Study on Sintering of Iron Ores. I : Reducibility of Iron Oxide Materials

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Reducibility of Iron Oxide Materials*

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Synopsis

The briquett-samples containing Fe_2O_3, SiO_2 and CaO were heated at 1,200°C and 1,300 C in the atmosphere of air or of mixed gas of CO and CO_2 so that the iron oxides might occur as hematite or magnetite or wüstite. These samples were deoxidized with CO or H_2 at 900°C, and their reducibility, expressed as a value of comparative reducibility, was determined from their own reduction curve.

The influence of composition of raw materials and of sintering atmosphere on reducibility was confirmed. Their porosity was determined, and also the relation between reducibility and porosity was discussed.

The results obtained from this investigation were as follows ; in the atmosphere of air, SiO_2 and CaO contents of iron oxide materials seemed to have little effect on reducibility of iron oxide, and it appears that reducibility varied directly with porosity when iron oxide mixtures were heated at 1,200°C, but there was found no longer such a clear relationship when heated at 1,300°C. In the reducing atmosphere, even a little amount of SiO_2 in the iron oxide materials gave undesirable effect on reducibility, and addition of CaO together with SiO_2 could not so much recover it as decreased it, till CaO was added enough for the content of SiO_2. There was found no direct relationship between reducibility and porosity, and the more reducing the atmosphere was more evident the tendency became.

I. Introduction

Sinters are forming an important and growing source of supply for blast-furnace burden with rapidly increasing production of iron and steel as well as with steady exhaustion of good resources of iron ores. In the early stage of development of sintering process, the process was employed to utilize fine ores, flue-dust and pyrite cinder, etc., that were unsuitable for the burden as they were. Sinters have been proved to be advantageous in improving the physical conditions in a blast-furnace because of the desirable physical character of sinters, therefore it has been emphatically stated that strength was the most essential nature of all.(1)(2)

This fact seems to have a very important bearing under such conditions as we see in Japan which is poor in strong cokes and in good lump ores. Under these conditions, strength may be considered to be predominantly essential since only a limited portion of sinters are to be used. But under the conditions that sinters are generally used in the burden as we see today, further information is necessary

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* The 35 th report of the Research Institute of Mineral Dressing and Metallurgy.

(1) G. Yamada, J. Iron Steel Inst. Japan, (in Japanese), **12** (1926), 431.

(2) G. M. Schwartz, Trans. A. I. M. E. Iron Steel Div., **84** (1929), 39.

about their reducibility.[3][4][5][6] Moreover, recent development in pelletizing process of iron ores will be sure to throw light on this problem.

As the reducibility of sinters widely varies with practical operation as well as with properties of raw materials, their reducibility is not always favorable in spite of their high porosity. While it has been often suggested hitherto[6][7][8][9][10][11] that reducibility was much affected by the degree of oxidation, and that of fusion as well as by minerallogical composition and porosity of sintered products, the information about them seems to be insufficient.

In sintering practice, the process is performed so complicatedly that it seems very difficult to establish the factors taking place in course of the process. This investigation, therefore, was undertaken in order to establish the fundamental facts on reducibility by determining the experimental conditions to be explained in the following section. Although these experimental conditions do not duplicate practical sintering conditions but rather make us think of those similar to briquetting or pelletizing conditions, the results derived from this investigation may be utilized in arriving at a clear understanding of reducibility of sinters and agglomerated materials.

II. Experimental merhod and raw materials

In this series of experiments, briquett-samples consisting of Fe_2O_3, SiO_2 and CaO were used, which were heated at 1,200°C or 1,300°C for 30 minutes in the atmosphere of air or of mixed gases of CO and CO_2 so that the ferric oxide in original samples might be converted to hematite or magnetite or wüstite repectively.

These specimens sintered were deoxidized in a cylindrical form as when they were made at 900°C with CO or H_2 and their reduction curves were plotted against the reduction period.

A porcelain combustion tube, 20 mm in inner diameter and 70 cm long, which was equipped with water-cooled glass caps at both ends, was inserted in the heating furnace with heating elements of silicon carbide. Samples were introduced in this tube. As a reduction arrangement, a silica spring balance was employed as graphically shown in Fig. 1. Inside a fused quartz tube, 26 mm in inner diameter and 35 cm long, a thin crucible of silica, 15 mm in diameter and 5 mm deep, was suspended from the spring with a fine string of quartz. A specimen was placed on a thin plate of nickel in the crucible to prevent contamination with the silica crucible.

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(3) C. E. Agnew, Matals Tech., T. P. **956** (Aug. 1938).
(4) P. G. Harrison, Blast Furnace Steel Plant., **27** (1939), 372.
(5) J. H. Slater, Trans. A. I. M. E. Iron Steel Div., **145** (1941), 44.
(6) J. L. Mauthe, Iron Age, **162** (July 29, 1948)
(7) W. Luyken and L. Kräber, Mitt. K. W. Inst. Eisenforsch., **13** (1931), 247.
(8) T. L. Joseph, E. P. Barrett and C. E. Wood, Blast Furnace Steel Plant, **21** (1933), 1447.
(9) J. E. Greenawalt, Metals Tech., T. P. **963** (Sept. 1938).
(10) J. Klärding, Arch. Eisenhüttenwes., **12** (1938/39), 525.
(11) K. Croethe and J. Stoecker, Stahl u. Eisen, **55** (1935), 641.

Decrease in elongation of the spring taking place in course of deoxidation of specimens could be read by means of a telescope which has accuracy of 0.01 mm. As the spring employed had 37.8 mm elongation per gram, this arrangement had sensibility of about 0.3 mg.

CO and CO_2 were reserved in gas reservoir tanks separately, in which water level was kept constant by means of the apparatus illustrated in Fig. 2, and velosities of flows of gases were adjusted by the water heads and needle valves. CO and CO_2 were mixed in the desired ratio by means of flowmeters and the composition of mixed gas was determined by Orsat micro-gas analysis apparatus.

