

THE EFFECT OF WATER VAPOR ON THE RATE OF REDUCTION OF IRON ORE BY HYDROGEN

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Synopsis

The measurements were done at the temperature range of 600 to 900°C with respect to the temperature gradient of the rate of reduction and the relation between reduction ratio and produced metallic iron pct., and at 700 and 900°C to the relation between the addition of water vapor to hydrogen and the rate of reduction. The results obtained were as follows. The rate of reduction of hematite to magnetite was not affected by the presence of water vapor, as expected from thermodynamic calculations. The rates of later steps of reduction were decreased considerably as the ratio of partial pressures of steam to hydrogen was increased. Particularly, the rate of the last step, the production of metallic iron, is strongly affected.

I. Introduction

It has been found much study on the reduction of iron ores with reducing gases, which deals with its mechanism and the rate of reaction. The results obtained are, however, not satisfactorily. It is because that there are several processes other than chemical reactions in the mechanism, and that the observed rates of reduction are dependent on experimental conditions such as the flow rate of reducing gas and particle size of ore. It has been stated by Edström *et al.*¹⁾ from their experimental results including the microscopic observations that iron ores are reduced by hydrogen in steps Fe_2O_3 - Fe_2O_4 - FeO - Fe accompanying the evolution of water vapor as a by-product. The processes, which were assumed as the rate determining steps by the respective authors, are classified into the following three groups: transportation of reducing gas and product gas through the boundary layer in the gas phase, the interfacial reaction and diffusion of iron in oxide^{1) 2) 3)}, and the transportation of reducing gas and product gas through pores of ores⁴⁾. In the present paper, effects of addition of steam to the reducing gas on the rate of reduction are studied and the mechanism of reduction of ores is elucidated.

II. Experimental

Apparatus. A schematic diagram of an apparatus used for the reduction is shown in Fig. 1. It consisted of two parts, one is an apparatus for measuring the standard reducibility of iron ores (coarse grains) recommended by the Japan Society of the Promotion of Science, and the other a water vapor saturater which gives water vapor of definite constant pressure to the reducing gas. The saturater consisted of a water filled bottle as a preliminary saturater and an accurate

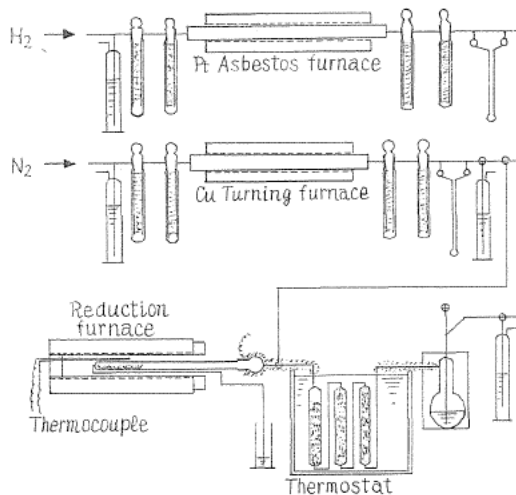


FIG. 1. Schema of experimental apparatus.

TABLE 1. Chemical composition of used hematite

Total Fe	SiO ₂	CaO	Mn	P	Cu	S	Zn	Pb
63.80	2.54	—	0.16	0.052	0.02	0.008	—	—

controller dipped in a thermostat which can be regulated to $\pm 0.02^\circ\text{C}$.

Sample. Iron ore used here was hematite mined in India, composition of which is shown in Table 1. The ore was crushed and sieved to 5–10 and 9–28 mesh and after being roasted at 120°C for 2 hrs. to remove moisture, it was stored in a desiccator.

Operation. 2 or 5 g of ore taken in a quartz boat was settled in a reaction tube. After replacing the air in the tube by nitrogen, the tube was inserted into a resistance furnace which was maintained at the reaction temperature, and the sample was roasted for 20 min. After the sample was cooled it was weighed again. The weight loss was attributed to the chemically hydrated water. The sample was held in the reaction tube again as mentioned above and then nitrogen gas was replaced by the reducing gas. After reduction proceeded for a given time, the atmosphere was changed quickly to nitrogen, and the sample was cooled to room temperature in nitrogen stream to avoid re-oxidation. This weight loss of the sample was attributed to oxygen removed by the reduction during reaction time t , and a ratio of this amount to that of total oxygen was denoted R . The weight loss of ore by the reduction with hydrogen for 5 hrs. at 1000°C was taken as the total weight of oxygen removable by reduction. The flow rate of hydrogen was 500 cm^3 (NTP)/min, and the water vapor was added to this stream. The flow rate of nitrogen which was used as a neutral gas before and after reduction, was 300 cm^3 /min. The accuracy of each flow rate was $\pm 1\%$. Temperatures at which the measurements were done were 600, 700, 800, and 900°C , respectively and the duration of reduction was less than 25 min.

