KINETICS OF DIRECT REDUCTION OF IRON ORE PARTICLES BY HYDROGEN IN A FLUIDIZED BED REACTOR

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الخلاصــة :

هذا البحث يتعلق بالاختزال المباشر لحبيبات خام حديد وادي فاطمه (المملكة العربية السعودية) بعد تركيزه بواسطة غاز الايدروجين فى جهاز من نوع الطبقة المتميعة . وقد تم تقدير معدل سرعة التفاعل بطريقة النقص فى الوزن . وتم تقدير تأثير كل من ظروف التفاعل على درجة الاختزال . وكانت ظروف التفاعل كالآتي : درجة الحرارة - حجم الحبيبات - سرعة الغازات وتركيز غاز الايدروجين . ووجد ان طاقة تنشيط التفاعل تساوي ٧,٠٣٤ كيلو سعر لكل جزىء اكسجين مزال وذلك فى درجات حرارة من ٤٠٠ الى ٧٠٠ درجة مئوية . وقد تم استنباط معادلة لحساب معدل سرعة التفاعل بدلالة ظروف التفاعل .

ABSTRACT

Particles of Wadi Fatima (Saudi Arabia) iron ore concentrate were directly reduced by hydrogen in a fluidized bed reactor. Rate of reaction was determined by loss-in-weight method. The effects of temperature, particle size, gas velocity, and hydrogen concentration on extent of reduction were determined. The activation energy of the reaction in the temperature range 400–700°C was found to be 7.034 kCal per mol oxygen removed. A rate equation was developed to express the reaction rate as a function of operating conditions.

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NOMENCLATURE

A	Constant
C	Mole fraction hydrogen in the gas
D_p	Particle size, cm
ΔE	Activation energy, kCal per mol oxygen removed
k	Constant
k_0	Frequency Factor
n_1, n_2, n_3	Constants
r	Rate of reaction, mol oxygen removed per hour
R	Universal gas constant. $1.987 \mathrm{cal\,mol^{-1}K^{-1}}$
t	Reaction time, min
T	Temperature, K
V/V_{mf}	Ratio of gas velocity to that at minimum fluidization
X	Fraction of Fe_2O_3 reduced

INTRODUCTION

Iron metal and its alloys are considered to be the structural basis of our modern civilization since iron is the most important of the metals and the most widely used. Different iron ores are found in nature in numerous places around the globe. Most iron minerals are oxides, *e.g.*, hematite (Fe_2O_3), limonite ($Fe_2O_3.x\ H_2O$), magnetite (Fe_3O_4), and geothite ($HFeO_2$). Many of these ores are lean, therefore, they have to be processed to improve the iron content and reduce the impurities.

One of the main iron ore deposits in the Kingdom of Saudi Arabia is the Oolitic Iron Ore of Wadi Fatima [1]. The deposit is located in the western part of the Kingdom between Jiddah and Makkah. The estimated reserve of the deposit is about 70 million tons [1]. The oolite size ranges from 1 to 2 mm. The ore has an average hematite content of about 46%. [1]

As early as 1850, steel producers were interested in the possibility of producing iron directly from its ores in the solid state. Since that time many new ideas have been proposed but none played a major role in steel production until the middle of the 1950's [2]. The iron, produced by direct reduction, was mainly of importance as a scrap substitute. It could also be used as a part of the blast furnace burden to increase productivity and decrease coke consumption [3]. Sibakin [2] and Sastri [3] were among those who published reviews on the different reduction processes. Different types of reducing agents were used ranging from solids, single gas (hydrogen or carbon monoxide), simple binary mixture of hydrogen and carbon monoxide, or complex mixture of reducing gases (reformed natural gas) [4].

Of the different direct reduction processes, the fluidized bed direct reduction process has proved versatile [5–9]. The Fluidized Iron Ore Reduction (FIOR) process had its first commercial plant use in 1976 in Venezuela. The process involved the use of multiple-bed reactors in which iron ore was reduced up to 94% metallization, using steam-reformed natural gas containing 90% hydrogen. The reduction process was followed by hot briquetting of the iron fines produced [9]. One of the main drawbacks of the fluidized bed process is the tendency of particles to sinter, thus causing defluidization of the bed and sticking of particles to the vessel [7]. The sintering tendency was found to increase with increase in particle size, increase in gas velocity, or decrease of operating temperature [10]. Sintering was also found to depend on the extent of reduction. For example, in the case of hydrogen reduction of hematite at 600°C, sintering starts at 76% reduction, at 700°C it starts at 54% reduction, while at 800°C particles tend to sinter at only 36% reduction [11]. Rates of reduction of iron minerals were also found to depend on other associated minerals [12].

In this work, particles of crushed Wadi Fatima iron ore concentrate were reduced directly by hydrogen in a fluidized bed reactor. The rate was determined by the weight loss method. Effects of hydrogen concentration, particle size, gas velocity, and operating temperature on rate of reduction were determined.

MATERIALS USED

Wadi Fatima Iron Ore

The ore was subjected to an upgrading operation before reduction [4, 13, 14]. This consisted of three successive steps [14]:

1. oolite liberation by grinding in a rod mill under controlled conditions so as to affect liberation of the oolites from the cementing gangue minerals;

2. fluidized-bed washing of the oolites to remove any adhered gangue fines; and
3. calcination of the washed oolites at 450°C so as to convert the geothite into hematite.

