HOKKAIDO UNIVERSITY

Title	The Rates of Reduction of Iron Ore and Water-Gas Shift Reaction
Author(s)	Ishii, Kuniyoshi; Akiyama, Tomohiro; Kashiwaya, Yoshiaki; Kondo, Shin-ichi
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 17(1), 1-13
Issue Date	1986-12
Doc URL	http://hdl.handle.net/2115/38021
Type	bulletin (article)
File Information	17(1)_1-14.pdf

The Rates of Reduction of Iron Ore and Water-Gas Shift Reaction

Kuniyoshi Ishii[*1], Tomohiro Akiyama[*2]
Yoshiaki Kashiwaya[*1] and Shin-ichi Kondo[*3]
(Received June 30, 1986)

Abstract

Hematite ore was reacted with Ar-H_2-H_2O-CO-CO_2 multi-component gas at temperatures of 900-1100℃ under the condition that only water-ges shift reaction (WSR) concurrently proceeded with reduction of ore. The process was pursued by gas analysis using QMS. The samples were treated as a fixed bed having the distribution of fractional reaction in the longitudinal direction and analyzed by using the reaction kinetic models and the parameter fitting method.
(1) It was confirmed that the rate constant of H_2 reduction was about 10 times as large as that of CO reduction. (2) The rate constant of WSR was expressed by $K_{WSR}=1.4\times10^9$ exp($-5400/T$). (3) WSR was not so fast as both reductions by H_2 and by CO. Therefore, in the reduction with Ar-H_2-CO_2, the reaction tended to proceed beyond the limitation of gas equilibrium because of the extremely fast reduction with H_2. On the other hand, it was hardly expected in Ar-CO-H_2O that the reduction would be accelerated by H_2 regenerated through WSR.

1. Introduction

In the ironmaking processes, such as blast furnace process or any direct-reduction processes, iron ores react with multi-component gas. However, numerous work on reduction have been mainly carried out hitherto for the reactions with simple CO-CO_2 or H_2-H_2O mixtures.

$$Fe_mO_n + CO = Fe_mO_{n-1} + CO_2 \tag{1}$$
$$Fe_mO_n + H_2 = Fe_mO_{n-1} + H_2O \tag{2}$$

In recent years, although the studies of reduction of iron ore with CO-CO_2-H_2-H_2O are increasing, the amount of information is extremely less than those of binary mixtures. For example, the effect of H_2 addition to Ar-CO mixture on the reduction have been already investigated by many workers[1-9] and it was reported that they could not neglect

---

*1 Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University.

*2 The Research Institute of Mineral Dressing and Metallurgy, Tohoku University.

*3 Formerly, Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University.

the improvement of reducibility. However, their magnitudes and causal relations are not clear as yet. When multi-component gas is reacted with iron oxide, several reactions simultaneously take place in the system.

The main reaction is water gas shift reaction (WSR), and in the case of coexistence of solid carbon or a low concentration of oxidant gas such as CO_2 and H_2O, it is considered that Boudouard reaction (BR) and water gas reaction (WR) proceed also together.

$$WSR : H_2 + CO_2 = H_2O + CO \tag{3}$$

$$BR : C + CO_2 = 2CO \tag{4}$$

$$WR : C + H_2O = H_2 + CO \tag{5}$$
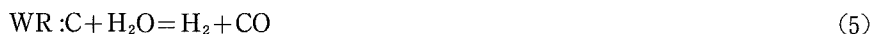
However, it is worthwhile to know how these reactions proceed and affect to each other especially under the condition where industrial processes are actually performed. If we clesire to investigate these matters, it is impossible only by conventional thermo-gravimetry, because the weight change merely gives a sum of changes of each element. Although the method for pursuing the process by using gas analysis is not perfect as yet in order to separate the complicated reactions individually the following advantage are also recognized.

a) Reduction and gasification (deposition) of carbon can be separately measured from the oxygen and carbon balances of gas compounds participating in the reactions, respectively.

b) When we limit the five reactions considered to BR, WR, WSR, CO reduction (CMR), and H_2 reduction (HR), if two of them can be expected in any fashion it is possible that the rates of three remaining reactions can by individually decided.

c) The apparent contributions of CMR, HR, and direct reduction with carbon (CR) could be estimated from the differences between inlet and outlet mass flow rate of CO_2, H_2O, and $C(=CO+CO_2)$, respectively. Moreover they are useful for designing practical furnace.

On the other hand, the gas analysis method has also the following demerits.

d) The gas analysis is less sensible than thermogravimetry. Therefore, in order to measure the rate of reaction with a high accuracy, it is necessary to set a large difference between the inlet and outlet concentrations of gas. The distribution of fractional reaction could not be neglected in the layer of sample.

e) Since the sample can not be regarded as a differential bed, the rate of reaction must be analyzed by considering the distribution of gas concentration in a fixed bed.

