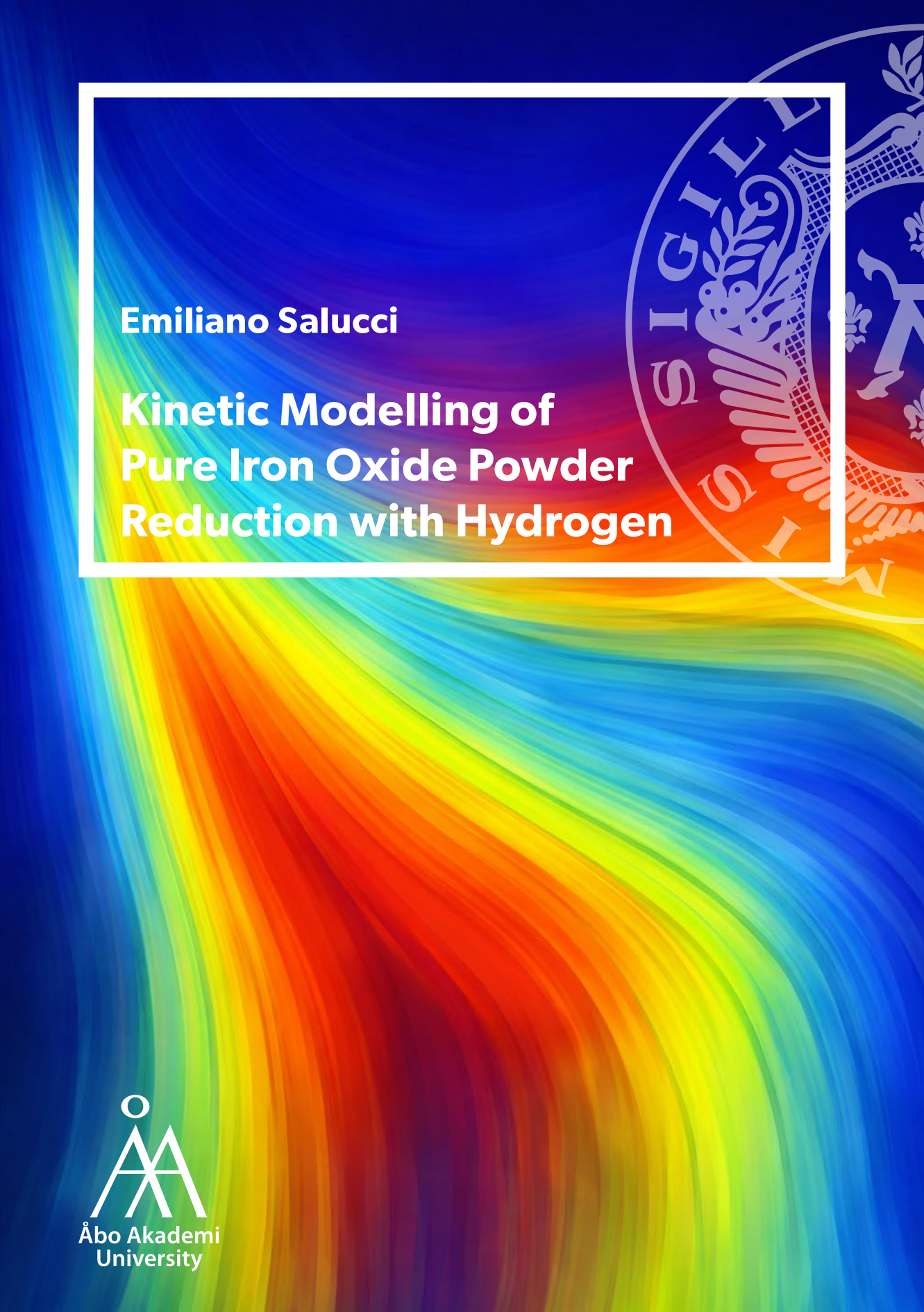




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**Kinetic Modelling of
Pure Iron Oxide Powder
Reduction with Hydrogen**



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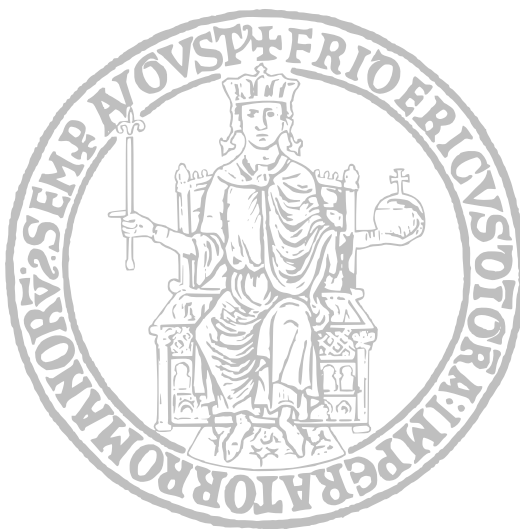
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Kinetic Modelling of Pure Iron Oxide Powder Reduction with Hydrogen

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Preface

The present PhD thesis marks the culmination of a long, intense, and transformative journey that actually started more than four years ago. Looking back at the path from the very beginning to this final stage, I realize how profoundly this experience has shaped me — not only as a researcher, but as a person. The scientific challenges faced, the ideas explored, and the results achieved are the visible outcome of years of dedication. Yet, none of this would have been possible without the people who guided, supported, and believed in me along the way.

My deepest gratitude goes to Prof. Henrik Saxén, whose mentorship has been far more than academic supervision. With patience, rigor, and unwavering dedication, Henrik taught me how to approach scientific problems with critical thinking and intellectual honesty. The countless discussions have always been accompanied by an irrepressible desire to solve any problem with the dedication of someone who loves not only science but knowledge in its entirety, with an ever-present touch of irony and lightheartedness. What I will never forget is the invaluable and complete trust that was placed in me. Working alongside him has been both a privilege and an inspiration.

I am equally grateful to Prof. Henrik Grénman, whose experience and perspective have enriched this work immensely. The ability to see clarity in complexity, to transform obstacles into opportunities, and to push ideas further than I thought possible has left a lasting mark on my development. What I can express in just a few lines is only a small part of my gratitude, but I sincerely thank him for all the precious time dedicated to me by a person whom I respect and consider not only a leader, but also a friend.

A heartfelt thank you goes to Prof. Vincenzo Russo for his constant support and for standing by me in both the technical and the most challenging moments of work and life. Ours is a collaboration that has lasted nearly a decade, yet what remains clear in my mind is the profound sense of sacrifice and meritocracy that he represents. What for many may appear as a distant figure is, more than ever, an inspirational benchmark to strive toward. Thank you for your continuous support, “socio.”

I also wish to acknowledge all the colleagues, collaborators, and friends who contributed to this journey. To Antonio, Guanwei, Tommaso, and Salvatore, thank you for the stimulating discussions, the shared efforts, and the moments of genuine camaraderie. Thanks to you, the working life here has been not only easier to face but has also allowed me to engage with realities different from my own, both professionally and personally.

To Professors Mazzoleni and Giannino, and to Fabrizio Cartenì, I express my gratitude for having had a significant impact on the kind of researcher I am today. You taught me what it means to expand one's thinking laterally and place it at the service of understanding the world around us.

I would also like to acknowledge the FFS1 and FFS2 projects and Walter Ahlstrom Foundation, which significantly contributed to the financial support of this research and enabled collaboration with academic and industrial institutions of great scientific and technological impact, such as the University of Oulu and SSAB.

To my students, Francesco, Luigi, and Eleonora, thank you for your enthusiasm, dedication, and trust. Watching your projects develop has been one of the most rewarding aspects of this experience.

My warmest gratitude goes to my family. Your unconditional support has been my foundation, keeping me grounded through successes and setbacks alike. Every sacrifice, every word of encouragement, and every silent gesture of love has carried me forward more than you can imagine.

To my closest friends, these years have been filled with important moments, even if lived at a distance. I was once told that if time does not seem to have passed when you meet again, even after a long while, it represents the truest synonym of friendship. With you, who have shared laughter, doubts, long conversations, and unforgettable moments, this sentence could not be truer.

Finally, to L and MG, thank you for your unwavering support. We often ask ourselves what might be missing in our lives, and sometimes we learn the answer only by living it day by day.