A sample of mixture of 1 g was pressed in a cylindrical form, 10 mm in diameter under 5 kg load, then it would have 7~10 mm height, depending on its composition. It was placed in a porcelain boat, sometimes with a plate of nickel to prevent any reaction with the boat, then it was introduced to the furnace center gradually in a combustion tube which was maintained at a desired temperature, and through which flowing gas passed at the rate of 100 cc/min. After heating for 30 minutes, the gas was displaced with N_2 and the boat was pulled out by an end

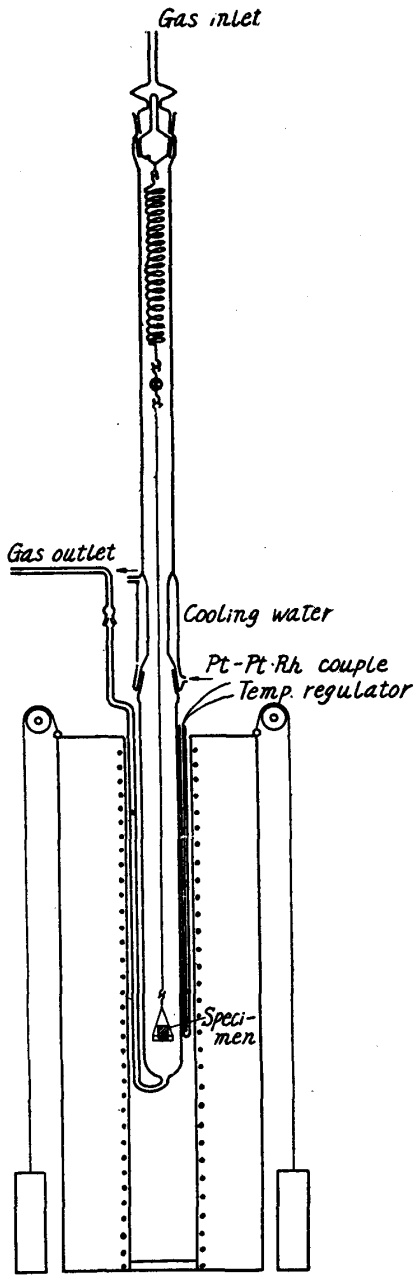

Fig. 1. An arrangement for reduction tests.

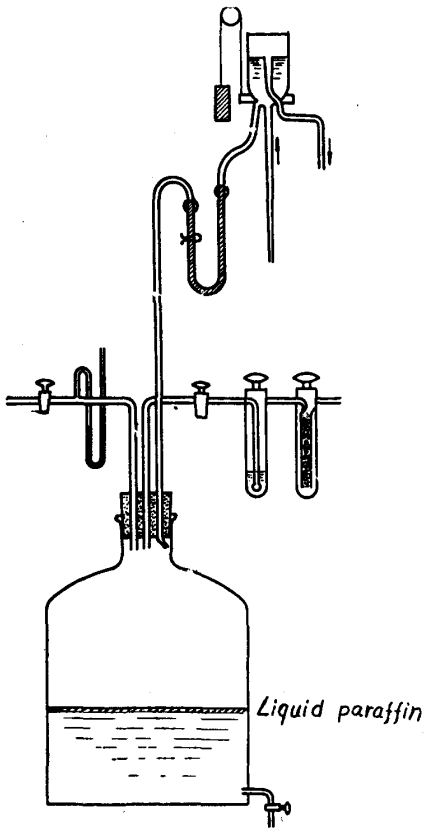

Fig. 2. An gas reservoir tank.

of the tube and allowed there to cool in N_2 to prevent reoxidation of the sample.

A specimen sintered was then weighed with accuracy and placed in the crucible, suspended from the spring balance. After a preliminary evacuation, N_2 was introduced and the furnace was lifted up which was maintained at 900°C. After the specimen reached 900°C, reducing gas was passed through at the rate of 50 cc/min by turning cocks. The temperature of the specimen was controlled by an automatic regulator. The degree of decrease in the weight of the specimen was recorded at 1~5 minutes intervals. When deoxidation proceeded no more, the reducing gas was displaced with N_2, and the specimen was allowed to cool in N_2 by pulling the furnace downwards.

The gases used were prepared as follows: CO was obtained from formic acid and sulphuric acid, CO_2 from limestone and hydrochloric acid, H_2 from electrolysis of kalium hydroxide aqueous solution, and N_2 from a commercial bomb. These gases were purified by the usual procedure for purification. The iron oxide used in this investigation was pure chemically precipitated Fe_2O_3, and SiO_2 was prepared from silica sand of 99.5% SiO_2 content which was ground under 200 mesh and washed with hydrochloric acid. CaO was prepared by igniting precipitated calcium oxalate at 1,000°C.

The compositions of samples used in this investigation were given in Table 1 in molecular fraction and in weight percentage with denotations.

Table 1. Composition of original samples.

No	Denotation	Mol Fraction			Weight Percentage		
		Fe_2O_3	SiO_2	CaO	Fe_2O_3	SiO_2	CaO
1	Fe	100	0	0	100.0	0	0
2	10S	90	10	0	96.0	4.0	0
3	20S	80	20	0	91.4	8.6	0
4	40S	60	40	0	80.0	20.0	0
5	50S	50	50	0	72.7	27.3	0
6	20S10C	70	20	10	86.4	9.3	4.3
7	20S20C	60	20	20	80.5	10.1	9.4
8	20S30C	50	20	30	73.5	11.0	15.5
9	20C	80	0	20	92.0	0	8.0

III. Experimental results

The reduction curves obtained in each series of experiments are presented in Figs. 3~8, in which reduction degree is denoted as the ratio of the oxygen removed from the sample for the available oxygen. The available oxygen was computed on the fact that iron oxides in the original samples would be entirely converted to hematite or magnetite or wüstite, though, strictly speaking, the case seems to be impossible.

