Redution Kinetics of Hematite and Magnetite Pellets

Containing Coal Char*

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Synopsis
The rate of reduction of hematite and magnetite pellets containing coal
char in a nitrogen atmosphere and at the temperatures between 800 °C and
1200 °C was investigated. The reduction rate was found to increase
with increasing temperatures, and increasing calcium oxide content of the
pellets. The reduction was not stepwise. That is, iron, hematite, mag-netite and wustite were detected by X-ray analysis as coexisting phases during early stages of the reduction process. Large temperature differences were found between the core and surface o f the pellets, indicating that the reduction process occurred under non-isothermal conditions.
Calculated values for the apparent activation energy ranged between 38 kcal/mol to 51 kcal/mol. These values are lower than those reported by previous workers, but still within the accepted range for chemically con-trolled processes. The rate of the carbon gasification reaction and the rate of heat transfer from the furnace wall to the reacting pellet were found to exert the strongest influence on the overall rate of the process. Considering the observed non-isothermal conditions, the highly endotermic nature of the carbon gasification reaction and the large increase in the reduction rate with increasing temperature, it appeared that the overall process was heat transfer controlled.

I. Introduction

The direct reduction of iron oxides by carbon has been extensively investigated in recent years.l-5) The work done has demonstrated that such process occurs via the gaseous intermediates CO and CO2. Initially, the carbon monoxide is produced by a reaction of carbon with oxygen from the oxide in contact with the char, graphite, coke, etc., or with oxygen entrap-ped within the system. This carbon monoxide re-duces the oxides, producing carbon dioxide which reacts with carbon to form more CO; thus restoring the reducing potential of the gas phase that allows the reduction to continue.
Most of the studies done to present have dealt with
the behavior of either powder mixtures of iron oxide
and carbon or agglomerates of iron oxides containing carbon. In dealing with powder mixtures of particle size ranging from - 65 M to - 325 M and covering
temperatures from 900 to 1 300 °C, the works of
Otsuka and Kuni,5~ Abraham and Ghosh,6~ Rao,2~ and Fruehan7~ have demonstrated that the rate of re-duction is highly sensitive to the form of carbon used, and that it increases with increasing temperature, in-creasing percentage of carbon used and decreasing

particle size. These studies have agreed that the re-duction process was controlled by the rate of carbon gasification reaction. Similar results have been ob-

tained regarding the influence of temperature, per-centage of carbon and particle size on the reduction of agglomerates. However, there is no agreement concerning what controls the reduction ofagglomerates of iron oxide and coal char. Srinavasan and Lahiri,8~ working with pellets at the temperature range be-tween 950 °C and 1 060 °C concluded that the process was initially controlled by the rate of the carbon gasifi-cation reaction, but changed to control by the reduc-tion of wustite to iron during the final reaction stages. Ghosh,9~ working between 950 °C and 1 100 °C, con-cluded that the reduction of hematite pellets contain-ing char was limited by the rate of reduction of wus-tite to iron.

Although the studies to date have considered that solid reduction of iron oxides occurs isothermally, it is difficult to truly achieve such conditions when work-ing with pellets of iron oxide and coal char. Among the factors that complicate the establishment of ther-mal equilibrium are :
(1) The reduction will begin before reaching the desired experimental temperature if such temperature is greater than the minimum temperature4~ required to start the reaction.

(2) Once the process starts, the highly endotermic Boudouard reaction would act as a heat sink prevent-ing the pellets from reaching thermal equilibrium.
(3) The heat transfer through the porous oxide plus char pellet or from the heat source to the pellet may be slow.
The effect of these factors has been overlooked, and their importance underestimated. Based on the con-sideration of their combined effects, one might predict that the reduction of oxide pellets containing coal char does not occur under isothermal conditions. In-

stead, the reduction takes place under significant tem-perature gradients, and the process might be con-trolled by heat transfer, by chemical reaction or by a combination of both. The purpose of this work is to examine the reduction behavior of hydrothermally agglomerated pellets made of iron oxide and coal char. The reduction kinetic is analyzed and the effect of heat transfer on the process is demonstrated.

