INTRODUCTION

With increasing stress being placed on expanding steel production capacity, especially in areas lacking high grade iron ore and metallurgical coke, attention has been directed towards developing and expanding other techniques for the production of iron. One such alternative promising method is the direct reduction of iron ore. The words 'direct reduction' refer to the process, wherein the ore is reduced with either solid or gaseous reductants to the solid product without the intermediate liquid product, namely, molten metal. Briefly, the factors which stimulate much of the interest in processes other than the blast furnace are as follows:

1. The increasing availability of ore fines and of high grade ore concentrates from low grade ores.
2. The decreasing reserves of metallurgical coking coal.
3. The need for steel production in small concentrated market areas remote from major steel producing centres, i.e., in small scales with output less than 1000 tons.

4. High cost and limited supply of steel scrap in the case of developed countries and lack of large capital in the case of developing countries.

Thus the direct reduction is one possible way of considerable technical promise. Many economic and process studies of specific application of direct reduction by pilot plant operations[1-8] have shown it to be at least competetive and for some reasons the preferred route for additional hot metal and steel capacity. Wild[9] has considered in a concise and comprehensive way the fuel requirements for iron ore reduction. His main conclusions are:

1. The process using prepared ore and fuel and electricity has the highest efficiency.

2. Other processes are having low efficiencies, however, their flexibility in using the locally available fuel makes them promising processes.

While pilot plant studies have shown that this process is viable from economic point of view, the fundamental reduction processes occurring in the direct reduction are not well understood.

The possibility of reduction of a specimen of iron ore or any ferruginous material by a reductant has to be judged from the point of view of equilibrium consideration or in other words, a thermodynamic approach has to be made for the reaction system under study. Thermodynamic data of interest for iron making are available in literature[10]. Schenck[11] and Baukloh[12] have stressed the importance of chemical equilibrium and explained its application in the reduction of iron oxide. If for example, the oxygen partial pressure of the gaseous atmosphere in contact with the ferric oxide is equal to or greater than the dissociation pressure of the oxide, then the gas with that composition in contact with the metal oxide will not reduce it. Darken and Gurry[13] have drawn the phase diagram showing the equilibrium compositions of metallic iron and its oxides with oxygen partial pressure.

Haematite (Fe_2O_3) can have the following reduction sequence as indicated by the equilibrium phase diagram

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe \quad (\text{above } 570^\circ C)$$

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow Fe \quad (\text{below } 570^\circ C)$$

Russian workers[14-16] have recorded the presence of wustite (FeO) below even 570°C. Generally speaking, however, the possibility of the formation of FeO is very remote below this critical temperature. When the equilibrium in the system is favourable for the reduction of the oxide, the process has to be normally kinetically controlled.

Study of the rate of reduction of the oxide, under favourable thermodynamic conditions, is of interest to understand the mechanism of reduction, when the reaction is kinetically controlled. There is a wealth of information available in literature on the reduction of iron oxide. Reviews showing the periodical progress made in the study of the reaction have also appeared. For example, Hauffe[17] in 1955 has made an assessment on the scientific aspects of the reduction process. In 1967, Engell and Bogdandy[18] have made an exhaustive survey on this aspect. A brief outline of the various aspects of this problem is presented in the following pages.

Reduction of a lump of iron ore or oxide presupposes an elementary process of heterogeneous chemical reaction between solid oxide and solid or gaseous reducing agent. In the discussion to follow, attention will be limited to the reduction by gaseous reductants only, with specific reference to hydrogen. In order that chemical reaction may go on, the gas must come in contact with the solid at the interface or phase-boundary of the gas/solid and further the gaseous products of reaction must be transported away from the reaction site. The reduction of a lump of ore in a current of reducing gas involves at least two elementary processes, namely, chemical reaction and diffusion of gases through the pores of the lump.