In this article, firstly, gas analysis method was used in the system in which only reduction and water gas shift reaction were simultaneously performed. And then the respective rate constants of reaction were determined by the kinetic analysis against a fixed bed.

2. Apparatus and Procedures

2. 1. Methods of gas analyses

In this study, experiments were carried out with Ar–CO–CO_2–H_2 mixtures of various compositions. As a result of tracing reactions, it was neccssory for the gas analyzer to have a high resolution sensitiety for change of gas composition and an ability for continuous measurement. Gas chromatography was not used since it was not suitable for the requirements. We used two kinds of equipment, which were conventional infrared CO and CO_2 gas analyzers and a quadruple mass spectrometer (QMS). While the infrared absorption method was completed for a process gas analyzer, it could not detect non–polar molecules such as H_2 gas. Although another QMS could detect any gas regardless of the polarity of the molecule, it has searcely been used for quantitative analysis of high concentration gas. To overcome this difficulty, the following relationship was found and used for the calibration curves[10].

$$I_i/I_{40} = a + \Sigma \ b_i V_i/V_{Ar} \tag{6}$$

where, I ; ion peak intensity, V ; mass flow rate, j ; mass to electric charge ratio (m/e) of the ion used for detecting the target molecule, i ; constituent of sample gas except inert component, a, b ; constant. As the flow rate of Ar was precisely regulated during run by thermal mass flow controller (MFC), if the constants, a and b_i, were previously determined by measuring the standard gas prior to final measurement, the flow rate of each ingredient could be decided by simultaneously solving equations having the same form as equation (6). Fig. 1 shows the apparatus equipped with QMS and infrared gas analyzers (IRGA), The operating conditions of QMS (Anelva AGA–100) were as follows : working pressure : 4×10^{-6} torr, ionizing voltage ; 30volt, and emission current ; 1.2mA.

In the gas analysis by QMS, it was very difficult to directly analyze the gas containing much H_2O. If H_2O concentration was less than a few percent, or thereabouts C_2H_2 could
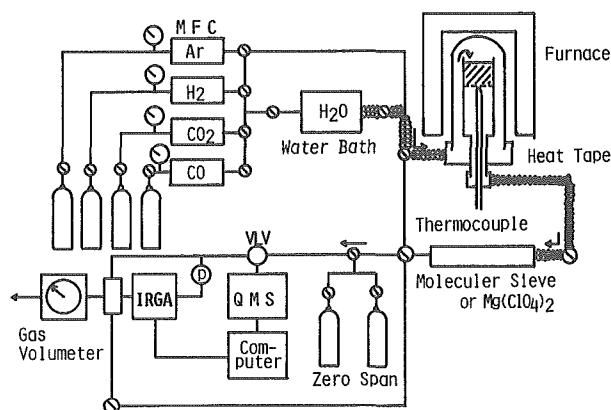

Fig. 1 Experimental apparatus equipped
with QMS and IRGA.

be detected as an alternative of H_2O, that reacted with CaC_2 for generating C_2H_2. However, the conversion proceeded imperfectly in higher H_2O concentrations[10]. Since H_2O concentration in the present study, depending on experimental conditions, was expected to be above 10% or thereabouts sample gas was dried by passing it through a column of magnesium perchlorate anhydride or molecular sieve 3A and introduced to QMS. The flow rate of H_2O was finally obtained by calculation based on H_2 balance.

2. 2. Calculation of reaction rates

The overall rate of reduction is composed of reactions with CO, H_2, and C. The apparent rate of each reduction is obtained from the respective mass balance.

with CO : $(R_{CO})_{app} = [CO_2]_{out} - [CO_2]_{in}$ (7)

with H_2 : $(R_{H2})_{app} = [H_2O]_{out} - [H_2O]_{in}$ (8)

with C : $(R_C)_{app} = [CO + CO_2]_{out} - [CO + CO_2]_{in}$ (9)

Where, [ ] denotes the mole flow rate per bed-volume of each constituent ($= Vi$/bed volume, $mole/cm^3,s$). The overall rate is represented as the sum of these rates.

$$R = (R_{CO})_{app} + (R_{H2})_{app} + (R_C)_{app} \qquad (10)$$

2. 3. Experimental procedures

In order to evaluate the water gas shift reaction that concurrently proceeds with reduction, isothermal experiments were conducted at 900 to 1100℃ with high purity Brazil ore as shown in Table 1. The ore was graded to 9–16 mesh (1–2mm) and in most

Table 1 Chemical Composition of Iron Ore employed (wt%).