Samples were heated in air at 1,200°C and 1,300°C and then deoxidized with CO at 900°C in the series A and B respectively. In the series A, any one of the samples had good reducibility and addition of SiO_2 and CaO gave no undesirable effect on their reducibility as illustrated in Fig. 3. For the series B, the results are shown

in Fig. 4, in which deoxidation of hematite itself was considerably retarded in com parison with that heated at 1,200°C, and although addition of SiO_2 alone rather seemed to improve the reducibility, simultaneous addition of SiO_2 and CaO gave some undesirable effect on it. Even when iron oxide occurred as hematite, iron oxide could be deoxidized only to the vicinity of 95 per cent. of reduction degree in the deoxidation with CO and it could not be completed to nearly 100 per cent. till H_2 was introduced after CO.

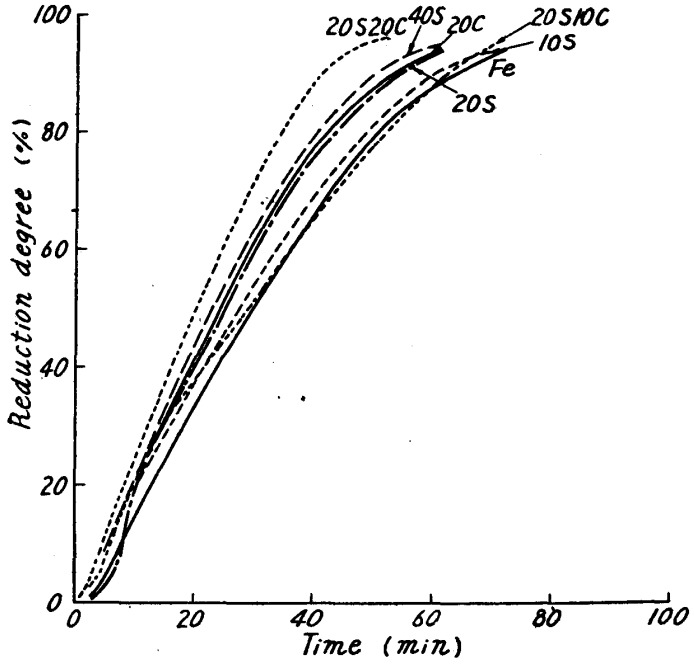

Fig. 3. Reduction curves in the series A.

Samples in series C and D were heated at 1,200°C in the mixed gas of 10%CO and 90% CO_2, and at 1,300°C in the mixed gas of 7%CO and 93% CO_2 respectively, and then deoxidized with CO at 900°C. In these cases iron oxide of original samples might possibly be converted to magnetite, so that the available oxgen was computed as the oxygen content combined with iron when iron oxide was entirely converted to Fe_3O_4.

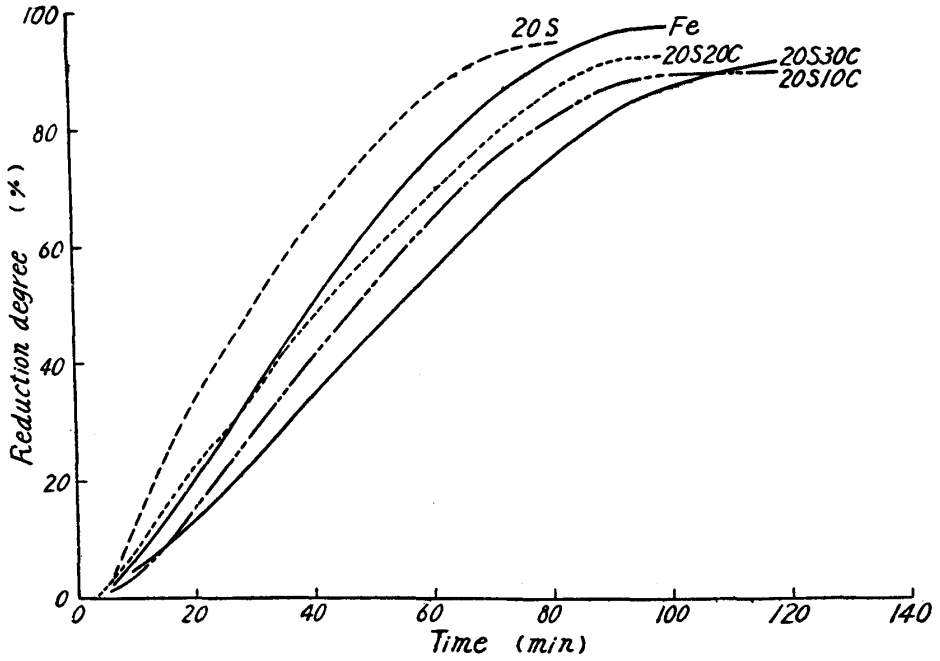

Fig. 4. Reduction curves in the series B.

The results of series C and D are illustrated in Figs. 5 and 6, in which magnetite itself was not so easily deoxidized as hematite, especially in series D. SiO_2 had a bed effect on reducicility and CaO added together with SiO_2 gave a worse effect

on it up to 20S20C of CaO content, and could not recover it till CaO was added up to 20S30C of CaO content.

In the series E and F where iron oxides existed as wüstite, samples were heated at 1,200°C in the mixed gas of 40% CO and 60% CO_2, and then deoxidized with CO