Thus, the reduction process involves the following sequence:

i. transport of hydrogen from the bulk gas stream to the surface of the iron oxide pellet through a stationary boundary layer.

ii. diffusion of hydrogen through the iron product layer and the pores in the pellet to the reaction surface.

iii. reaction of the reducing gas with oxide at reaction surface to give rise to product gas. This may include several steps like adsorption chemical reaction, nucleation, etc.

iv. diffusion of the product gas through the pores of the metal layer formed, to the surface of the pellet.

v. transport of the product gas from the pellet surface to the bulk of the gas stream through the boundary layer.

One of these five steps will be the slow step controlling the overall rate of reduction.

Excepting step (iii) all the other steps involve the diffusion of the gaseous species, while step (iii) is the surface reaction. This surface reaction may be layer-wise over the surface or it may be taking place throughout the entire available surface of the solid. Both types of these surface reactions have been observed[19,20] in the reduction of iron oxide.

RATE CONTROLLING STEP

Diffusion through the gas film:

That the flow rate of gas influences the rate of reduction of iron ores has been long known[21,22]. When the gas velocity is too small ($\leq$ 100 cc/min) there can be local depletion of the concentration of the reductant since the gas product formed will be adsorbed on the surface or will be present near the surface of the product which can inhibit the approach of the reductant to the oxide. The results obtained by Marek *et al*[21] pertain to this region of gas velocity so that the diffusion through the boundary layer is theslow step. Woods[22] has considered this diffusional resistance in detail. When the flow rate of gas is gradually stepped up, the rate of reduction will increase but above a certain flow rate, further increase in flow rate will have little or no effect on the rate of reduction indicating that the boundary layer is no longer hindering reduction kinetics. This has been confirmed by Udy and Lorig[23], Feinmann *et al*[24] and Schurmann *et al*[25]. The following relation[26] will hold good for the diffusion through the film

$$t \;\alpha\; (x) \qquad .. \quad (1)$$

where x is the amount reacted at time t.

Diffusion through the product layer as rate determining:

Bogdandy and Janke[27] from their studies on the reduction of pellets of 31 mm diameter, have concluded that the slowest step in the reduction of iron oxide is the diffusion of the gases through the product iron layer. Bogdandy and Günrer[28] and Henderson[29] attributed the slow rate to **the protective** layer which inhibits the gas diffusion. This has been confirmed by Wilhelm and Pierre[30], Turkdogan and Vinters[31] and Quets *et al*[32]. The general equation[26] for such a model is

$$\left[\frac{1}{2} - \frac{(1-x)^{2/3}}{2} - \frac{x}{3}\right] \alpha \;\; t/r^2 \qquad .. \quad (2)$$

where r is the radius of the original pellet. Hill and Tiemann[33] obtained evidence for this model. In reducing low grade iron ores, they found that above

900°C, the reduction never went to completion because of sintering. Due to sintering the pores were closed, thereby increasing the diffusional resistance by the product layer.

Reaction at the interface as rate controlling:

A majority of investigators[34-37] have concluded that the rate is controlled by the surface reaction at the interface of oxide/metal. McKewan[38] found that the rate of reduction increased with the partial pressure of hydrogen and the linear relationship for the following equation[26] has been obtained for the interface reaction

$$[1 - (1 - x)^{1/3}] \propto t/r \qquad .. \quad (3)$$

Several investigators[39-41] working under different experimental conditions have confirmed the importance of the reaction at the interface.

In deriving the above equation (3), for the topochemical model a tacit assumption has been made that stepwise reduction of iron oxide occurs layer by layer i.e., only after reducing the outer layer, the reductant can react with the subsequent lower layer. For example, in the reduction of Fe_2O_3 the first layer will be reduced to Fe_3O_4. Further reaction of this magnetite with reductant gas will convert it to wustite (FeO) above 570°C or directly to iron below 570°C. The wustite formed above 570°C will be reduced to metallic iron. Thus, above 570°C, in a partially reduced oxide, one will find all the four phases, namely, Fe_2O_3 / Fe_3O_4 / FeO / Fe and below 570°C the three phases Fe_2O_3 / Fe_3O_4 / Fe.

