CARNEGIE INSTITUTE OF TECHNOLOGY

COLLEGE OF ENGINEERING AND SCIENCE

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Master of Science

TITLE REDUCTION OF HEMATITE ORES WITH HYDROGEN IN FIXED BEDS

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CHAIRMAN — December 21, 1966 — DATE

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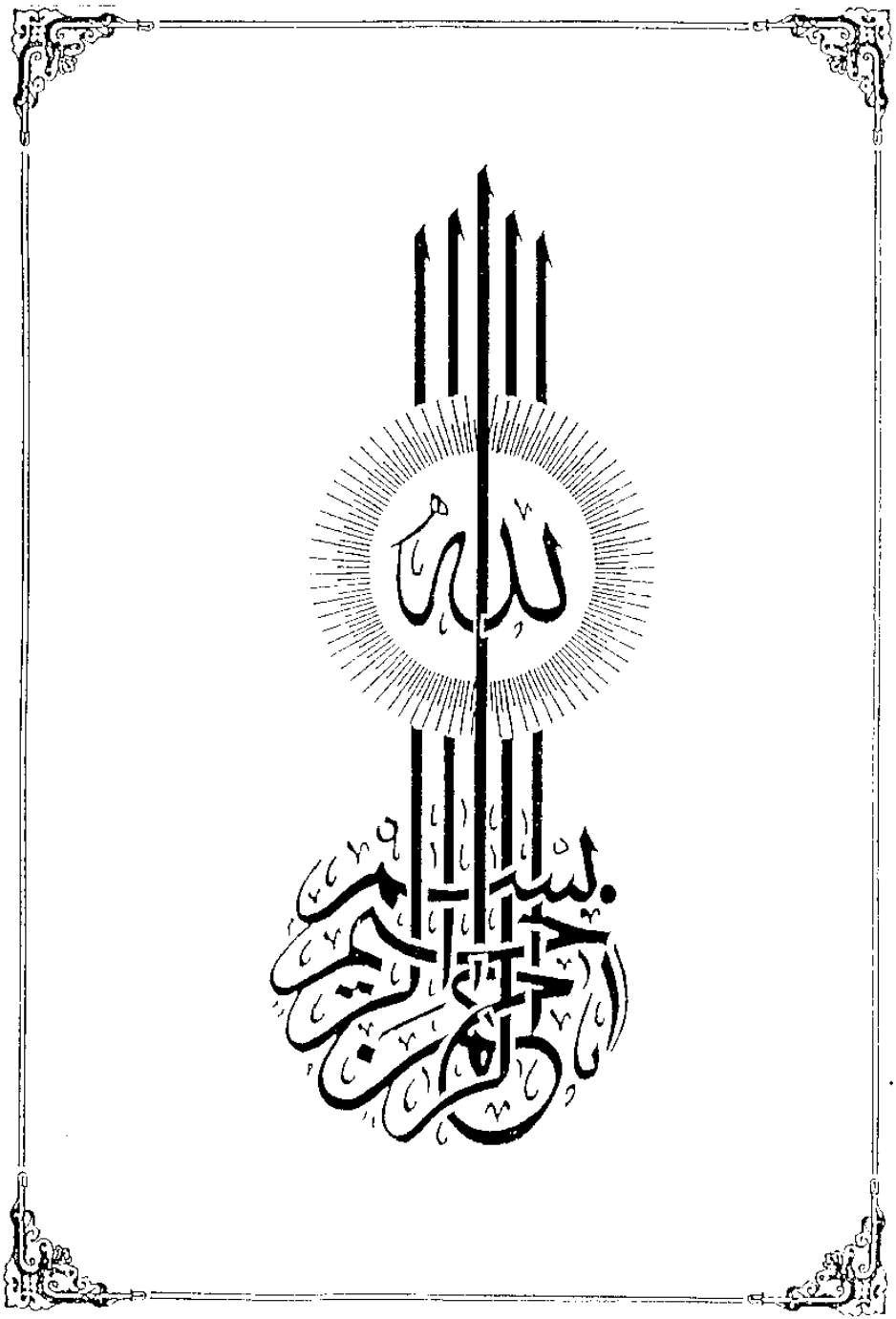
ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to his faculty advisors, Dr. F. S. Manning and Professor W. O. Philbrook, for their helpful suggestions and guidance.

The American Iron and Steel Institute, whose support made this study possible.

The United Arab Republic government for supporting the author's studies.



