas mixtures, the relative contribution of each gas to the overall reduction rate depends on the activity of its molecules and their selective adsorption on the iron oxide surface.

2. Temperature Effect on the Reduction Rate

Turkdogan and Vinters³³⁾ found that the measured overall reduction rate is not equivalent to the specific rate of the chemical reaction but it also depends on the active surface area of the oxide and the diffusion

Fig. 3. Reduction curves of dense briquettes with a 50% CO/ H_2 mixture

coefficient of the reducing gas. Accordingly, activation energy values obtained from plots of the overall reduction rate against reciprocal of absolute temperature, does not necessarily correspond to the specific rate of chemical reaction but more reasonably to whatever process is controlling. Strangway³⁴⁾ could classify apparent activation energies for the reduction of iron oxide in ranges corresponding to the rate controlling process.

Figure 4 presents Arrhenius plots for the reduction of dense briquettes* with different gas compositions. The activation energy values assessed from these lines varied according to the gas composition as shown in Table 3, which implies the variation of the rate controlling process with gas composition.

3. Microscopic Examination

Partially reduced briquettes reveal the lack of sharp boundaries between phases which interfere in rather wide bands. (Hematite and magnetite will not be included in this investigation since the transformation of wustite to iron is considered as rate controlling). Photograph 1(a) represents the iron-wustite intergrowth in a briquette partially reduced with a 50% CO/H₂ mixture. It shows irregular growth of iron within the wustite phase which is highly porous. This does not significantly differ from the structure of CO reduced briquettes. On the other hand, H₂ reduction showed that wustite patches are surrounded by iron layers³¹⁾ in a shrinking core type of reaction.

It is also observed that for reduction with CO or CO/H₂ mixtures, the iron phase always consists of two zones (Photo. 1(b)), the outer is more porous and is mainly iron carbide (as will be shown by X-ray analysis), the inner being iron. For H₂ reduction, one iron zone is usually detected.

Table 2. Standard free energy changes for reduction of Fe₂O₃ with H₂ and CO at 1000°C

Reaction	ΔF° (kcal)
$\text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O}$	-36.00
$\text{Fe}_2\text{O}_3 + 3\text{CO} = 2\text{Fe} + 3\text{CO}_2$	-31.00

Table 3. Activation energies for reduction of dense briquettes

Reducing gas	E (kcal/mol)
100%CO	7.55
75%CO + 25%H ₂	8.94
50%CO + 50%H ₂	9.59
25%CO + 75%H ₂	10.83
100%H ₂ ³¹⁾	12.80

4. Mechanism of Reduction

For H₂ reduction the initial parts of the reduction curves are mostly linear (up to 50~90% reduction depending on temperature) indicating a constant rate of reduction.³¹⁾ The activation energy value obtained for this case (12.8 kcal/mol) indicated a chemically controlled process. However, linear rates here are mainly chemical rates without interference of diffusion resistances which may change the rates. As the microstructure showed the formation of iron layer around wustite particles, this may also explain that reduction is chemically controlled till a dense iron layer is formed and prevents gas diffusion.³¹⁾

On the other hand, reduction with CO shows gradual decrease in the rate with progress of reduction (Fig. 1) revealing the creation of an increasing resistance to the chemical reaction. The activation energy value reported for CO reduction signifies a mixed controlled process by both the chemical reaction and gaseous diffusion.³⁵⁾ The decreasing rate with progress of reduction in this case is due to diffusion of gases through an increasing thickness of a porous iron layer. During reduction with CO, other side reactions occur between the iron phase and CO gas

Fig. 4. Arrhenius plots for the reduction of dense briquettes

(a)

(a) Wustite-iron intergrowth

(b)

(b) Left: the inner dense iron zone

Right: the outer porous iron carbide

Photo. 1. Photomicrographs for a dense briquette, 60% reduced at 1000°C with a 50% CO/H₂ mixture ($\times 900$) ($\times 4/5$)

* The rates of reduction were taken at 50% reduction to avoid errors of measuring initial rates and to correspond to the wustite-iron transformation.

or deposited active carbon which result in the formation of iron carbide. These additional reactions would change the reduction mechanism, especially from the point of gaseous diffusion through the porous iron carbide layer formed (Photo. 1(b)).

For CO/H₂ reduction, as the rates are intermediate between those for reduction with pure gases, it would be expected that the rate controlling process in this case will also be a combination of those prevailing in reduction with pure gases. However, the activation energy values obtained for CO/H₂ mixtures reveal also a mixed controlled process³⁴⁾ with more contribu-

tion of the gaseous diffusion factor as the CO ratio in the mixture increases. This is reasonable since as the CO ratio increases, the greater will be the amount of iron carbide formed and hence the greater will be the resistance to diffusion of gases.