The upgraded oolites were then crushed and sieved into different size fractions. The concentrate produced had the following compositions: 87.11 wt % Fe_2O_3, 3.57 wt % SiO_2, 4.12 wt % MgO, and 5.20 wt % Al_2O_3 [4, 14].

Hydrogen Gas

Hydrogen was used as the gaseous reducing agent. The grade used was of 99.5% minimum purity.

Nitrogen Gas

Nitrogen was used as a diluent for hydrogen and as an inert fluidization gas during heating-up and cooling of the fluidized bed. The grade used was of 99.9% minimum purity.

APPARATUS

Figure 1 shows the fluidized bed experimental arrangement. Hydrogen and nitrogen gases were each passed individually through a pressure regulator, flow controller and a rotameter, before being mixed and allowed to enter the reactor from the bottom. Pressure drop across the reactor was measured by a U-tube water manometer. Details of the fluidized bed reactor are shown in Figure 2. The reactor was made of steel tube of 43 mm inside diameter and about 30 cm long. The first 10 cm of the tube from the bottom was filled with copper wire to act as a gas preheater and remove any traces of oxygen in the nitrogen gas. Heating was applied via 6 semi-cylindrical heating units insulated from the outside by high-temperature cement which, in turn, was covered with a layer of asbestos cement. The temperature of the fluidized bed was measured by a thermocouple and controlled by a power regulator controlling power input to the heating units. The reactor set-up was placed on an electronic digital balance with precautions to prevent deviation of reading due to power and other connections. The range of the electronic balance was 1500 g with an accuracy of ±0.5 g. The thermocouple output was recorded on a $y-t$ chart recorder. The whole arrangement was placed in a fumehood.

EXPERIMENTAL PROCEDURE

The power supply was checked, and the chart recorder and balance turned on. The reactor was placed on the balance and its weight was recorded. Nitrogen gas was allowed to flow through the reactor at a predetermined rate. This rate was selected as a function of the minimum fluidization velocity at the operating conditions [15].

A weighed amount of solid particles was charged into the reactor; about 100 g were used which were equivalent to an initial bed height of 6–7 cms. Final weight of the set-up was recorded. Power was switched on and heating was continued until reaction temperature was attained and then maintained for about 5 minutes. At each 50°C interval, the rate of flow of nitrogen was adjusted to the predetermined value.

Reducing gas was then allowed to replace the nitrogen. The weight of the set-up was recorded every five minutes (in some cases every two minutes and in other cases every ten minutes). Oscillation of the manometer reading was taken as an indication of the uniformity of fluidization.

When the predetermined reaction time was elapsed, nitrogen was allowed to replace the reducing gas and the heating power was switched off. The set-up was allowed to cool down to room temperature while fluidized with nitrogen.

Finally, the reactor was emptied and a sample of the produced material was analysed (by X-ray diffractometer).

Blank experiments were done at all operating conditions to determine loss in weight due to carry-over of fines.

RESULTS

The only result measured was the weight loss of the bed after certain time intervals for each experiment. These figures could not be directly used in the kinetic study, but had to be corrected as follows.

> The percentage weight loss recorded in the blank experiment was subtracted.
>
> The final product remaining in the bed was collected and then analysed to determine its content of magnetite and iron (in addition to unreduced hematite, if present). Percentage weight loss was then calculated from the result of the analysis.
>
> The average weight loss was calculated as the average of two values: from bed weight and from X-ray analysis.