	T.Fe	FeO	Fe_2O_3	SiO_2	CaO	Al_2O_3	MgO
lump ore	68.42	0.73	97.01	0.40	0.06	0.92	0.04

experiments 5 g of ore were packed in an aluminum container having an inner diameter of 20mm and mumerous perforations at the bottom. Then a fixed bed of 7mm height was formed. Half of mixed gas was Ar and the compositions of the remainder that consisted of CO, CO_2, H_2, and H_2O, was prepared according to the purpose. The inert Ar and reactant gases of CO, CO_2, and H_2 were mixed after each flow rate was regulated by MFC, and the mixture was introduced into a steam generator in a constant-temperature water bath as required. The flow rate of each constituent gas was kept within $0.5Ncm^3/min$ of the given value. The total flow rate was $2000Ncm^3/min$ and it was equivalent to the superficial velocity of 0.11m/s at STP. The reaction chamber was composed of outer silica tube and inner alumnum tube. The gas mixture was introduced from the bottom of reaction chamber and entered the sample bed from the top of container shown in Fig. 1. The reactant gas was preheated while it was made to up between both tubes. The product gas, that was made to flow out from the bottom of inner tube, was dehydrated and sent to the gas analysis systems. Finally, the exhaust gas was collected in a wet gas volumeter

and the flow rate was checked.

Samples was heated in an inert atmosphere of Ar, when reaching the temperature desired, the reactant gas that was prepared in another path was passed into the reaction chamber by switching a three-way cock. A lapse of time until beginning of the reaction was short due to the small accumulation volume in tubing. The data such as furnace and bed temperatures, epicyclic time of wet gas volumeter, peak intensities of QMS, etc., were recorded by a data acquisition system and the rate of reactions were calculated by on –line processing.

3. Results and Discussions

3. 1. Accuracy of gas analysis by QMS.

Before presenting the experimental results, the accuracy of gas analysis by QMS should be confirmed. Fig. 2 illustrates the relationships between analytical values and real flow rates. The real flow rates were measured by using a wet gas volumeter as a standard
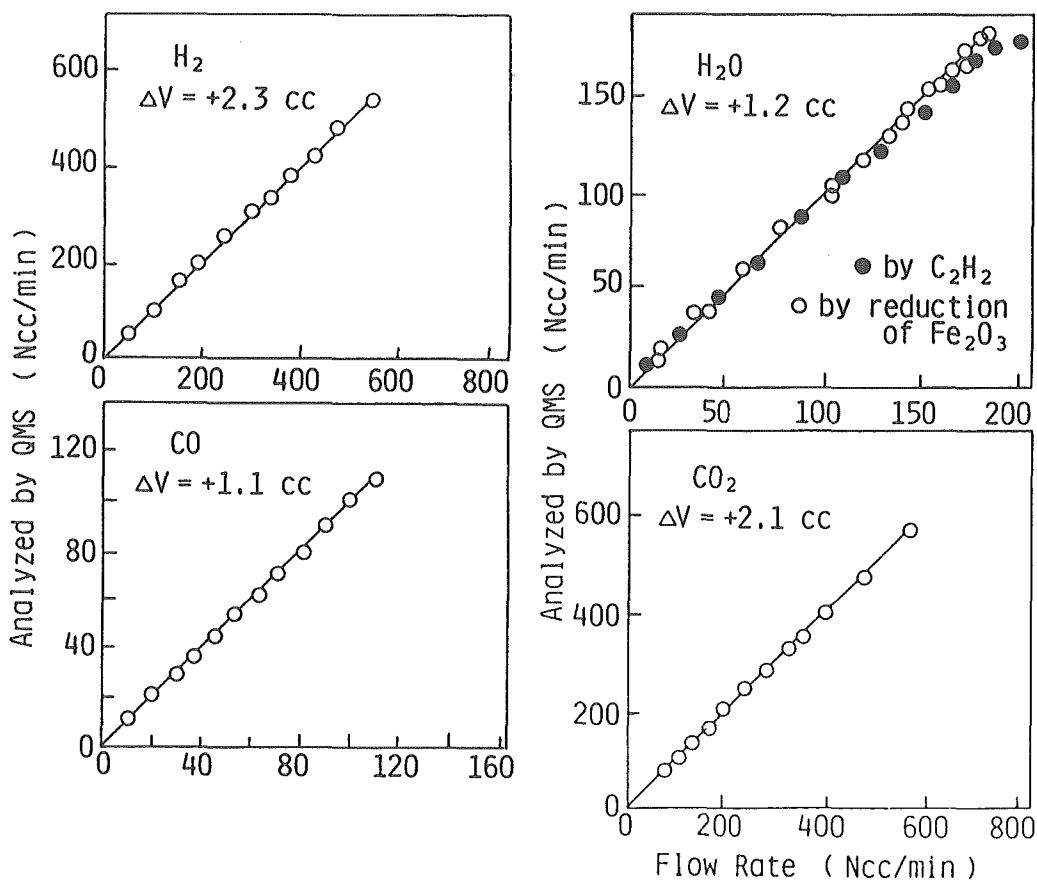

Fig. 2 Comparison of flow rates determined by
QMS with the measured by wet gas volumeter.

flowmeter, An apparent flow rate, that was obtained from epicyclic time of volumeter, was converted to a normal value by correcting for temperature and pressure. The values by QMS consisted of the real ones within astemdord error of about 2Ncm³/min over the discharge range required in practice. This accuracy was sufficient to measure the rate of reaction in the present study.