These past years have transformed my life in ways I could not have foreseen. To everyone who has been part of it, I offer my sincere and lasting gratitude.

Abstract

The aim of this doctoral thesis is to model key phenomena governing the reduction of pure iron oxide powders in the presence of hydrogen based on novel experimental data. This objective is strongly associated with the urgent need to reduce the carbon footprint of metallurgical processes involved in large-scale iron and steel production, which remains one of the industrial sectors most in need of ecological transition.

The main goal was to elucidate and describe the fundamental aspects of the series of reductions that characterize the reactive network through a rigorous mathematical framework based on a dynamic shrinking-core model. The ultimate purpose was to identify the controlling regimes and to estimate and validate the associated kinetic parameters. The results of this study provide a solid basis for the scale-up of more complex reactor systems that may serve as a realistic alternative to current production chains or contribute to their optimization by increasing hydrogen use in existing facilities.

A research strategy was developed that alternated between mathematical modelling and experimental investigation, including a detailed characterization of solids under transient conditions. Such an approach is crucial, since mathematical models must consistently describe emerging phenomena through sound assumptions, while simulations—however preliminary—can support the interpretation, inspire the design of new experimental campaigns, and confirm the key mechanisms of the process.

In the first stage, an extensive review of the scientific literature was conducted to assess the wide experimental and modelling variability associated with hydrogen-based iron-oxide reduction. This survey highlighted the heterogeneity of kinetic parameters reported over the past six decades and the consequent need to establish an experimental methodology capable of generating accurate and reproducible data for reliable regime and kinetic evaluation.

Accordingly, reduction experiments were carried out in a fixed-bed reactor loaded with pure hematite and magnetite powders, using a chemisorption analysis device equipped with a thermal conductivity detector for exhaust-gas analysis. The experimental work was supported by the development of a comprehensive mathematical model capable of describing both the reactive

solid-bed dynamics and the reaction of individual particles, including the motion of multiple reaction fronts. To ensure physical consistency, a mathematical constraint was introduced to prevent the overlap of the reaction fronts. The final model, which combines a classical axial-dispersion formulation with the shrinking-core model, was used to describe the solid conversion over time, with its consistency and flexibility evaluated through an in-depth parametric analysis.

A dedicated comparison between the experimental results of thin-layer reduction tests and the corresponding model simulations was then carried out. For this purpose, an innovative numerical-mathematical method was developed to correlate the evolution of the thermal conductivity of the exhaust gases with the overall reduction degree of the solids. By incorporating granulometric data from sample analysis, the model enabled the precise evaluation of the kinetic parameters for each reaction step involved in the reduction sequence.

Finally, the estimated kinetic parameters were successfully validated through an extensive experimental dataset obtained from the reduction of iron-oxide beds under a wide range of operating conditions. The mathematical model thus provided a refined microscopic description of the reduction process, elucidating the implications of the reversible nature of the reactions and offering a robust interpretative framework for future hydrogen-based ironmaking technologies.

Referat

Syftet med denna doktorsavhandling är att modellera och experimentellt undersöka de centrala fenomen som styr reduktionen av järnoxidpulver i närvaro av väte. Målet är nära kopplat till det akuta behovet av att minska koldioxidavtrycket från metallurgiska processer för storskalig järn- och ståltillverkning, som fortfarande är en av de industrier som mest kräver en ekologisk omställning.

Det huvudsakliga målet var att fördjupa förståelsen och beskriva de grundläggande aspekterna av de seriereaktioner som kännetecknar systemet under studium, genom en noggrant utvecklad matematisk modell baserad på en dynamisk krympande-kärn-modell. Målet var att identifiera kontrollregimer samt att bestämma och validera de tillhörande kinetiska parametrarna. Resultaten från arbetet ger en solid grund för uppskakning av mer komplexa reaktorsystem som kan utgöra ett realistiskt alternativ till dagens produktionskedjor eller bidra till deras optimering genom ökad användning av väte i befintliga anläggningar.

För att uppnå detta utvecklades en forskningsstrategi som växelvis fokuserade på matematisk modellering och experimentellt arbete, inklusive noggrann karakterisering av den fasta fasen under transienta förhållanden. Detta alternerande tillvägagångssätt är centralt eftersom matematiska modeller konsekvent måste beskriva de observerade fenomenen genom välgrundade antaganden, medan simuleringar – även i ett tidigt skede – kan stödja tolkningen och vägleda utformningen av nya experiment och bekräfta de mest centrala mekanismerna i processen.

I den inledande fasen genomfördes en omfattande litteraturöversikt över experiment och modellering av vätgasbaserad reduktion av järnoxider. Studien påvisade en betydande spridning av rapporterade kinetiska data under de senaste sextio åren och därmed behovet av en experimentell metodik som kan generera tillförlitliga och reproducerbara data för korrekt bestämning av kinetik och reaktionsregimer.

Reduktionsexperiment utfördes därför i en fastbäddsreaktor med rent hematit- eller magnetitpulver i ett kemisorptionsinstrument utrustat med en detektor för värmeledningsförmågedetektor, med vilken vätehalten i avgaserna kunde

detekteras. Det experimentella arbetet stöddes av resultat från en omfattande matematisk modell som utvecklades för att beskriva både den reaktiva fasta bäddens dynamik och reaktionen hos enskilda partiklar, inklusive flera dynamiska reaktionsfronter i partiklarna. För att säkerställa fysisk konsistens infördes ett matematiskt villkor som förhindrar dessa fronter att överlappa eller passera varandra. Modellen, som kombinerar en klassisk axiell dispersionsbeskrivning med krympande-kärn-modellen, användes för att beskriva den fasta fasens konversion utvärderades genom en detaljerad parametrisk analys.

En jämförelse mellan resultaten från reduktionsförsök med tunna bäddskikt och simuleringar gjordes för att kontrollera de uppmätta värdena. För detta utvecklades en innovativ numerisk-matematisk metod som korrelerade avgaser-
nas värmeledningsförmåga med den totala reduktionsgraden hos den fasta fasen. Genom att integrera granulometrisk data från proverna möjliggjordes en noggrann bestämning av de kinetiska parametrarna för varje steg i reduktionssekvensen.

Slutligen validerades dessa kinetiska parametrar framgångsrikt med hjälp av ett omfattande experimentellt data för reduktion av järnoxidbäddar under ett brett spektrum av driftförhållanden. Den matematiska modellen ger här en detaljerad mikroskopisk beskrivning av reduktionsprocessen och klargör de reversibla reaktionernas inverkan. Modellen är ett värdefullt redskap för analys av framtida vätebaserade järnframställningsteknologier.

Sinossi

L'obiettivo di questa tesi di dottorato è la modellazione e l'indagine sperimentale dei fenomeni chiave che governano il processo di riduzione di polveri di ossidi di ferro puri in presenza di idrogeno. Tale obiettivo è strettamente connesso all'urgenza di ridurre l'impronta carbonica dei processi metallurgici destinati alla produzione su larga scala di ferro e acciaio, uno dei settori industriali che più necessitano di una transizione ecologica.

A tal fine, il principale scopo del lavoro è stato quello di approfondire e descrivere gli aspetti fondamentali delle riduzioni in serie che caratterizzano il network reattivo, attraverso un rigoroso modello matematico basato su un dynamic shrinking-core model. L'obiettivo finale è stato identificare i regimi controllanti, stimare e validare i relativi parametri cinetici. I risultati ottenuti forniscono basi solide per la scale-up industriale di sistemi reattoristici più complessi, potenzialmente in grado di rappresentare un'alternativa reale alle catene produttive attuali o di supportarne l'ottimizzazione mediante un maggiore impiego di idrogeno negli impianti esistenti.

Per raggiungere questo scopo è stata sviluppata una strategia di ricerca basata sull'alternanza tra modellazione matematica e sperimentazione, comprendente anche una accurata caratterizzazione dei solidi in transiente. Tale approccio integrato è risultato cruciale: da un lato, la modellazione matematica deve descrivere coerentemente le proprietà emergenti attraverso assunzioni fisicamente fondate; dall'altro, le simulazioni, anche nelle loro fasi preliminari, possono supportare l'interpretazione dei dati, orientare la progettazione di nuove prove sperimentali e confermare i meccanismi fondamentali del processo.