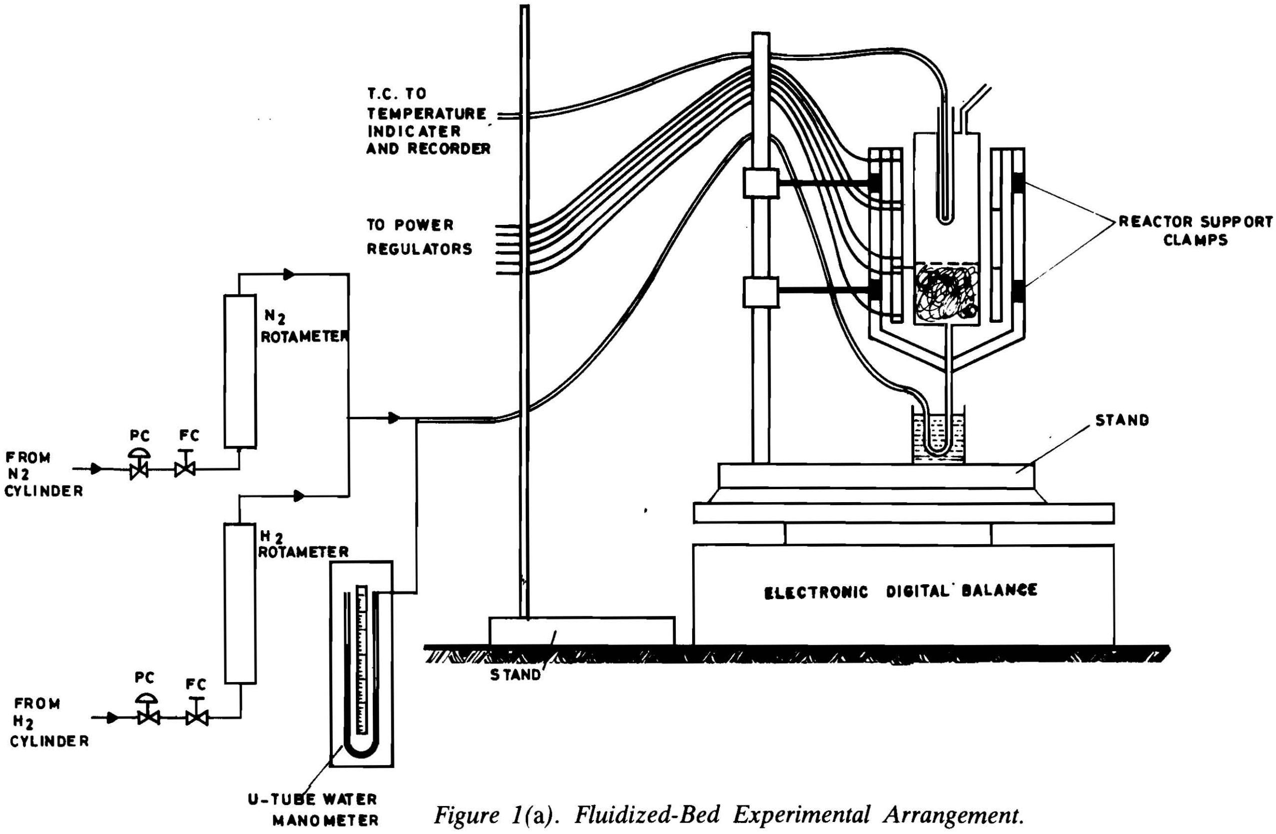

Figure 1(a). *Fluidized-Bed Experimental Arrangement.*

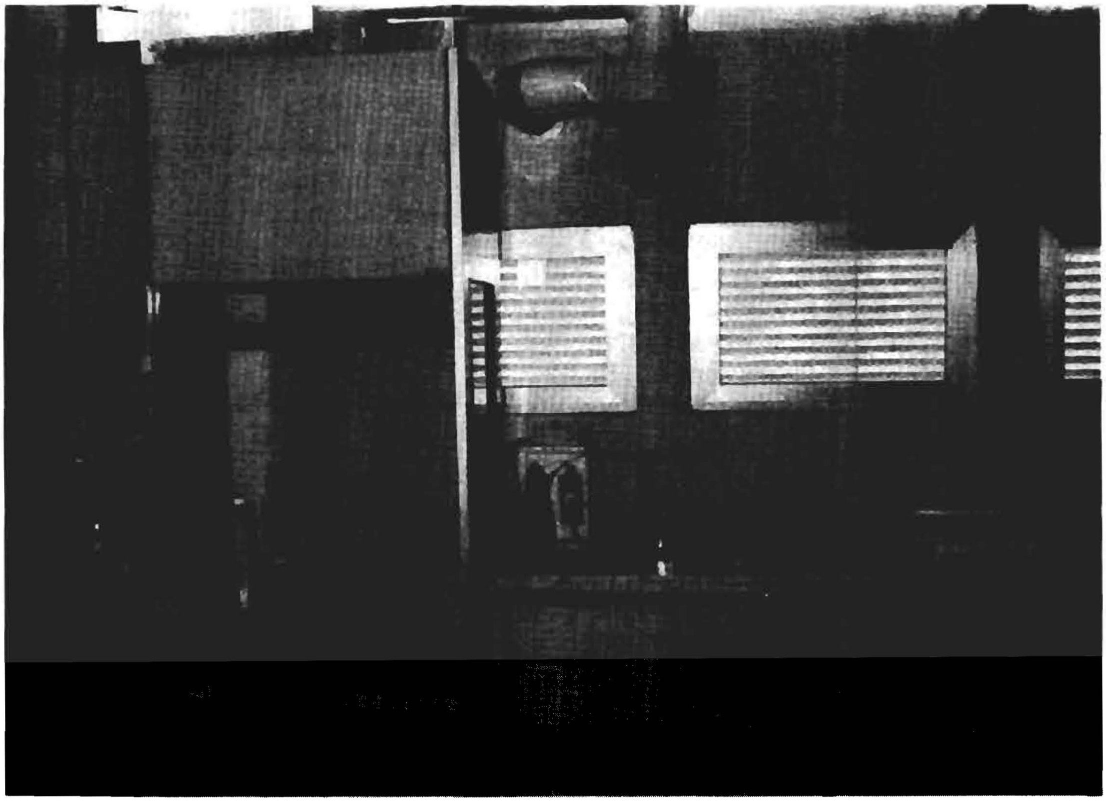

Figure 1(b). *Pictorial View of the Experimental Arrangement.*

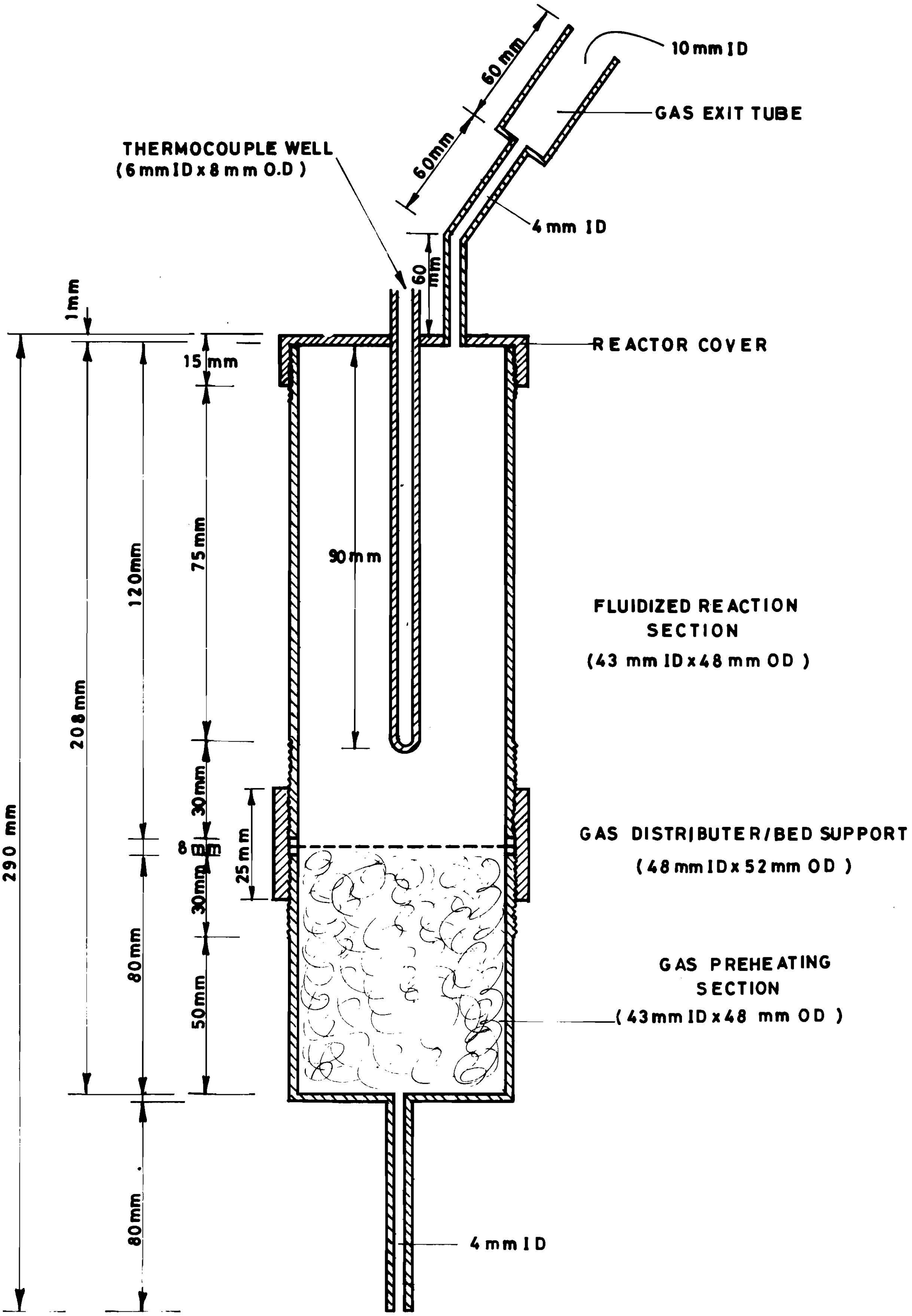

Figure 2. Details of the Fluidized-Bed Reactor.

Using the average value of the final product, the value at each time interval was then corrected and used in the kinetic study.

Table 1 shows the detailed calculations for Experiment number 1. Table 2 lists the corrected values for all experiments. Results are also presented in Figures 3 through 8. It can be noticed in some of these figures that early rates of reaction are not of the same order as for longer reaction times. This is usually due to the presence of fine particles which react much faster due to its larger specific surface areas.

Reduction of hematite by hydrogen involves two successive reactions [4]:

$$Fe_2O_3 \xrightarrow{H_2} Fe_3O_4 \xrightarrow{H_2} Fe.$$

Effect of Hydrogen Concentration

Figure 3 shows the effect of hydrogen concentration on reduction. As can be noticed, decrease in hydrogen concentration results in a decrease in the extent of reduction.

Effect of Gas Velocity

Figure 4 illustrates the effect of gas velocity on reduction. It was noticed that the extent of reduction increases with increase in gas velocity. At a gas velocity of about 4.3 times the minimum fluidization velocity, carry-over of fines became very significant. This is due to extensive bubbling and possible slugging. Therefore, fluidized bed reduction should be carried out at gas velocities less than 4.3 × V_{mf}.