3. 2. Reduction of iron ore with H_2-CO_2 and $CO-H_2O$.

In order to clarify the effect of WSR on reduction, isothermal experiments were conducted with gas mixtures corresponding to the reactant (H_2, CO_2) or the product (H_2O, CO) of reaction (3). The ratios of $H_2/CO_2=4/1$ and $CO/H_2O=4.6/0.6$ were selected as gas compositions that were capable of reducing hematite to metallic iron in the thermodynamic equilibrium at 1000°C. Likewise, the ratios $H_2/CO_2=3/2$ and $CO/H_2O=3/2$ corresponded to wustite near Fe–Fe_xO equilibrium, and wustite equilibrated in $H_2/CO_2=1/4$ was expected to have the composition close to by Fe_xO–Fe_3O_4. Thus equilibria was calculated by the method of Rao et al.[11] using JANAF thermochemical data[12]. Typical data for the reduction of hematite ore with these gas es at 1000°C are shown in Fig. 3 by thinned-out plotting. The features of reaction are then represented as fractional reduction, f.

$$f=(1/[0]_o)\int_t R\ dt \tag{11}$$

where, $[O]_o$ is the initial amount of oxygen combined with iron in the bed (moleoxygen/cm³). The fraction reduced was larger in Ar–H_2–CO_2 than that in Ar–CO–H_2O. And above all things it was surprising for us to see in Fig. 3 that in both cases of $H_2/CO_2=6/2$ and 1/4 reduction proceeded beyond the Fe_xO–Fe limitation (f=0.3) in equilibrium. The same tendency was observed at other temperatures until H_2/CO_2 was decreased to about 1/6. It was considered that such abnormal reduction was caused by the extremely
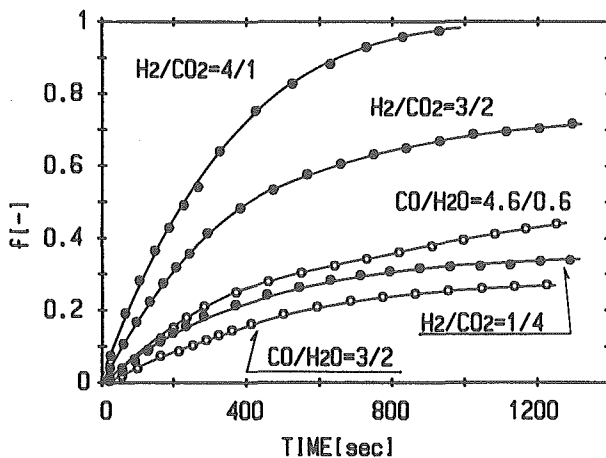

Fig. 3 Reduction curves of Brazil(MBR) ore
with H_2–CO_2 and CO–H_2O mixtures.
(1000°C, 5g)

rapid reduction with H_2. If the oxidation of reduced product with CO_2 and/or the shift reaction was as rapid as reduction with H_2, the equilibrium of gas phase shuld be more easily established. Although the shift reaction would be essentially the exchange reaction of oxygen between H_2 and CO_2 (or CO and H_2O) on iron catalyst, it was indistinguishable from the oxidation-reduction reaction in this expriment. However, since the apparent rate of reduction measured, in the case of no carbon gasification (deposition), is equal to the sum of rates of true reduction and shift reaction, if reduction can be truly estimated in any manner, it is possible to decide the rate of shift reaction.

$$(R_{CO})_{app} = (R_{CO})_{true} - S \tag{12}$$

$$(R_{H2})_{app} = (R_{H2})_{true} + S \tag{13}$$

Where, S symbolizes the rate of shift reaction($mol/cm^3 s$).