Nella fase iniziale è stata condotta un'ampia revisione della letteratura scientifica relativa ai processi di riduzione con idrogeno, evidenziando la notevole variabilità sperimentale e modellistica riportata negli ultimi sessant'anni. Tale analisi ha sottolineato la necessità di sviluppare un approccio sperimentale dedicato, capace di fornire dati accurati e riproducibili per una stima più affidabile dei regimi e dei parametri cinetici.

Sono quindi stati condotti esperimenti di riduzione in reattore a letto fisso caricato con polveri pure di ematite e magnetite, utilizzando un sistema di analisi di chemisorbimento dotato di rivelatore a conducibilità termica per l'analisi dei

gas in uscita. Il lavoro sperimentale è stato accompagnato dallo sviluppo di un modello matematico avanzato in grado di descrivere sia la dinamica del letto solido reattivo, sia la reazione delle singole particelle, includendo il moto di fronti di reazione multipli e dinamici. A garanzia della coerenza fisica, è stato introdotto un vincolo matematico volto a evitare la sovrapposizione dei fronti di reazione. Il modello, che combina una formulazione classica di dispersione assiale con lo SCM, è stato utilizzato per descrivere l'evoluzione temporale della conversione del solido, valutandone la coerenza e la flessibilità attraverso un approfondito studio parametrico.

Il confronto tra i risultati sperimentali di prove di riduzione di strati fini di solido e le corrispondenti simulazioni numeriche ha consentito di verificare l'accuratezza dei dati sperimentali. A tale scopo è stato sviluppato un innovativo metodo numerico-matematico per correlare l'evoluzione della conducibilità termica dei gas in uscita con il grado di riduzione complessivo dei solidi. Integrando i dati granulometrici delle polveri, il modello ha permesso la valutazione accurata dei parametri cinetici di ciascuna reazione del processo riduttivo.

Infine, tali parametri cinetici sono stati validati con successo attraverso un ampio set di dati sperimentali relativi alla riduzione di letti di ossidi di ferro condotti in diverse condizioni operative. Il modello matematico sviluppato fornisce quindi una descrizione microscopica raffinata del processo di riduzione, chiarendo le implicazioni della reversibilità delle reazioni coinvolte e offrendo un solido quadro interpretativo per le future tecnologie siderurgiche basate sull'idrogeno.

List of publications

- I. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxèn, "Review on the Reduction Kinetics of Iron Oxides with Hydrogen-Rich Gas: Experimental Investigation and Modeling Approaches", *Industrial & Engineering Chemistry Research* 64 (2024), 1, DOI: 10.1021/acs.iecr.4c03136.
- II. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxèn, "Modelling of iron oxide reduction with hydrogen in a small fixed bed", *Chemical Engineering Science* 292 (2024), 119934, DOI: 10.1016/j.ces.2024.119934.
- III. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, and H. Saxén, "Kinetic modeling and parameter estimation of thin-layer iron oxide reduction with hydrogen in a fixed-bed reactor," *Chemical Engineering Journal* 529, (2026), 172848 DOI: 10.1016/j.cej.2026.172848.
- IV. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxèn, "Validation of kinetic parameters based on fixed-bed experiments for hydrogen reduction of iron oxides", submitted manuscript.

The author's contribution to the articles

The author of the thesis has contributed to the appended four papers as outlined below.

- I. Methodology, Conceptualization, Writing - Original Draft, Data Curation, Writing – review and editing.
- II. Writing – original draft, Validation, Software, Methodology, Formal analysis, Writing – review and editing.
- III. Methodology, Software, Formal analysis, Data curation, Validation, Writing - Original Draft, Writing – review and editing.
- IV. Methodology, Software, Formal analysis, Data curation, Validation, Writing - Original Draft, Writing – review and editing.

The co-authors of these four papers have contributed as outlined below.

Antonio D'Angelo: Investigation, Data Curation

Vincenzo Russo: Conceptualization, Writing - Review & Editing, Supervision

Henrik Grénman: Conceptualization, Project administration, Writing - Review & Editing, Supervision

Henrik Saxén: Methodology, Writing - Review & Editing, Conceptualization, Project administration, Funding acquisition

Conference presentations related to the thesis

Oral Presentations

- I. **E. Salucci***, S. Ghosh, V. Russo, H. Grénman, H. Saxén, “Modelling of hydrogen-based reduction of iron oxides”, H₂ and Fossil-free Steel, Oulu, November 9, 2022.
- II. **E. Salucci***, S. Ghosh, V. Russo, H. Grénman, H. Saxén, “Modelling of iron oxide reduction with hydrogen”, The 33rd European Symposium on Computer-Aided Process Engineering (ESCAPE-33), Athens, June 18 – 21, 2023.
- III. **E. Salucci***, S. Ghosh, V. Russo, H. Grénman, H. Saxén. Modeling of iron oxide reduction with hydrogen, “10th International Conference on Modelling and Simulation of Metallurgical Processes in Steelmaking (SteelSIM23), Warwick, September 11 –13, 2023.
- IV. **E. Salucci***, A. D’Angelo, S. Ghosh, V. Russo, H. Grénman, H. Saxén, 14th European Congress of Chemical Engineering and 7th European Congress of Applied Biotechnology (ECCE 14), Berlin, September 17 – 21, 2023.
- V. **E. Salucci***, A. D’Angelo, V. Russo, H. Grénman, H. Saxén, “Some challenges in describing the kinetics of iron oxide reduction in hydrogen atmospheres”, FFS2 Towards Fossil-Free Steel, Phase 2 (FFS2), Helsinki, January 30, 2025
- VI. **E. Salucci***, A. D’Angelo, V. Russo, H. Grénman, H. Saxén, “Kinetic Study of Pure Iron Oxide Reduction with Hydrogen Using a Dynamic Triple Reaction Front Shrinking Core Model”, 11th International Conference on Modelling and Simulation of Metallurgical Processes in Steelmaking (SteelSIM25), Trinec, September 02 –04, 2025.

- VII. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxén, "Application of thermal conductivity detector for the estimation of kinetic parameters of reduction of pure iron oxides with hydrogen." Hybrit - FFS2 Towards Fossil-Free Steel, Phase 2, (H-FFS2), Oulu December 3, 2025.
- VIII. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxén, "Kinetic Modelling of Pure Iron Oxide Powder Reduction with Hydrogen." FFS2 Towards Fossil-Free Steel, Phase 2, Final Seminar (FFS2), Oulu December 11, 2025.

Poster Presentations

- IX. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxén, "Mathematical modeling of hydrogen reduction of iron oxides" Finnish Catalysis Society – Young Scientist Forum 2024, Helsinki, April 6, 2024.
- X. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxén, "Mathematical modeling of hydrogen reduction of iron oxides", 28th International Symposium for Chemical Reaction Engineering (ISCRE 24), Turku, June 16 – 19, 2024.
- XI. **E. Salucci***, A. D'Angelo, V. Russo, H. Grénman, H. Saxén, "Kinetic study of pure iron oxide reduction with hydrogen using a dynamic triple reaction front shrinking core model", 15th European Congress of Chemical Engineering and 8th European Congress of Applied Biotechnology (ECCE 15), Lisbon, September 08 – 10, 2025.

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Chapter 1–Introduction (I)

*“Being cultured does not mean remembering every piece of knowledge but
knowing where to find it.”*

U. Eco

1.1 Anthropogenic decarbonization

One of the major ecological and economic challenges of the modern world is undoubtedly represented by the enormous production of greenhouse gases, which translates into the necessity of reducing the carbon footprint of all human activities. Rapid technological progress, coupled with competitive industrial development, has indirectly contributed to an increase in the planet's surface temperatures. It is estimated that this increase ranges between 0.8 °C and 1.3 °C,¹ with cascading impacts on climate change, desertification, and natural meteorological disasters that severely affect all ecosystems. The global objective has been to focus scientific and economic efforts on limiting the increase in Earth's temperature, aiming not to exceed, by the end of the century, an average temperature rise of 1.5 °C.²

To achieve rapid decarbonization of anthropogenic activities, it is necessary to study valid alternatives to the current technologies used in transportation, energy conversion, and especially in the industrial sector. Among these, the industrial sector is the most complex to evolve, due to both the extensive exploitation of non-renewable natural resources and the complicated ecological conversion of existing plants, or in the worst case, their complete replacement.