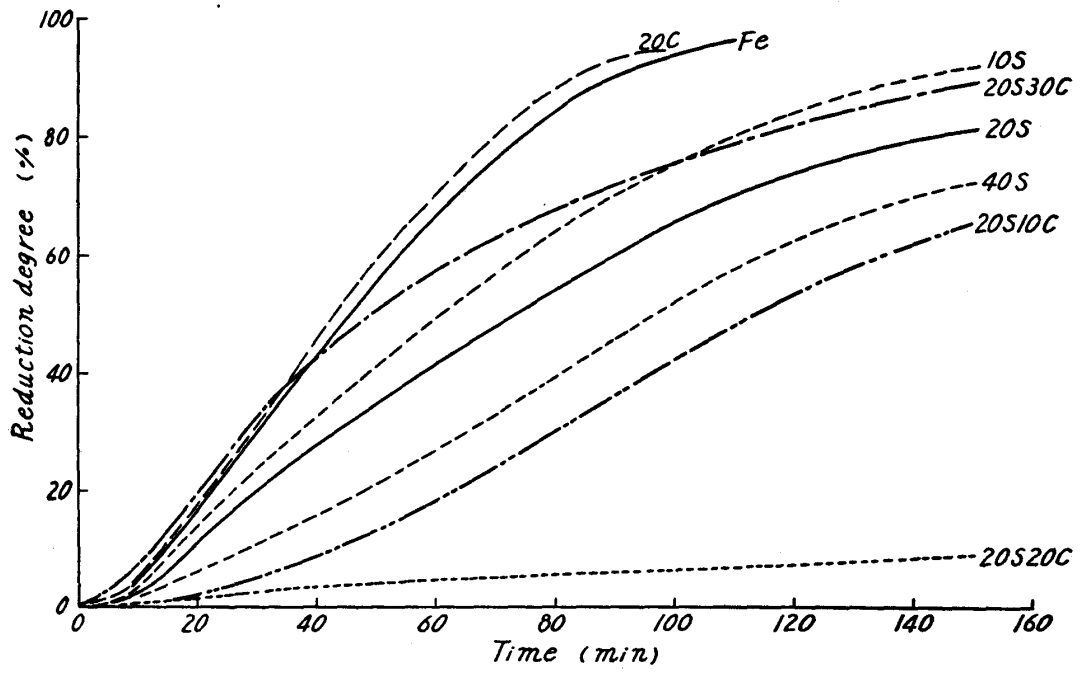

Fig. 5. Reduction curves in the series C.

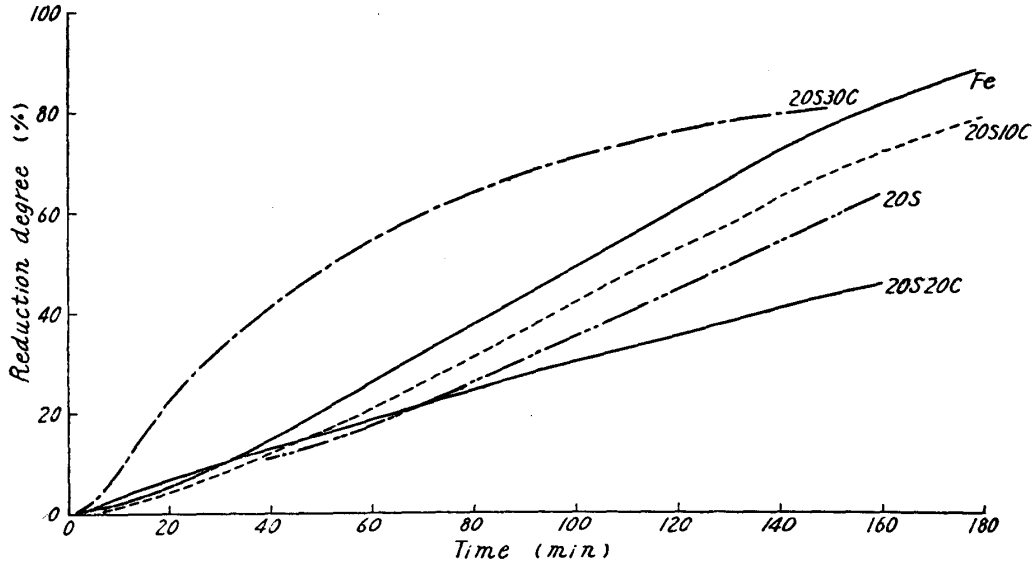

Fig. 6. Reduction curves in the series D.

or H_2 respectively. Their results are shown in Figs. 7 and 8. Wüstite which was in equilibrium with the above mixed gas at 1,200°C contained about 0.24% oxygen,[12][13] so that the available oxygen was computed on this fact. In this case a little addition of SiO_2 gave a very bed effect on the reducibility, and they were deoxidized with H_2 since most of them could not be satisfactorily deoxidized with CO.

(12) R. Schenck and Th. Dingman, Z. anorg. allgem. Chem., **166** (1927), 113.
(13) K. Sanbongi, Sci. Rep. RITU, A 1 (1949), 213.

The similar effect as that shown in Fig. 5 may clearly be observed in Fig. 8.

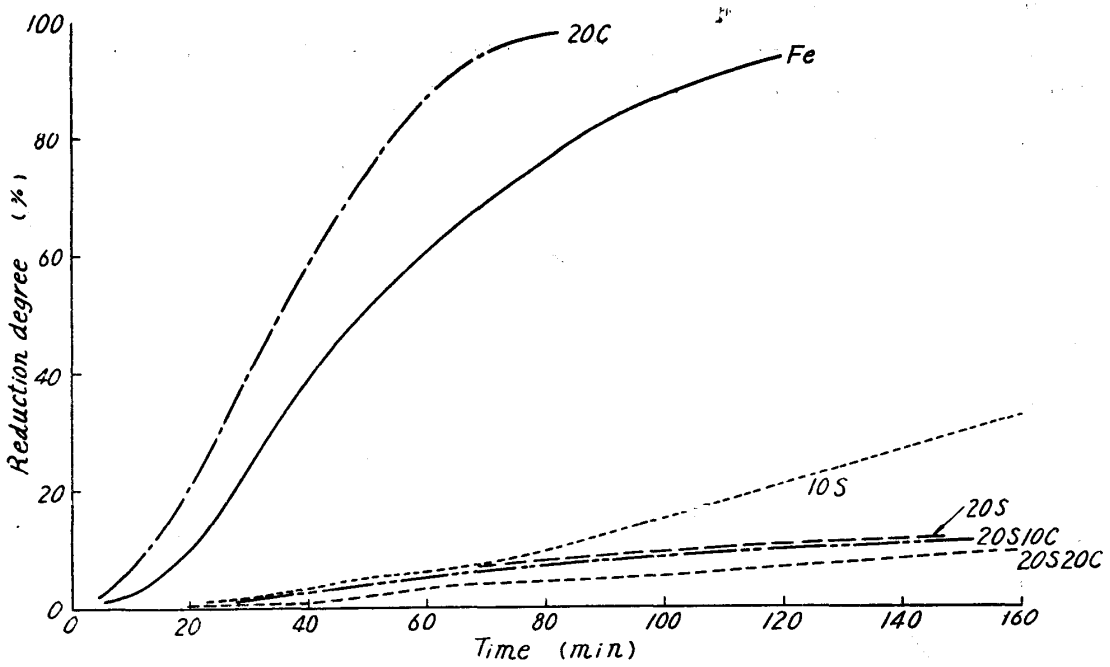

Fig. 7. Reduction curves in series E.

