



Reduction and sintering of fluxed iron ore pellets—a comprehensive review

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Synopsis

Iron ore pellets with or without additives are commonly used as alternate charge material in both conventional and newer ironmaking processes. The performance characteristics of these pellets are normally assessed on the basis of their reducibility values, reduction strength and resistance to clustering. These properties depend mainly on the type and amount of additives and on the sintering phenomena of the pellets during firing. In the case of composite pellets (ore-coal pellets), reduction and sintering of the iron ore fines occur simultaneously. The thermodynamic and reaction mechanisms of the processes involved in the reduction of iron ore pellets with and without reductants, additives, etc., may not necessarily be identical.

The reduction and sintering characteristics of pellets greatly influence the reaction mechanism and the surface morphology of the reduced pellets. The approaches in the literature to the analysis of these reduction and sintering phenomena are broadly categorized as follows: (i) empirical models, (ii) models based on kinetics, and (iii) models based on morphological changes. The relative merits and de-merits of these models are illustrated by their application to the reduction of fluxed ore-coal composite pellets. A critical analysis of the investigations that have been conducted on the reduction and sintering behaviour of such pellets is given.

It is shown that, although elegant empirical models and kinetic equations have theoretical significance and can be usefully employed in elucidating the reaction mechanisms of iron ore lumps, they are sometimes not directly applicable to fluxed ore-coal composite pellets. In studies of the latter, the approach should be to correlate the morphological changes with the reduction mechanism. The paper also gives a brief account of an investigation on the reduction and sintering aspects of fluxed composite reduced iron pellets.

Introduction

Although the reaction of iron ore has been a subject of research and discussion for many years, it is still beset with uncertainties, with inconsistent experimental data, and with conflicting theories. The practical application of many studies has been severely limited because most of them have been confined to controlled experiments and idealized conditions, which are very different from the conditions in industrial practice. Although several investigations have been carried out on the gaseous and solid reduction of iron

oxides (ore), uncertainties arise because of the complex nature of these oxides. These studies, which generally simulate the conditions of blast furnace or direct reduced ironmaking, may not necessarily be applicable to the conditions prevailing in the combined processes of direct reduction and smelting reduction (DR-SR).

The production of liquid iron from the DR-SR route conceptually avoids the cokemaking and ore-agglomeration processes. But these process routes which are at different stages of their development, cannot directly utilize ore fines and coal fines like conventional processes. The feed is generally in the form of lumps and/or pellets of selected size. However, the lumps/pellets of iron ore should exhibit adequate reducibility, and their green and reduction strength characteristics should be suitable under given process conditions. The complexities in the case of pellets arise from uncertainties in their chemical composition due to impurities, flux additions, other additives, and binders.

The presence of impurities or additives can alter the intra-crystalline structure, lattice diffusivity, porosity, surface orientation, non-stoichiometry, and even the reduction sequence of the iron oxides during reduction. The nature and composition of the reducing gases, and the type of reductant, are as important as the temperature in determining the kinetic parameters. Iron oxides can form mixed crystals or compounds with other oxides, which affect the thermodynamic driving force for their reaction and can alter their stability ranges. For instance, Von Bogdandy and Engel¹ have shown that, when $\text{SiO}_2\text{-CaO}$ was added to iron oxide, the magnetite stage disappeared from the decomposition sequence of the iron oxide.

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Reduction and sintering of fluxed iron-ore pellets

Most of the studies in the literature on reduction and sintering phenomena in fluxed composite iron ore pellets generally deal with one or more of the following:

- experimental measurement of the progress of reaction by weight loss due to oxygen removal and chemical analysis in isothermal and non-isothermal conditions
- microscopic investigation of the reduction and sintering behaviour of pellets
- development of mathematical models to predict the effect of process parameters on the reduction and sintering of pellets.

The present paper describes and analyses various aspects of these studies, showing that the correlations established do not necessarily elucidate the reaction mechanism of fluxed composite iron ore pellets. A brief summary of an ongoing investigation on such pellets is also presented.

Thermodynamic aspects of reduction

Reduction of iron ore

Thermodynamically, the reduction of iron oxide occurs in steps. Of all the iron oxides, hematite is the richest naturally-occurring form. Accordingly, the following stable iron oxides can occur during the reduction (above 570°C): hematite (Fe_2O_3), magnetite (Fe_3O_4), and non-stoichiometric wustite (Fe_{1-Y}O , Y = metal deficit).

Magnetite and wustite exist within the temperature range shown in Figure 1. During the stepwise reduction of hematite to magnetite, wustite, and metallic iron, changes occur in the crystal structure. In hematite, the oxygen atoms are arranged in a closely packed hexagonal structure but, in magnetite and wustite, they form a face-centred cubic structure.

Hematite has one of two lattice structures: rhombohedral corundum (Al_2O_3 type of structure) or a spinal type of structure as magnetite. The latter is metastable and can be obtained³ by the oxidation of magnetite below 400°C.

Wustite is markedly non-stoichiometric, and it has a cubic face-centred, closely packed oxygen lattice with the ferrous ions arranged in the octahedral sites between the large oxygen ions⁴. At 1000°C, the oxygen-to-iron atomic ratio varies from 1.05 to 1.14 in equilibrium with the Fe and Fe_3O_4 respectively. Above 850°C, the composition of wustite in equilibrium with iron is almost constant (Figure 1). The lattice parameter of wustite varies linearly⁵ with the oxygen content from 4.301 to 4.2816 Å at 22.2 to 23.92 per cent oxygen (by weight) respectively, with corresponding densities of 5.728 to 5.613 g/cm³ at 25°C. The increase in lattice parameter and density as the oxygen-to-iron atomic ratio approaches unity indicates the formation of cation vacancies^{5,6}.

Edstrom³ has shown an increase in volume of 25 per cent in the transformation of hematite to magnetite, and a further 7 to 13 per cent increase in its transformation to wustite. However, owing to shrinkage in the metal, the overall increase in volume during reduction is about 25 to 27 per cent. Edstrom also found that, when natural magnetite crystals are reduced to metal, there is no corresponding volume increase but there is a shrinkage of about 4 to 5 per cent in the final product. This helps to explain why the reducibility is greatly improved when magnetite is oxidized to hematite before it is reduced.

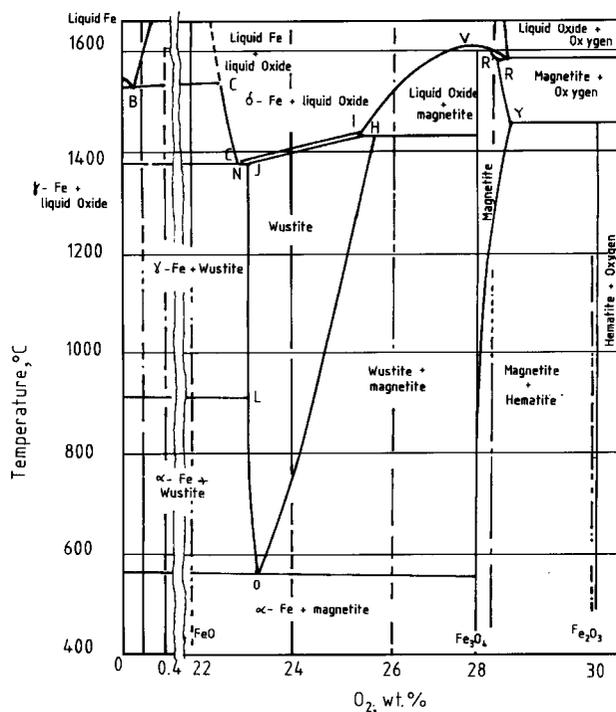


Figure 1—Iron-oxygen equilibrium diagram²

Magnetite's lack of expansion during reduction results in the formation of dense layers of metallic iron surrounding remnants of wustite, which cut off the access of the reducing gas to the oxide and prevent complete removal of the oxygen⁷.

Reduction of iron oxide composites

Owing to the expansion of the wustite phase field with an increase in temperature, larger amounts of foreign ions can be substituted. Wustite forms a continuous solid solution⁸ with MgO and MnO. It can dissolve⁹ 28 per cent of CaO at 1100°C, and 5 per cent and 1 per cent of Cr_2O_3 at 1350°C and 850°C respectively.

The changes in free energy accompanying the reduction of various iron-oxide composites are discussed by Ward¹⁰ and by Richardson and Jeffes¹¹. In composites, the oxygen potential corresponding to the reduction to metallic iron is decreased, and the thermodynamic driving force is lowered. Any elimination of oxygen in this case results in an enrichment of the second phase in the oxide.

Richardson and Jeffes¹¹ demonstrated the effect of a change in the activity of an element or its oxide in dilute solutions at the minimum reduction temperature and a given oxygen potential. The presence of additional phases would introduce thermodynamic activity gradients at fixed temperatures and applied pressures, and would alter the available degree of freedom of the system. Fujii and Meussner¹² reported a decrease in the equilibrium oxygen pressure of wustite with dilute chromium solutions. It is generally agreed that the addition of only small amounts of foreign ions produces significant effects on the volume changes and reduction rates^{3, 13-20}. Small additions of Na_2O , K_2O , CaO, and Li_2O retard the Fe_2O_3 to Fe_3O_4 reduction, but enhance the

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FeO to Fe reduction²¹. While the addition of SiO₂ accelerates the initial stages of iron oxide reduction, Al₂O₃ decelerates it at 550°C.