A rapid and potentially impactful approach is the development of innovative technologies that can be easily integrated into well-defined production processes, supporting the transition towards technologies that are not yet mature but are potentially highly sustainable from both economic and ecological perspectives.

The steel industry is one of the sectors that requires significant efforts to drastically reduce greenhouse gas emissions. Annual production has tripled in

¹ V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B. R. Matthews, T. K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou, *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change; Technical Summary*, (2021).

² M. Fischedick, J. Marzinkowski, P. Winzer, and M. Weigel, 'Techno-economic evaluation of innovative steel production technologies', *Journal of Cleaner Production*, 84 (2014), 563–80.

the last 20 years, reaching about 2 billion tons of steel (tSteel).³ Global production remains dominated by China, which accounts for about 53%.⁴

To achieve this level of production, in 2011 the World Steel Association estimated the consumption of about 2 billion tons of iron ore, 1 billion tons of coal, and 575 million tons of recycled steel.⁵ This resulted in a specific emission of approximately 1.85 tons of carbon dioxide (CO₂) per tSteel, which falls within the range of 7–9% of global direct CO₂ emissions.⁶

This figure, representing approximately 2.5 Gt/year of CO₂, is comparable to the amount of greenhouse gases produced annually by the entire European community (about 4 Gt/year), considering all sectors, both industrial and non-industrial (e.g., energy, manufacturing, transportation, etc.).⁷

Furthermore, it has been estimated that the complex production chain requires approximately 32 EJ of energy to meet the current production demand.⁸ This inevitably translates into a huge contribution, currently not plausible, required directly or indirectly from renewable sources. The current impossibility of using such technologies is due to both the low efficiency of the processes and the poor stability of energy supply over time.

An alternative to the current carbon-based steel production chain is represented by the option of introducing or almost completely replacing carbon-based sources with hydrogen (H₂).⁹

As will be emphasized and explained in detail in the following sections of this doctoral thesis, several steps must be taken to promote the use of hydrogen. The in-depth study of phenomena at both micro and macroscopic scales, which occur in production processes, is crucial both for economic and energy optimization

³ World Steel Association, *2022 World Steel in Figures*, (2022).

⁴ J. Kim, B. K. Sovacool, M. Bazilian, S. Griffiths, J. Lee, M. Yang, and J. Lee, 'Decarbonizing the iron and steel industry: A systematic review of sociotechnical systems, technological innovations, and policy options', *Energy Research & Social Science*, 89 (2022), 102565.

⁵ 2011 World Steel Association, *Raw Materials*, (2011).

⁶ J. P. Birat, 'Society, materials, and the environment: The case of steel', (2020).

⁷ V. Vogl, M. Åhman, and L. J. Nilsson, 'The making of green steel in the EU: a policy evaluation for the early commercialization phase', *Climate Policy*, 21/1 (2021), 78–92.

⁸ IRENA, *Reaching Zero with Renewables: Eliminating CO₂ Emissions from Industry and Transport in Line with the 1.5 °C Climate Goal*, (2020).

⁹ F. Patisson and O. Mirgaux, 'Hydrogen ironmaking: How it works', *Metals*, 10/7 (2020), 1–15.

purposes and for obtaining steel with a value not inferior to that produced using conventional methods.

What proves to be crucial in studies of this kind is to establish a solid foundation aimed at ensuring the understanding of the emerging phenomena and their description through accurate experimental data and sophisticated yet efficient mathematical models.

1.2 Steel production chain

The origins of steelmaking can be traced back several centuries; however, modern steel production commenced in the 19th century with the invention of the Bessemer process (1856), which enabled the large-scale manufacture of steel.¹⁰ The most relevant technical innovation that laid the foundations for future mass production was the introduction of coke in the blast furnaces, as it served as a cost-effective source of heat and reactants.¹¹ After several decades, according to the World Steel Report 2020, still 73.7% of global steel production is obtained using the classic Blast Furnace (BF) – Basic Oxygen Furnace (BOF) process.¹² Figure 1.1 displays how a BF typically operates.¹³

This production process initially consists of the pre-treatment of raw materials, coal, and iron ore (or iron oxides), which are agglomerated by coking and sintering/pelletizing, respectively. With a global consumption between 10% and 18%, this sector represents the largest industrial coal consumer.¹⁴ Generally, the solid materials are fed into the blast furnace at the top alternately, while hot oxygen-enriched air and pulverized coal are injected laterally into the lower BF through tuyere holes.¹⁵

¹⁰ M. F. Ashby and D. R. H. Jones, *Engineering Materials 2*, (Elsevier, 2013).

¹¹ S. J. Davis, N. S. Lewis, M. Shaner, S. Aggarwal, D. Arent, I. L. Azevedo, S. M. Benson, T. Bradley, J. Brouwer, Y.-M. Chiang, C. T. M. Clack, A. Cohen, S. Doig, J. Edmonds, P. Fennell, C. B. Field, B. Hannegan, B.-M. Hodge, M. I. Hoffert, E. Ingersoll, P. Jaramillo, K. S. Lackner, K. J. Mach, M. Mastrandrea, J. Ogden, P. F. Peterson, D. L. Sanchez, D. Sperling, J. Stagner, J. E. Trancik, C.-J. Yang, and K. Caldeira, 'Net-zero emissions energy systems', *Science*, 360/6396 (2018).

¹² World Steel Association, *Steel Statistical Yearbook 2020 concise version*, (2020).

¹³ The National Iron & Steel Heritage Museum, 'Blast Furnace Process', (2012).

¹⁴ U.S. Energy Information Administration, *Industrial sector energy consumption*, (2016).

¹⁵ Geerdes M., Chaigneau R., Lingardi O., Molenaar R., van Opbergen R., Sha Y., and Warren P., *Modern Blast Furnace Ironmaking an introduction*, (2020).

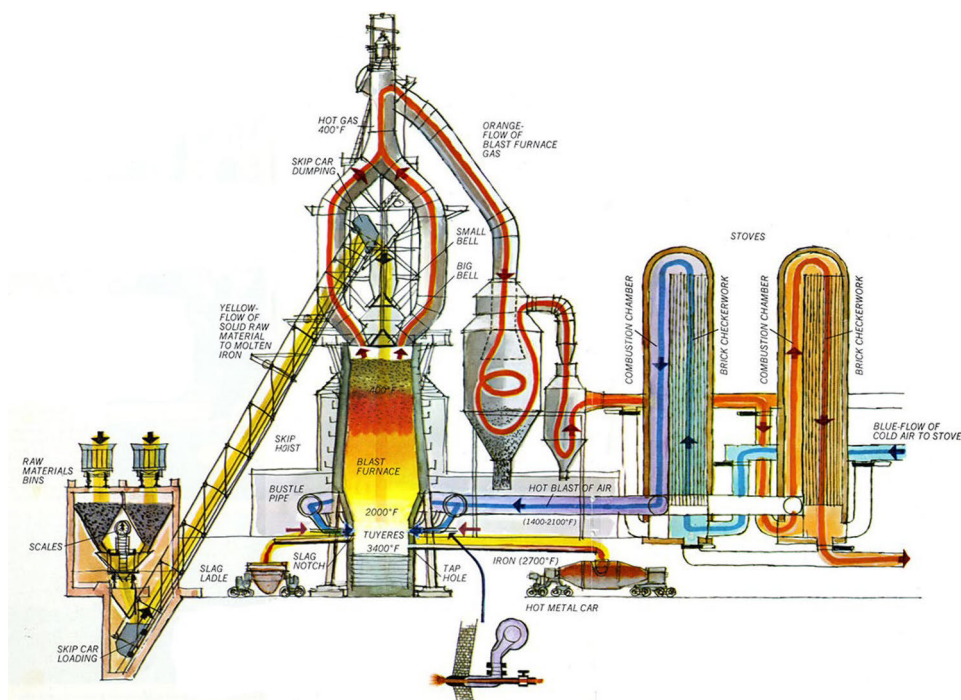


Figure 1.1 Blast furnace plant scheme.¹³

The interaction between oxygen, coke, and injected hydrocarbons leads to the partial combustion of carbon, which not only enables the formation of carbon monoxide (CO) but also provides heat for furnace operation. The CO produced acts as a reactant, allowing the removal of oxygen from iron oxides until their complete reduction to metallic iron. As can be imagined, this inevitably leads to the formation of carbon dioxide (CO₂). This section of the production chain is responsible for around 70% of the steel industry's CO₂ emissions.¹⁶ The entire production process is extremely complex and also includes the formation of slag, which consists of inorganic byproducts and molten iron separated due to density differences in the furnace hearth.¹⁷

The molten iron, containing dissolved carbon, is sent to the BOF, where pure oxygen is blown onto the liquid surface. This process reduces the carbon content

¹⁶ C. C. Xu and D. Cang, 'A brief overview of low CO₂ emission technologies for iron and steel making', *Journal of Iron and Steel Research International*, 17/3 (2010), 1–7.