II. Experimental Procedure
The magnetite pellets used in these experiments

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Transactions ISIJ, Vol. 23, 1983 (491)

were produced by the hydrothermal agglomeration

process described elsewhere.10~ One batch of mag-netite pellets, and two of hematite containing 2 and 7 % of calcium oxide were made. The variation on the calcium oxide content was done in order to observe its influence on the kinetic and on the microstructural

changes that accompany the reduction of hematite. The raw materials used to make the pellets were mixed as indicated by the weight percentages shown in Table 1.

The chemical composition of the magnetite and hematite concentrates and the bituminous coal char

are given in Table 2. The screen size range of the char was 100 % passing 325 M. High purity reagent grade lime and silica were used, and their screen size ranges were 100 % passing 200 M and 100 % passing 325 M, respectively.
Pellets were reduced in a mullite tube 30 inches

long by 1.5 inches inside diameter which was mounted horizontally in a Varian furnace. The furnace was resistively heated and capable of reaching 1 300 °C. The temperature control setting was held constant dur-ing an experiment. The temperature of the reaction zone was monitored with a chromel-alumel thermo-

couple. During normal operating conditions, the furnace had a constant temperature zone with ±2 °C over a length of 2 inches. Gas inlet and outlet ports were attached to the ends of the mullite tube. A

constant nitrogen flow of 800 cm3/min (STP) was maintained throughout the reduction tests in order to

avoid accumulation of reaction products, mainly CO and CO2, inside the reaction tube.
For the determination of the reaction rates, dried

pellets of equal diameter (14 mm) were placed inside the hot zone of the tube furnace. Temperatures be-tween 800 °C and 1200 °C were tested. The pellets were weighed before and after exposure, and the per-centages of weight lost under different temperature and time conditions were recorded. The identifica-

tion of iron and its various oxide phases present for different reduction times was done by X-ray analysis of powder samples. The temperature changes occur-ring near the surface and at the center of the pellets were monitored by placing Pt-Pt-Rh thermocouples at those locations.

III. Results

The results of the reduction experiments on both the magnetite and hematite pellets are presented in the form of fractional reaction, f, res. time, t, plots in Figs. 1 and 2. Figure 2 also shows the effect of calcium oxide on the reduction of hematite. As Figs. 1 and 2 indicate, the rate of reaction increases with increasing temperature, and the reduction of hematite appears to be enhanced by increasing the calcium oxide content. Notice also that, at lower tempera-tures (1000 °C) hematite pellets reduce faster than the magnetite ones. This finding is consistent with the observed greater porosity of the wustite grain resulting from thereduction of hematite.
The shape of the curves shown in Fig. 2 along with the results from X-ray analysis of powder samples shown in Table 3 indicate the existence of two fairly distinguishable stages during the course of reduction. The first stage comprises the fast reductions of hematite and magnetite to wustite with the reductions of wus-tite to iron overlapping to some extent. The second stage corresponds to the reduction of wustite to iron.

Table 1. Raw materials used for pellets.

Table 2. Chemical compositions of raw materials.

Fig. 1. Fractional reaction res. time for magnetite pellets.

(492) Transactions ISIJ, Vol. 23, 1983

It is in the second stage where the bulk of reduction occurs, as the oxygen in the wustite amounts to about 70 % of the total amount of oxygen to be removed by reduction.