Mixed control model:

It is normally considered that the rate controlling step is the interaction of the gaseous reductant with the solid at the Fe / FeO interface, on the basis that the solid diffusion is fast. One implication of this model is that only very thin layers of the intermediate oxides are formed so that diffusion through them will be negligible. Warner[42] on the other hand found thick layers of the intermediate oxides which offered considerable resistance to the gas diffusion and hence concluded that the reduction is not controlled either by diffusion through the pores or the interface reaction alone and derived an equation for the mixed control model. Gray and Henderson[43] also arrived at a similar conclusion. Spitzer <u>et al</u>[44,45] have derived a generalised mathematical equation for the reduction of haematite. Seth and Ross[46] combining equations 2 and 3 derived the following equation for the mixed control model.

$$\frac{A}{r^2}\, t = \frac{B}{r}\left[1 - (1 - x)^{1/3}\right] + \left[\frac{1}{2} - \frac{(1-x)^{2/3}}{2} - \frac{x}{3}\right] \quad .. \ (4)$$

where A and B are constants involving concentration gradient and reaction rate constant.

Baranski <u>et al</u>[47] have found that this relation holds good for the data on the reduction of industrial iron catalyst. Initially, the rate is controlled by the reaction at the interface of iron and wustite because very little resistance is given by iron formed. As the layer of iron grows, resistance to the transportation of gas increases and hence subsequently this becomes the slow step[48]. This situation will be applicable when dense pellets of large diameters(> 10 mm) are used, so that the product iron formed as a thick dense film, offers resistance in the reduction of ores at high temperatures. Engell et al[49] have found that the mixed control model is operative in the reduction of ores. Wei-Kao Lo[50] has also derived another equation for the mixed control model.

St. Clair[51] on similar considerations derived an equation for the mixed control model taking into account the diffusion through the stagnant film in addition to the interface reaction and diffusion through the product layer.

Uniform reaction over the entire cross section of the solid:

In the previous sections, the rate equations for the interface reaction have been derived assuming layer by layer reduction. On the other hand if a lump of ore is very porous, then the reducing gas can travel through such pores toward the interior and back, reacting simultaneously with equal velocity, throughout the mass of the oxide; then the entire lump will be reduced step-wise. Starting with haematite it will be converted completely to magnetite. When no haematite remains, magnetite will start getting reduced to wustite and so on.

As pointed out by Schenck[52] loose and porous agglomerates may get reduced in this manner. This is explained in terms of Thiele and Zeldowitsch theory and several treatments on this are available[53-55]. A general equation for this is

$$\ln (1 - x) \propto t \quad .. \quad (5)$$

Bogdandy and Riecke[20] using different sizes of pellets have found that for pellets less than 4 mm diameter, the concentration of the reducing gas is uniform throughout the pellet to obey the above equation. Wethrill and Furnas[56] and Meissner and Schora[57] have supported this view. El Mehairy[58], Levin and Wagner[59] obtained a linear relation for the above equation which they attributed to the first order rate equation.

Actual mechanism of the reduction:

Whatever be the rate controlling step for the reduction to take place, the reductant should react with oxygen in the lattice to produce the product vapour and the metal. In the reduction of Fe_2O_3 to metal, the $Fe_2O_3 \longrightarrow Fe_3O_4$ reaction represents 11 per cent reduction, the step $Fe_3O_4 \longrightarrow FeO$ another about 22 per cent and the step FeO ⟶ Fe accounts for the rest of about 67 per cent. The reducing gas is therefore in contact with wustite during major part of the reduction time.

In order to explain some features of the reduction of wustite, it becomes necessary to take into account the lattice vacancy disorder of the wustite phase which is a cation deficient p-type semiconductor.

In wustite the iron/oxygen ratio is variable but is always less than the stoichiometric ratio[60]. Depending upon the oxygen partial pressure of the gas in contact and temperature, the wustite lattice contains a large number of Fe^{2+} ion vacancies, the vacant sites forming 5 to 11 per cent of the total iron ion sites. Electrical neutrality is maintained through the presence of Fe^{3+} ions as shown in Fig.I.I.