2. Reduction of Porous Briquettes

1. Rate of Reduction

Porous briquettes give faster reduction rates than dense briquettes due to larger surface area. Figures 5 and 6 represent the reduction curves with CO and a 50%CO/H₂ mixture. Both figures show that

Fig. 5. Reduction curves of porous briquettes with CO

Fig. 6. Reduction curves of porous briquettes with a 50%CO/H₂ mixture

Fig. 7. Effect of temperature on the rate of reduction of porous briquettes with CO

some reduction curves overlap each other at certain temperatures. By plotting the rates of reduction against temperature it indicates a rate minimum at 975°C for CO reduction (Fig. 7) and another minimum at 1 025°C for reduction with CO/H₂ mixtures (Fig. 8).

2. Effect of Temperature on the Reduction Rate

Arrhenius plots for reduction of porous briquettes were made and the activation energy values were given in Table 4. The values are much lower than those obtained for dense briquettes but vary also with gas composition.

3. Microscopic Examination

Porous briquettes show more diffuse reaction zones than dense briquettes; also two iron zones were observed for reduction with CO and CO/H₂ mixtures. At the rate minimum temperature most of the wustite particles were entrapped inside iron shells (Photo. 2). Above or below the rate minimum temperature the wustite iron intergrowth does not show such isolated wustite areas (Photo. 3).

4. Mechanism of Reduction

Activation energies for reduction of porous briquettes suggest a gaseous diffusion controlled reaction³⁴⁾ for all gases used. Due to fast chemical reaction

Fig. 8. Effect of temperature on the rate of reduction of porous briquettes with a 50% CO/H₂ mixture

Table 4. Activation energies for reduction of porous briquettes

Reducing gas	<i>E</i> (kcal/mol)
100% CO	2.28
75% CO + 25% H ₂	3.00
50% CO + 50% H ₂	3.66
25% CO + 75% H ₂	4.11
100% H ₂	5.14

Photo. 2. Photomicrograph of porous briquette, 60% reduced with CO at 975°C (×1 800) (×4/5)

rates of porous briquettes, the rate of gaseous diffusion through the briquette became the slowest step. At the rate minima temperatures, which are rather high, sintering of iron (or iron carbide) around wustite grains isolated them from direct contact with the reducing gas and hence hinders reduction rate.

Reduction with CO/H₂ mixtures does not significantly vary from CO reduction except for a 50°C shift in the rate minimum temperature. This is most probably due to the fact that the amount of iron carbide formed during CO reduction is greater than that formed in case of CO/H₂ mixtures, and allows the same degree of sintering at a lower temperature in the former case.

3. Correlation of Activation Energy with Gas Composition

From Tables 3 and 4, it is interesting to find a linear relation between the activation energy of reduction and the corresponding gas composition as shown in Fig. 9. From these lines, the activation energy E_m corresponding to a certain gas mixture X_{H_2} (for example) could be represented by;

$$E_m = E_{CO} + bX_{H_2} \dots\dots\dots(1)$$

where, E_{CO} : the activation energy for reduction with pure CO

Photo. 3. Photomicrograph of porous briquette, 60% reduced with CO at 1 100°C (×1 800) (×4/5)

Fig. 9. Relation between reducing gas composition and the activation energy of reduction

b: a constant representing the slope of the line.

A similar expression could be written in terms of the CO ratio in the gas mixture.

Substituting for the values of E_m and E_{CO} in Eq. (1), from the Arrhenius form;

$$K = Ae^{-E/RT} \dots\dots\dots(2)$$

we finally get;

$$K_m = K_{CO} \cdot A_m / A_{CO} e^{-bX_{H_2}/RT} \dots\dots\dots(3)$$

where, K_m and K_{CO} : the reaction rate constants for a certain gas mixture and pure CO respectively

A_m and A_{CO} : the corresponding constants of the Arrhenius relation.

From Eq. (3) the reaction rate constant K_m varies exponentially with the corresponding gas composition X_{H_2} , provided that all other factors are constant. Actually, K_{CO} and A_{CO} are constants for pure CO, and A_m is found to be constant in the range of gas compositions used (plotting $\log K_m$ vs. X_{H_2} gives straight line).