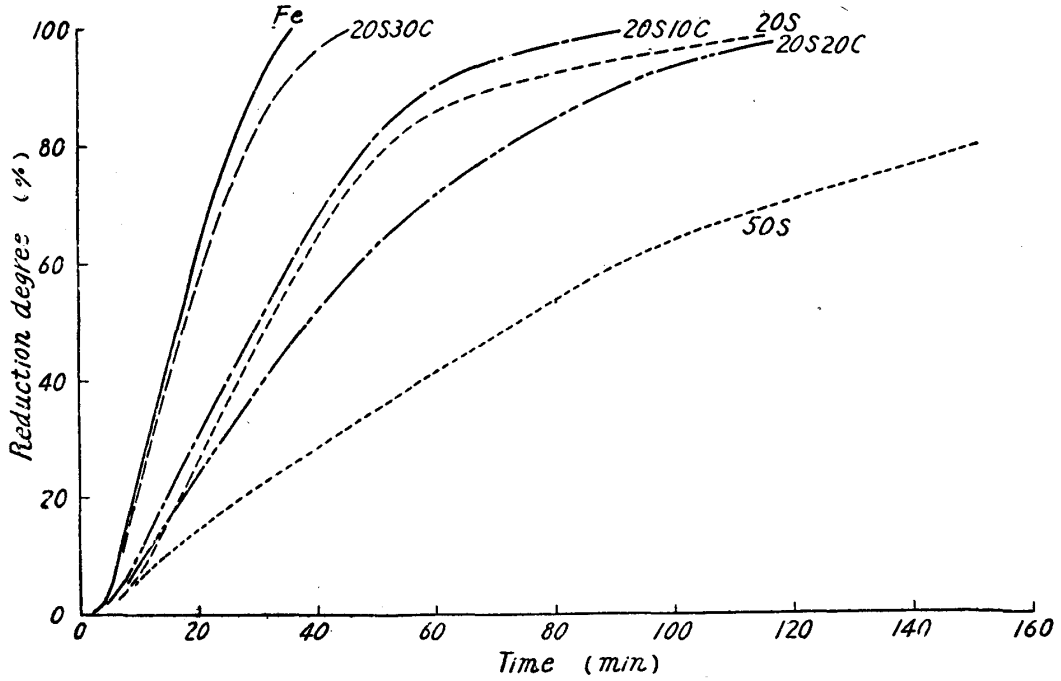

Fig. 8. Reduction-curves in the series F.

IV. Determination of value of comparative reducibility and porosity

The rate of deoxidation of iron oxide materials is affected not only by kind of materials but also by particle size and amount of the materials, kind and velocity of reducing gas, and temperature of deoxidation as well.[14] A survey of the papers

(14) W. H. Wetherill and C. C. Furnas, Ind. Eng. Chem., **26** (1934), 983.

published hitherto reveals that there are discordance regarding the relation between the above factors, and the feature of deoxidation is not clarified so well, although general tendency of these variables seem to be accepted. Therefore, the method of expressing the reducibility is different with investigators and most of them seem to be nothing but conventional.[8][15][16][17]

It has been pointed out that the rate of deoxidation is controlled by something going on within the ore and it is very likely that this something is the diffusion of reaction gas from the seat of reaction to the gas phase.[18][19] The present writer considered the feature of deoxidation in this experiments on the basis that the rate of deoxidation was controlled by the rate of diffusion of the reaction gas through the deoxidized layer. If the amount of the deoxidized layer is substituted by the reduction degree, the relation may be expressed as follows:

$$dw/dt = k \cdot 1/w$$

$$w^2 = k't$$

where w denotes degree of reduction in weight ratio and t denotes time in minutes. From this, a linear relationship may be established between w^2 and t. When we plot the value of w^2 against t from the above reduction curves, we may find a reasonable portion of straight line in the plotted curves as shown in Fig. 9 for an example. From the inclinations of these lines, we can get k' which are designated