At all temperatures, there is an initially high reac-tion rate which comprises the pyrolisis of the remain-ing volatile in the char, the reduction of hematite and magnetite to wustite and part of the convertion of wustite to iron. This is confirmed by the results of the X-ray diffraction analysis shown in Table 3. They indicate that the steps Fe2O3 - Fe3O4 --f FeO and Fe3O4 -> FeO took place rapidly and during early stages of the reduction. This also indicates that the temperature and reducing potential of the CO/CO2 gas mixture needed for hematite and magnetite con-version are reached early in the process.
The results of the temperature measurements at the core and surface of the pellets are shown in Figs. 3 and 4. The figures clearly indicate that the process occurs under non isothermal conditions. As can be

seen, 15 and 27 min were needed for the pellets to reach thermal equilibrium at 1 000 and 1 100 °C, re-spectively. 10 min were needed to reach it at 1200 °C. Notice also how the temperature difference becomes

greater as the pellet reaches the zone where the car-bon gasification reaction proceeds to a larger extent. Then, the temperature gradient decreases and disap-

pears when the reduction has gone to completion (1 100 and 1 200 °C), or when the process comes to a virtual halt as it happens at 900 °C.
From the X-ray results, it could be concluded that the reduction did not take place in a stepwise manner throughout the pellet. Magnetite, wustite and iron were present at early reduction stages. This was con-firmed by metallographic observations which revealed the presence of iron at the pellet surface while hema-tite, magnetite and wustite were found near the core.

Fig. 2. Fractional reaction vs, time for hematite p ellets.

Table 3. Iron bearing phases i
fraction analysis.

dentified by X-ray dif-

Fig. 3. Temperature measurement at
magnetite pellets.

surface and core of

Fig. 4. Temperature measurement
hematite pellets.

at surface and core of

Transactions ISIJ, Vol. 23, 1983 (493)

This is caused by the temperature gradient which lead to condition where the conversion of wustite to iron was possible near the surface, but not at the center of the pellet.

Iv. Discussion of Results

1. Analysis of Kinetic Data
The results have shown that the reactions to con-

sider during the reduction of iron oxides pellets con-taining coal char are:

FeO(S)+CO(g) = FeS(s)+CO2(g) ....(1)

C02(g)+C(s) = 2C0 (g) ....(2)

Reaction (1) represents the reduction of wustite to iron, while reaction (2) represents theBoudouard reac-tion.

The derivation of a fundamental rate equation that would take into account the reaction and trans-

port steps involved, and that would describe, satis-factorily, the experimental results would require knowledge of the intrinsic rate of the heterogeneous reactions involved, as well as information concerning gas partial pressure, local temperature, pore size characteristics. Such data can not be obtained

under conventional experimental techniques. Due to this difficulty, simpler approach were undertaken by Rao2~ and Fruehan7j who considered that the reduc-tion was chemically controlled and assumed the Bou-douard reaction to be rate limiting step. With these assumptions and in light of the first order behaviorll~ observed for reaction (2), the weight change as a function of time for the measured reduction rate

could be approached to the following equation:

dW
dt0 = -KWc ....(3)

where, WC : the mass of carbon
K: the rate constant.

Integrating Eq. (3) for Wc= Wc,o at t=0, and Wc= Wc,t at t =t, gave Eqs. (4) and (5) for hematite and magnetite, respectively :

In (1-0.98 f) _ -Kt ....(4)

ln(1-1.037f)=-Kt ....(5)

If reaction (2) is rate controlling, the overall rate measured should approach that given by Eq. (3) and the experimental data must fit Eqs. (4) and (5). This is shown in Figs. 5 and 6 where ln(1 f) vs. time plots are drawn. As can be seen from Figs. 5 and 6, the reduction of hematite and magnetite pellets fol-low the first order expression up to f values of 0.7, but it deviates from linearity as the plateau of the reduc-tion curves shown in Figs. 1 and 2 is reached. Simi-lar results were obtained by Fruehan7~ and Wright et a1.121 They explained the nonlinearity of the curves as caused by the formation of oxides compounds such as FeO • SiO27~ or CaO •A12O3 •S1O212~ which blocked

the surface of the unreduced wustite. Although these compounds may form, the lowering of the reduction

rate would depend on how fast their rate of forma-tion is in comparison to that of oxide reduction. In general solid-solid reaction tend to be slower than gas-solid reactions. Therefore, one should not ex-pect such oxide compounds, at the fast reaction rates attained at 1 100 and 1200 °C, to seriously affect the reduction process. The observed deviation of the ln(1 f) res. t plots may represent the influence of sev-eral factors. Among them are the decrease on the surface area of both wustite and char as the reduction