The addition of CaO or CaCO₃ increases the reducibility of hematite by hydrogen. This is attributed to an increase in porosity, which promotes the wustite dissociation mechanism^{14,22}. CaO and SiO₂ are major slag-forming oxides during induration of the pellets, and their ratio is important in governing the basicity of the gangue. Turkdogan and Vinters²³ found that an addition of CaO (up to 4 per cent by weight) and SiO₂ (up to 5 per cent by weight) affects the gaseous reduction of synthetic Fe₂O₃ and of ore pellets by carbon monoxide differently: in the former reaction, it reduced the swelling of synthetic material but showed no pronounced effect on swelling in the case of the pellets.

CaO²⁴⁻²⁶ and sodium oxide^{24, 26-28} cause abnormal swelling during reduction, but SiO₂ and Al₂O₃ additions reduce swelling^{28, 29} mainly because of the improved slag bonds and the removal of basic oxides. The inability of MnO and MgO to promote swelling is a result of their higher mobility and solubility in iron oxide.

El-Geassy and his co-workers³⁰ studied the effect of the degree of crystallization of silica on the reduction kinetics of Fe₂O₃ briquettes. They observed that the crystalline silica acted as a surface promoter and accelerated the reduction of iron oxide owing to the higher number of active sites for gas-solid reaction. However, they found that amorphous silica retards the reduction because of the formation of fayalite (Fe₂SiO₄).

The effects of additions have been reported to vary with the anionic nature of the compound. In the reduction of alkali chlorides and carbonates added to reagent-grade hematite, Bitsianes³¹ reported a catastrophic disintegration. Catastrophic swelling with Na₂CO₃ was observed by Lu²⁶. Fuwa and Banya²⁸ report that NH₄Cl and FeCl₃ added to iron ore formed whiskers of metallic iron, and Khalafalla and Weston¹⁵ observed that chloride and sulphide ions poisoned the promoters of wustite reduction, although nitrate ions had no effect. Na⁺ was a better promoter when added as a hydroxide than as a chloride. When Fuwa and Banya²⁸ decreased the NaCl content of pellets that had shown catastrophic swelling from 0.3 to 0.08 per cent, there was no significant effect on the swelling. The absorption of sulphur on wustite surfaces inhibited the chemical reactions, and promoted the growth of whiskers²⁷.

Mechanism of reduction

The reduction of iron ore or any ferruginous raw material with a reducing material involves stepwise reactions (Figure 2). In the first stage of reduction, oxygen atoms undergo a severe re-adjustment, which results in an increase in volume³ of about 25 per cent. This tends to open up the structure and facilitates the subsequent reduction stages. In the transformation of magnetite to wustite, the oxygen lattice remains unchanged while iron atoms diffuse to fill the vacant sites in the iron lattice. This can be accommodated with only a small increase in volume. Because wustite has a variable composition, there is also a small increase in volume as its composition changes from that in equilibrium with magnetite to that in equilibrium with metallic iron. On the other hand, the

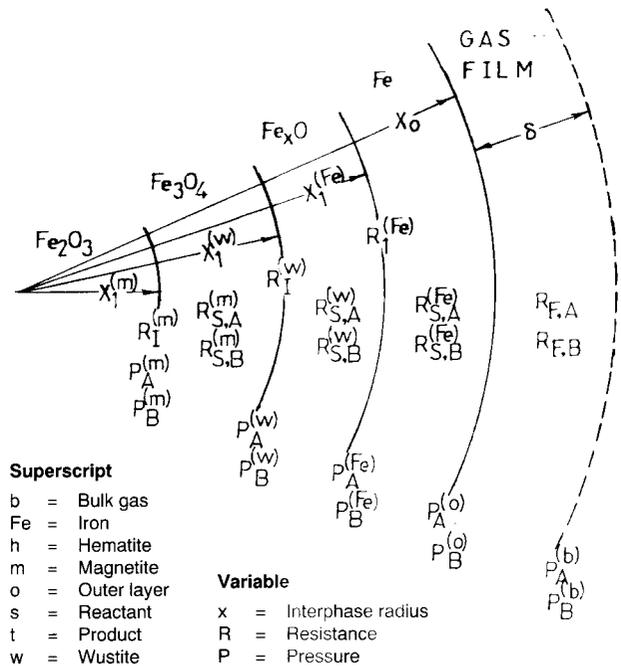


Figure 2—Representation of a model with three interface concentric shells

nucleation growth of iron crystals results in shrinkage and a large increase in the porosity of the metallic phase, which greatly facilitates the diffusion of the reducing gases from the outer surface of the particle to the wustite-iron interfaces.

Indirect reduction

For indirect reduction to take place, oxygen has to be removed by the contact of the reducing gas with the surfaces of iron oxide.

The fundamental steps involved in the reduction of iron oxide are as follows:

- diffusion of the reducing gas across the boundary layer
- intraparticle diffusion of the reducing gas to the reaction interface
- phase-boundary reaction: migration of Fe⁺⁺ and electrons to the iron nucleus
- intraparticle diffusion of oxidized gas from the reaction interface
- diffusion of oxidized gas across the boundary layer.

Diffusion control of the gas film

When the resistance of the gas film controls the reactions, the concentration profile for the gas-phase reactant is as shown in Figure 3.

The mass transfer of the boundary-layer gas film becomes negligible in the reaction of solids with a gas stream flowing above critical gas velocities. Different kinetic models can be used for the various reduction mechanisms.

Control of the phase-boundary reaction

Control of the chemical reaction at the interface occurs when the reaction product is porous and offers no diffusional resistances. At temperatures above 550°C, it was found

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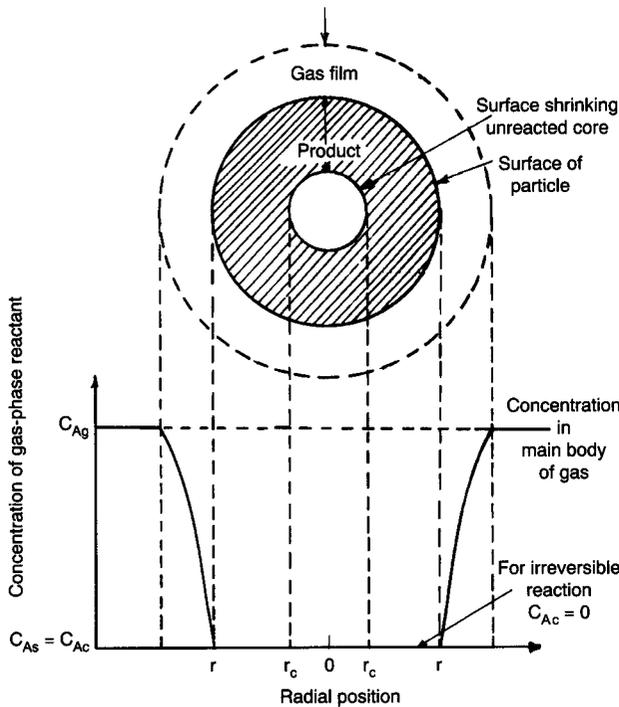


Figure 3—Representation of a reacting particle when gas-film diffusion is the controlling resistance³²

experimentally that, when the rate of reduction, \bar{r}_0 , is given in mol-cm⁻¹-s⁻¹, the reduction of iron oxide by H₂ or CO is shown by equation [1]³³:

$$\bar{r}_0 = k[p_0 - p_i] \quad [1]$$

where p_0 and p_i are the pressures of the reducing gas at the oxide surface and at the interface respectively.

The rate constant k for the phase-boundary reaction depends on which of the iron oxides is reacting with the gas. McKewan³⁴, in his study of the kinetics of iron oxide reduction, expressed phase-boundary reaction control as a shrinking-core model in terms of the fraction reacted, R :

$$\rho_0 r_0 [1 - (1 - R)^{1/3}] = kt \quad [2]$$

where r_0 is the initial radius of the pellet and ρ_0 is the density. The reaction rate dR/dt in equation [2] is proportional to $(1 - R)^{2/3}$. Spitzer *et al.*³⁵ indicated that the summation of the removal of oxygen at arbitrary points could possibly be proportional to $(1 - R)^{2/3}$. However, this rate equation does not denote the mechanism unambiguously. Figure 4 illustrates the concentration gradients within the particle when a chemical reaction controls the rate.