3. 3. Intrinsic rates of reduction with H_2 and CO

The ordinary reduction experiments by $CO-CO_2$ and H_2-H_2O, therefore, were carried out, in order to investigate fundamental features of the reduction used under the present conditions. The reduction curves are illustrated in Fig. 4 as representative. The reduction with H_2-H_2O was faster than that with $CO-CO_2$ and the initial rate of the former rose to a few times of the latter under the same conditions. This indicates that the intrinsic reduction by H_2 is extremely fast as compared with that by CO. It is also seen that the reduction curve obtained by $Ar/H_2/CO_2 = 5/3/2$ shown in Fig. 3 is comparable or slightly larger them the curve by $Ar/CO = 5/5$. The reduction rates rose as the height of bed (weight of sample) was decreased and the flow rate of reacting gas was increased. Hovever, it was not considered that the change of rates were controlled by the mass transfer such as gas film diffusion and intraparticle diffusion, because in the preliminary analysis using the unreacted shrinking core model the resistances resulting from these both
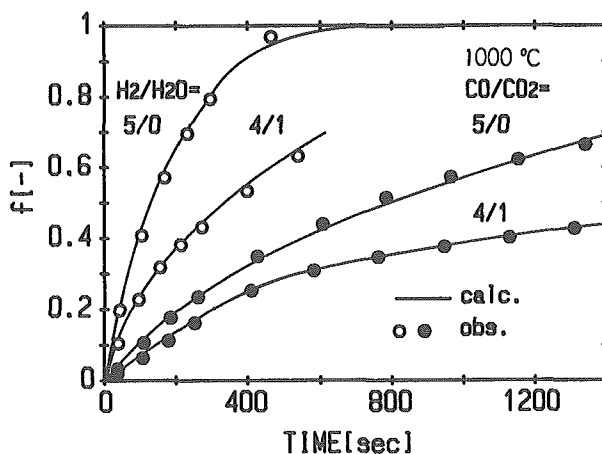

Fig. 4 Reduction curves of Brazil (MBR) ore
with H_2-H_2O and $CO-CO_2$ mixtures.
(1000℃, 5g)

processes were estimated together as less than about 10% even in the reduction by $Ar/H_2 =$ 5/5. The result could be explained by the consideration that the sample bed behaved as an integral flow reactor and not as a differential flow reactor regardless of how the bed height was, 7mm for a 5g sample. This was supported the following facts. On examining microstructure of particles partially reacted, it was seen that the extent of reduction varied according to the distance in the direction of gas flow, although a particle was reduced almost homogeneously from the outer surface towards the interior. The reduction was therefore analyzed by applying a homogeneous reaction model to the fixed bed of ore sample.

The rate equation of reduction for particles is

$$R_x = k_x(1-f)(P_x - P_{xo}/K_x)/RT \qquad (14)$$

Where, R; rate of reduction (mole-oxygen/cm^3·s), f; fractional reduction(−), k; rate constant (1/s), K; equilibrium constant of reduction (−), P; partial pressure (atm), R, T: gas constant and absolute temperature, x, xo: subscripts expressing H_2 or CO, and H_2O or CO_2, respectively. Fquation (14) was applied while changing the values of k and K depending on the fractional reduction, f, at the value of 0.11 ($Fe_2O_3 \rightarrow Fe_3O_4$) and 0.3 ($Fe_3O_4 \rightarrow Fe_xO$). On the other hand, the sample were taken as an isothermal fixed bed with voidage of ε composed of homogeneous particles. The material balances were derived by assuming a steady state and piston flow of gas. The governing equations may be written as follows:

for gas phase   ; $U(\partial P_x/\partial z) + \varepsilon(\partial P_x/\partial t) = -R_x RT \qquad (15)$

for solid phase ; $\partial f_x/\partial t = R_x/[O]_o \qquad (16)$.

where, t; time(s), z; distance from top of bed (cm), U; gas velocity (cm/s).

Equations (14), (15), and (16) were converted to ordinary differential equations by using the characteristic curve method and rate constants were numerically obtained by the data fitting method according to the simple rule of Euler. A finite increment of 1mm was selected for longitudinal distance in order to ensure that the numerical integration remained stable. The rate constants determined for CO and H_2 reductions are listed in Table 2. The solid lines shown in Fig. 4 are calculated by using those rate constants. It is also found that the data observed are in good a greement with the calculated curves

Table 2 Rate Constants of Reduction with H_2-H_2O and CO-CO_2(1/s)

	temperature	$Fe_2O_3 \rightarrow Fe_3O_4$	$Fe_3O_4 \rightarrow Fe_xO$	$Fe_xO \rightarrow Fe$
	930	40	40	50
H_2	1000	50	50	75
	1080	70	70	130
	930	8	7	3.5
CO	1000	9	9	7
	1080	14	14	14

throughout various conditions.

The rate constants for H_2 reduction are roughly 10 times those for CO reduction. The reduction of Fe_2O_3 and Fe_3O_4 are equally fast and these rate constants are not necessarily large as compared with that of Fe_xO reduction. The temperature dependence of Fe_xO reduction is 19kcal/mol for H_2 reduction and 30kcal/mol for CO reduction, respectively and fairly agrees with some in formation in the literature[13].