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ABSTRACT

Closely-sized vermillon ore particles were reduced with hydrogen in packed beds at 700°c and 1 atmosphere. Photographs of sections of partially reduced pellets indicated that both stage-wise and topochemical reduction occurred due to the variation in individual particle porosity. Overall reduction rates as reflected by the observed weight losses could be fitted using Barner's (7) method of predicting fixed bed reduction rates and Spitzer's porous model 'B' single particle kinetics (18). The fit was better for the middle part of the bed than in the top or bottom parts. The increase in reduction rate with increase in reducing gas mass velocity was correlated empirically.

INTRODUCTION

With the large increase in pig iron production in the last decade, it has become of great industrial importance to have an accurate model for predicting the reduction behavior of different ores under widely varying operating conditions in the blast furnace in order to optimize its operation. Barner (6) presented a mathematical model for the isothermal reduction of hematite ores in fixed beds in which single particle kinetics was used to predict packed bed reduction. Spitzer (17) using different kinetic expressions for single particle modified Barner's model and presented three models describing the reduction of hematite ores in packed beds, the experimental data available for the use of hydrogen as a reducing agent in the bed was not adequate to permit fully testing the three models and the need for more data arose.

The present work provides experimental data for the fractional reduction and exit gas composition as a function of time and the effect of gas velocity in the bed on the reduction rate to test the different models.

The reduction of hematite ores in packed beds is investigated as a start for predicting blast furnace and other direct reduction processes. A simplification

to the analysis is to consider the isothermal reduction in fixed beds with hydrogen or carbon-monoxide, however with the appropriate modification this analysis can be extended to the reduction with a mixture of reducing gases and to the adiabatic case which are the cases encountered in the industrial processes.

LITERATURE REVIEW

Because the reduction of iron ores has received very extensive coverage in the literature, this review is limited to reduction using hydrogen. Reduction of packed beds and single particles are treated separately.

1 - Packed beds

Udy and Lorig (1) reduced fixed beds of magnetite ores using hydrogen. The reduction rate was reported to increase with rising temperature until 600°C. Above 600°C the rate decreased considerably until 700°C when it increased again. Varying the gas velocity in the bed at 700°C they found that at relatively slow rates of flow the percentage reduction increased with increasing rate of flow, but a critical flow rate can be reached beyond which no further increase in reduction rate was noticed. Bostovtesv and Em (2) studied the reduction of hematite ores in packed beds at 800°C and determined the fractional conversion at set positions in the bed as a function of time. Privaloc, Timofeev and Bokovikov (3) presented an empirical formula relating the rate of reduction of iron ores in fixed beds to the reducing and product gas concentrations, gas velocity, bed height, external surface of ore lumps per unit volume of the bed and cross sectional area of the bed.

El-Mehairy and Philbrook (4) investigated the

combined effects of bulk gas flow and chemical reaction in an isothermal fixed bed of hematite particles under constant pressure drop. Except at high pressure differentials, the hydrogen flow rate varied as the square of the particle diameter as indicated by the Carman-Kozeny equation. However, the total particle surface area was inversely proportional to the particle diameter. At very small particle sizes the gas flow rate was very slow, and this produced a very small conversion. However, at a constant pressure drop very large particles would result in a higher flow rate, but now the available surface area per unit bed volume would be small and hence the overall reduction would be low. Bed reduction rates would reach a maximum between these two extremes. El-Mehairy predicted the overall reduction of the bed as a function of particle diameter but was unable to operate in the range of particle diameter where maximum reduction rate exists, so he only approached but did not reach the maximum rate. Osman (10) repeated El-Mehairy's data in regions where possible back diffusion of by-passed hydrogen would have been serious.

Barner (5, 6) modelled mathematically the reduction process in isothermal packed beds. He estimated the reducing gas flow rate through the bed and used McKewan's (7) single particle kinetics to relate the changes in reducing gas consumption to the particle conversion by material balance equations and was able to predict the optimum

particle diameter for reduction under constant pressure differentials.

Spitzer, Manning and Philbrook (9) modified Barner's model to permit the formation of intermediate oxides by gaseous reduction in portions of the bed where the gas no longer has enough reducing power to produce metallic iron. This modification was suggested by experimental data (10) which indicated that hydrogen may be consumed almost completely during early stages of reduction. Three alternative models were proposed, dense particle model, porous particle models A and B. In the three models the assumption was made that all gaseous reduction steps are controlled at the reagent-product interface, i.e. transport resistances were neglected.