Diffusion through the product layer

Figure 5 illustrates the situation in which the resistance to diffusion emanates from the product layer and controls the reaction. Diffusion control occurs when the phase-boundary reaction is faster than the rate of supply or than the removal of the reactants or products. When the geometry is spherical and the texture porous, the rate-controlling model as developed by Crank, Ginstling and Brownshtein (CGB)³² is as follows:

$$1 - (2/3)R - (1 - R)^{2/3} = \frac{D_e(\rho_0 - \rho_i)}{\rho_0 r_0 RT} t \quad [3]$$

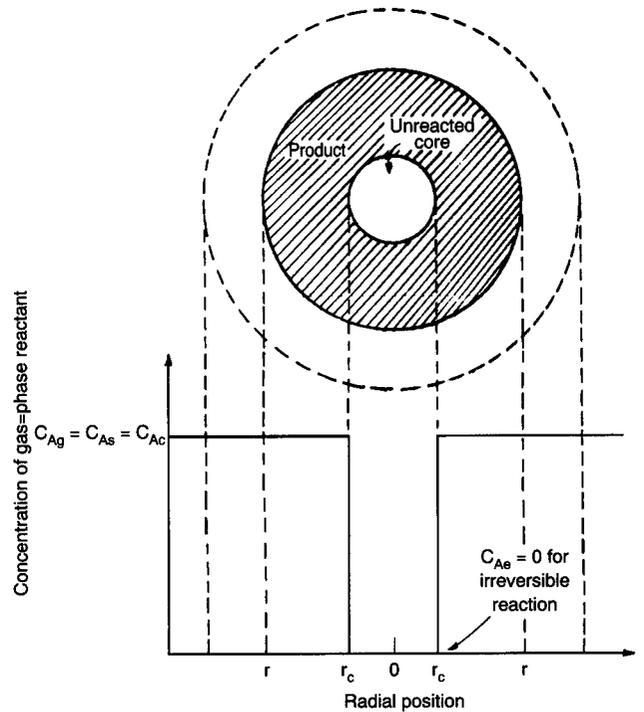


Figure 4—Representation of a reacting particle when the chemical reaction is rate controlling^{32, 36}

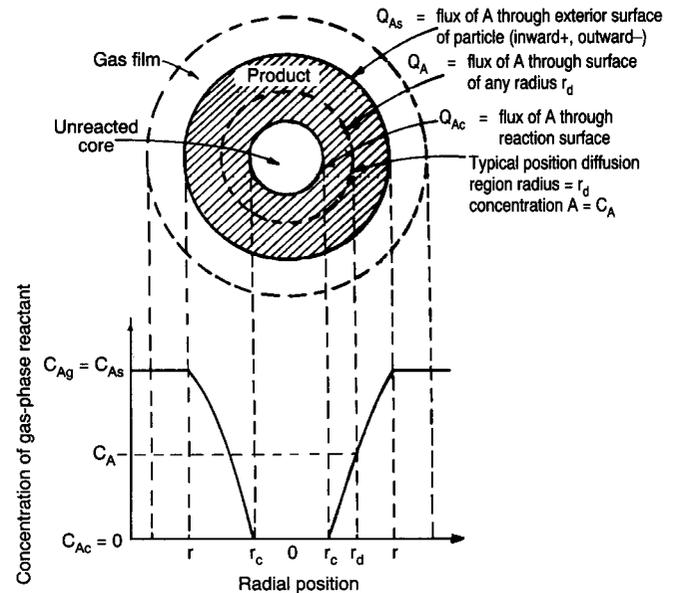


Figure 5—Representation of the situation in which product-layer diffusion controls the reaction^{32, 36}

where D_e is the effective gas diffusivity (i.e. the coefficient of porous diffusion of the gas).

Mechanism of mixed control

Mixed reaction control occurs when the rate of reaction is governed both by the phase boundary and by diffusion-control processes.

Seth and Ross³⁷ developed an equation assuming rate control by both the transportation of gas through the porous

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product layer and the interfacial reaction. The equation is as follows:

$$1 - (1 - R)^{1/3} + \frac{r_0 k_p [(1/2) - (R/3) - (1 - R)^{2/3}]}{2k_d} = \frac{k_p (C^0 - C)}{r_0 \rho_0} t, \quad [4]$$

where C^0 and C are the bulk-phase and equilibrium concentration of the reducing gas, ρ_0 is the density, and k_p and k_d are proportionality constants with the units of $M/L^2 t \text{ conc.}$ and $M/L t \text{ conc.}$ respectively.

A similar model had been proposed earlier by Lu³⁸.

Model of nucleation and growth

When nucleation of the product at various preferential active sites in the crystal accompanied by the growth of these nuclei is the rate-limiting step, equation [5]³⁹ applies:

$$\ln \left[\frac{R}{1 - R} \right] = kt. \quad [5]$$

This equation is derived from the Prout and Tompkins kinetic model, which assumes that the reaction starts at a series of active centres. The Johnson-Mehl or Avrami-Erofev equation has also been used⁴⁰ to empirically describe the nucleation and growth type of reaction mechanism. The rate of reduction seems to be governed by the structure of the iron formed by reduction because of its influence on the processes of chemical reaction and diffusion. If the iron formed during reduction is distributed over the surface of the FeO, and if it is difficult to disperse along the FeO and it grows vertically to the FeO, the rate of chemical reaction becomes faster because the sum of the co-existing lines in the three phases per unit area of the FeO surface becomes larger. The equation is

$$R = 1 - \exp(-kt)^n. \quad [6]$$

Composition of the reducing gas³²

The Fe-O-C (Figure 6) and Fe-O-H equilibrium diagrams¹ show that, thermodynamically, CO is a more efficient reductant than H₂ below 820°C, and *vice versa* at higher temperatures. Reduction to lower oxides can be carried out by the use of controlled oxygen potentials and gas mixtures of CO or H₂ with their oxidized forms.

Investigations⁴¹⁻⁴³ of reductions with H₂-CO mixtures in gas-based direct-reduction plants have shown that water-gas equilibrium is not attained at temperatures less than 1000°C. Turkdogan and Vinters⁴¹ explain the internal reduction in H₂-CO mixtures as consisting of two parallel reactions with H₂ and CO. Significant carbon deposition was obtained with 25 per cent CO or more. This can be attributed to the catalytic effect of the reduced iron⁴² and an inability to attain the water-gas equilibrium in H₂-CO or H₂-CO₂ mixtures⁴¹. The reduction rates increase with an increase in H₂ content.

The surface reaction rate is expected to decrease in proportion to the degree of dilution when inert gas diluents such as Ar or N₂ are used with H₂ or CO. Rao and Al-Kahtany⁴⁴ reduced magnetite in H₂-He, H₂-Ar, and H₂-N₂ mixtures at 487°C and concluded that

- H₂-He mixtures conform to first-order behaviour with respect to the partial pressure of H₂
- there are small retardations in reduction rate in H₂-Ar
- nitrogen has a strong poisoning effect on the reduction kinetics.

Dam⁴⁵ reported an enhancement of the kinetics by nitrogen in the reduction of hematite in H₂-N₂ and H₂-Ar mixtures at 900°C.

Effect of temperature

The effect of temperature on the reaction rate is given by the Arrhenius equation:

$$k = A \exp(-E/RT), \quad [7]$$

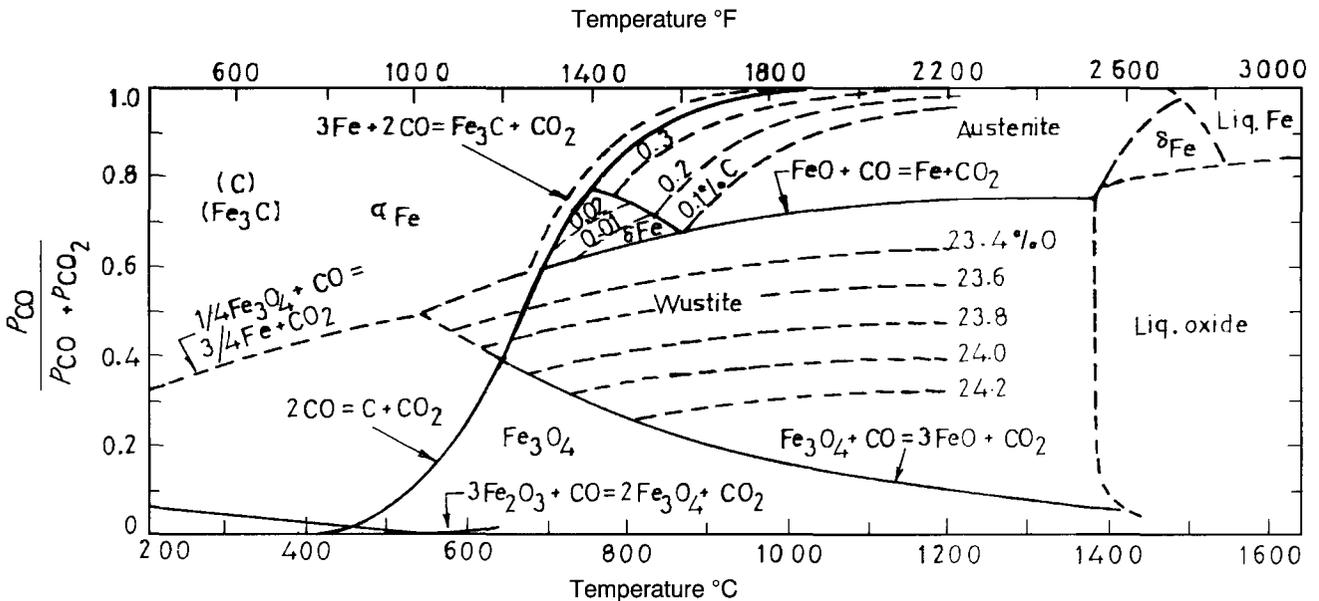


Figure 6—Equilibrium gas composition versus temperature for the Fe-O-C system, including the cementite equilibrium³²

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where E is the apparent activation energy and A a frequency factor. Gas-solid non-homogeneous reactions include physical processes in addition to the interfacial reaction.