progresses, the penetration of inert7~ gas inside the pel-let with the subsequent lowering of CO and CO2 par-tial pressure, and the decrease on the heat flux needed for the Boudouard reaction as the pellet reaches the furnace temperature.
At temperatures of 900 °C and below, the reduc-tion rate is slow, decreases with the onset of wustite reduction, and comes to a virtual halt shortly after having started. Between 900 °C and 1 000 °C, the reaction rate increases with temperature, the reduc-tion does not stop, but it shows the same tendency toward lower values as reduction progresses. This sluggishness of the reduction reaction at the above

Fig. 5. Test of Eq. (5) using experimental
fractional reduction f, and time t.

values for the

Fig. 6. Test of Eq.
fractional re

(4) using
duction f,

experimental
and time t.

values for the

(494) Transactions ISIJ, Vol. 23, 1983

mentioned temperatures has been reported previous-ly, but no explanation has been given for it. A potential explanation is based on the widely accepted assumption of reaction (2) being rate controlling, and on Ross et a1.13) affirmation that the rate of the gasification of carbon reaction might be controlled by the rate of heat transfer from the heat source to the reacting material. It is postulated that the rate decreases due to the lowering of the carbon monoxide generation caused by a deficiency in the energy available for reaction (2) to proceed. This defi-ciency is produced by a decrease on the heat flux from furnace walls to the pellet as the latter reaches the furnace temperature. It is also possible that under the slow reduction rate, and the close contact between calcium and iron oxide, the rate of forma-tion of oxide compounds or solutions may become competitive to that of oxide reduction. This would also contribute to lower the reduction rate as it

would lower the activity of wustite, and raise the CO/CO2 ratio needed for the convertion of wustite to iron.

Apparent values of the activation energy were ob-tained from the slopes of the Arrhenius type plot shown in Fig. 7. The calculated value for magne-tite pellets was 38 kcal/mol, while values for hematite pellets varied from 57 to 30 kcal/mol. These values are less than those obtained by Rao2~ (72 kcal/mol), Fruehan7~ (70 to 80 kcal/mol) and Srinavasan and Lahiri8~ (99 kcal/mol), but are comparable to those that Walker14> reported for the catalyzed oxidation of carbon. Considering these values alone, it could be concluded that the process is chemically controlled, that the lower activation energy obtained reflects the reported catalytic effect of iron and alkaline com-pounds on the rate of the carbon gasification reac-tion,7~ and that there appears to be a change of mechanism on the reduction of hematite as the

process temperature is switched from low to high values.

The conclusion that the process is chemically controlled must be critically examined in light of the non-isothermal conditions present in our work. Obviously, the calculations of the rate constants are not strictly correct, but, if the difference between the measured rate and that of a theoretically isothermal process could be calculated, the magnitude of the activation energy should still lay within the accepted range for chemically controlled processes. The key question is whether or not it is valid to rule out other possibilities, and conclude, based on the magnitude of the activation energy, that the carbon gasification reaction controls the rate of the overall process. For instance, knowing the temperature gradient, consider-ing the great rate increase with increasing tempera-ture, and taking into account the strong endothermic nature of the process, one could conclude that the re-duction would proceed at a rate which depends upon the amount of energy available for the gasification of carbon reaction to continue. That is, the process is heat transfer controlled. This reasoning should apply to the work of Ghosh and Tiwari,9~ Srinavasan

and Lahiri,8~ and Abraham and Ghosh6~ dealing with the reduction of iron oxide and char agglomerates, and perhaps to powder mixtures of the same. The experimental evidence does not provide a basis to de-termine which of the two mechanisms (heat transfer or chemical) is responsible for limiting the rate of the overall process. One possibility could not be excluded from the other based on the values of the activation

energy, or in the analysis derived from the applica-tion of Eqs. (3) to (5) which do not consider the fun-damental aspects of the reactions involved, and the complex nature of the reduction process.