Following the removal of oxygen from the surface the wustite layer becomes supersaturated with Fe^{2+} ions, this will lead to the formation and growth of iron nuclei. Richardson et al[61,62] and Wagner[63] have formulated such a picture. During the reduction process a concentration gradient of Fe^{2+}

$O^{=}$	Fe^{++}	$O^{=}$	Fe^{+++}	$O^{=}$
Fe^{++}	$O^{=}$	Fe^{++}	$O^{=}$	Fe^{++}
$O^{=}$	Fe^{+++}	$O^{=}$	$\square$	$O^{=}$
Fe^{++}	$O^{=}$	Fe^{++}	$O^{=}$	Fe^{++}

Fig.I.1. Wustite lattice showing the cation vacancy ions is also built up across the wustite layer, the subsurface being unattacked by the gas. The Fe^{2+} ions may therefore migrate from the surface to the interior and react at the subsurface with the magnetite layer according to the following equation:

$$Fe + Fe_3O_4 \longrightarrow 4FeO$$

Thus, the wustite layer grows at the expense of magnetite. This has been established by Edstrom[64]. Hauffe[17] has given the following mechanism to explain the above process.

$$H_2 + \oplus \rightleftharpoons 2H^+ \text{ (chemisorption)}$$
$$FeO + 2H^+ + Fe\Box \rightleftharpoons H_2O \text{ (Reaction)}$$

At the surface

$$Fe^{2+} + 2e^- \text{ (gas/oxide interface)} \longrightarrow \text{diffusion through the solid} \longrightarrow Fe^{2+} + 2e^- \text{ (FeO/Fe}_3\text{O}_4 \text{ interface)}$$

$$Fe_3O_4 + Fe^{2+} + 2e^- \rightleftharpoons 4FeO \text{ (Reaction at FeO/Fe}_3\text{O}_4 \text{ interface)}$$

$\oplus$ = electron defect, $Fe\Box$ = bivalent cation vacancy.
Engell and Kohl[65] have concluded that the rate is controlled by this solid state diffusion process.

Below 570°C where FeO is unstable, a similar process is probable for the reduction of magnetite to metallic iron as the magnetite is known to have cation vacancies.

The following reduction sequence is well established for the reduction of iron oxide.

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe \qquad \text{(above } 570^{\circ}C\text{)}$$

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow Fe \qquad \text{(below } 570^{\circ}C\text{)}$$

As a consequence of the assumption of layer by layer reduction it is imperative that all the species in the reduction sequence should be present during reduction. Many authors have supported this view. On the contrary, when uniform internal reduction occurs, (i.e., when the reduction kinetics obeys the equation $\ln(1-x) \propto t$) the reduction will proceed in steps. Magnetite formed from haematite will be reduced to wustite, only when all the haematite has been converted to magnetite and further reduction of wustite to metal will start after completion of reduction of magnetite to wustite.

Many authors, notably Russian[66,67] and Japanese[68,69], have supported the stepwise mechanism for the reduction of Fe_2O_3 to metal.

In the reduction with hydrogen below 570°C, the first step of the process, namely, Fe_2O_3 to Fe_3O_4 is exothermic and the further reduction to metal is highly endothermic, with carbon monoxide, however, both the steps are exothermic[70]. Thus, employing the method of differential thermal analysis, Keely[71] showed the stepwise reduction of Fe_2O_3 to Fe_3O_4. Recently, Walker and Ford[72] and Dobovisek and Rosina[73] also have used the same technique for following the reduction of iron oxide. Colombo et al[74] and Gazzarini and Lanzavechia[75] have obtained a break in the kinetic curves which they have attributed to the change in the reduction rate due to stepwise reduction and tried to explain this with the help of defect structure of the oxide.