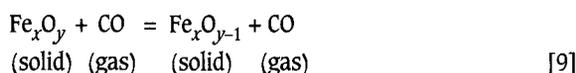
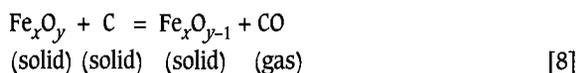
Some remarkable retardations in reduction rates have been observed at various temperatures. Minimum rates have been reported at 600°C for the reduction of magnetite, at 650°C for the reduction of dense hematite in H_2 , and at 975°C and 1025°C for the reduction of porous hematite with CO and CO/ H_2 respectively⁴³. The lower reduction rates between 900 and 950°C with H_2 or H_2 -rich gas mixtures have been attributed to the α - γ -iron transformation⁴⁵ at about 912°C. Moukassi *et al.*⁴⁶ attributed the minimum rate between 700 and 900°C in the dry reduction of wustite by hydrogen to the formation of a dense layer of metal that acts as a barrier against the diffusion of gas through the pores.

Direct reduction

The thermodynamic aspects of the complex systems in iron-ore reduction are well known and easily understood. However, not much about the kinetics of the direct-reduction process is accepted universally. Some kinetic aspects are briefly summarized here. It is now accepted that there is neither any universally accepted mechanism nor any particular value of activation energy. The rate is controlled by one or more of several possible mechanisms, depending on the physical nature of the system and the experimental conditions used to test it.

The direct reduction of iron oxides by solid carbon can be characterized as reactions between a solid proceeding through gaseous intermediates. Strictly speaking, such a reaction can be truly visualized in an evacuated system, where the carbon monoxide product is removed as fast as it is formed.

The reduction of iron oxide by solid carbon is generally represented as follows, being based on two general hypotheses for when a mixture of oxide and carbon (coke, graphite, coal, char, deposited carbon, etc.) is heated:



where

$$x = 1, 2, \text{ or } 3$$

$$y = 1, 3 \text{ or } 4.$$

The reaction between the two solid phases can begin only at points of contact between the carbon and the particles of iron oxide. Contact is disrupted as soon as metallic iron appears as an intermediate phase between the other two. From then on, reduction can proceed only by the diffusion of carbon atoms through the layer of metallic iron to the metal oxide interface. However, because carbon monoxide is one of the reaction products, it is generally accepted that the reduction of iron oxides by carbon proceeds indirectly by carbon monoxide, and that the carbon dioxide formed then reacts with carbon to re-form carbon monoxide, as shown in equation [10].

Baldwin⁴⁷ studied the reduction of a heated bed of iron oxide and coke, and confirmed the mechanism given by

equations [9] and [10]. According to him, the rate of dissolution of carbon is much slower than the reduction of iron oxides at higher temperature, and is the rate-controlling step. This view is largely supported by Ostuka and Kunii⁴⁸, Szendrei and Van Berge⁴⁹, Abraham and Ghosh⁵⁰, and Srinivasan and Lahiri⁵¹. Ghosh and Tewari⁵², however, report that the reduction of iron oxide is more likely to be rate-controlling. Their view is based on the estimation of activation energy values. They did not attempt to develop any kinetic model, but reported kinetic data as a function of temperature, particle size, ratio of reactants, etc.

Rao⁵³, working with synthetic mixtures of ferric oxide and graphite powder, proposed a model based on the assumption that the rate-controlling step in the overall reduction process is the reaction between solid particles of carbon and carbon dioxide. He proposed the following equation:

$$\log(1.743 - f) = (-R/2.303) t + \log(1.743). \quad [11]$$

In equation [11], the degree of reduction is expressed in terms of pseudo-kinetic parameters defined as the ratio of weight loss at time t to the maximum possible weight loss. This is not necessarily a true kinetic equation. However, the equation was found to represent the kinetics of reduction quite satisfactorily. It was seen that the addition of small quantities of Li_2O greatly enhanced the reaction rate, while the addition of ferrous sulphide retarded it. This was to justify the assumption since the Boudouard reaction was the rate-controlling step for the overall reduction process.

Equations for the reduction of hematite and magnetite pellets containing coal or char were proposed by Seaton *et al.*⁵⁴ as follows:

for hematite,

$$\ln(1 - 0.98f) = -kt \quad [12]$$

and, for magnetite,

$$\ln(1 - 1.037f) = -kt. \quad [13]$$

The f in these equations is also not clearly related to the degree of reduction.

Equations [12] and [13] are similar to that given by Turkdogan and Vinters⁵⁵ for the gaseous reduction of porous pellets. Seaton *et al.*⁵⁴ say that the rate of iron oxide reduction is controlled by the chemically controlled Boudouard reaction. They also postulate that the overall rate may be controlled by heat transfer, which affects the carbon-gasification reaction. The gasification of carbon by CO_2 is highly endothermic ($\Delta H = 41\,220$ cal/mol) and requires a high temperature to proceed at an appreciable rate. The overall reduction rate is rate-controlled by the rate of gasification of carbon^{53, 56}. This conclusion is based on the observation of a temperature gradient in the system, the high endothermicity of the carbon-gasification reaction, and the significant increase in the overall rate with an increase in the temperature of the reaction.

Elguindy and Davenport⁵⁷ report that, at temperatures below 1020°C, the reduction mechanism of an ilmenite-graphite system is solid-solid interaction that depends on the contact points. However, at temperatures above 1020°C, the mechanism of reduction is represented by diffusion of the product layer, namely,

$$1 - (2/3)R - (1-R)^{2/3} = kt, \quad [14]$$

where CO has been suggested as the diffusing species.

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Maru⁵⁸ has shown that the reaction between CO and carbon controls the overall rate for the reduction of chromium oxide and chromium carbide. At low conversion levels, he represented his experimental results in terms of chemical-reaction control. He explained the resistance, and indicated that the complete range of reduction could possibly be expressed by mixed control involving interfacial reaction and product-layer diffusion, as proposed by Seth and Ross⁵⁷.

The rate of gasification of carbon by carbon dioxide depends on the reactivity of the carbon, the temperature, and the availability of heat to maintain the reaction at the reaction temperature. Therefore, the rate of carbon gasification that controls the rate of reduction in the reduction of solid carbon will, in turn, be controlled by the rate of heat transfer from the heat source to the reacting materials.

The rate of heat transfer will be affected by the thermal conductivity of the material through which the heat must pass and by the distance between the heat source and the reaction sites. Little can be done to improve the conductivity of the materials involved in the reduction of iron ore but, in the design of the equipment, consideration should be given to the location of the point of heat production as close as possible to where the heat is needed. In this respect, it is interesting to note that, in the Wilberg process⁵⁹, the gasification of carbon and the reduction of iron oxide take place in separate vessels, and this provides better heat transfer than in processes where the carbon and the iron oxide are mixed. Hogana's process⁶⁰, which has been in use in Sweden for many years, uses large amounts⁶¹ of iron-ore fines and coke fines packed in alternate layers or concentric rings in ceramic saggars. Prakash *et al.*^{62, 63} ascertained the possibility of producing iron directly from ore and coal fines through the RESINESS route (RE: REDuction, SIN: SINtering, ESS: Electro Slag Smelting), and studied kinetic aspects and heat transfer in this process, which was developed at the National Metallurgical Laboratory in Jamshedpur. They inferred from their studies that, like the reducibility of iron ores, the reactivity of carbonaceous materials varies widely from one material to another and from batch to batch of the same material. The surface area of the carbon available to provide reaction sites for the carbon dioxide is the important feature, and this is determined by the particle size and, more importantly, by the porosity of the material.

The choice of reductant is a factor in the determination of the operating cost and energy efficiency of direct-reduction processes. Processed materials such as charcoal, char, and coke are more porous and reactive than natural carbon-bearing materials such as wood, coal, and graphite. Charcoal is generally more reactive than coke, and both low-temperature coke and char are more reactive than hard, burnt coke. Coke made from different types of coal may have an important influence. Some as components or additives have a definite catalytic effect. Rao⁵⁵ found lithium oxide to be one of these. Nickel oxide has a similar effect⁵⁶. On the other hand, the gasification of carbon is inhibited by the presence of sulphur in the carbon⁵³.

Fruehan⁵⁶ studied the reduction of iron oxide by carbon in two stages, and his observations indicate that the carbon monoxide formed by the gasification of carbon is consumed as fast as it is produced. This supports the claim that the Boudouard reaction is rate-controlling.

Similarly, in the second stage of reduction, the CO-to-CO₂ ratio of the off gas was found to be close to and slightly

greater than the wustite-iron equilibrium, at least during the first 50 per cent of the reduction, but increased considerably during the last 20 per cent. This slowing down of the reduction rate is usually attributed to the sintering and recrystallization of the newly formed metallic iron, which occurs readily at temperatures above about 650°C and drastically decreases the porosity of the particles. Seth and Ross⁵⁷ showed that the porosity of hematite pellets sintered at 1160°C and reduced in hydrogen at 800°C increased as the reduction proceeded up to 50 per cent, and then decreased drastically beyond that point. This also shows that the gasification of carbon is still rate-controlling, although the reduction rate of iron oxide decreases during the final stages.