Effect of Particle Size

As can be seen in Figure 5, and as expected, the extent of reduction decreases with increase in particle size.

Effect of Temperature

Figure 6 shows the effect of temperature on extent of reduction. Reduction rate increased with increasing temperature. Also at 700°C, and gas velocity equal to 3.2 times the minimum fluidization velocity for particles of size range −60+65 mesh, residence time for complete reduction was estimated to be one hour.

Arrhenius Plot

The Arrhenius plot for the overall reaction is illustrated in Figure 7. Activation energy of this

Table 1. Detailed Calculations For Experiment No. 1

Time,	Blank Experiment, Cumulative Weight Loss		Experimental, Cumulative Weight Loss		Net Percentage Cumulative Weight Loss	Percentage Weight Loss From X-Ray Analysis	Average Percentage Weight Loss	Corrected Percentage Weight Loss
	g	%	g	%				
2	1.5	1.40	–	–	–			–
4	1.5	1.4	–	–	–			–
6	2.5	2.34	10.5	10.34	8.00			6.83
8	3.0	2.80	12.0	11.82	9.02			7.70
10	4.5	4.21	14.5	14.29	10.08			8.61
12	5.0	4.67	15.5	15.27	10.60			9.05
14	5.0	4.67	16.5	16.26	11.59			9.90
16	5.0	4.67	18.0	17.73	13.06			11.15
18	5.5	5.14	19.5	19.21	14.07			12.02
20	6.0	5.61	21.0	20.69	15.08			12.88
25	7.0	6.55	24.0	223.65	17.10			14.60
30	8.5	7.94	26.5	26.11	18.17			15.52
35	9.0	8.41	29.5	29.05	20.64			17.63
40	9.5	8.88	31.5	31.03	22.15			18.92
45	10.0	9.35	35.0	34.48	25.13			21.46
50	10.5	9.81	37.0	36.45	26.64	18.86	22.75	22.75
Initial Weight, grams	107.0		101.5					