3. 4 Rate of water-gas shift reaction

In order to analyze the data observed in the reduction with H_2–CO_2 and CO–H_2O, the additivity was assumed between H_2 and CO reduction. Then replacing equation (16) with equation (17), integration was performed by use of the same parameters as hitherto
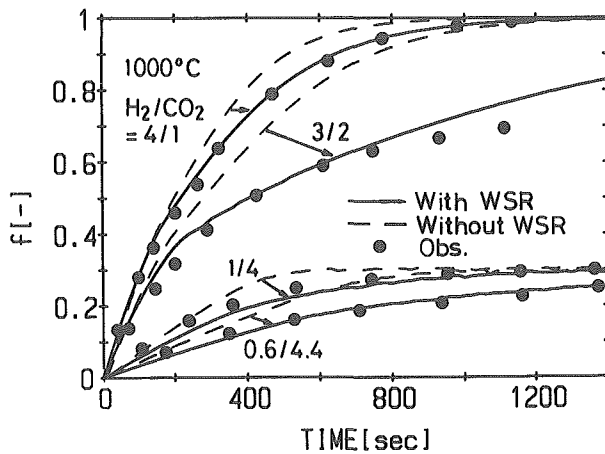

Fig. 5 Comparison of the observed fractional
reduction with the caluculated by considering
water-gas shift reaction. (H_2–CO_2, 1000℃, 5g)

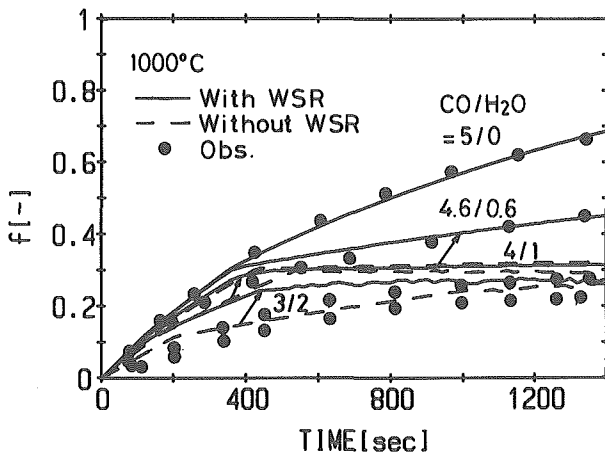Fig. 6 Comparison of the observed fractional
reduction with the caluculated by considering
water-gas shift reaction. (CO–H_2O, 1000℃, 5g)

described.

$$\partial f/\partial t = (R_{CO} + R_{H_2})/[O]_O \qquad (17)$$

The curves calculated by considering only reduction, are illustrated as broken lines in Fig. 5 and 6.   The calculation was inconsistent with the observed data and the curves were overestimated in the reduction with H_2–CO_2 as shown in Fig. 5 and in contrast underestimated in the reduction with CO–H_2O(Fig. 6).   Considering that H_2 acted as a stronger reducing agent than CO, these findings would be explained by the presence of another equilibria which made the ratio of P_{H_2O}/P_{H_2} balance to some extent, namely, water gas shift reaction(WSR), reaction (3).   WSR retarded or accelerated the reduction through increasing or decreasing P_{H_2O}/P_{H_2}, respectively.   The presence of WSR in this study had been directly verified by the facts that CO or H_2 was observed in exhaust gas. In order to evaluate the contribution of WSR for reduction, the macroscopic but well –known rate formula was adopted[14].

$$S = k_{WSR}(P_{H_2}P_{CO_2} - P_{H_2O}P_{CO}/K_{WSR})/(RT)^2 \qquad (18)$$

where, k_{WSR} is rate constant for WSR (cm^3/mol·s) and K_{WSR} is the equilibrium constant of WSR.   In a thin layer divided of the sample bed, let us think that WSR proceeds concurrently and independently with two kinds of reduction.   And then the change of molar flow rate ascribed to each reaction are added and the sum becomes a reacting gas for the next layer.   Equation (15) should be rewritten as follows:

$$U(\partial P_x/\partial z) + \varepsilon(\partial P_x/\partial t) = -(R_x + S)\cdot RT \qquad (19)$$

Applying this idea to interpret the experimental data, equations (14) for the respective reduction, (17), (18), and (19) for each component were simultaneously
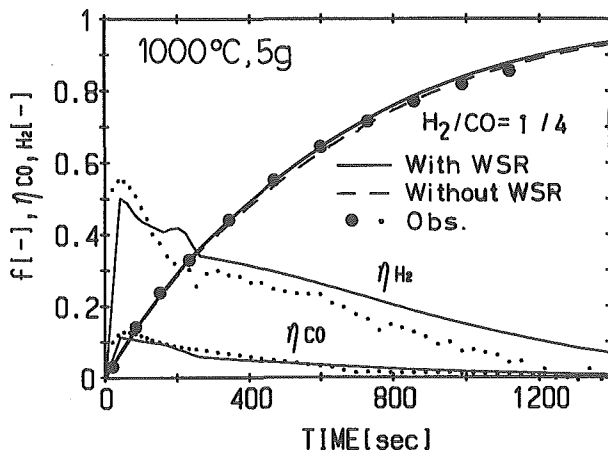