In a similar manner, carbon can be gasified by water vapour, and iron oxides can be reduced by hydrogen produced by the gasification of carbon by water vapour. Again, because the gasification reaction is highly endothermic and requires high temperature to proceed at an appreciable rate, the factors affecting the rate of the reaction involving hydrogen are the same as those for the gasification of carbon dioxide.

Of course, these laboratory experiments were conducted in isothermal reactors in which heat transfer was not a factor. Therefore, the translation of these results to an actual process would have to be accompanied by proper accounting of the heat-transfer mechanism.

From the preceding discussions, it is seen that, in contrast to gas-solid reactions, not many kinetic studies have been made on solid-solid reduction. Elguindy and Davenport⁵⁷, Rao⁵³, and Maru⁵⁸ used equations analogous to those developed for non-porous gas-solid systems. Rao⁵³ developed a model of his own, but his data fitted very well to the model proposed by McKewan⁶⁴ for the special case of Li₂O added as a catalyst. He considered the equilibrium relationship of the CO-to-CO₂ ratio in the reducing gas mixture with each of the three oxides of iron: Fe₂O₃, Fe₃O₄, and FeO.

It can thus be seen that models developed for non-porous gas-solid systems can also be used for the interpretation of experimental data relating to solid-solid systems reacting through gaseous intermediates.

Szekely *et al.*⁶⁵, in their review of work done by various workers^{3, 7, 66, 67} on the reduction of iron oxide by carbon, remark that, although the experimental results can be interpreted by the use of Jander's or Ginstling Brownshtein's equation, such interpretations serve only as indirect proof that the overall rate is controlled by the reaction of CO₂ with carbon. It should be noted that these models are somewhat insensitive at a low degree of solid conversion and, in most of the studies, good fit is obtained only for low values of the conversion. More conclusive proofs are required before investigators will be able to pin-point the exact mechanism involved. Hence, further theoretical and experimental work is required in this area for a proper understanding of the system.

Kinetically, a solid-solid reaction is expected to be much slower than a gas-solid one for the following two reasons:

- (1) the solid-solid contact area is much smaller than the gas-solid contact area
- (2) solid-state diffusion is much slower than mass transfer in gases.

An attempt has been made by several investigators⁶⁸⁻⁷¹ to measure the rates of true direct reduction, viz the solid-solid reduction between iron oxide and carbon, by

Reduction and sintering of fluxed iron-ore pellets

continuous evacuation of the chamber in the overall temperature range 700 to 1150°C at pressures of 5×10^{-4} to 10^{-2} torr. The underlying assumption in their investigations was that the gas phase is substantially eliminated by the evacuation, and hence the rates obtained represent those of solid–solid reaction. It can be concluded from these results that the rates under inert gas flushing are even smaller than some of those obtained under evacuated conditions.

There is no experimental evidence to support the theoretical expectation that the rate of solid–solid reaction should be much slower than that of gas–solid reaction. However, although the chamber was evacuated in these experiments, the pressure inside the fine pores of the pellets was likely to have been appreciable because the flow of CO and CO₂ from the interior of the pellet to the chamber would require a substantial pressure difference. It was found that, in order to allow the flushing of CO and CO₂ out of the pellet, the pressure inside the pellet should be appreciable (10 mm Hg). If that is so, the gas phase cannot be ignored in such experiments^{68–71}.

Reduction and sintering mechanism

The production of liquid iron outside the blastfurnace has attracted considerable attention in the past ten to fifteen years. The development of smelting–reduction processes is an innovative approach as an alternative route to steelmaking. However, these processes require very selective grades of raw materials: both the iron ore and the coal have to be fed in the form of lumps of selected size. The fines of ore, blue dust, or coal produced during mining or crushing cannot generally be utilized in these processes. Some of the new smelting–reduction processes use a fluidized bed for the pre-reduction of iron ore. Although fluidized beds can use iron-ore fines directly (without their agglomeration), sticking problems occur during the reduction. This unintentional agglomeration is the reason for numerous breakdowns in fluidized beds.

Fluxed composite reduced iron pellets

The concept of fluxed composite iron pellets requires that well-balanced amounts of fluxes are added to the mixture of iron-ore fines and coal, and that, on being reduced by a solid or gaseous reductant, the mixture produces well-sintered fluxed composite reduced iron pellets⁷². During melting or smelting, such pellets will generate their own slag and carbon. This is intended to reduce the residual oxygen of the iron oxide in the molten slag while the slag remains in chemical balance with the furnace lining, giving the necessary assimilation of impurities like S, P, V,^{73, 74} as well.

However, one of the most important properties of such pellets is their strength during their transportation, reduction, and smelting to liquid iron. This depends largely on the composition and quality of the gangue in the ore and on the additives. The development of pellets began with acid pellets as early as 1940⁷⁴, and continued until pellets of neutral and basic composition were gradually introduced in the 1970s^{74, 75}. The basicity of these pellets has been reported in the range 1.0 to 1.5. Edstrom^{3, 68}, in his studies, found a notable improvement in reduction properties when lime was added to magnetite concentrate with a low content of gangue—0.5 per cent (SiO₂ + Al₂O₃). These improvements were attributed mainly to the formation of a binding phase consisting of calcium diferrite, CaO–2Fe₂O₃.

Based on investigations^{69–77} into the gaseous reduction of iron oxide pellets, it was concluded that the rate-determining mechanism can be described as a combination of interparticle gaseous diffusion through the reduced layer and chemical reaction at the interface between the reduced and the unreduced layers. Several other investigators^{78–84} also support this view. The extent of reduction and its structural changes depend greatly on various operating variables^{69, 77, 79, 80}. The most critical of these is gaseous diffusion through the reduced layer, which depends on the porosity of the pellets. Abraham and Ghosh⁵⁰ predicted a significant resistance to mass transfer in the oxide. The mass-transfer limitations modify the rate but do not influence the activation energy significantly. Thus, a high activation energy exists in spite of partial control by mass transfer. It further implies that, if composite pellets of ore and reductant can be used, the rate of the process can be enhanced by at least an order of magnitude. Rao⁵³ found, in an investigation of the reduction kinetics of mixtures of hematite and carbon powders in the temperature range 850 to 1087°C, that the reduction process is characterized in terms of the availability of carbon monoxide. A solution-loss reaction occurs between the carbon particles and the carbon dioxide within the mixture, and this governs the overall reduction process.

Although several investigators have attempted to characterize the reaction mechanism and rate-controlling steps in terms of mathematical expressions, there is now much experimental evidence based on microscopic studies to suggest that temperature, carbon particle size, hematite-to-carbon ratio in the mixture, additions of catalysts, binders, fluxes, etc. all affect the reaction kinetics. It is also almost certain that, at temperatures of 900 to 1000°C, the overall rate of reduction of iron oxide by carbon is influenced significantly by the rate of gasification of the carbon by carbon dioxide.

With a more sophisticated approach, investigations on the reduction and sintering behaviour of fluxed ore and coal have been carried out to test the influence of CaO and SiO₂, the sintering temperature, and the sintering period on changes in the iron morphology. Qi *et al.*⁸² reported a chronological observation by scanning electron microscope (SEM) of the reduction of iron ore. The reduction temperature was varied between 600 and 1000°C, and different gas compositions were used. It was found that every precipitate could be assigned to a main area in the equilibrium diagram (Figure 7). The chemical composition had a strong influence on the precipitation morphology of the iron⁸². Prior to the reduction of the material, the iron oxide was sintered at different temperatures and periods in an atmosphere of oxygen. Qi *et al.*⁸² observed that the precipitation of metallic iron took less time than that of pure hematite. Consequently, the CaO can be referred to as an active compound. The results of the investigation are illustrated in Figure 8.

According to Philips and Muan's phase diagram⁸³, calcium diferrite (CaO, 2Fe₂O₃ = CaFe₄O₇) is stable between 1155 and 1126°C in air at 1 atm., as shown in Figure 9. Bergman⁸⁴ recently found that calcium diferrite (CF₂) was formed at about 140°C at 1 atm. in air. This apparent deviation can be attributed to the local oxygen potential at which it was formed, which differed from that of the ambient atmosphere.