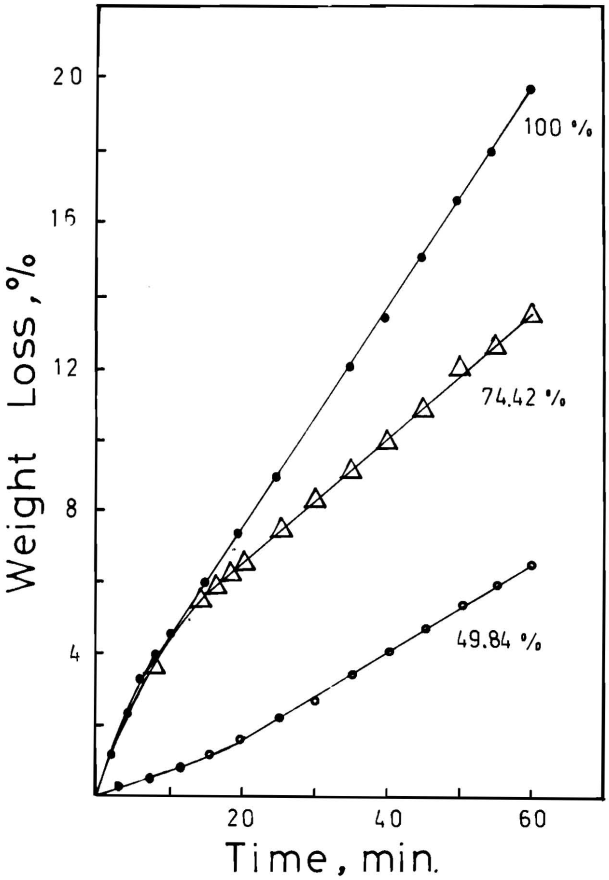

Figure 3. Effect of Hydrogen Concentration on Reduction of −60+65 Mesh Particles at 700°C and Gas Velocity = 1.2 Times V_{mf}.

reaction was calculated to be 7.034 kCal mol^{-1} oxygen removed in the temperature range 400−700°C.

The Rate Equation

Rate of reduction in a fluidized bed reactor may be expressed as a function of operating variables. For this set of experiments the rate equation is as follows:

$$r = k_0 \exp\left(\frac{-\Delta E}{R\,T}\right) C^{n_1}\, D_p^{\,n_2}\, (V/V_{mf})^{n_3}\,. \qquad (1)$$

The best values for the constants k_0, n_1, n_2, n_3 were evaluated by a non-linear regression analysis (range of deviation = 6.66%, $\sigma_n = 0.3112$ and $\sigma_{n-1} = 0.3409$); these values were:

$k_0 = 7.771 \times 10^{-3}$, $n_1 = 1.349$, $n_2 = -0.847$ and $n_3 = 0.240$.

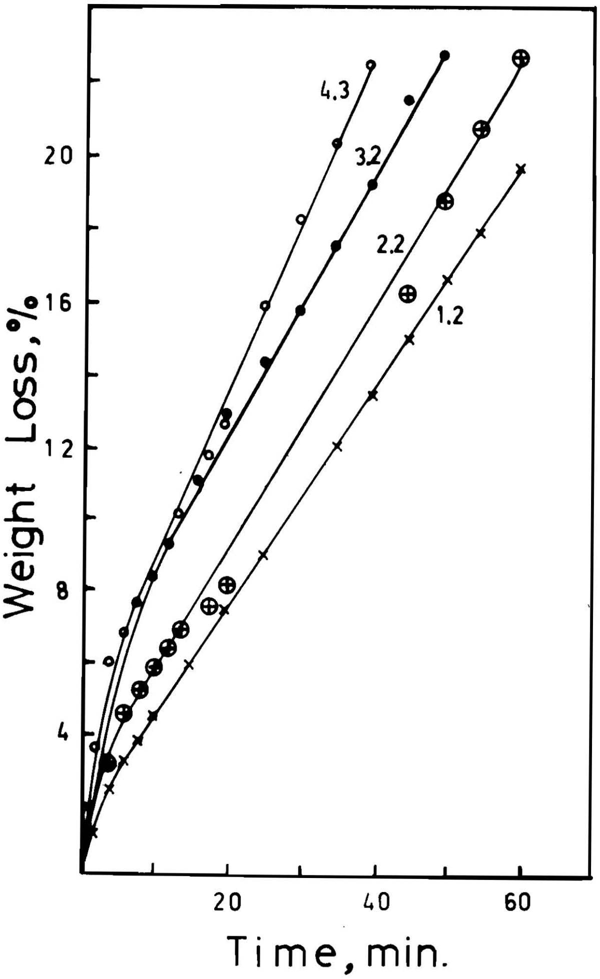

Figure 4. Effect of Gas Velocity on Reduction at 700°C, −60+65 Mesh Particles Using 100% Hydrogen. Values are Multiples of V_{mf}.