Fig. 7   Variation of fractional reduction and
compositions of exhaust gas as function of time.
(H_2/CO_2=4/1, 1000℃, 5g)

integrated so as to fit the observed data.   The available parameter for WSR over almost experiments had the values of 1.5×10^7, 2.0×10^7, and 2.5×10^7 cm^{3}s^{-1} mol^{-1} at 930°, 1000°, and 1080℃, respectively.   The results recalculated by using the parameter at 1000℃ are shown in Fig. 5 and 6 as solid lines.   The WSR is a catalytic reaction and it has been frequently said that metallic iron as the catalyzer is more active than oxides[15].   Inspection of Fig. 5, however, shows that a single parameter is applicable in explaining the experiments even if fractional reduction exceeds 0.3 when formation of metallic iron immediately sets in this reduction model.   It would be considered in the H_2-CO_2 that metallic iron had been already formed at the early stage of reaction and numbers of active site at the moving gas/solid reaction interface were kept at a constant state during reduction.

Fig. 7 shows the comparison between the data observed and the calculation for the variations of outlet gas composition for 5g sample in $H_2/CO_2 = 4/1$ at 1000℃.   The correlation is good and within the limits of accuracy imposed by the experiment.   The exit concentrations of each constituent are almost held at some constant values after about 1000 s when reduction was almost completed.   Then the observed gas ratio for WSR ($= CO \cdot H_2O/H_2 \cdot CO_2$) is 0.5 (0.62 in calculation) and differs from 1.62 in equilibrium.   It is indicated in this fact that WSR is not so rapid that an equilibrium is readily established.

On the other hand, in CO-H_2O mixtures, the parameter has a tendency to overestimate the fractional reduction when especially it is at lower degrees less than 0.3 , except where the CO/H_2O ratio is large.   Because CO is a less reactive reducing agent than H_2, and H_2O is a strong oxidant.   Thus it may be considered that the active sites on the surface of metallic iron are blocked by oxygen dissociated from H_2O in the low CO/H_2O ratio.   This assumption might be supported with a recent study of Munster and Grabke[16].   They observed the surface of Fe_xO by Auger spectroscopy, and found that the surface coverage by oxygen increased with the increasing Po_2.

The present data are relate to temperature by relationship (20) of the Arrhenius form.

$$k_{WSR} = 1.4 \times 10^9 \exp(-5400/T) \qquad (20)$$

The apparent activation energy agreed well with Moe's data[14] determined for iron-base shift catalyst but the absolute values are much larger by about one order.   The present works also became 4 to 8 times as large as the recent data by Ishigaki et al.[15] who examined the rate of only WSR by using a fixed bed reactor with the catalyst of prereduced iron pellets.   Although it may be explained due to the, larger specific area of this sample than the pellet, it is rather reasonble that the fresh surface subsequently was renewed, while the reduction succeeding, supplies the active sites for adsorption-decomposition of oxidant, that have been similarly described by Meschter et al.[17].   They studied the rate of WSR on thin-foiled Fe_xO and obtained the activation energy of 124.7KJ/mol, assuming that decomposition of CO_2 was the rate limiting step:

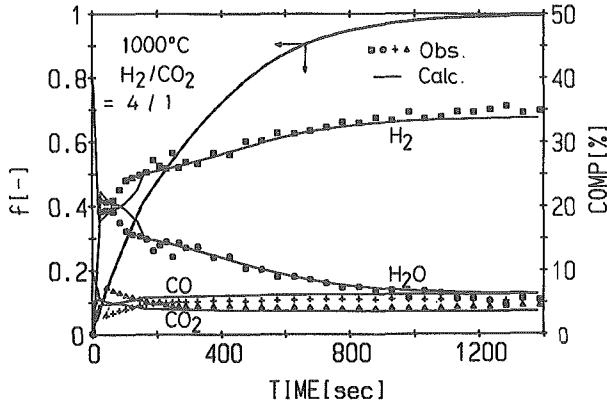$$CO_2(g) \rightarrow CO(g) + O(ads) \qquad (21)$$

Fig. 8   The fractional reduction and utilization
of H_2 and CO.
($H_2/CO_2 = 1/4$, 1000℃, 5g)

Relating rate equation (18) to their more rigorous equation, it is seen that our rate constant also includes the terms with respect to the adsorption decomposition isotherm of $H_b O$:

$$H_2O(g) \rightarrow H_2(g) + O(ads) \tag{22}$$

It might be explained for this reason why the activation energy apparently observed became small in this study.

