

Iron oxide reduction using hydrogen as green reducing agent

Antonio D'Angelo^{1,2*}, E. Salucci^{1,2}, V. Russo², H. Grénman², H. Saxén²

1 Åbo Akademi University, Åbo FI-20500, Finland;

2 Università degli studi di Napoli Federico II, Napoli IT-80125, Italy

**Corresponding author: antonio.dangelo@abo.fi*

Highlights

- Iron oxide reduction study in a packed bed reactor.
- Intrinsic kinetic of the system.
- Diffusion and Mass transfer phenomena evaluation.

1. Introduction

The steel industry plays an important role in the world economy and the yearly production is huge, approaching 2000 million tons. Unfortunately, this industry sector is also a very large emitter of carbon dioxide, about 8 million tons per year, as a major part of the iron is produced from iron ore with coal-based reduction: today, more than 70% of the iron production is made in blast furnaces (BF). In the BF, iron oxides are reduced by carbon monoxide produced by combusting coke or coal. The coke and iron oxides are charged at the top part of the BF, descend through the shaft where they are preheated and react. The partial oxidation of coke produces CO which starts to reduce the iron oxide, eventually yielding liquid iron and slag, as well as CO₂. The most promising candidate for decarbonization of ironmaking is a shaft furnace where the reduction is carried out in solid state by a reducing gas, yielding direct reduced iron (DRI). In the present DR furnaces, the reduction is carried out at a lower temperature (< 1273K) using reformed natural gas with a H₂/CO ratio of about 3. Part of the exhaust gas is mixed with natural gas and reformed, and the remainder is combusted to preheat the reformer gas. Broader application of DR furnaces represents a first important step towards the decarbonization of the ironmaking process, but fossil feedstock is used in them and considerable amounts of CO₂ are still emitted. Recently, a shift to hydrogen reduction has attracted increasing attention for cutting CO₂ emissions, but this requires further development of the DR process. The focus of the present work on the reduction kinetics of iron oxide using hydrogen as the sole reductant (Fig. 1). The seemingly simple overall reaction displays interestingly complex behavior, which depends on gas phase, surface and solid phase phenomena. This may be the reason for partly contradictory observations and interpretations presented in literature, e.g., with respect to kinetic parameters such as activation energies. It is important to stress that a deep understanding of these fundamental issues is crucial for designing and operating new steelmaking processes.

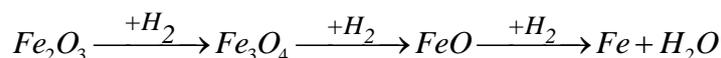


Figure 1. Reaction scheme of hematite reduction

2. Materials and Methods

The kinetics of hydrogen reduction of fines of pure hematite (Fe₂O₃) and industrial ironmaking materials (pellets consisting of mainly hematite) reduction were studied utilizing a precisely controlled fixed bed reactor system (Autochem II) with a thermal conductivity detector (TCD) for analyzing the outgoing gas. Moreover, a micro-GC (Agilent 990) was used to analyze online the composition of the gas. Experiments were performed with a monolayer of hematite fines to study the intrinsic kinetics and with a bed of fines to evaluate the influence of the bed dynamics on the overall reactions. Solid-state properties were also analyzed to assess the morphology, and crystal structure of the material.

3. Results and Discussion

The TCD signal which reflects the gas composition is sensitive to hydrogen in the gas as the thermal conductivity of hydrogen is much larger compared to the other gases in the mixture. As can be seen in Fig. 2, which depicts the normalized output of the TCD signal, the reduction kinetics differs between pure and commercial samples. In order to study the solid phase properties during the process, a physical-

chemical characterization of the material (before, during and after reaction) at various experimental conditions was performed. The results indicate that the local thermodynamics influences the overall kinetics especially in the iron oxide bed. Moreover, diffusion limitations exist inside the particles and is influenced by morphology changes occurring during the reduction. The observations are supported by data obtained on the gas composition and solid-state properties of the pure oxide and commercial samples obtained with SEM, nitrogen physisorption and mercury porosimetry.