III. Results

Reduction curves of ore with dry hydrogen at various temperatures are shown in Fig. 2, where the reduction ratio, R , in per cent are plotted against the reduction time, t , in min. Errors of reduction time due to the replacement of reducing gas with nitrogen, and to the cooling of sample to room temperature for weighing, were found to be negligibly small in the limit of experimental errors.

The amounts of metallic iron in the ore of various reduction ratios were analysed and the results are shown in Fig. 3, where it is to be noted that no metallic iron is detected until the reduction ratio reaches about 20%. To reduce all of Fe_2O_3 in ore to Fe_3O_4 , about 11% of removable oxygen must be removed, and to form FeO about 33% of oxygen must be removed. A full line and a broken line in Fig. 3 represent respectively the two theoretical courses, along one of which the reduction may proceed in such a way that the metallic iron was produced directly from Fe_3O_4 , and along the other via FeO . Since the experimental results fall on between

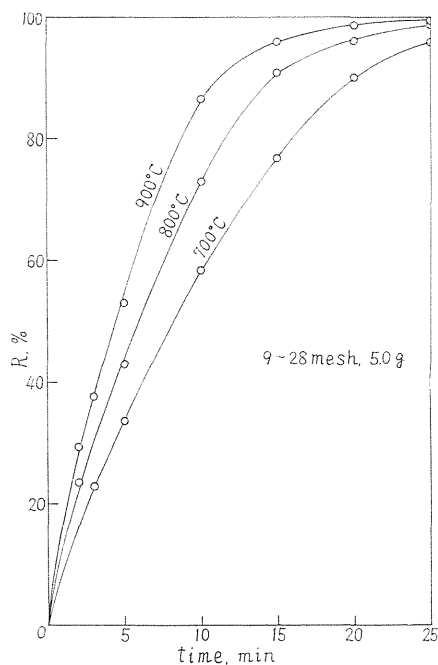


FIG. 2. Reduction curves with pure hydrogen at various Temperatures.

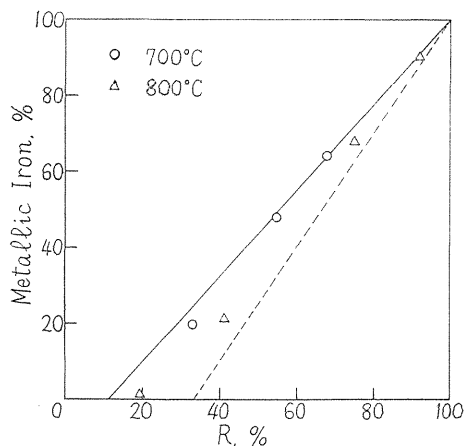


FIG. 3. Relation between reduction ratio and metallic Fe/total Fe in ore.

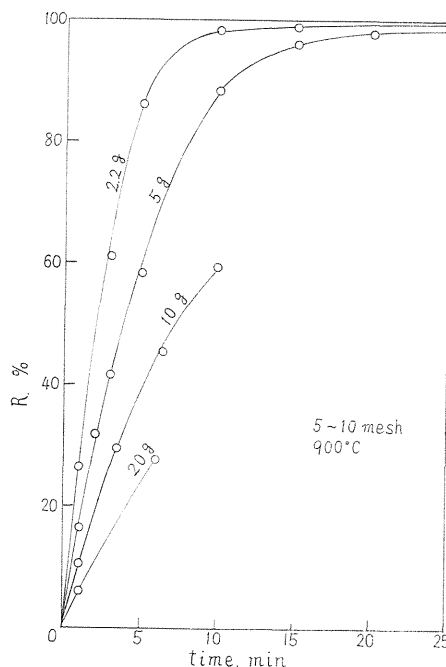


FIG. 4. Variety of reduction curves with its amounts and particle size.