Reduction and sintering of fluxed iron-ore pellets

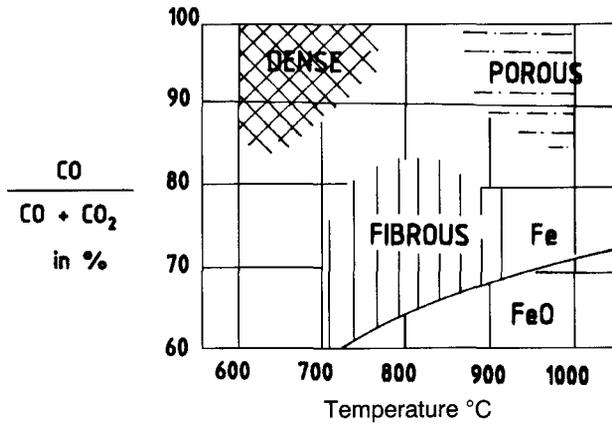


Figure 7—Main regions of the different precipitation morphology of iron during the reduction of iron ore⁸²

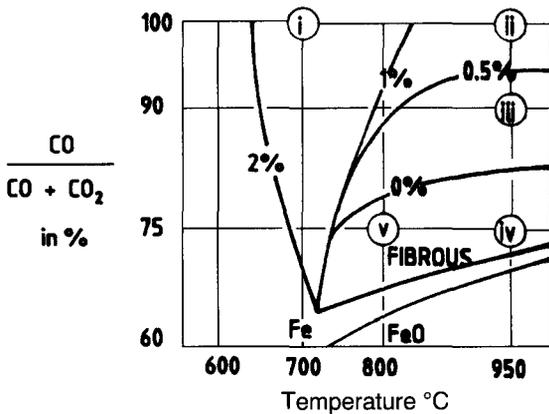


Figure 8—Changes in the precipitation of iron at different CaO contents in the five zones of gas composition and temperature used in the study⁸²

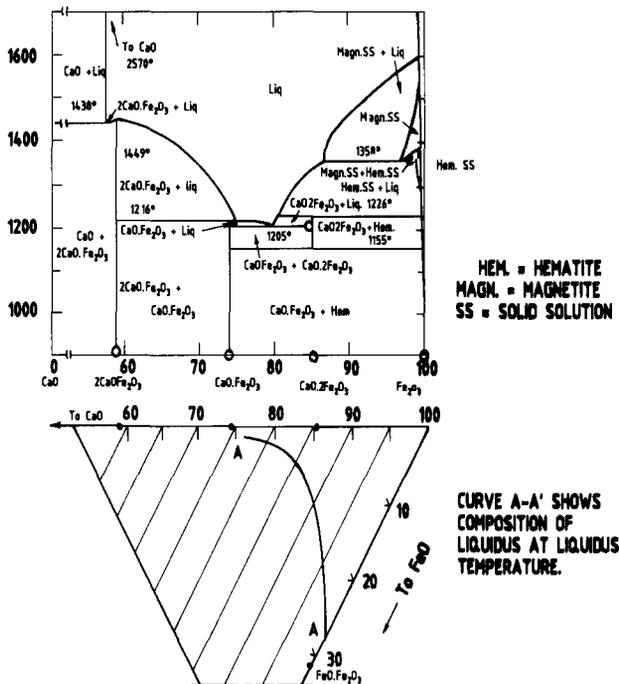


Figure 9—The CaO-Fe₂O₃ system (in air)⁸³

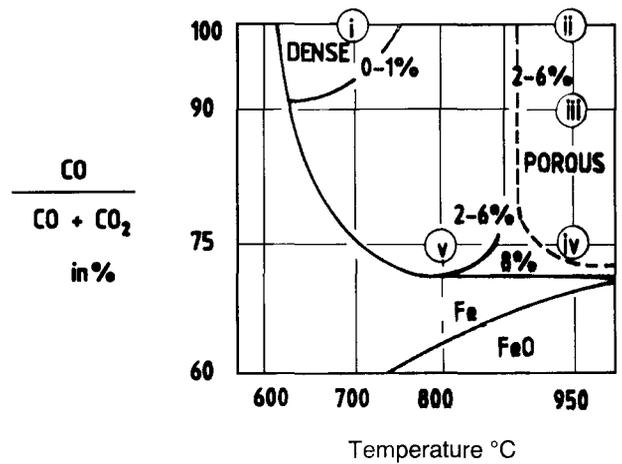


Figure 10—Changes in the precipitation of iron at different SiO₂ contents in the five zones of gas composition and temperature used in the study⁸²

As in the case of CaO, SiO₂ cannot be reduced in the temperature range 600 to 1000°C. In contrast to CaO, SiO₂ can form only the chemical compound fayalite (2FeO·SiO₂), which also cannot be reduced by CO. Consequently, SiO₂ can be referred to as a sluggish compound that hinders the reduction of iron oxide. The influences of SiO₂ and CaO on the iron morphology are shown in Figure 10.

Under identical changes of temperature and CO-CO₂ reducing-gas composition, Qi *et al.*⁸² assigned different zones, (i) to (v), to each precipitate, as shown in Figures 8 and 10. These five zones comprise various combinations of the gas composition and temperature under which the iron-precipitation morphology was studied.

All the investigations on the influence of CaO and SiO₂ have shown that different concentrations of foreign compounds result in a change in iron morphology under different reduction conditions. These changes are characterized by fibrous, porous, and dense morphology. Fibrous and dense morphologies are the two extreme cases, and porous morphology is an intermediate stage between these two.

A schematic representation of the effects of different factors on surface morphology is shown in Figure 11.

One of the main problems during reduction in a shaft retort under unfavourable conditions is clustering. This can result in uneven gas distribution and problems during discharging. The pellets therefore need to be tested for their properties such as porosity, green and compression strength after reduction (CSAR), and sticking characteristics. However, the standard methods of test are rather rough simplifications of the process steps and treatments that they are intended to simulate. Thus, there is a danger that one may concentrate on optimizing the behaviour of an ore product under test conditions rather than its properties under actual process conditions.

In order to minimize smelting costs, it is essential that the sponge iron should be highly reduced, and to achieve this without sacrificing productivity in the direct-reduction furnace needs an easily reducible burden. The limiting factor is usually the shape of the reduction curve towards the end of reduction. The time required for a reduction of 90 per cent under isothermal conditions can be minimized⁵⁵ by the use of a reductant in the fluxed pellets.

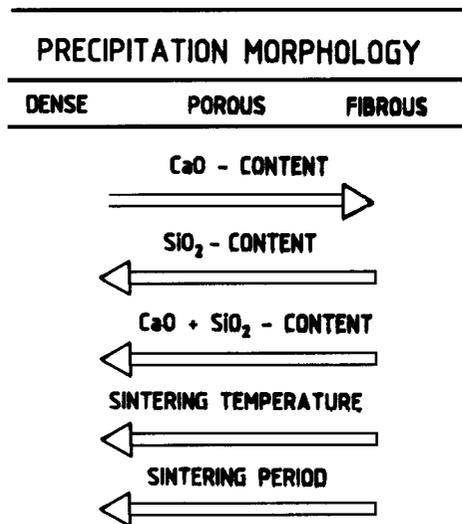


Figure 11—Effects of different factors on surface morphology⁸²

Results and discussions

Prakash *et al.*⁸⁵⁻⁸⁷ recently conducted laboratory studies on the reduction and sintering behaviour of fluxed composite reduced iron pellets. The starting material was chemical grade iron oxide (85 per cent Fe₂O₃, the remainder being made up of non-FeO at a particle size of -0.1 + 0.03 mm), commercial-grade graphite powder (99.8 per cent C at a particle size of -0.01 mm), lime powder (99.8 per cent CaO at a particle size of -300 mesh) and a binder. In all the experiments, various proportions of these ingredients were used to make fluxed composite (iron oxide and solid reductant) reduced iron pellets. The CO generated *in situ* served to reduce the pellets.

To maintain a reducing atmosphere inside the furnace, excess CO was passed through the bed (Figure 12). The pellet samples were heated to pre-determined reduction temperatures of 1073, 1173, 1273, and 1323 K for specific reduction times.

Experiments were also carried out on the effects of the Fe-to-C ratio and the quantity of flux on the reduction characteristics. The plots of the fraction reacted (calculated from weight-loss data) against time are shown in Figure 13 and were subjected to isothermal kinetic analysis.

The fluxed composite reduced iron pellets were fractured for a study under the SEM of the changes in microstructure during simultaneous reduction and sintering after known reaction intervals. These results, illustrated in Figures 14 to 16, show that, with an increase in time and temperature (Figure 14), the ferrite phase tends to grow on a substrate of wustite, progressively producing bridges that consolidate and form aggregated particles. However, apparently in the initial stages, the pores opened up due to gas pressure inside them and were further increased by the reduction from wustite to metallic iron. As a result of this, there was a significant variation in the pore-size distribution. The SEM photographs at the higher temperatures indicate the enhanced melt formation⁸⁹⁻⁹¹, presumably CaO-FeO-SiO₂. However, the liquid did not close the pores, and reduction continued. These photographs show significant changes in morphology due to the presence of CaO, and these must account for the changes in reducibility. These results corroborate the findings of Gudenau and Schiller⁹².