Effect of products of reduction on the rate of reduction:

In the experiments reported in this thesis, the products of reduction are water vapour and solid metal. It has been shown that water vapour generally retards the reduction rate, its effect is more pronounced on the reduction of Fe_3O_4 to Fe than on the Fe_3O_4's [redacted] formation from Fe_2O_3[76]. The retardation has been explained on the basis of equilibrium conditions.

Similarly, studies on the effect of added metallic iron have given some interesting results. In 1963, Pokhvisnev and Abdelrassul[77] have found that the metallic iron powder has a catalytic effect on the reduction of iron oxide. Korneeva and Vorontsov[78] have found that platinised platinum has a similar effect in the reduction of Fe_2O_3. Similar catalytic effect by metals on the reduction of metal oxides have been reported[79-84]. Recently, Boudart _et al_[85] have tried to explain the catalytic effect of metals like platinum and palladium on the reduction of metal oxides like tunstic oxide and ferric oxide, on the basis of the adlineation theory orginally proposed by Schwab and Pietsch[86]. According to this theory the hydrogen is adsorbed on the metal surface and is transported to the oxide-metal interface through the portholes of moisture. The exact nature of the species that is being transported has not yet been established. An excellent review[87] on this spillover mechanism is now available.

Roman and Delmon[88] from their studies on the catalytic effect of metal on the reduction of NiO/SiO_2 concluded that the acceleration in the rate is due to the stabilisation of the nuclei and creation of more sites for growth. This has been concluded by them on the basis of decrease in the rate of reduction of NiO/SiO_2 compared to that of pure NiO and further in the former the reaction does not go to completion. Further studies[89] led them to conclude that the molecular hydrogen is activated by adsorption on the metal surface. The activated hydrogen species, which are mobile on the surface, are transferred to the reducing oxide particle. Bogdandy et al[90] have shown the significance of the formation of the nuclei in the reduction process, by their studies on tempering the lattice stress. Moraweitz and Schaefer[91] have given supporting evidence for the above observations.

Effect of added impurities on the reduction kinetics:

Effect of foreign metal oxides on the reduction kinetics of NiO[92] and CoO[93] have been studied in a systematic way. Russian workers[94,95] have studied the catalytic effect of halides and carbides of various metal ions and attributed the effect to the change in the electronic properties of the material. But similar effect with inert oxides has not been clearly established[96,97]. It has been found[94] that carbonates forming ferrites impede the reduction rate. Turkdogan and Vinters[98] have studied the effect of doping with CaO on the reduction of iron oxide. They have found that the haematite is present till 90 per cent reduction is over. This, they have attributed to the blocking of inter-connecting pores in the haematite by the calcium ferrite formed and have concluded that the partially reduced ferrites remaining in the pores of the iron layer hinder the gas diffusion. Engell and Kohl[99] from similar studies on mixed oxides concluded that the oxide with lower free enthalpy of formation gets reduced and as the reduction proceeds the less noble metal (i.e., the one with lower free enthalpy of formation) diffuses with the formation of the metal phase inside the oxide. Further studies on complex iron oxides like ores and solid solutions have led him[100] to conclude that the separation of oxygen and iron requires a diffusion process in the solid phase. Similar conclusion has also been arrived at by Tittle[101] for the reduction of iron oxide by hydrogen present in granular calcined bauxite.

According to him, the reduction is in two steps as follows:

$$Fe_2O_3 + 2Al_2O_3 \xrightarrow{H_2} 2FeAl_2O_4$$

$$FeAl_2O_4 \xrightarrow{H_2} Fe + Al_2O_3$$

In this sequence, the first step is considered to be fast and the second one is considered to be the slow step.

Methods of following the reduction:

For accurate measurements, a closed high vacuum unit is employed. At the start of the reaction the reducing gas is enclosed in the reaction vessel to a predetermined pressure. As the gas reacts with the solid inside the reaction chamber, the gaseous reaction product is frozen out and the resulting pressure of the reducing, non-condensable, gas is measured as a function of time. This is the common principle used in the various experimental arrangements employed in the reduction of the oxides[102-106].