¹⁷ R. Dippenaar, 'Industrial uses of slag (the use and re-use of iron and steelmaking slags)', *Ironmaking and Steelmaking*, 32/1 (2005), 35–46.

of the alloy, allowing the desired carbon fraction in the steel to be achieved, which determines its mechanical properties.¹⁸ Simultaneously, the temperature rises, which is necessary since the melting point of steel is much higher than that of hot metal due to the lower carbon content. From this perspective, the role of coke is essential, as it ensures sufficient carbon content in the hot metal (above 4%) before BOF treatment and, crucially, maintains the gas and liquid permeability of the BF by providing coke slits in the cohesive zone and a permeable dead man in the hearth.¹⁹

Another steel production process parallel to BF–BOF is the electric arc furnace (EAF). In this process, steel is produced exclusively by melting scrap. EAF is the most important scrap recycling process. On a global scale, steel produced through EAF accounts for 25%.²⁰ This overview makes it clear that a chemical alternative to CO is required to reduce CO₂ emissions.

As an alternative, the Direct Reduction (DR) process replaces coal as the primary reducing agent and produces a solid product, called direct reduced iron (DRI) or sponge iron, by solid–gas reactions at considerably lower temperatures (i.e., 800–1200 °C) than in the BF.²¹ This process, carried out in a Shaft Furnace (SF) coupled with an EAF, enables the production of iron using mixtures of reducing gases (e.g., H₂ and CO) that remove oxygen from iron ore in its solid state. The concept behind this process originated in the 1960s due to the lack of coal in areas rich in iron ore. For this purpose, natural gas was used as the source of energy and reductants through reforming processes.

The fundamental difference between BF–BOF and SF–EAF lies in the reactants used and overall energy efficiency. It is estimated that using the SF–EAF process route can reduce CO₂ emissions by half compared to the BF–BOF process, with an estimated value of about 0.97 tCO₂ per tSteel.²² This technology encompasses various processes based on different feedstocks, reactors, and reducing agents. Furnaces using standard gas-based direct reduction consist of three parts: an

¹⁸ T. S. Naidu, C. M. Sheridan, and L. D. van Dyk, 'Basic oxygen furnace slag: Review of current and potential uses', *Minerals Engineering*, 149 (2020), 106234.

¹⁹ Y. Pan, H. Zuo, J. Wang, Q. Xue, G. Wang, and X. She, 'Review on improving gas permeability of blast furnace', *Journal of Iron and Steel Research International*, 27/2 (2020), 121–31.

²⁰ P. Cavaliere, 'Blast Furnace: Most Efficient Technologies for Greenhouse Emissions Abatement', *Clean Ironmaking and Steelmaking Processes*, (Cham: Springer International Publishing, 2019), pp. 167–273.

²¹ B. L. Hans and S. Peter, *History, developments and processes of direct reduction of iron ores*, (2022).

²² J. Ling, H. Yang, G. Tian, J. Cheng, X. Wang, and X. Yu, 'Direct reduction of iron to facilitate net zero emissions in the steel industry: A review of research progress at different scales', *Journal of Cleaner Production*, 441 (2024), 140933.

upper part with a pellet charging system, a middle part with a reaction zone and a reducing gas charging system, and a lower part containing a cooling and carburization zone, and discharge systems.²³ Figure 1.2 displays a typical layout of a direct reduction reactor.

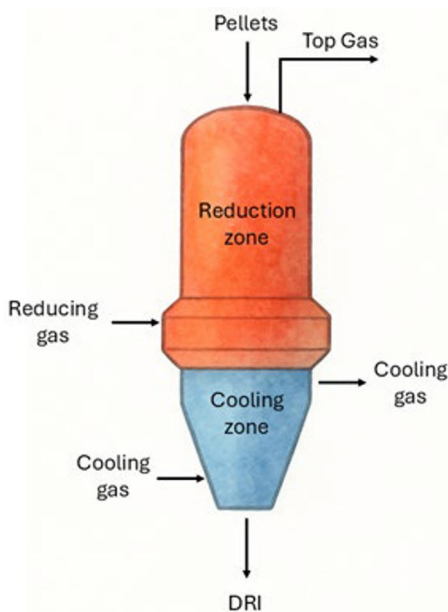


Figure 1.2 Shaft Furnace scheme.

Midrex²⁴ and HYL-III²⁵ are examples of industrially operated DR processes that use SF as a reactor. In general, the HYL-III process operates with twice the $H_2:CO$ ratio of Midrex and under higher temperature and pressure conditions. Other examples of industrial DR processes are Circored²⁶ and Finmet²⁷, which use fluidized beds (FB) as reactors. The differences between these systems and the previous ones lie not only in the source of the reductant gas but mainly in the

²³ B. Anameric and S. K. Kawatra, 'Properties and features of direct reduced iron', *Mineral Processing and Extractive Metallurgy Review*, 28/1 (2007), 59–116.

²⁴ Atsushi M., Uemura H., and Sakaguchi T., *MIDREX process*, (2010).

²⁵ M. Ahmed, M. Shahin, M. Elzeky, and M. Ahmed, 'Effect of HYL Process Parameters on the Quality of Iron Ore Reduction', *Journal of Petroleum and Mining Engineering*, 18/1 (2016), 54–60.

²⁶ D. Nuber, H. Eichberger, and B. Rollinger, *Circored fine ore direct reduction*, (2006).

²⁷ S. Parvathaneni, B. Kodukula, and M. W. Andrade, 'Iron-Ore Reduction in Fluidized Beds: Review of Commercial Technologies, Status, and Challenges', *Industrial & Engineering Chemistry Research*, 63/44 (2024), 18724–33.

type of reactor used. A comparison between different DR processes and BF is provided in Table 1.1.^{28 29}

Table 1.1 Comparison of DR and BF processes.^{28 29}

	Midrex	HYL III	Circored	Finmet	Classic process
Reactor	SF – EAF (External reformer)	SF	Circular FB	Multi FB (External reformer)	BF
Feed	Lump and/or pellets	Lump and/or pellets	Fine ore	Fine ore	Coke, sinter 70%, pellet 20, lump 10%
Reductant	Reforming syngas (55% H ₂ , 36% CO)	Syngas + CH ₄	100% H ₂	Reforming syngas	In situ partial combustion CO
Temperature [°C]	750 – 1000	930 – 1050	630 – 650	400 – 800	1200 – 2000 Regional thermal profile
Energy consumption [GJ/tDRI]	10.4	9.4 – 11.2	~11.5	14	~24
CO₂ emission [tCO₂/ tSteel]	1	0.2 - 0.5	0	~1	~2.3

As can be observed, in terms of direct emissions solely from the reactors, it is estimated that in this H₂-based production chain the amount of CO₂ could be further reduced to about 0.2–0.5 tCO₂ per tSteel in the best-case scenario, with total emissions reduced by 89–97%.³⁰ This reduction is due not only to the use of H₂ but also to the possibility of operating at temperatures significantly lower than those in the conventional process.

As previously mentioned, the percentage of steel produced by these alternative industrial routes remains negligible compared to the demands of the modern market. This becomes even more evident when estimating the considerable

²⁸ P. Cavaliere, 'Direct Reduced Iron: Most Efficient Technologies for Greenhouse Emissions Abatement', Clean Ironmaking and Steelmaking Processes, (Springer International Publishing, 2019), pp. 419–84.