2. Heat Transfer Effect
The effect of heat transfer over the rate of chemi-

cal reactions has been demonstrated by Hills15~ in regard to the calcination of limestone, and by Linch and Elliott16~ in regard to the oxidation of calcium sulphide. In conection to this work, there is a clear influence of heat transfer on the rate of the endother-mic Boudouard reaction. Influence that is reflected

on the following considerations:
(1) The occurrence of the carbon gasification re-action at a significant rate requires a continuous supply of energy from the heat source. Heat is transferred through the pellet by conduction, but the heat flux to the pellet is supplied by radiation from the furnace wall to the pellet surface at a rate that decreases with increasing pellet temperature.
(2) The occurrence of the carbon gasification re-action at a significant rate requires a much greater amount of calories than those needed to heat the pellet up to reaction temperature. This is an important consideration, since it implies that a pellet at a given temperature would not be able to react to completion without external heat supply. It also implies that the larger portion of energy supplied to the pellet is con-sumed by the carbon gasification reaction, and that the raising of the system temperature is adjusted ac-

Fig. 7. Arrhenius plot of log of rate constants vs, the re-ciprocal of absolute temperature.

Transactions ISIJ, Vol. 23, 1983 (495)

cordingly. This explains the observed temperature gradient.
(3) The experimental results indicate a high reac-tion rate during early stages of the process. This is consistent with the larger heat flux from furnace wall to the pellet that is present at that moment. At 1 100 and 1200 °C, the reaction rate is fast and pro-ceeds to virtual completion within the first 15 min of reaction. At 1 000 °C and below the heat flux to the

pellet is not enough to grant an appreciable rate of the carbon gasification reaction. Therefore, the re-duction rate is slow and the process does not advance to completion.
The mathematical treatment of the problem for the conditions of this study is extremely complicated. As it was shown, the reduction is non-isothermal. Fur-thermore, the thermal properties of the pellets vary as a function of time. The pellet temperature dis-tribution is a complex function of heat radiation from the furnace walls, heat conduction through the solid pellet framework and heat consumption by the Bou-douard reaction. A simple treatment, however, could be developed to demonstrate the importance of heat transfer. Let's consider, for the sake of simplicity, the results at 1 100 °C and use the information generated by the reduction of magnetite pellets. At this tem-perature, in agreement with previous findings, a shell core structure develops after about 3 min with the shell composed of porous iron, and the core composed of iron, wustite and char. Heat is transferred by ra-diation from the furnace wall to the pellet. The heat flux to the pellet surface is transferred through by con-duction. This heat is used to raise the pellet tempera-ture and to keep to carbon gasification reaction going. A heat balance on the pellets would require that:

QRad = QR+QG+QS (6)

where, QG, QS : the heat fluxes related to the tem-perature increase of the CO-CO2
offgas and remaining solids
QRad: the heat flux from the furnace to
the pellet surface
QR : the heat consumed by the chemical
reactions of the overall process.
The heat radiated to the pellet can be expressed as follows :

QRad = y DoeFe(T f- T)..................(7)

where, D° : the pellet outside diameter
e : the iron emissivity
Q : the Boltzman constant
Tf, TS are the furnace and pellet surface temperature. The heat consumed by the chemical reaction will be approximated to that needed for the carbon gasifi-cation reaction, and the measured overall rate would be assumed to equal that of the Boudouard reaction. Assumption that is consistent with the fact that reac-tion (2) is rate controlling. The heat consumed by the chemical reaction would be:

dH/ dW01 Q
-R l2 l dt J (8)

where, 4H: the heat consumed (41 200 kcal/mol) by the carbon gasification reaction
dWc/dt: the reaction rate.