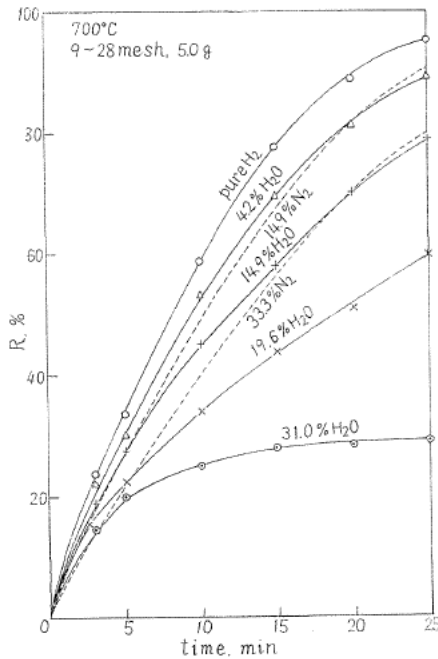


FIG. 5. Reduction curves with various hydrogen-steam mixtures at 700°C

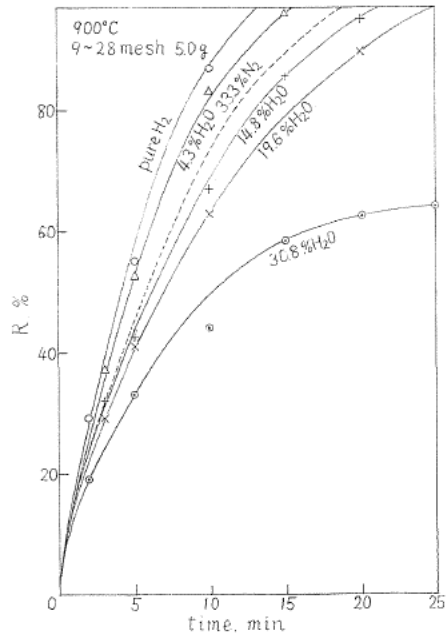


FIG. 6. Reduction curves with various hydrogen-steam mixtures at 900°C.

two lines, it is reasonable to suppose that at the initial period of reduction, metallic iron was not produced.

The relation between the amounts of ore and the rate of reduction was observed. Results are shown in Fig. 4. It is clear that the more the amount of sample, the slower the reduction, and the reduction ratio becomes low. It will be considered later that the rate of formation of H_2O , however, increases slightly with increase of the amount of ore.

Experiments were done on the effects of addition of steam to reducing gas. Reduction curves of iron ore with various hydrogen-steam mixtures at 700° and 900°C are shown in Figs. 5 and 6, respectively. For the sake of comparison, the reduction curves with hydrogen-nitrogen mixtures are shown also by broken lines in these figures.

IV. Considerations

The activation energy of this reaction was determined by using the reduction curves with pure hydrogen (Figs. 2 and 4). In the present study, the gradient of each curves at a constant value of R was taken as the value directly proportional to the rate constant of reduction, and was plotted against the reciprocal of absolute temperature. The results are shown in Fig. 7. It is seen obviously from Fig. 7. that when $R=0$, the apparent activation energy at a constant flow rate of hydrogen varies widely with the other experimental conditions such as the amount and particle size (average) of ore. On the contrary, it is seen that

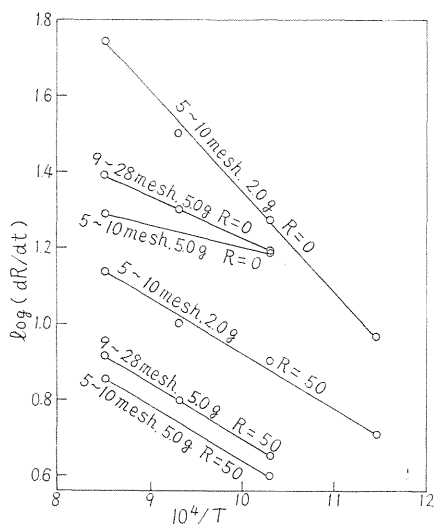


FIG. 7. Relations between temperature and the rate of reduction at various experimental conditions.

when $R=50\%$, the activation energy appears to be constant, *i. e.*, 6.9 ± 0.05 kcal/mole, in spite of the variety of the other experimental conditions. The difference is thought to be resulted from a fact that with the increase of amount of ore, the flow rate of hydrogen becomes so low compared with the rate of its expenditure that the over-all rate is determined almost by the flow rate of hydrogen. Let dW/dt denote the rate of evolution of H_2O which is evaluated directly from the rate of decrease of weight of sample used. Variation of dW/dt with the experimental conditions are shown in Table 2. It is seen clearly that at $700^\circ C$, the increase of dW/dt is to be explained by the increase of surface area of ore, where the packing of particles are taken into consideration. At $900^\circ C$, however, dW/dt approached to