²⁹ H. Y. Sohn, 'Energy Consumption and CO₂ Emissions in Ironmaking and Development of a Novel Flash Technology', *Metals*, 10/1 (2019), 54.

³⁰ V. Vogl, M. Åhman, and L. J. Nilsson, 'Assessment of hydrogen direct reduction for fossil-free steelmaking', *Journal of Cleaner Production*, 203 (2018), 736–45.

amounts of hydrogen required for the transition, estimated at about 70,000 m³ STP/h for 1 million tSteel per year.³¹

The challenges associated with hydrogen use are well known, including safety (i.e., wide flammability range), transport and storage,³² low volumetric energy density, and costs (green H₂: 9–10 €/kg; grey H₂: <2 €/kg).³³ It is also evident that the enormous amount of hydrogen required is far beyond any current production capacity. From this perspective, the overall scenario could become even more complex if other industrial sectors also turned to hydrogen, for example, as a simple energy carrier.³⁴ Even in such a scenario, it has been predicted that by 2050 the steel sector will still be the main consumer of hydrogen and will be 18–50% dependent on hydrogen by that time.³⁵

For this reason, the only viable solution is for transition-friendly policies to support the scientific community and industrial companies in working together to improve the efficiency and continuous applicability of green electrolysis, or chemical loop technologies.³⁶ In this context, the ULCOS (i.e., Ultra-Low CO₂ Steelmaking) program was launched in Europe during the 2000s, with the goal of evaluating the entire hydrogen-based pathway for steel production.³⁷ The project also includes other possible alternatives such as iron oxide electrolysis and carbon capture storage. Several industrial initiatives are investing time and

³¹ F. Patisson, O. Mirgaux, and J. P. Birat, 'Hydrogen steelmaking. Part 1: Physical chemistry and process metallurgy', *Materiaux et Techniques*, (EDP Sciences, 2021).

³² H. Nazir, N. Muthuswamy, C. Louis, S. Jose, J. Prakash, M. E. Buan, C. Flox, S. Chavan, X. Shi, P. Kauranen, T. Kallio, G. Maia, K. Tammeveski, N. Lympieropoulos, E. Carcadea, E. Veziroglu, A. Iranzo, and A. M. Kannan, 'Is the H₂ economy realizable in the foreseeable future? Part II: H₂ storage, transportation, and distribution', *International Journal of Hydrogen Energy*, 45/41 (2020), 20693–708.

³³ H. Nazir, C. Louis, S. Jose, J. Prakash, N. Muthuswamy, M. E. M. Buan, C. Flox, S. Chavan, X. Shi, P. Kauranen, T. Kallio, G. Maia, K. Tammeveski, N. Lympieropoulos, E. Carcadea, E. Veziroglu, A. Iranzo, and A. M. Kannan, 'Is the H₂ economy realizable in the foreseeable future? Part I: H₂ production methods', *International Journal of Hydrogen Energy*, 45/27 (2020), 13777–88.

³⁴ M. A. Rosen and S. Koohi-Fayegh, 'The prospects for hydrogen as an energy carrier: an overview of hydrogen energy and hydrogen energy systems', *Energy, Ecology and Environment*, 1/1 (2016), 10–29.

³⁵ A. Sgobbi, W. Nijs, R. De Miglio, A. Chiodi, M. Gargiulo, and C. Thiel, 'How far away is hydrogen? Its role in the medium and long-term decarbonisation of the European energy system', *International Journal of Hydrogen Energy*, 41/1 (2016), 19–35.

³⁶ W. Liu, J. Y. Lim, M. A. Saucedo, A. N. Hayhurst, S. A. Scott, and J. S. Dennis, 'Kinetics of the reduction of wüstite by hydrogen and carbon monoxide for the chemical looping production of hydrogen', *Chemical Engineering Science*, 120 (2014), 149–66.

³⁷ K. Meijer, M. Denys, J. Lasar, J.-P. Birat, G. Still, and B. Overmaat, 'ULCOS: ultra-low CO₂ steelmaking', *Ironmaking & Steelmaking*, 36/4 (2009), 249–51.

resources in the development of pilot plants combining large-scale green electrolysis facilities with DRI production units (i.e., HYBRIT, H₂ Green Steel).³⁸

The transition could also involve the use of H₂ in traditional steelmaking plants. The increased use of hydrogen as a reductant in BF_s has led to intense debate in the metallurgical sector. This raises several questions, particularly regarding the delicate balance of reducing agents and the safety of systems not designed to use hydrogen at temperatures above 2000 °C.³⁹ In addition to safety concerns, certain phenomena require further investigation in both kinetic and thermodynamic terms. The endothermic nature of hydrogen reduction must be considered, as it negatively affects the energy balance of the furnace and requires an external energy input.⁴⁰

Another relevant point is that the morphological evolution of the solid during reduction appears to differ significantly when using H₂ compared to CO, which can be attributed to the higher diffusivity of hydrogen within the solid.⁴¹ Furthermore, the effect of water vapor, especially during the rapid initial reduction step, should be investigated in more detail. Other important aspects are the possible effects on coke and its gasification rate, as well as on the permeability and temperature of the burden bed, including the cohesive zone.⁴²

Several studies propose simulations in which hydrogen is used as an auxiliary reductant injected with the hot blast as a partial or total substitute for pulverized coal.⁴³ Using a maximum hydrogen content not exceeding 20 vol%, lower CO₂ and slag production, better bed permeability, and improved slag properties were observed. Various authors have conducted detailed modelling studies on the introduction of H₂ in BF to evaluate different operating conditions and energy

³⁸ M. Åhman, O. Olsson, V. Vogl, B. Nyqvist, A. Maltais, L. J. Nilsson, K. Hallding, K. Skånberg, and M. Nilsson, *Hydrogen steelmaking for a low-carbon economy A joint LU-SEI working paper for the HYBRIT project*, (2018).

³⁹ F. Mauret, M. Baniasadi, H. Saxén, A. Feiterna, and S. Hojda, 'Impact of Hydrogenous Gas Injection on the Blast Furnace Process: A Numerical Investigation', *Metallurgical and Materials Transactions B*, 54/4 (2023), 2137–58.

⁴⁰ Y. Zhai, L. Shao, C. Zhao, X. Zhang, and H. Saxén, 'A Numerical Study of the Thermochemical and Aerodynamic States of H₂ -intensive Direct Reduction Shaft Furnace', *steel research international*, (2024).

⁴¹ D. Spreitzer and J. Schenk, 'Reduction of Iron Oxides with Hydrogen—A Review', (2019).

⁴² F. Chen, Y. Mohassab, T. Jiang, and H. Y. Sohn, 'Hydrogen Reduction Kinetics of Hematite Concentrate Particles Relevant to a Novel Flash Ironmaking Process', *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 46/3 (2015), 1133–45.

⁴³ Y. Qie, Q. Lyu, C. Lan, S. Zhang, and R. Liu, 'Effect of H₂ addition on process of primary slag formation in cohesive zone', *Journal of Iron and Steel Research International*, 27/2 (2020), 132–40.

requirements.⁴⁴ However, it is evident that hydrogen can only partially substitute coke and cannot entirely replace it in conventional blast furnace processes. Several alternative approaches have been proposed; for example, some authors have suggested the use of ammonia as a green energy carrier. The concept relies on producing hydrogen in situ and employing different process configurations to enhance the overall efficiency of the system.⁴⁵

1.3 Iron and iron oxide

Iron is the fourth most abundant element on Earth. Over 300 minerals contain iron, but the main sources of iron ore containing oxygen are hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite, and maghemite (i.e., allotropes of hematite).⁴⁶ Among these, the first three are of major importance due to their occurrence in large, economically mineable quantities.⁴⁷ An overview of the presence of oxygen in the lattice is provided by the Fe–O phase diagram (i.e., oxygen content in mol % vs. temperature) in Figure 1.3 (data extracted from FactSage 8.2).⁴⁸

This diagram depicts the various stability regions of pure and mixed solid phases, including different allotropes and liquid phases. It is well known that above 570 °C, the Fe–O phase diagrams display the presence of a eutectoid point from which the stability region of FeO originates and expands with increasing temperature. In the literature, wüstite is commonly denoted as Fe_{1-x}O , reflecting that the iron–oxygen ratio is not strictly constant or exactly equal to unity.⁴⁹ Structurally, hematite, magnetite, and wüstite exhibit well-defined elementary cells that can be distinguished using X-ray diffraction (XRD).⁵⁰ Figure 1.4 displays the crystal structures of the three oxides together with their lattice parameters. Table 1.2

⁴⁴ V. Shatokha, 'Modeling of the effect of hydrogen injection on blast furnace operation and carbon dioxide emissions', *International Journal of Minerals, Metallurgy and Materials*, 29/10 (2022), 1851–61.