Rate Controlling Step

For gas−solid reactions there are three possible rate controlling steps, each with its characteristics rate expression.

Chemical Reaction at Gas−Solid Interface

The general rate equation for such reactions is [16]:

$$1-(1-X)^{1/3} = Y = kt + A \qquad (2)$$

Diffusion Through Product Layer

For this the rate equation is [17]:

$$\tfrac{1}{2} - \left(\frac{1-X}{2}\right)^{2/3} - X/3 = Y = 4\,t/D_p^{\,2} \qquad (3)$$

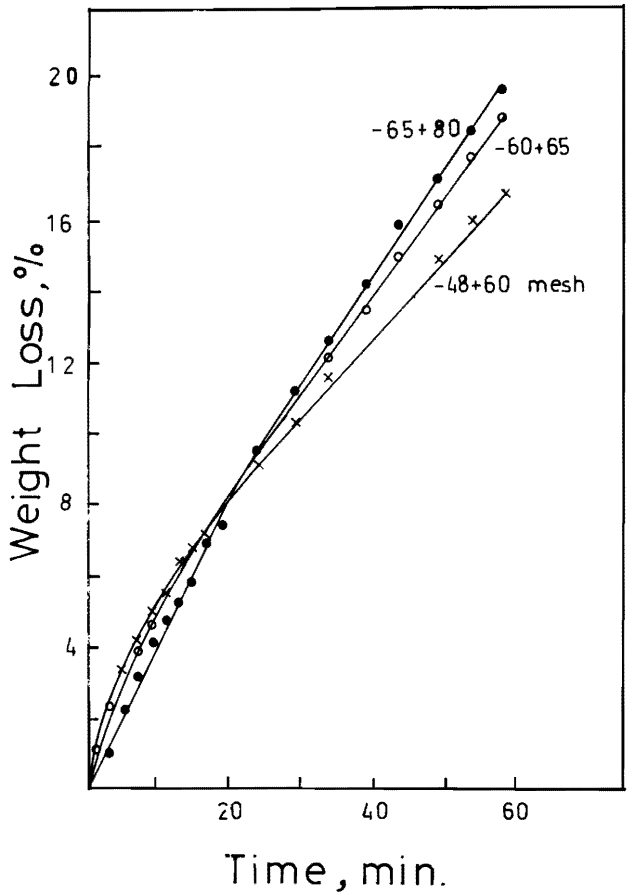

Figure 5. Effect of Particle Size on Reduction at 700°C, 100% Hydrogen and at Gas Velocity = 1.2 Times V_{mf}.

Mixed Control

The general rate equation is [18]:

$$\ln(1-X) = Y = kt + A\,. \qquad (4)$$

To determine the rate controlling step, the experimental data was expressed as by Equations (2), (3) and (4), and Table 3. Figure 8 shows a plot of Y against t. From the figure it is clear that Equation (2) is the one which best fits the experimental data. The constants for the equation were calculated to be:

$A = 0.06$ and $k = 0.007$.

CONCLUSIONS

1. Upgraded Wadi Fatima iron ore particles can be directly reduced by hydrogen in a fluidized bed reactor.
2. The direct reduced iron (DRI) produced had the following chemical composition [4]:

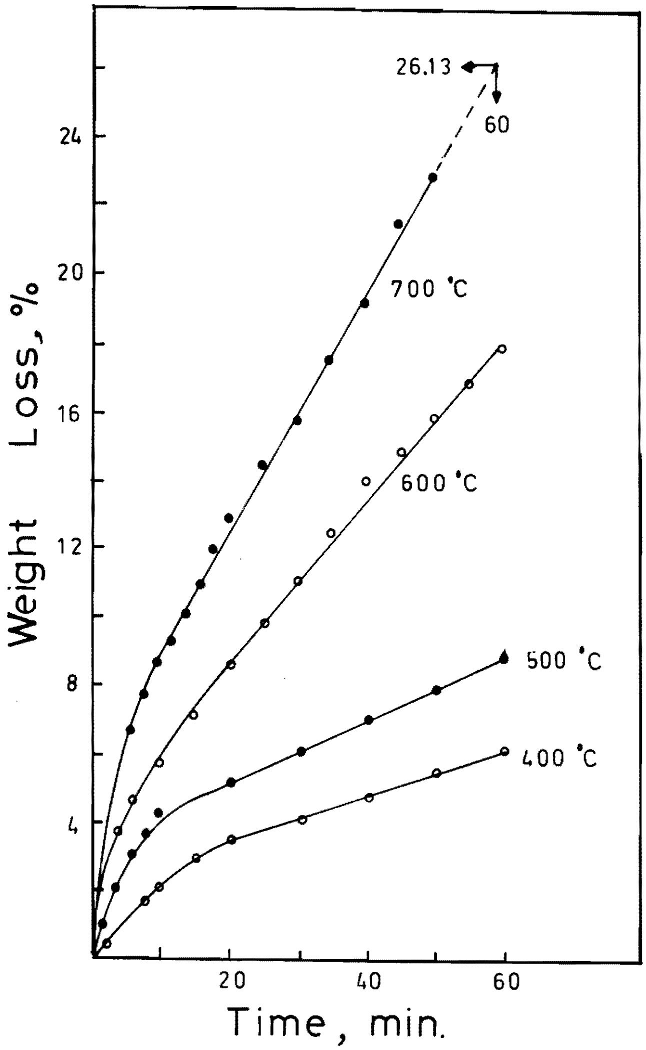

Figure 6. Effect of Temperature on Reduction of −60+65 Mesh Particles Using 100% Hydrogen and at 3.2 Times V_{mf}.