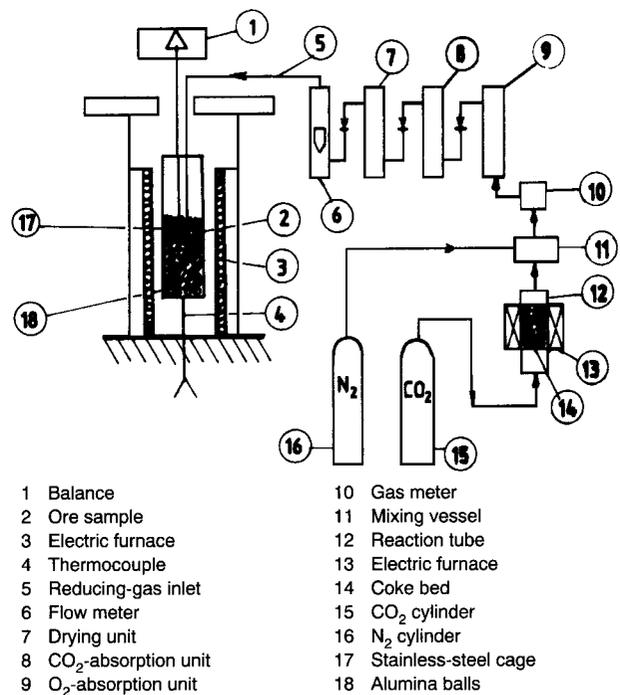
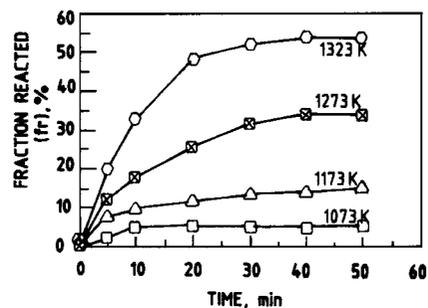
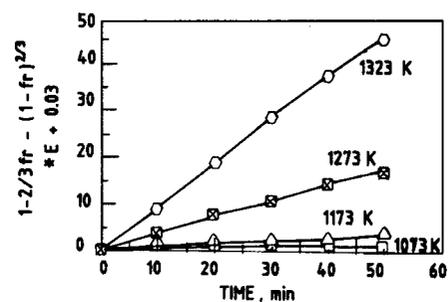


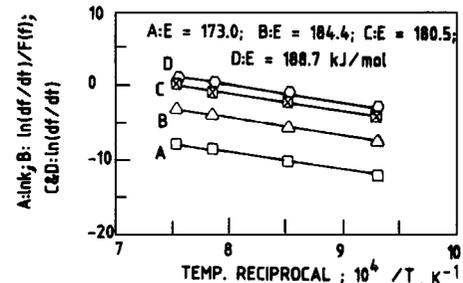
Figure 12—Schematic diagram of the isothermal setup⁸⁶⁻⁸⁸



(a) ISOTHERMAL f_r - time plot



(b) CGB MODEL - $g(f) - t$ PLOT (isothermal)



(c) ARRHENIUS PLOT - DIFFERENTIAL AND INTEGRAL METHODS

Figure 13—Evaluation of isothermal kinetic parameters (size: -0.1 + 0.04 mm; Fe/C = 2.9; %CaO = 2.0)

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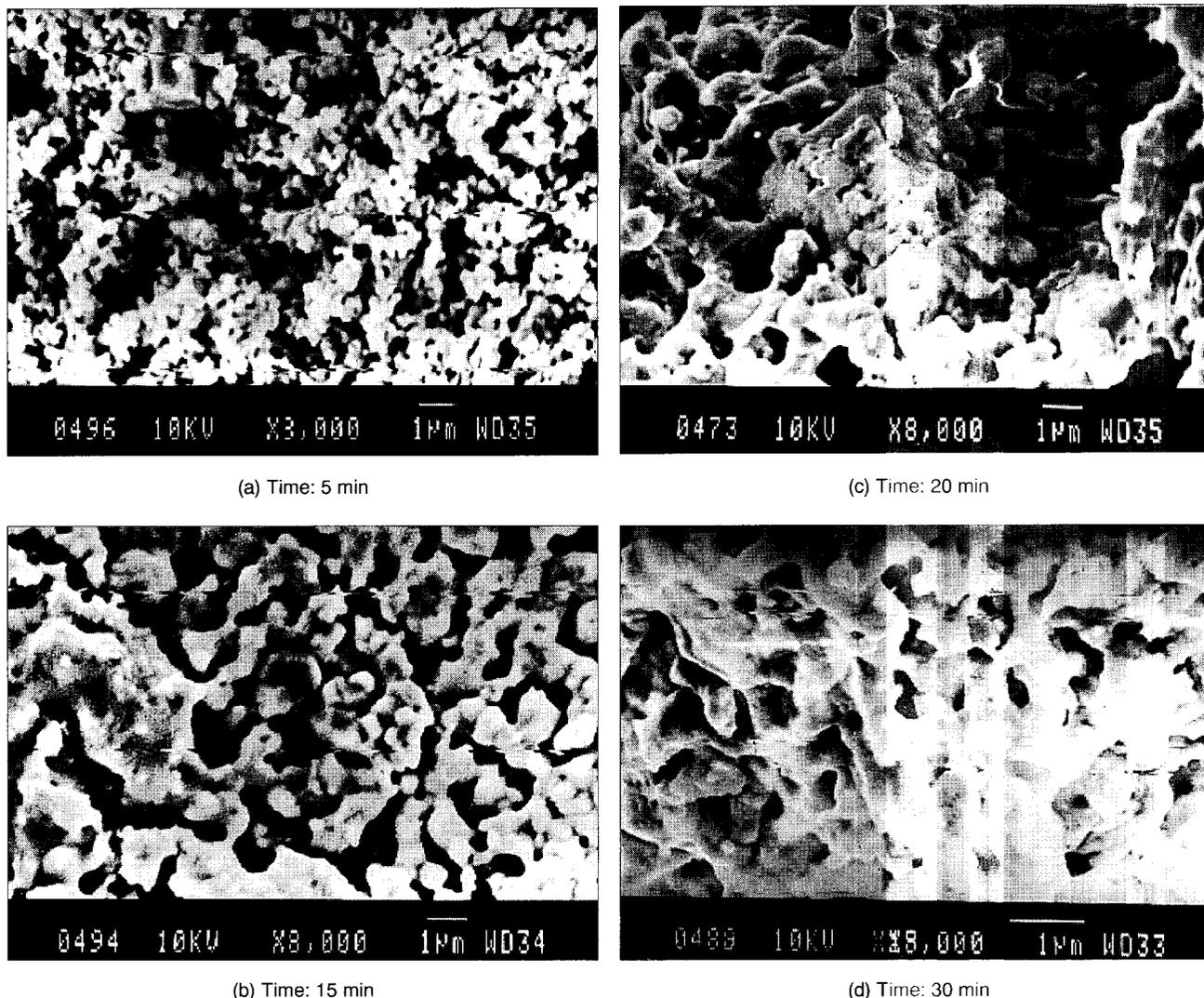


Figure 14—Changes in microstructure of the core part: variation in pore-size distribution, coarsening of the structure with an increase in residence time (Fe/C: 2.9; CaO: 2%; temp: 1273 K)

Summary

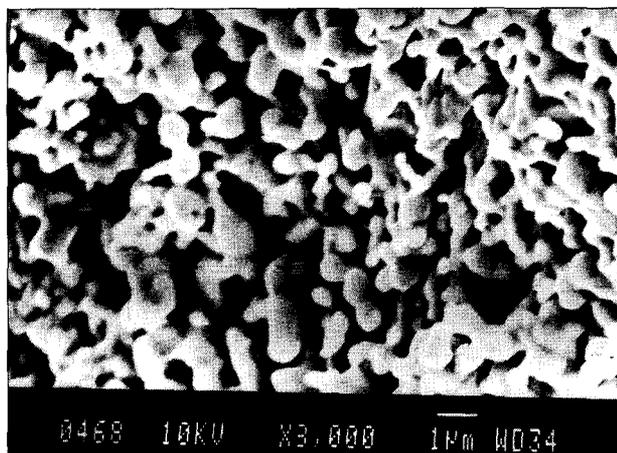
On the basis of the studies reviewed here, it can be concluded that, of the many possible parameters, the temperature and potential of the reduction gas are generally considered to be of great importance to the kind of iron precipitation that occurs. Every kind of iron precipitation is found in certain areas of the Baur-Glassner diagram (Figure 7) under corresponding potentials of temperature and reduction gas. The chemical composition and presence of foreign substances (CaO, SiO₂, etc.) have a strong influence on the surface morphology of the reduced iron.

In the quantitative analysis of the reduction of iron ore, ore-coal pellets, fluxed ore pellets, and fluxed composite pellets, the following three types of approaches were used: empirical models, models based on kinetics, and models based on morphological changes. The relative merits and limitations of these models were discussed, and the role of some of these approaches in the simulation of the reduction of fluxed (ore-coal) composite pellets was illustrated. It was, however, noted that gaseous diffusion through the product layer cannot be used alone as rate-limiting in the determina-

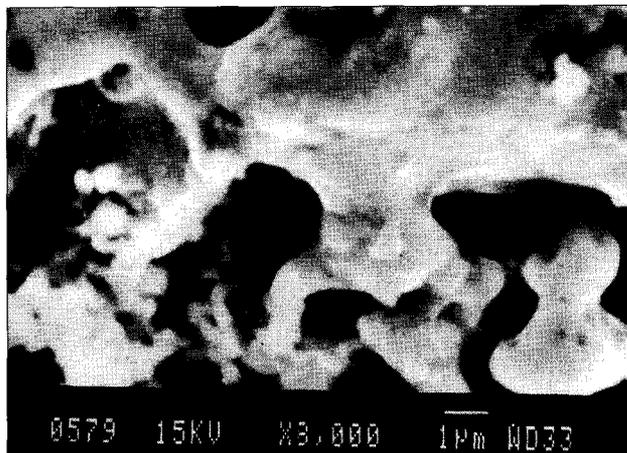
tion of the kinetic parameters: the mass-transfer process between the reducing gas and the iron oxide must also be considered. The reduction process can be characterized in terms of the availability of carbon monoxide. Although elegant empirical models and kinetic equations have theoretical significance and are indeed necessary for elucidating the reaction mechanism, they are sometimes not directly applicable in the kinetic study of fluxed ore-coal composite pellets. It is prudent to explore the possibility of correlating the change in iron-precipitation morphology with the reaction mechanism. Such correlations established for variations of parameters within specific ranges may significantly ameliorate the reduction and strength characteristics of fluxed pellets. However, fluxed ore-coal pellets have not been studied as widely as this.