Substituting Eq. (3) in Eq. (8) and solving Eq. (3)

to obtain Wo,r' the following expression is obtained:

QR = y KWc o ex (--Kt)

where, K: the rate constant
W0,0: the initial carbon content of the pellet.
From the Arrhenius plot in Fig. 7, the dependence of K with temperature was found to obey the following equation:

K =1.3904 X 105 exp (- 38196/R T) ......(10)

Replacing Eq. (10) in Eq. (9) :

QR = 4H We 01.3904 12

X 105 exp (-38196/RT) exp (-Kt) ...(11)

Using Eq. (11) together with the experimental data from Fig. 3, the values of QR and QRad were calculated and compared on Table 4. The selected values used to calculate QRad were : D0= 1.30 cm, e=0.40, i= 8.10 X 10-11 cal/min. cm2. °K4. Since no value has

been reported for the emissivity of iron resulting from reduction of iron oxide pellets, a mean value between the minimum and maximum reported177 values was taken.

Considering the approximations involved, the results given in Table 4 indicate that the agreement is good. The calculated heat consumption for the carbon gasi-fication reaction could be improved by using a mean temperature instead of the temperature at the core of the pellets. If this were the case, closer agreement would have been obtained provided that the assump-tion on the iron emissivity were correct. The impor-tant issue indicated by the calculations is that the maintenance of a constant rate for the carbon gasifi-cation reaction would not be possible under the con-tinuous variation in the heat flux from the heating source to the pellet. The overall rate should adjust accordingly, varying from very high to low reaction rates as the reduction progresses. This agrees with our findings, and is consistent with our previous ob-servation in the sense that the overall process might be heat transfer-controlled. Further research is under

way in order to approach this complex process form a more fundamental point of view.

Table 4. Calculated values of QRad and QR.

(496) Transactions ISIJ, Vol. 23, 1983

V• Conclusions

The experimental results of the present study, and the analysis thereof lead to the following conclusions:
(1) The reduction of hematite and magnetite pel-lets containing coal char occurred under non-isotherm-al conditions. The furnace temperature was first reached at the surface of the pellet, producing a non-stepwise mode of reduction where, at early stages, iron formed near the surface while the original iron oxide and oxides of lower oxygen content were pres-ent at the center.

(2) At all temperatures, the process is character-ized by an initial stage of high rate of reaction, and during which occurs most of the reduction. At 1 100 and 1200 °C, for instance, the reduction is virtually completed within the first 10 min of exposure to the furnace temperature. The second stage is character-ized by a lower reaction rate which decreases con-tinuously with time. In this stage, the covertion of wustite to iron is slow and the overall process tends to stop as it is indicated by the reduction data obtained at temperatures below 1 000 °C.
(3) The results of this work, in agreement with previous findings, indicate that the solid reduction of iron oxide pellets containing coal char proceeds via the gaseous intermediates CO/CO2. The key reac-tion of the overall process is the rate of carbon monox-ide generation by the carbon gasification reaction. In a strict sense, the rate of reduction of iron oxide is controlled by the rate of the Boudouard reaction, but this does not necessarily mean that the overall pro-cess is chemically controlled. The lowest step could be the rate at which energy is supplied to the system in order to maintain a significant rate of the carbon gasification reaction. This appears to be our case as it is indicated by the observed temperature gradient, the highly endothermic nature of the carbon gasifica-tion reaction and the great increase in the overall rate

produces by increasing the temperature of reduction.

Nomenclature

Do : Pellet outside diameter (cm)
EFe : Iron emissivity
f : Fraction of reaction

4H: Heat consumed by the Boudouard (cal/mol)
K: Rate constant (min-1)
a : Boltzman constant (J/cm2 • min • °K4)

QR : Heat consumed by chemical (cal/min)

reaction

reaction

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QG : Heat consumed in heating the offgas (cal/min)
Qs : Heat consumed to heat up the pellet (cal/min)
Q.Rad: Heat transferred from furnace wall to the pel-let (cal/min)
R : Universal gas constant (cal/mol • K)
Tf. Furnace temperature (K)
Ts : Surface temperature of the pellet (K)
W0,0: Weight of carbon in the pellet at t=0 (gm) Wc,t : Weight of carbon in the pellet at t = t (gm)

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