In the dense particle model it is assumed that in atmospheres reducing to wüstite, all the oxygen removal from the core occurs at the Fe/Fe_xO interface. Internal reduction of Fe_2O_3 to Fe_3O_4 to Fe_xO occurs by solid-state diffusion of iron ions and electrons into the dense oxide phases, as the reducing gas is no longer reducing to wüstite, this model suggests a shift in reduction mechanism to allow reaction to continue by gaseous reduction of magnetite to wüstite and similarily, by gaseous reduction of hematite to magnetite at P_{H_2}/P_{H_2O} ratios below Fe_xO/Fe_3O_4 equilibrium value. In the porous

particle models hydrogen is assumed to penetrate far into the core, producing product layers of each possible phase by gaseous reduction and be almost completely utilized in reducing hematite to magnetite, but water vapor effusing outward would then be oxidizing to wüstite and iron. Porous model 'A' considers that reoxidation of outer product layers by water vapor effusing outwards is rapid, i.e. step wise reduction so hematite particle has to be completely reduced to magnetite before any wüstite or iron is formed. Similarily, the magnetite formed has to be reduced to wüstite before any iron is formed and finally wüstite is reduced to iron, so only two phases may be present at a given time in a single pellet.

Porous model 'B' considers the reoxidation process to be so slow that it is neglected, i.e. reduction is occurring at the three interfaces (Fe/Fe_xO, Fe_xO/Fe_3O_4, Fe_3O_4/Fe_2O_3) simultaneously so that during the course of reduction the three interfaces are moving and it is possible that all four phases to coexist in the same pellet.

By choosing suitable values for the kinetic constants $K_r(Fe/Fe_xO)$, $K_r(Fe_xO/Fe_3O_4)$, $K_r(Fe_3O_4/Fe_2O_3)$ Spitzer (8) was able to fit the three models to El-Mehairy's experimental data and it appeared that these data were inadequate to fully test the three models and more experimental data showing the change of fractional reduction and the exit gas analysis with time become important to fully test the three models.

2 - Single particle

As discussed earlier all the models developed for reduction in packed beds use single particle kinetic expressions to predict the reduction of a fixed bed of ore particles. The reduction of dense hematite pellets involves the following steps:-

1) Transport of the gaseous reactant from the bulk gas phase to the outer surface of the particle.

2) Diffusion of the gaseous reactant through the pores of the product layer to the surface of the unreacted oxide core.

3) Chemical reaction between the gas and the solid oxide.

4) Diffusion of the gaseous product outwards through the product layer to the surface of the solid.

5) Transfer of gaseous product from the outer surface back to the bulk gas phase.

These steps offer resistance in series to the overall chemical reaction. If one is considerably slower than the others it may be identified as 'rate controlling step'. If two or more are found to be significant the reduction process is described to be under mixed control.

Below 560°C where wüstite is unstable the reduction involves the successive steps $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$, while above 560°C the sequence is $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe_xO \rightarrow Fe$ (x represents the ratio of iron to oxygen ions in the non stoichoimetric wüstite). McKewan (7) developed a rate expression based on Edström's (8) mechanism for dense hematite pellets in which the overall reaction is assumed to be controlled by the rate of gaseous reduction of wüstite to iron and the intermediate oxides are reduced

by the non controlling solid state diffusion of iron ions and electrons into dense oxide phase and the rate of oxygen removal must approach zero as the P_{H_2}/P_{H_2O} ratio approaches the Fe/Fe_xO equilibrium value.

Spitzer (11) presented a generalized model for the gaseous reduction of dense hematite pellets and showed that the linear rate of thickening of the product layer, which has been commonly taken as evidence of interface control, may be observed even though transport resistances play a dominant role in overall kinetics. Spitzer (17) showed that the reduction behavior of dense hematite pellets in packed beds by hydrogen/water vapor mixtures is described more appropriately by his porous pellet model in which gas-solid reduction is permitted at each of the three advancing interfaces (Fe/Fe_xO, Fe_xO/Fe_3O_4, Fe_3O_4/Fe_2O_3) and is controlled by a complex series - parallel sequence of chemical and transport steps. McKewan's experimental data (12, 13) showed that each interface was found to advance in a linear fashion and to approach zero rate at its own equilibrium composition. Spitzer, using very nearly the same ratio of the kinetic constants K_r (Fe/Fe_xO): K_r (Fe_xO/Fe_3O_4) : K_r (Fe_3O_4/Fe_2O_3) to the one obtained from McKewan's data, was able to fit the porous model 'B' to El-Mehairy's experimental data and concluded that the difference in the values of the kinetic constants obtained from single particle experiments (12) and those used in the packed bed model may be due to heat transfer effects and to a particle size dependence of the kinetic constants.