Basically, smelting-reduction processes should completely avoid ore agglomeration and cokemaking. The concepts of these processes are impaired⁹³ broadly because of the arrangements for the pre-reduction of iron-ore fines and the highly efficient post-combustion that occurs in the smelting vessel. Conceptually, fluxed composite iron-ore pellets

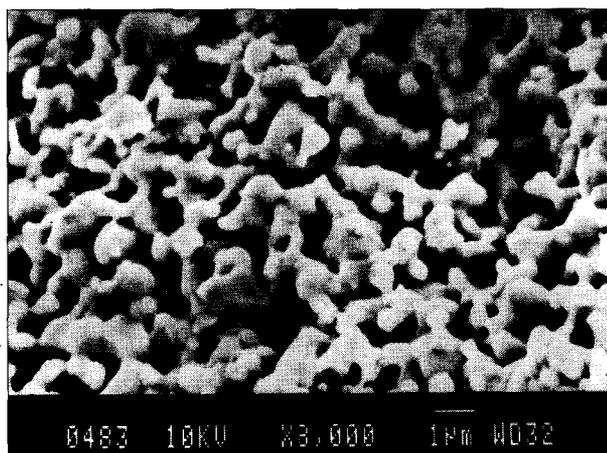
Reduction and sintering of fluxed iron-ore pellets



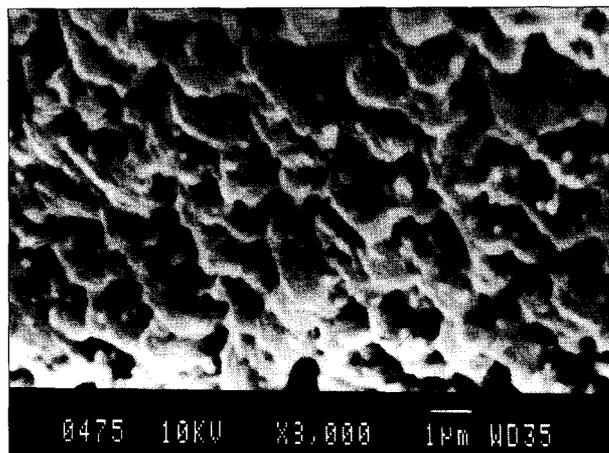
(a) Temperature: 1273 K



(Core) (c) Temperature: 1373 K



(b) Temperature: 1323 K



(Periphery) (d) Temperature: 1373 K

Figure 15—Microstructure of the fractured pellets, showing the effects of temperature (Fe/C: 2.9; CaO: 2%; time: 45 min)

utilizing ore and coal fines seem to be a better alternative charge material for DR–SR processes. However, these pellets should have the requisite properties relating to reduction and compressive strength after reduction.

Prakash *et al.*^{72, 85} obtained some very encouraging results on the reduction and strength characteristics of fluxed composite reduced-iron pellets (FCRIP). A laboratory study is being undertaken on the sintering and reduction properties of such pellets, and work is under way on the development of a process⁹⁴ for the production of FCRIP.

Acknowledgements

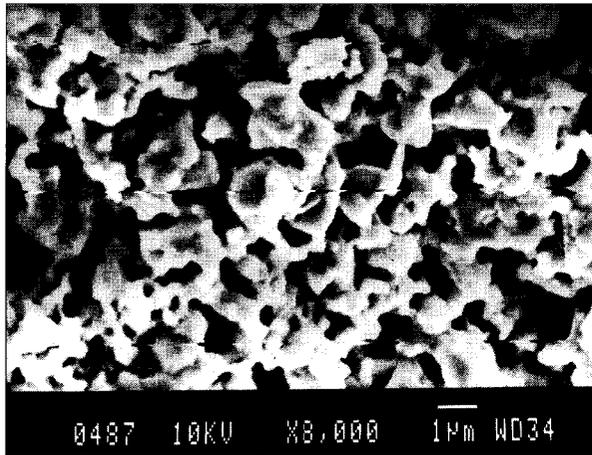
The author thanks Professor P. Ramachandra Rao, Director of the National Metallurgical Laboratory, Jamshedpur, for his advice and encouragement in the preparation of this review, for providing facilities for the experimental work, and for according permission to publish the paper.

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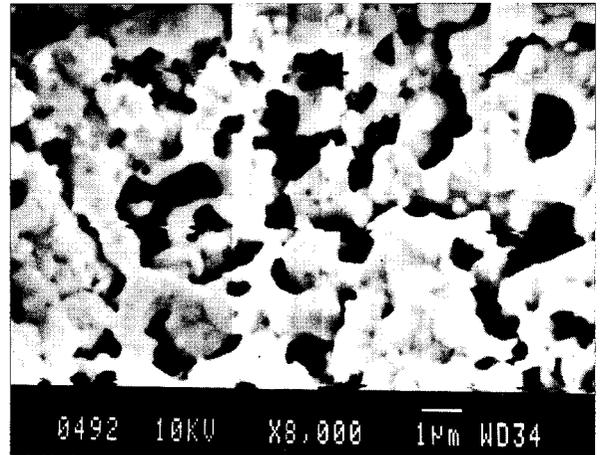
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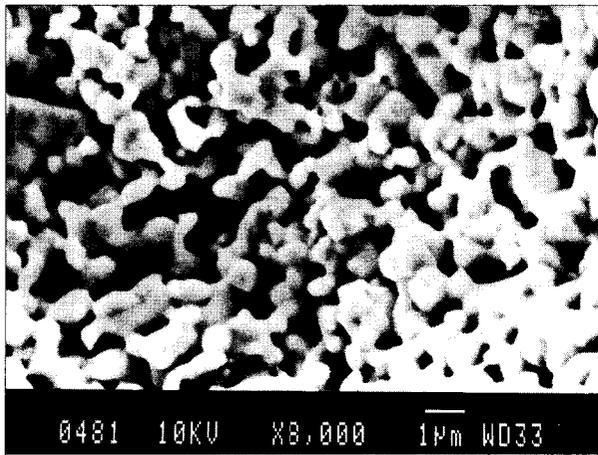
Reduction and sintering of fluxed iron-ore pellets



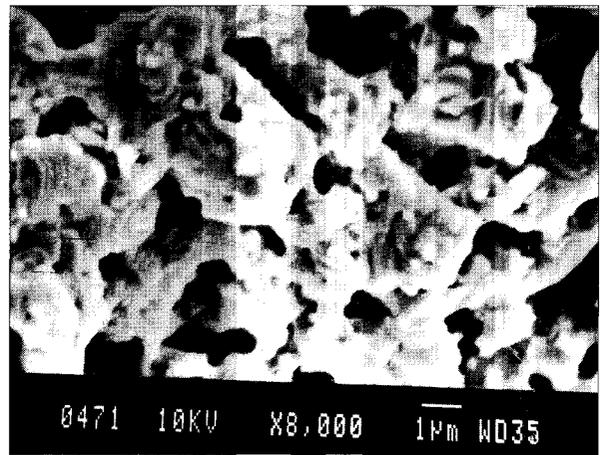
(a) Fe/C: 3, % Lime: 2



(c) % Lime: 2, Fe/C: 2.9



(b) Fe/C: 6, % Lime: 2



(d) % Lime: 8, Fe/C: 2.9

Figure 16—Effect of lime addition on Fe/C ratios (temp: 1273 K; time: 45 min.)

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SRK to undertake environmental audit in Mongolia*

Steffen, Robertson and Kirsten Consulting Engineers Inc. (SRK) has won a World Bank tender to complete a review of environmental conditions at Erdenet Copper Mine in northwestern Mongolia. The mine, situated about 350 km from the capital Ulaan Bataar, is of the open-pit type and produces more than 20 Mt of porphyry copper ore a year, the concentrate being sold to customers in Russia, China, and Japan. This large-scale activity generates about 60 per cent of Mongolia's gross domestic product.

Owing to Erdenet's pivotal role in the local economy, the World Bank is looking to implement a long-range development plan once environmental conditions at the facility are properly understood and controlled. After reviewing proposals from numerous international

consultants, the Bank commissioned SRK to conduct an environmental audit of the mine.

Members of the environmental team had spent ten days on site, during which time they completed a draft report on the main environmental concerns. These include the generation of dust from the tailings dam and potential pollution of the surface water systems as a result of seepage from the tailings dam and open pit. The stability of the tailings dam, which is of the valley-fill type, was also investigated. ◆

* Issued by Tish Stewart PR Associates.