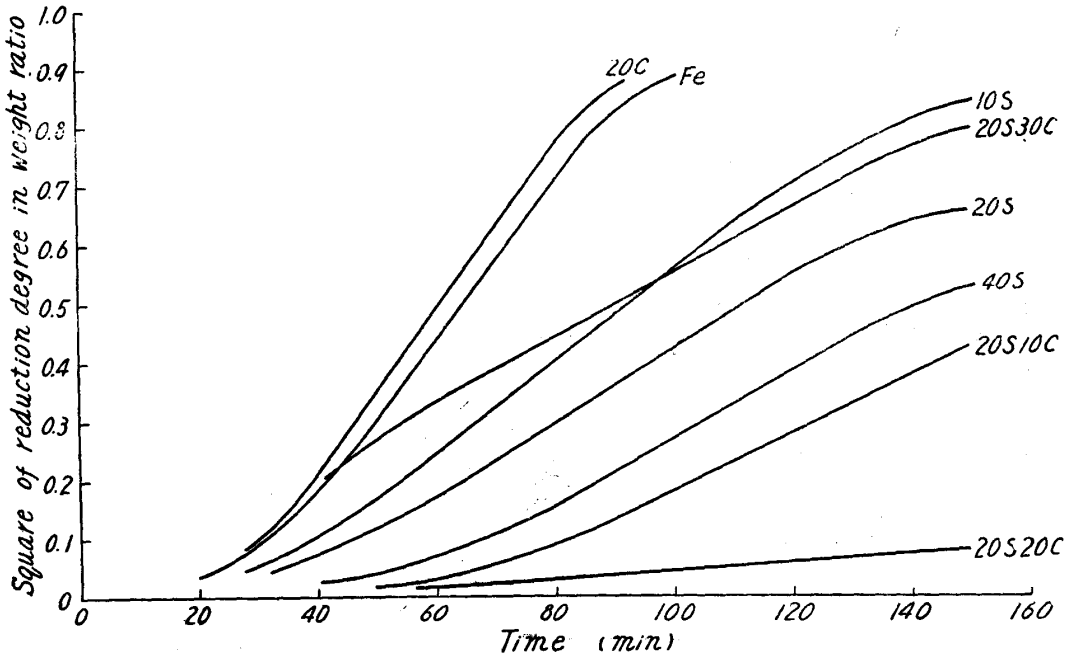

Fig. 9. Relation between Square of Reduction-degree and Time in series C.

(15) T. L. Joseph, Trans. A. I. M. E. Iron Steel Div., **120** (1936), 72.
(16) G. Oishi and K. Ishibe, J. Iron Steel Inst. Japan (Japanese), **17** (1931), 242.
(17) B. Stalhane und T. Malmberg, Stahl u. Eisen, **49** (1929), 1835; **50** (1930) 969; **51** (1931), 716.
(18) M. C. Udy and C. H. Lorig, Trans. A. I. M. E. Iron Steel Div. **154** (1943), 162.
(19) F. Wüst and P. Rütten, Mitt. K. W. Inst. Eisenforsch., **5** (1924), 1.

as values of comparative reducibility. These values obtained in this experiments are given in Table 2 and Fig. 10.

Table 2. Values of comparative reducibility.

No	Denotation	Series A	Series B	Series C	Series D	Series E	Series F*
		1,200°C Air	1,300°C Air	1,200°C 10% CO 90% CO_2	1,300°C 7% CO 93% CO_2	1,200°C 40% CO 60% CO_2	1,200°C 40% CO 60% CO_2
1	Fe	1.83×10^{-2}	1.50×10^{-2}	1.36×10^{-2}	0.76×10^{-2}	1.09×10^{-2}	4.56×10^{-2}
2	10S	1.91		0.79		0.15	
3	20S	2.09	1.64	0.65	0.50	0.04	2.02
4	40S	2.40		0.56			
5	50S						0.59
6	20S10C	1.71	1.28	0.50	0.56	0.04	2.09
7	20S20C	2.71	1.32	0.08	0.20	0.03	1.22
8	20S30C		1.17	0.65	0.55		3.60
9	20C	2.16		1.43		2.11	

* In the last column, samples were deoxidized with H_2, and in others with CO.

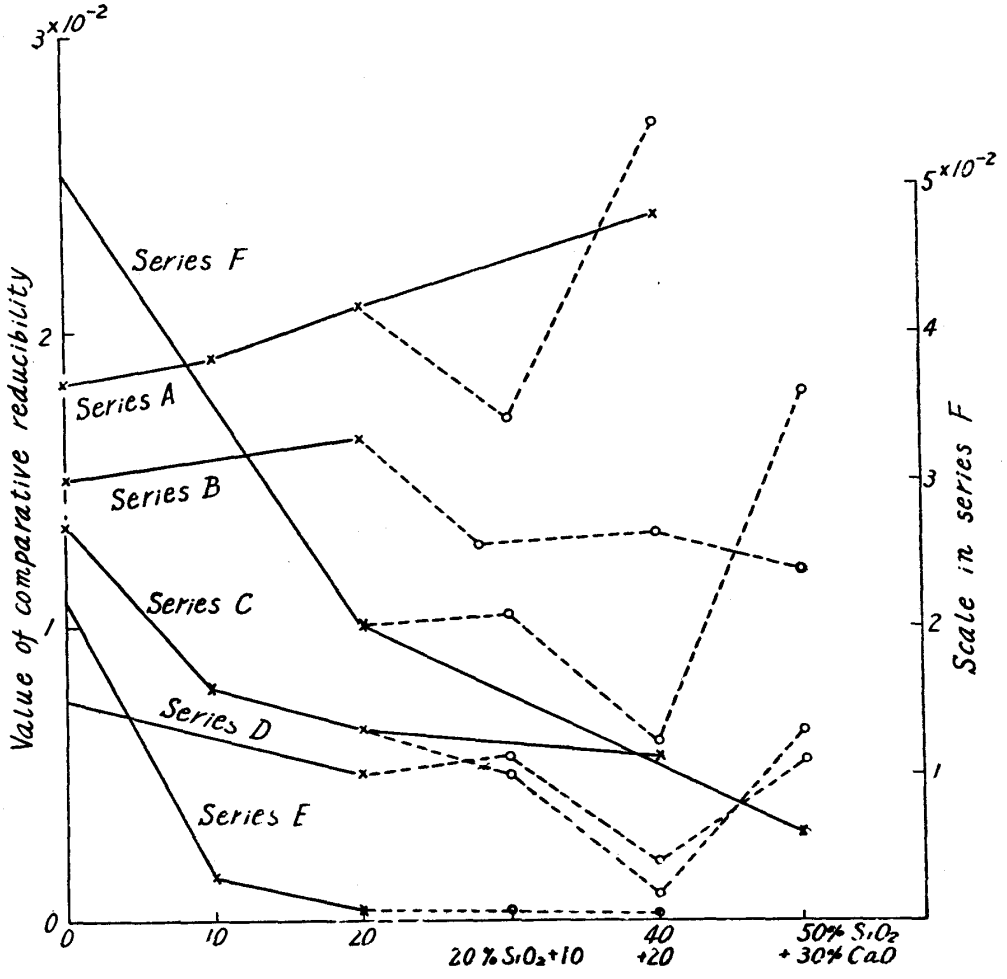

Fig. 10. Relation between Reducibility and Composition.