⁴⁵ F. Mauret, J. Ji, P. Kinzel, H. Saxén, and M. Baniyadi, 'Ammonia as a Green Energy Carrier to Lower Blast Furnace CO_2 Emissions', *ISIJ International*, 65/5 (2025), ISIJINT-2025-041.

⁴⁶ M. Yellishetty, P. G. Ranjith, and A. Tharumarajah, 'Iron ore and steel production trends and material flows in the world: Is this really sustainable?', *Resources, Conservation and Recycling*, 54/12 (2010), 1084–94.

⁴⁷ US EPA. Extraction and beneficiation of ores and minerals, Technical Resource Document Iron Extraction And Beneficiation Of Ores And Minerals Volume 3 .

⁴⁸ C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. E. Gheribi, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M.-A. Van Ende, 'FactSage Thermochemical Software and Databases - 2010 - 2016', (2016).

⁴⁹ L. S. Darken and R. W. Gurry, 'The System Iron-Oxygen. I. The Wüstite Field and Related Equilibria', *Journal of the American Chemical Society*, 67/8 (1945), 1398–1412.

⁵⁰ F. Izumi and K. Momma, 'VESTA, Three-dimensional Visualization in Powder Diffraction', *Proc. XX Conf. Appl. Crystallogr., Solid State Phenom.*, (2007), 15–20.

provides a summary of the crystallographic parameters for the unit cell of the three oxides, as well as for the allotropic form of iron.

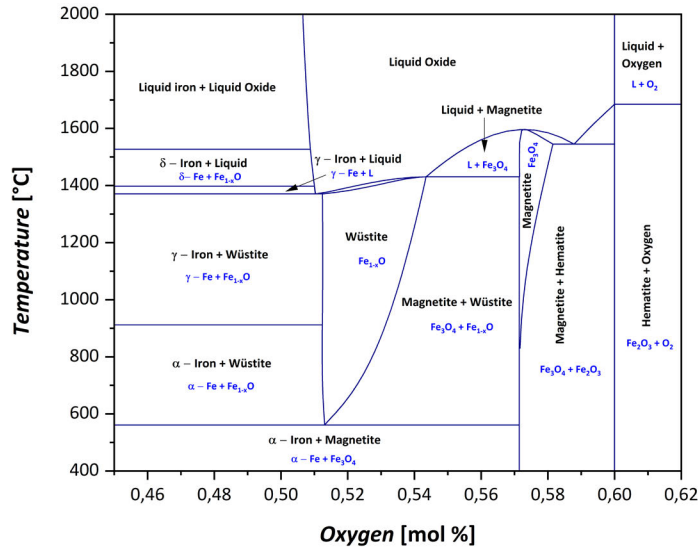


Figure 1.3 Fe–O phase diagram (FactSage 8.2).⁴⁸

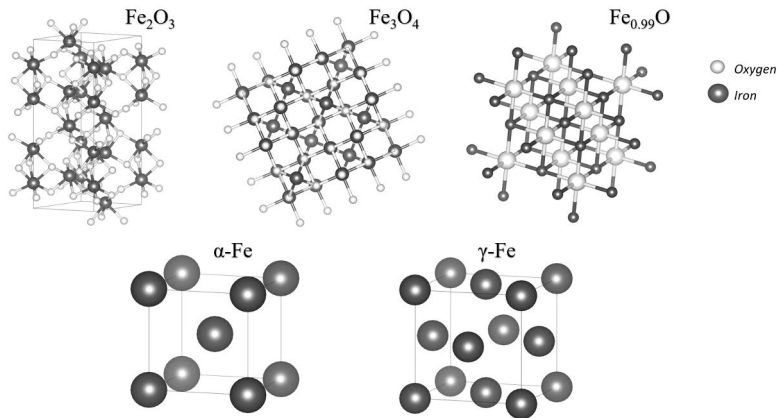


Figure 1.4 Crystal structure of the unit cells of Fe_2O_3 , Fe_3O_4 , Fe_{1-x}O , $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$.⁵⁰

Table 1.2 Resume of crystallographic parameters of Iron and Iron oxides.⁵⁰

Fe ₂ O ₃				Fe ₃ O ₄				Fe _{0.99} O			
R-3c				Fd-3m				R-3c			
a	5.035	α	90°	a	8.396	α	90°	a	4.310	α	90°
b	5.035	β	90°	b	8.396	β	90°	b	4.310	β	90°
c	13.754	γ	120°	c	8.396	γ	90°	c	4.310	γ	90°
α-Fe				γ-Fe							
R-3c				R-3c							
a	2.865	α	90°	a	3.581	α	90°				
b	2.865	β	90°	b	3.581	β	90°				
c	2.865	γ	90°	c	3.581	γ	90°				

Hematite has a trigonal crystal system and typically crystallizes in the rhombohedral R3c structure. Fe³⁺ cations occupy octahedral sites, while the oxygen lattice consists of compact hexagonal arrays. Magnetite has an isometric crystal system and crystallizes in octahedral and mixed tetrahedral/octahedral layers (Fd3m). The inverse spinel structure contains Fe³⁺ and Fe²⁺ ions, which occupy both tetrahedral and octahedral interstitial sites. Wüstite also exhibits an isometric crystal system and crystallizes in a hexoctahedral structure (C2/m). The compact cubic matrix contains anionic sites occupied by O²⁻, while the cationic sites are occupied by Fe²⁺ in octahedral interstices. Iron can assume the α or γ allotropic form depending on the operating temperature (with the γ form occurring at temperatures above 912 °C), and this phenomenon is often crucial due to the different density of the reduced metal, which can have a very negative impact on the reduction process.⁵¹

⁵¹ A. A. El-Geassy and V. Rajakumar, 'Influence of particle size on the gaseous reduction of wüstite at 900-1100.DEG.C.', *Transactions of the Iron and Steel Institute of Japan*, 25/12 (1985), 1202–11.

1.3.1 Iron ore

Most iron ore is mined in open-pit mines worldwide, transported by rail to dedicated ports, and then shipped to steel mills, mainly in Asia and Europe. Table 1.3 shows global iron ore production and import/export data.⁵²

Currently, China is clearly driving global demand for iron ore, as it is the largest and fastest-growing market for seaborne iron ore trade. Following in its footsteps are other developing countries such as Brazil, Russia, and Ukraine.

The notable increase in steel production over the last twenty years is mainly due to China's expansion in the metallurgical market. Comparing iron ore consumption in Europe and America over the same period reveals that steel production has slightly decreased. This suggests that China has filled a market gap that has emerged in the past two decades, during which several new industrial entities have begun to flourish.⁵³ Moreover, markets such as Australia are now considering processing locally the enormous quantity of iron ore produced annually, which is currently mostly exported. This development, in the absence of pre-existing facilities, could strongly drive the production of high-quality green iron.⁵⁴

Regarding gangue minerals, the samples mainly contain quartz (SiO_2), gibbsite, or generally alumina (Al_2O_3), along with other compounds such as oxides of magnesium, manganese, calcium, and small amounts of phosphorus (P) and sulfur (S).⁵⁵ One of the crucial characteristics that differentiates the classical process from direct reduction processes is precisely related to the quality of the raw material. In the BF, the quality of the material can be relatively low, but the presence of gangue can still cause several problems, such as an increase in the viscosity of the slag produced (e.g., aluminum content) and a deterioration of the steel properties (e.g., sulfur content).^{56 57}

⁵² World Steel Association, *2024 World Steel in Figures*, (2024).

⁵³ A. Dyczko, 'Production management system in a modern coal and coke company based on the demand and quality of the exploited raw material in the aspect of building a service-oriented architecture', *Journal of Sustainable Mining*, 22/1 (2023), 2–19.