81.78 wt% Fe, 7.39 wt% Al_2O_3, 3.35 wt% MgO, and 7.48 wt% SiO_2.

3. The rate of reaction is controlled by the chemical reaction at the gas−solid interface, this is as expected for such a low temperature range [19].
4. The activation energy of the reaction was calculated to be 7.034 kCal mol^{-1} oxygen removed. Reduction of Venezuelan hematite (64.12 wt % total iron, *i.e.*, 91.6 wt % FeO) by hydrogen was conducted in a static-boat apparatus [20] and in the temperature range 500−900°C, activation energy was reported to be 4.67 kCal mol^{-1} oxygen removed. Reduction of the same oxide in a fluidized bed reactor [8] in the temperature range 300−650°C gave a value for the activation

Table 2. Corrected Average Percentage Weight Loss

Experiment Number	1	2	3	4	5	6	7	8	9	10	11
Time, Min.											
2	–	2.12	3.60	1.46	–	0.52	1.30	1.21	2.82	1.03	0.52
4	–	3.22	6.00	2.88	0.17	1.05	2.16	2.41	3.76	2.06	1.05
6	6.83	4.75	6.81	3.46	–	2.10	3.46	3.32	4.70	3.09	1.05
8	7.70	5.34	7.61	3.74	0.50	3.16	4.33	3.94	5.17	3.77	1.57
10	8.61	5.85	8.41	4.61	–	4.21	5.19	4.54	5.64	4.46	2.08
12	9.05	6.36	9.21	5.18	0.84	4.73	5.62	–	–	–	–
14	9.90	6.87	10.01	5.47	–	5.25	6.48	–	–	–	–
15	–	–	–	–	–	–	–	5.93	7.06	–	3.13
16	11.15	6.87	10.81	5.76	1.22	5.78	6.92	–	–	–	–
18	12.02	7.46	11.62	6.05	–	6.84	7.35	–	–	–	–
20	12.88	7.97	12.42	6.34	1.56	7.36	7.78	7.30	8.47	5.15	3.65
25	14.60	8.99	16.02	7.49	2.23	9.46	9.07	8.98	9.89	–	–
30	15.52	10.09	18.43	8.35	2.73	11.03	10.38	–	11.30	6.18	4.18
35	17.63	11.70	20.43	9.22	3.45	12.62	11.68	12.03	12.71	–	–
40	18.92	13.23	22.43	10.09	4.12	14.19	12.97	13.42	14.12	7.21	4.70
45	21.46	15.94	–	10.95	4.84	15.76	14.27	15.09	15.06	–	–
50	22.75	18.57	–	12.10	5.51	16.97	15.13	16.59	16.00	7.89	5.74
55	–	20.69	–	12.67	6.02	18.39	16.00	17.79	16.94	–	–
60	–	22.81	–	13.54	6.57	19.44	16.87	19.70	17.89	8.93	6.26
Temperature,°C	700	700	700	700	700	700	700	700	600	500	400
Mole Fraction Hydrogen	1.0	1.0	1.0	0.7442	0.4989	1.0	1.0	1.0	1.0	1.0	1.0
Particle Size, mm	0.240	0.240	0.240	0.240	0.240	0.204	0.265	0.240	0.240	0.240	0.240
V/V_{mf}	3.2	2.2	4.3	1.2	1.2	1.2	1.2	1.2	3.2	3.2	3.2

energy = 7.5 kCal mol^{-1} oxygen removed. It worth mentioning that the reduction process in this type of heterogenous reaction is drastically affected even by small variations in the experimental conditions such as gas velocity, particle size, or porosity. Therefore attempts to compare the reduction of pure oxide directly to that of the ore or of one ore to another will not be justified. As for the effect of impurities on the activation energy, it was reported that the presence of impurities would result in an increase in the activation energy [12]. At the same time it was reported that kinetics of reduction of hematite is catalyzed by the presence of iron part particles (either added to hematite or a product of initial reaction) [3].

5. Gas flow should be less than 4.3 times the minimum fluidization velocity, since at higher velocities carry over of fines would be excessive.

6. The optimum operating conditions are: (*i*) 100% hydrogen; (*ii*) temperature = 700°C; (*iii*) gas velocity less than 4.3 times the minimum fluidization velocity; (*iv*) particle size range −60+65 mesh; (*v*) residence time for complete reduction at these operating conditions is one hour.

7. The developed rate equation as a function of operating conditions is unique since no similar equation has been cited in literature.

Table 3. Calculations for the Three Possible Rate-Controlling Steps.