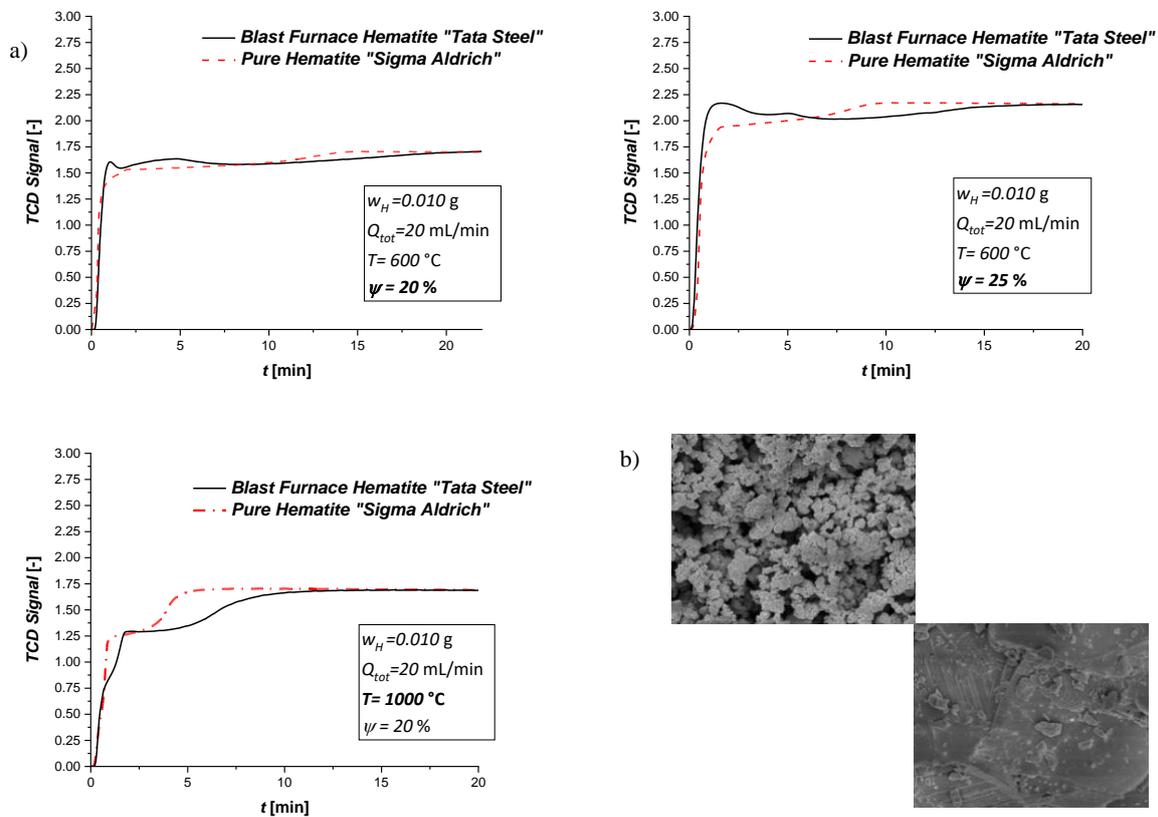


Figure 2. a) Hydrogen reduction experiments with pure and commercial hematite; b) SEM images of the samples.

4. Conclusions

In this work, monolayer and bed experiments with pure hematite and commercial samples were performed in various experimental conditions to investigate kinetics and mass transfer phenomena. To support the interpretation of the data, morphological and chemical-physical characterization was performed. The collected information provides a strong basis for understanding the overall reduction dynamics, and a starting point for developing a mathematic model describing the overall kinetics of the iron oxide reduction.

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Keywords

Iron oxide, hydrogen, kinetics, reduction experiments.