This assumption may be interpreted by the fact that sinters have more or less matrix formation in the microscopic structure, so that the reduction of iron oxides will proceed by diffusion of reducing gas or reaction gas through matrix.

It is well known that the rate of deoxidation varies directly with porosity or gas

permeability of ores in hematite or limonite, although this relation is not so clear in magnetite or sinters as in hematite.[15][19] Porosity measurements were made on some of samples used in reduction test. Apparent density was determined by the displacement method with Hg, and true density by the picnometer method. Porosity was calculated from these determinations. Samples containing CaO was determined with absolute alcohol to prevent CaO from dissolving in water. These results are tabulated in Table 3.

Table 3. Measurements of porosity.

No	Denotation	Series A			Series B			Series C			Series E & F		
		App. Density	Tru. Density	Poro-sity	App. Density	Tru. Density	Poro-sity	App. Density	Tru. Density	Poro-sity	App. Density	Tru. Density	Poro-sity
1	Fe	4.24	4.67	9.23	4.84	5.10	4.97	4.49	4.65	3.36	4.11	5.50	25.4
2	10S	4.02	4.45	9.80				4.23	4.46	5.05	4.12	4.98	17.2
3	20S	3.77	4.29	12.11	4.06	4.60	11.79	3.88	4.41	11.9	3.99	4.44	10.0
4	40S	2.93	3.54	17.06				3.14	3.90	19.5			
5	50S										3.55	3.99	11.1
6	20S10C	3.69	4.41	16.2	3.38	4.65	27.6	3.51	4.14	14.9	4.18	4.49	8.1
7	20S20C	3.03	4.62	34.5	3.64	4.36	16.6	3.90	4.61	15.7	3.92	4.39	10.9
8	20S30C				3.62	4.39	17.6				3.43	4.43	22.6
9	20C	3.57	4.81	25.8				4.57	5.30	14.1	4.43	5.67	21.9

When we consider this relationship between reducibility and porosity on the results obtained in this experiments, two straight lines may be found among the points obtained in the series A, one of which expresses the group that does not contain lime, and the other contains lime as shown in Fig. 11. In other cases so clear a

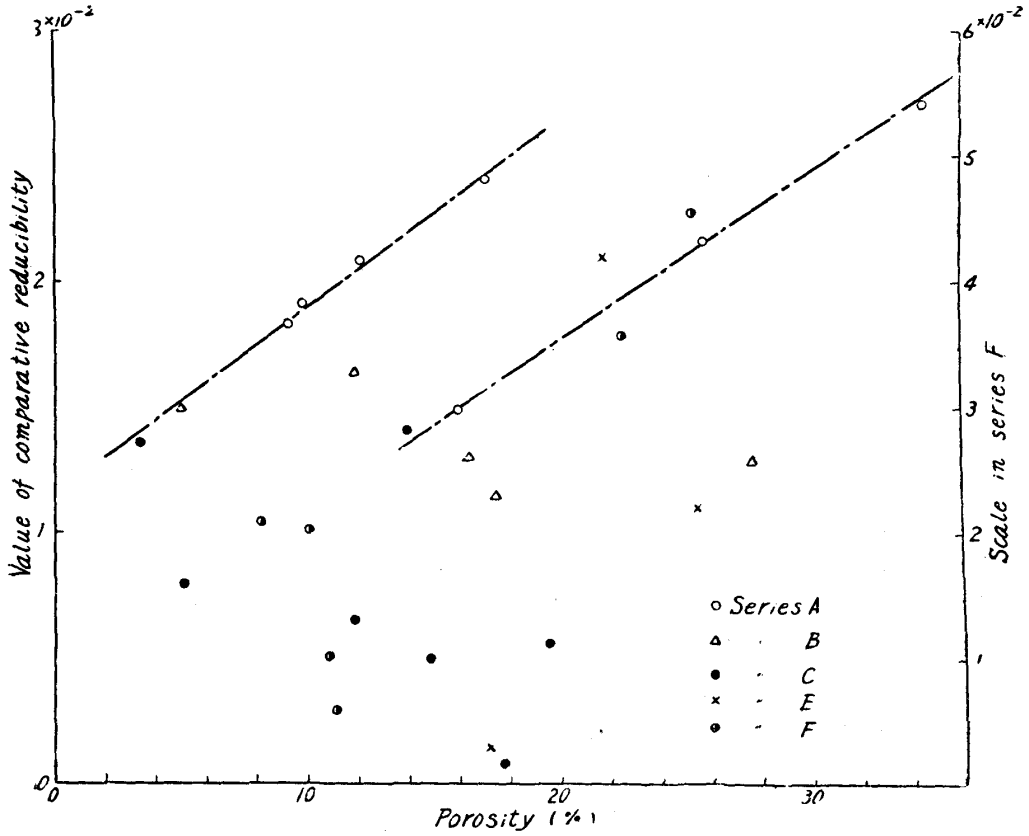

Fig. 11. Relation between reducibility and porosity.

relation cannot be found among them. It must be noted here that microscopically large pores as well as small pores are observable in the structures where matrix appears well-developed such as seen in wüstite series. Therefore, the porosity can express not only the microporosity, but includes the macro-pores occluded.

V. Discussions of the results

The microscopic structures of these specimens used in this experiments were observed and their results will be reported in another paper. These microscopic structures are, in general, considerably small compared with commercial sinters, but in the series D and E or F they seem to produce the material of about the same structure as commercial sinters. Under practical conditions, sintering temperature is considered to exceed 1,400°C, but for a very short period, so that may possibly be duplicated when heated to 1,200°C or 1,300°C for 30 minutes in some atmospheres. Here, some discussions will be made, with reference to these structures, on the relation of reducibility and chemical and minerallogical composition as well as porosity of sinters as follows:

(1) Iron oxide

It has been suggested and experienced by many investigators that the reducibility of iron oxides is much affected with their previous history. In this experiments hematite heated at 1,300°C showed less reducibility than that heated at 1,200°C, and magnetite prepared at 1,200°C had somewhat less reducibility compared with the latter, and magnetite prepared at 1,300°C had far less reducibility in comparison with magnetite prepared at 1,200°C. Apparently in magnetite prepared at 1,200°C and hematite heated at 1,300°C, their values of comparative reducibility seem to fall on the upper straight line as shown in Fig. 11, and their reducibility seems to be predominantly controlled by porosity.