TABLE 2. Rates of formation of H_2O in mg/min

Temp. ($^\circ C$)	R (%)	Mass of sample (g)			
		2.0	5.0	10.0	20.0
700	0	111	210	341	—
	50	55	74	82	—
900	0	308	330	358	387
	50	97	110	120	—

a value, 400 mg/min, which was the rate of conversion to H_2O when the all of hydrogen was converted to water. Therefore, to eliminate the influence of the rate of gas supply on the rate of reduction, that is to say, to remove the possibility of being the gas supply to reaction tube the rate determining step, the effective surface area of iron ore, where the reaction proceeded, must be diminished as small as possible, or the flow rate of reducing gas must be increased sufficiently in comparison with its expenditure. The measurements were repeated with 2.0 g of iron ore of 5-10 mesh at a constant flow rate of hydrogen, $500 \text{ cm}^3/\text{min}$ (Fig. 8). In these cases, the activation energy of the over-all reaction was found to be 11.2 kcal/mole at $R=0$. If a single ball of ore was used for the reduction, the activation energy would be larger. Since the activation energy at $R=0$ is different far from that at $R=50$, it is supposed that the rate determining steps at the initial period and at the later period of reaction are different from each other. The results shown in Fig. 3, together with these facts, suggest that at the initial period of reduction, Fe_2O_3 may be reduced to Fe_3O_4 , or rather to FeO , and that at the later period, the reduction of Fe_3O_4 and/or FeO to metallic iron may take place consecutively. This conclusion is seen

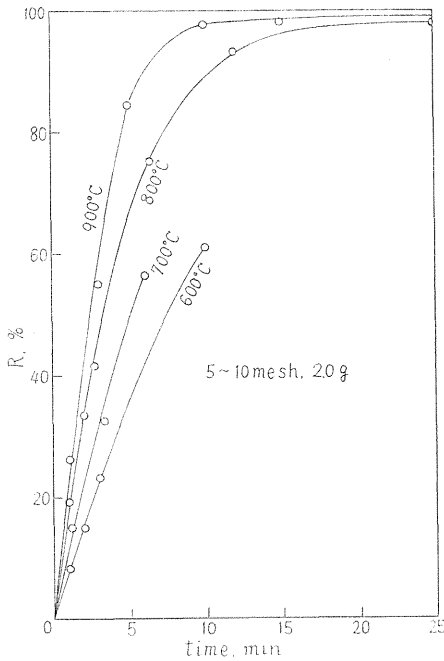


FIG. 8. Reduction curves with pure hydrogen at various temperatures.

to be supported by the following considerations on the effects of steam on the reduction.

It has been shown by McKewan⁵⁾ that when hematites were reduced by hydrogen-nitrogen mixtures, the rates of reduction were, independent of the presence of nitrogen, proportional to the partial pressures of hydrogen only. To express the rate of reduction, he applied the rate equation, $kt=1-(1-R)^{1/3}$, which he had proposed for the rate of reduction of hematite with hydrogen³⁾. More recently it is confirmed by Seth *et al*⁶⁾, that this equation can be derived from the more generalized equation which they have formulated on an assumption that both the interfacial area and the transportation of gas contributed in varying degrees towards controlling the rate of reduction. According to this equation, the results given in Figs. 5 and 6 are rearranged as shown in Figs. 9 and 10, respectively. It is noted readily that there is a remarkable difference between the effect of steam

and that of nitrogen on the rate of reduction. Thus, it is seen clearly that the equation holds well for the reduction with hydrogen and hydrogen-nitrogen mixtures only, but the reduction curves with hydrogen-steam mixtures cannot be expressed by the equation. On the reduction curve, the values of specific

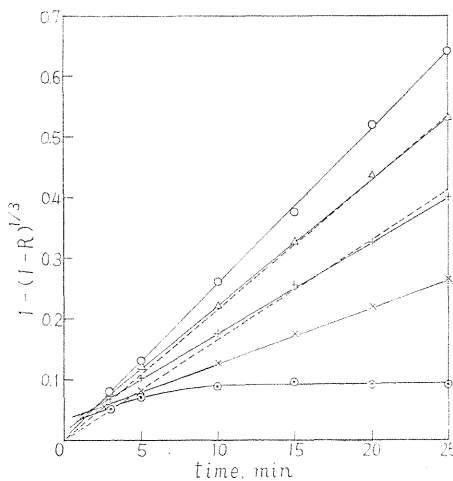


FIG. 9. Rearrangement of Fig. 5 in terms of $1-(1-R)^{1/3}=kt$.