Time, Minutes	X	Chemical Control $Y = 1-(1-X)^{1/3}$	Mixed Control $Y = \ln(1-X)$	Diffusion Control $Y = \frac{1}{2} - \left(\frac{1-X}{2}\right)^{2/3} - X/3$
2	–	–	–	–
4	–	–	–	–
6	0.261	0.096	−0.302	−0.102
8	0.295	0.110	−0.350	−0.097
10	0.330	0.125	−0.400	−0.092
12	0.346	0.132	−0.425	−0.090
14	0.379	0.147	−0.476	−0.085
16	0.427	0.169	−0.557	−0.077
18	0.460	0.186	−0.616	−0.071
20	0.493	0.203	−0.679	−0.065
25	0.559	0.239	−0.819	−0.051
30	0.594	0.260	−0.901	−0.043
35	0.675	0.312	−1.124	−0.023
40	0.724	0.349	−1.287	−0.008

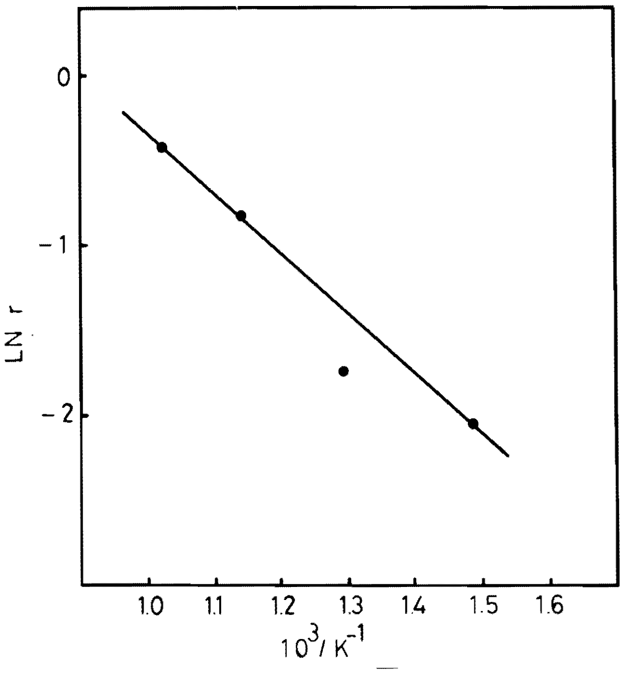

Figure 7. Arrhenius Plot of the Reduction Reaction.

ACKNOWLEDGEMENT

The author wishes to acknowledge the financial assistance of the Saudi Arabian National Center for Science & Technology. Appreciation is due to the Directorate General of Mineral Resources for supply of samples and to the Central Laboratories of the Saudi Arabian Ministry of Housing & Public Works in Riyadh for the X-ray diffraction and chemical analysis of the samples and experimental reduction products.

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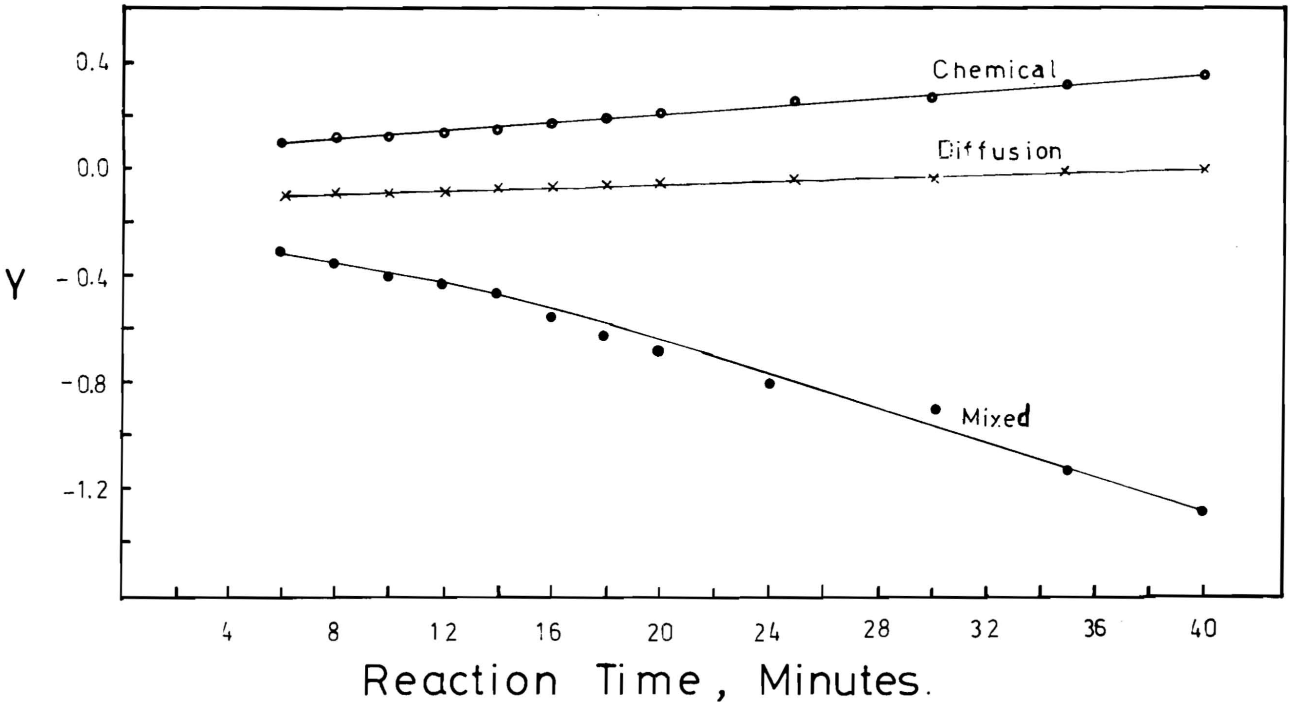

Figure 8. Y−t *Plots for the Three Possible Rate-Controlling Steps.*

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Paper Received 13 April 1986; Revised 3 September 1986.