Wüstite in the series E, however, has less reducibility than magnetite in the series C in spite of its higher porosity, and its value falls considerably below this line. Magetite in the seies D which has the value of only 0.65 must be far below this line. These facts suggest that there exists an interesting and much complicated feature of deoxidation in relation with crystalline state or minerallogical state of iron oxides, but it is impossible to treat this problem here.

(2) Effect of SiO_2 alone

In general, it is recognized that there is no compound or solid solution between Fe_2O_3 and SiO_2. In the series A, a linear relationship is found among the specimens of 10, 20 and 40 mol% SiO_2 content and SiO_2 is found rather to improve the reducibility proportionally to the porosity as shown in Fig. 11. But in the series B, though the specimen of 20 mol% SiO_2 content shows a litter reducibility than hematite, it does not increase proportionlly to the porosity, and its value falls considerably below the straight line. Slight dissociation of ferric oxide at this temperature resultıng in the formation of iron silicate, seems to be responsible for this fact, though the formation of iron silicate could not be determined microscopically.

In the case of magnetite-series and especially of wüstite-series, SiO_2 has clearly so bad an effect that deoxidation is much retarded, and this fact may by attributed more or less to the formation of iron silicate.

(3) Efect of CaO alone

Some calcium-ferrites are well-known compounds to be formed from Fe_2O_3 and CaO, but the relation between CaO and Fe_3O_4 or wüstite remains as yet uncertain. CaO added to Fe_2O_3 does not retard deoxidation in itself, but in relation with the porosity, calcium-ferrite has not so good a reducibility as Fe_2O_3, but their effect is not so serious.

When CaO is added alone to Fe_3O_4 and wüstite, the reducibility becomes rather good, and it may be said that CaO added to iron oxide has no toublesome effect on the reducibility in the case of any degree of oxidation of iron.

(4) Combined effect of SiO_2 and CaO

In the diagram of the system of iron oxide-SiO_2-CaO, a certain part of the system of FeO-SiO_2-CaO has been well investigated, and the existence in wide range of Ca-olivine is well known, but in the part with which iron oxide of higher oxidation degree is concerned, this relation still remains uncertain.

Simutaneous addition of SiO_2 and CaO in the series A does not show so bad an effect on the reducibility, but their reducibility is yet low, taking into consideration their high porosity. There is, however, an ineresting fact that another straight line seems to be found between the specimen containing CaO such as 20C, 20S10C, and 20S20C.

Owing to the observation of the microscopic structures, the structure of 20C is found to consist of hematite embeded in matrix which may be calcium-ferrite. Therefore, there appears a considerable amount of well-developed matrix and well-crystallized grains of hematite, but in the structure of 20S10C and 20S20C grain growth of hematite is slow and matrix is not yet sufficiently formed.

In the heating at 1,300°C, grains of hematite developed considerably well, and the matrix was also formed enough to envelop the grains, which resulted in a decrease in the reducibility, and the direct relationship of the reducibility and porosity was no longer found. At any rate, the existence of SiO_2 and CaO had not so much influence on the reducibility in the case of hematite.

In the series C and D, the combined influence of SiO_2 and CaO appeared pronouncedly, that is to say, CaO added up to 20S20C of CaO content, did not so much recover the reducibility as decreased it compared with 20S, and it could not be recovered till CaO was added up to 20S30C of CaO content.

In the series D in which a considerable decrease in the reducibility was already found in magnetite itself, an additional influence of SiO_2 and CaO did not look so remarkable as that in the series C, but had the same tendency as the series C. This fact might possibly be explained on the basis that CaO had a stronger affinity with SiO_2 than FeO at the elevated temperature. 20S in the series C has but a little amount of matrix and small grain of magnetite in its microstructure, but matrix and grain size increase with addition of CaO progresively such as in 20S10C

and 20S20C, and magnetite grains become enveloped completely with matrix. Therfore, undesirable effect in 20S10C and 20S20C may probably be attributed to this to some extent.

In the case of wüstite-series, deoxidation with H_2 had the same feature as in magnetite-series, and it shows that it is impossible to recover the reducibility till the excess of CaO is added.

(5) Reducing action of CO and H_2

Deoxidation of some materials with CO at 900°C seems to be much retarded as shown in the series of magnetite and wüstite, and the reducing power of CO is not progressively recovered, but stops further deoxidation in course of deoxidation and there are also observed some materials, in which deoxidation is retarded especially in the first stage of deoxidation. However, when they are deoxidized with H_2, they can be deoxidized without delay.

These facts which suggest the difference of reducing action between CO and H_2 seem to be related with the problem of activation for deoxidation of the reacton surface. In the deoxidation of sinters, which usually contains more or less such materials in their constitution, this difference should duly be taken into consideration.

VI. Conclusions

The results obtained in this investigation may serve to prove conclusively that the reducibility of sinters would be much affected by sintering atmosphere and sintering temperature, as well as the composition of iron oxide materials so that the reducibility ought to be considered duly in sintering practice.

It is advisable, from the point of view of reducibility, to produce sinters in the oxidizing atmosphere as much as possible, and this has been emphasized in Swedish sinters. Under such condetions, SiO_2 and CaO occuring in raw materials scarcely have any influence on the reducibility.

In a reducing atmosphere, even a small amount of SiO_2 has very bad effect on the reducibility, and CaO together with SiO_2 cannot recover it till CaO is added enough to SiO_2 content. Since the more reducing the atmosphere is, the more evident this tendency becomes, further discussions seem to be necessary for improving the reducibility of sinters containing considerable amounts of SiO_2 by adding CaO to them.

It is not until strength and reducibility of sinters could be controlled as they wish, that sinters can be expected to win honor of having excellent properties such as chemical and physical uniformity as well as high porosity.

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