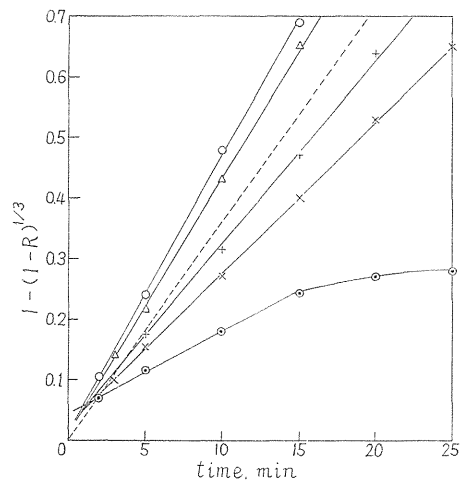
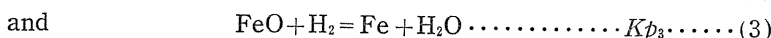
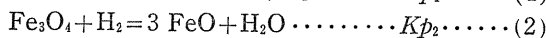
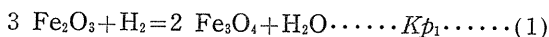


FIG. 10. Rearrangement of Fig. 6.

constant, k , evaluated by this equation at the reduction ratio R less than 15-20% and those at the ratio higher than 20% are different. That is to say, for the reduction with hydrogen-steam mixtures, rate constants over the whole range of reactions cannot be represented by this simple equation. The variation of k , calculated by this equation at $R=0$ and $R=25\%$ with the partial pressures of steam in reducing gases are shown with full lines and points in Fig. 11.

The equilibrium constants for each stepes of reaction which are supposed to take place in the reduction of hematite were considered. The values of Kp (p_{H_2O}/p_{H_2}) of reactions:



are evaluated from the thermodynamic data⁷⁾ and the results are listed in Table 3. From these values, it is considered to be reasonable that the reaction (1) proceeds almost completely to the right at each temperatures when hydrogen is present. Accordingly, the influence of addition of steam on the rate of reaction (1) is thought to be not due to the backward reaction, but to the decrease of partial pressure of hydrogen.

On the contrary, the equilibrium constants of reactions (2) and (3), Kp_2 and Kp_3 , are not so large that the backward reactions due to the addition of steam

TABLE 3. Equilibrium constants of reactions (1), (2) and (3)

T °K	Kp_1	Kp_2	Kp_3
900	7.9×10^4	0.470	0.376
1000	6.9×10^4	0.895	0.465
1100	5.9×10^4	1.61	0.539
1200	5.3×10^4	2.42	0.633

should be taken into account for these reactions.

Thus the fact that there is no appreciable differences between the effects of addition of steam and that of nitrogen in the range of reduction ratio upto about 15-20% may be explained as follows. The occurrence of backward reaction was not detectable because almost only reaction (1) is taking place at the initial period of reduction. On the other hand, in the later period of reduction it is supposed that, because the reaction (3) or reactions (2) and (3), each of which is to be affected strongly by the existence of steam, is taking place, the rate of reduction decreases widely with the increase of partial

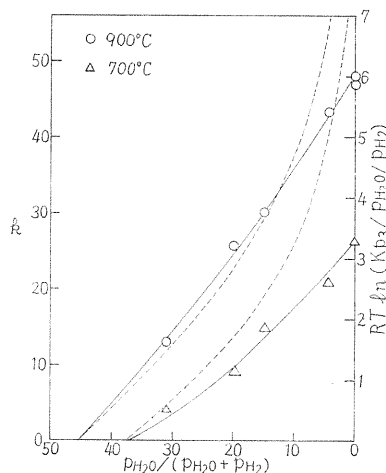


FIG. 11. Relations between k and partial pressure of steam in reducing gas.

pressure of steam.

On the basis of the present considerations, the activation energy of reductions with pure hydrogen at $R=50\%$ is too small to be explained by the assumption that the rate of reduction is controlled by chemical reactions. This fact is thought to mean that the diffusion of reactant and product gases becomes to play main role in rate determining.

Broken lines in Fig. 11 illustrate schematically the change of $RT \ln (Kp_3/p_{H_2,0}/p_{H_2})$ with $p_{H_2,0}/p_{H_2}$. This term corresponds to the driving force of reaction (3).

V. Conclusion

Results obtained here are as follows. The rate of reduction of hematite to magnetite was not affected by the presence of water vapor, as expected from thermodynamic calculations. The rates of later steps of reduction were decreased considerably as the ratio of partial pressures of steam to hydrogen was increased. Particularly, the rate of the last step, the production of metallic iron, is strongly affected, and at 700°C it is seemed to be negligibly small in the reducing gas containing about 30% water vapor.

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