3. 5   Contribution of WSR in blast furnace

Incidentally, it seems to be widely said in blast furnace operation that WSR is in equilibrium at the part of higher temperatures than about 800℃ [18] and hydrogen acts as a powerful reductant as if it has passed a few times the actual addition because of the regeneration from H_2O with the extremely fast WSR.   In order to confirm whether the mechanism was realistic or not, 5g sample was reacted at 1000℃ with the mixture of $H_2/$ CO=1/4 in which WSR was estimated to be most effective for the reclamation of product gas on the basis of calculation.   The results are plotted in Fig. 8 as the fractional reduction and the utilization factors of CO and H_2, $\eta_{CO}(=CO_2/(CO+CO_2))$ and $\eta_{H2}(=H_2O/(H_2+H_2O))$, respectively. The data measured are approximately consistent with calculation. η_{H2} is about times as large as η_{CO} because of large rate constant of H_2 reduction.   In any event it appears that the WSR that should improve the utilization of CO, hardly proceeds. Finally, it is conclude from this experiment that a major use for CO is not to regenerate H_2 by WSR but to substantially reduce oxide.

4.   Concluding Remarks

In order to investigate the reduction of iron ore with Ar-CO-CO_2-H_2-H_2O multi -component gas mixture, the process was pursued by gas analyses. The observed data were regarded as a fixed bed having the distribution of fractional reaction in the

longitudinal direction and analyzed by using the reactien kinetic models and the parameter fitting method.   Firstly, hematite ore was reacted at temperatures of 900–1100℃ under the condition that only watergas shift reaction (WSR) concurrently proceeded with reduction of ore.   In summary, the important results obtained by the experiments were as follows : (1) The rate constants of H_2 reduction was about 10 times as large as that of CO reduction. (2) The rate constant of WSR was expressed by $K_{WSR} = 1.4 \times 10^9 \exp (-5400/T)$. (3) WSR was not so fast as both reductions by H_2 and by CO.   There fore, in the reduction with Ar $-H_2-CO_2$, the reaction tended to proceed beyond the limitation of gas equilibrium because of the extremely fast reduction with H_2.   On the other hand, it was hardly expected in Ar $-CO-H_2O$ that the reduction would be accelerated by H_2 regenerated through WSR.

5. References

1.   H. K. Kohl and B. Marincek ; Helv. Chim. Acta, 48(1965), 8, p. 1857
2.   Q. T. Tsay, W. H. Ray, and J. Szekely ; AICHE. J., 22(1976), 6, p. 1064
3.   E. T. Turkdogan and J. V. Vinters ; Met. Trans., 3B(1972), 3, p. 1561
4.   V. Croft ; Met. Trans., 10B(1979), No. 2, p. 121
5.   R. Takahashi, S. Kurozu, and Y. Takahashi ; Tetsu–to–Hagane, 66(1980), 3, p. 336
6.   T. Chida, N. Sakai, and T. Tadaki ; Tetsu–to–Hagane, 67(1981), 9, p. 1485
7.   N. Towhidi and J. Szekely ; Ironmaking Steelmaing, 8(1981), 6, p. 237
8.   T. Murayama, K. Kawakami, and Y. Ono ; Tetsu–to–Hagane, 71(1985), 6, p. 680
9.   N. Kasai, Y. Kashiwaya, K. Ishii, and S. Kondo ; Tetsu–to–Hagane, 70(1984), 12, p. s97.
10.   K. Ishii, T. Akiyama, Y. Kashiwaya, and S. Kondo,; Bull. Fac. Eng., Hokkaido Univ., 132(1986) , in press.
11.   Y. K. Rao and H. G. Lee ; Met. Trans., 15B(1984), 3, p. 396
12.   D. R. Stull and H. Prophet ; JANAF Thermochemical Tables, 2nd ed., U. S. Government Printing Office, Washington, 1971
13.   M. Tokuda, H. Yoshikoshi, and M. Otani ; Tetsu–to–Hagane, 56(1970), 14, p. 1899
14.   J. M. Moe ; Chem. Eng. Prog., 58(1962), 3, p. 33
15.   M. Ishigaki, R. Takahashi, and A. Takahashi ; Bull. Res. Inst. Min. Dress. Met., Tohoku Univ., 38(1984), 1, p. 35
16.   P. Munster and H. J. Grabke ; Arch. Eisenhuttenwes. 51(1980), 8, p. 317
18.   P. J. Mescter and H. J. Grabke ; Met. Trans., 10B(1979), 5, p. 323
19.   Y. Shimomura and T. Sugiyama ; Report of 54th Committee of JSPS., No. 54–1600(1982)