The conventional method employed in the reduction of oxides, ores and agglomerates is to use flowing gas and to measure the weight of the reacting solid phase or the weight of gaseous products like water or carbon dioxide or to analyse the exit gas. The two methods are not comparable. The rates and energies of activation obtained from the former may be used as reference data for the particular reaction, whereas the latter one will yield only the apparent rates and energies of activation.

The flow rate of the gas should not be too small if the diffusional resistance through the stagnant boundary layer of gas film is to be avoided. This condition has to be satisfied, since kinetic data obtained under experimental conditions of diffusional resistance will not give information on the mechanism of reduction.

Attempts to follow the kinetics of reduction of iron oxide by magnetic susceptibility measurements have been made by Chekin and Syrovatskii[107]. Recently gas chromatogrphic technique[108] has been successfully used for the study of the kinetics of iron oxide reduction. Dutta _et al_[109] have made use of electrical conductivity measurements to follow the reduction of iron ores by hydrogen.

Methods for analysis of product distribution in the solid phase:

As pointed out earlier, in the reduction of haematite to the metal, there can be as many as four phases present at any time during the reduction. Thus an analysis of product distribution in the solid will give valuable information on the course of reduction of the oxide which could be made use of in proposing a proper model for the kinetics of reduction. Thus metallographic analysis and X-ray diffractometry have been used as analytical tools for the identification of solid phase in partially reduced ores[110-114].

Kölbel and Kuspert[115] and Romanov et al[116] have used the Mössbauer spectroscopy for the phase analysis during the reduction of iron oxides.

Wenzel et al[117] and Pluschkell and Sarma[118] have used the hot stage and scanning electron microscopy for the study of the morphological changes occurring in iron oxide during reduction with hydrogen.

Scope of the present investigation:

From the foregoing review, the following inferences may be drawn.

1. The rate determining step in the reduction of iron oxide is still controversial.

2. The influence of foreign metal oxides on the kinetics of the reduction of iron oxide has not been systematically studied.

3. The actual role of the added metal oxide on the reduction of iron oxide, whether it is electronic or structural, has not been identified.

4. The mechanism of the reduction of the ores has not yet been unambiguously established.

5. The presence of water vapour in the reducing gas stream affects the reduction kinetics in more than one way. The exact role of water vapour, the nature of the species involved and the mode of operation of reduction reaction in presence of water vapour, have not been identified.

The principal aims of the present investigation are to obtain experimental data on these five aspects of the reduction of iron oxide so as to resolve some of the controversies existing in literature as well as to elucidate the mechanism of the reduction of ores and of haematite in presence of water vapour. To achieve these aims, the reduction experiments have been carried out below 570°C so that the number of possible solid phases that can be present simultaneously is reduced to three, namely, $Fe_2O_3/Fe_3O_4/Fe$ instead of four. The flow rate of the reducing gas has been fixed to at 280 ml/min so that the gas diffusional problems will not be affecting the kinetics of reduction.

The strategy employed to achieve the principal aims of this investigation is to follow the kinetics of the reduction of pure haematite and haematite doped with different amounts of oxides like lithium oxide, magnesium oxide, aluminum oxide, titanium dioxide etc., by using the techniques of weight loss measurements, thermogravimetry and differential thermal analysis and the phases present at any stage of reduction have been analysed using, X-ray diffractometry, Mössbauer spectroscopy and micro-graphy.

The results obtained by these studies form the subject matter of Chapters III and IV of the present thesis. The reduction kinetics of natural haematite and magnetite ores have also been followed by using the same techniques and the results obtained pertaining to the mechanism of reduction reaction have been presented in Chapter V of this thesis.

In order to identify the actual part played by the presence of water vapour in the reducing gas stream, a series of experiments have been carried out on the reduction of ferric oxide in presence of various metal powders as well as varying amounts of water vapour. The results obtained from these experiments have been presented and analysed critically to identify the role played by water vapour in Chapter VI.

The overall mechanism of the reduction of iron oxide evolved from the present investigation is outlined briefly in Chapter VII.