4. Carbon Deposition

X-ray analysis of reduced briquettes revealed the presence of iron carbide and free carbon up to 900°C, while at higher temperatures only iron carbide is detected. Tables 5 and 6 represent carbon analysis and the phases present in reduced samples. However, iron carbide which was microscopically detected may be formed in one of the following ways:

- (1) Below 900°C, fine deposited carbon ($2CO \rightleftharpoons CO_2 + C$) reacts with freshly formed iron to give iron carbide. Solid-state solubility of carbon in iron depends mainly on temperature. The most favourable factor is the size of carbon atoms as compared with that of iron which enables the former to enter the octahedral holes of the iron lattice.³⁵⁾
- (2) Above 900°C, carburization of the reduced iron by the reaction $3Fe + 2CO = Fe_3C + CO_2$ occurs.³⁵⁾

The values listed in Tables 5 and 6 indicate that the amounts of carbon deposited during reduction de-

Table 5. X-ray and carbon analysis for reduced dense briquettes

Temp. (°C)	Reducing gas*	Reduction (%)	Total carbon (%)	Phases present
700	CO	42	2.10	Fe ₃ O ₄ , FeO, α-Fe, Fe ₃ C, C
	CO/H ₂	65	0.82	Fe ₃ O ₄ , FeO, α-Fe, Fe ₃ C, C
800	CO	85	1.63	FeO, α-Fe, Fe ₃ C, C
	CO/H ₂	92	0.49	FeO, α-Fe, Fe ₃ C, C
900	CO	100	0.85	α-Fe, Fe ₃ C, C
	CO/H ₂	100	0.40	α-Fe, Fe ₃ C, C
1 000	CO	100	0.51	α-Fe, Fe ₃ C
	CO/H ₂	100	0.12	α-Fe, Fe ₃ C
1 100	CO	100	0.25	α-Fe, Fe ₃ C
	CO/H ₂	100	0.03	α-Fe, Fe ₃ C

* Mixtures are 50% of both gases.

Table 6. X-ray and carbon analysis for reduced porous briquettes

Temp. (°C)	Reducing gas*	Reduction (%)	Total carbon (%)	Phases present
700	CO	60	1.70	Fe ₃ O ₄ , FeO, α-Fe, Fe ₃ C, C
	CO/H ₂	80	1.25	FeO, α-Fe, Fe ₃ C, C
800	CO	88	1.52	FeO, α-Fe, Fe ₃ C, C
	CO/H ₂	95	0.91	FeO, α-Fe, Fe ₃ C, C
900	CO	100	0.65	α-Fe, Fe ₃ C, C
	CO/H ₂	100	0.32	α-Fe, Fe ₃ C, C
975**	CO	100	0.89	α-Fe, Fe ₃ C, C
1 000	CO	100	0.48	α-Fe, Fe ₃ C
	CO/H ₂	100	0.21	α-Fe, Fe ₃ C
1 025**	CO/H ₂	100	0.37	α-Fe, Fe ₃ C
1 100	CO	100	0.13	α-Fe, Fe ₃ C
	CO/H ₂	100	0.06	α-Fe, Fe ₃ C

* Mixtures are 50% of both gases.

** Rate minimum temperature

crease with both rise in temperature and the presence of hydrogen.

In direct reduction processes where the degree of metallization does not usually exceed 95 to 96%, the carbon deposited on pellets acts as reducing agent for the remaining oxides during smelting for steelmaking. It is also an advantage in steelmaking if the charged materials already contain sufficient carbon as iron carbide to produce specific steel grades. Carburization could be controlled by adjusting both the reduction temperature and the gas composition to maintain the carbon content of the metallized material within certain limits.

IV. Summary and Conclusions

The reduction mechanism of pure Fe₂O₃ briquettes with CO/H₂ mixtures was found to depend on the

original structure (porosity and grain size) as well as the reducing gas composition. These factors significantly affect the structure of the phases formed during reduction.

Reduction of dense briquettes with H_2 is chemically controlled at the initial stages, and becomes mixed controlled by both the chemical reaction and gaseous diffusion for reduction with either CO or CO/ H_2 mixtures, with more contribution of the gaseous diffusion part as CO ratio in the gas increases. The rates of reduction with CO are much slower than those with H_2 , and are intermediate for gas mixtures. Chemical rates predominate for reduction with H_2 , but due to the formation of a porous iron carbide layer during reduction with CO, it causes a diffusional resistance for gases which contributes to the overall rate.

Reduction of porous briquettes is gaseous diffusion controlled for all gases.

The activation energy of reduction varied linearly with gas composition, while the overall reduction rates exponentially varied with gas composition.

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