⁵⁴ G. Brooks, P. H. Jensen, S. Petrie, and E. Webster, 'Can Australia Become a Green Iron Powerhouse?', *Australian Economic Review*, 57/4 (2024), 413–21.

⁵⁵ Liming Lu, *Iron Ore*, (Elsevier, 2015).

⁵⁶ S. Mahiuddin, S. Bondyopadhyay, and J. N. Baruah, 'A study on the beneficiation of indian iron-ore fines and slime using chemical additives', *International Journal of Mineral Processing*, 26/3–4 (1989), 285–96.

⁵⁷ M. P. Srivastava, S. K. Pan, N. Prasad, and B. K. Mishra, 'Characterization and processing of iron ore fines of Kiriburu deposit of India', *International Journal of Mineral Processing*, 61/2 (2001), 93–107.

Table 1.3 Iron ore production and import/export in the world.⁵⁴

Region	Production (Mt)	Exports (Mt)	Imports (Mt)	Apparent consumption (Mt)
France	–	0.1	11.2	11.1
Germany	1.2	0.9	33.4	33.8
Netherlands	–	16.9	24.4	7.5
Sweden	29.2	27.1	0	2.2
Other EU	3	0.7	32.9	29.1
European Union (27)	36.4	46.3	104.1	95.8
Turkey	7.9	2.2	9.9	15.6
United Kingdom	–	0	7.1	7.1
Other Europe	3	1.8	1.4	2.6
Europe	47.2	51.5	120.3	116.1
Russia & Other CIS + Ukraine	203.1	86.1	8.2	125.2
Canada	58.8	55.1	7.1	10.7
Mexico	11.4	1.9	1.5	11
United States	38.6	10.4	5.2	33.3
USMCA	108.7	67.5	13.7	55
Brazil	391	342.6	0.2	48.6
Chile	15	17	0.2	-1.8
Peru	8.9	11.6	0	-2.8
Central & South America	418.4	374.0	10.6	55.0
Mauritania	13.5	14.1	–	-0.6
South Africa	69	65.5	0	3.5
Other Africa	5.7	0.5	23.2	28.4
Africa	98.4	90.2	23.2	31.4
Middle East	53.6	10.4	25.1	68.3
China	270.5	15.6	1170.4	1425.2
India	203.8	52	0.7	152.5
Japan	–	0	99.4	99.4
South Korea	0.3	0.3	70.4	70.5
Other Asia	17.9	40.9	78.9	55.9
Asia	492.6	108.8	1419.8	1803.6
Australia	922.5	873	0.9	50.4
World	2342.2	1659.0	1616.8	2300.0

In DR, only high-grade ores are fed into the reactors to minimize the effects of impurities on the system, since the downstream EAF process can only handle moderate amounts of slag. Table 1.4 shows examples of iron ore composition by weight (Article I).

Table 1.4 Composition in percent by weight of Fe content and of the gangues in ferrous minerals (Article I).

Country	Ore Quality	Fe [%]	SiO ₂ [%]	Al ₂ O ₃ [%]	S [%]	P [%]
Brazil	H	68.9	0.35	0.6	0.01	0.03
Brazil	H	67.3	0.79	0.72	0.005	0.037
China	M	63.4	6.28	1.17	0.11	-
Australia	M	62.7	4.2	2.73	0.016	0.059
Australia	L	54.4	21.3	0.23	0.04	0.01
India	L	57.8	2.5	6.5	0.02	0.04
India	M	64	2.5	2.5	0.05	0.1
Russia	M	60.7	2.4	2	0.03	0.004
Russia	L	52.2	10.1	1.25	0.1	0.6
USA	L	57.5	10.1	0.7	0.01	0.06
USA	M	63	8.1	0.4	0.003	0.025

As can be seen, the purity of the ore and the proportion of other compounds vary depending on the extraction location, leading to large fluctuations in ore composition. Iron ore is characterized by its Fe content and is classified as high (H), low (L), or medium (M) depending on whether its mass percentage is above 65%, below 55%, or between these values, respectively.

1.4 Reduction

The reduction of iron oxides using CO or H₂ as reducing agents occurs gradually. Generally, the reduction begins with hematite (Fe₂O₃), the most abundant iron oxide on Earth, and proceeds through intermediate oxides before metallic iron (Fe) is obtained. Industrially, the reduction takes place via a series of reversible steps from Fe₂O₃ to magnetite (Fe₃O₄), then to wüstite, and finally to metallic iron (Fe).⁵⁸ The number of intermediate reactions depends on the operating

⁵⁸ W. Zhang, J. Zhang, Q. Li, Y. He, B. Tang, M. Li, Z. Zhang, and Z. Zou, 'Thermodynamic Analyses of Iron Oxides Redox Reactions', Proceedings of the 8th Pacific Rim International Congress on Advanced Materials and Processing, (Cham: Springer International Publishing, 2013), pp. 777–89.

temperature. In particular, the final reactive step may involve the reduction of wüstite to metallic iron if the temperature is above 570 °C, or, conversely, a direct reduction from Fe_3O_4 to Fe. Generally, wüstite is represented by the molecular formula Fe_{1-x}O , due to the non-stoichiometric ratio between iron and oxygen. However, for simplicity, this chemical species will be referred to as FeO.

Therefore, the atomic interactions between reducing species and the solid surface include the reactive network of two- or three-step reactions, the mass and electron transport of redox reactions through the solid medium, and the resulting interactions and crystallographic changes of the unit cell. As is well known, gas–solid reactions occur mainly at sites of high reactivity formed by structural defects.⁵⁹ Figure 1.5 (Article I) shows the reaction scheme of an atomic model of the interface systems hematite/magnetite,⁶⁰ and wüstite/iron.⁶¹

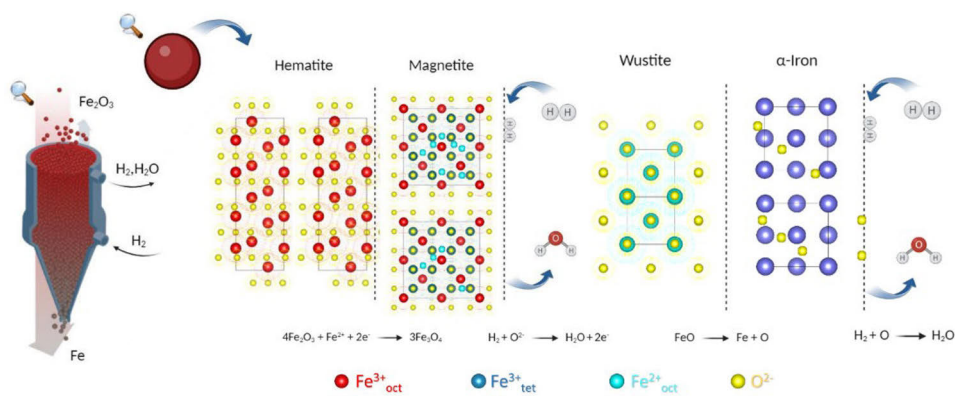


Figure 1.5 Atomic model surface reduction mechanism (Article I).

The hydrogen reduction proceeds via dissociative adsorption on oxide surfaces: the first H_2 forms surface hydroxide ions by abstracting lattice oxygen, and the second H completes H_2O formation and release. These steps are coupled with electron release and transport required for reduction. The rate depends on the

⁵⁹ R. Dieckmann, 'Point defects and transport in non-stoichiometric oxides: Solved and unsolved problems', *Journal of Physics and Chemistry of Solids*, 59/4 (1998), 507–25.

⁶⁰ C. Feilmayr, A. Thurnhofer, F. Winter, H. Mali, and J. Schenk, 'Reduction Behavior of Hematite to Magnetite under Fluidized Bed Conditions', *ISIJ International*, 44/7 (2004), 1125–33.

⁶¹ S. H. Kim, X. Zhang, Y. Ma, I. R. Souza Filho, K. Schweinar, K. Angenendt, D. Vogel, L. T. Stephenson, A. A. El-Zoka, J. R. Mianroodi, M. Rohwerder, B. Gault, and D. Raabe, 'Influence of microstructure and atomic-scale chemistry on the direct reduction of iron ore with hydrogen at 700°C', *Acta Materialia*, 212 (2021).

near-surface gas composition and surface diffusion at defects or pores.⁶² In hematite/magnetite systems, Fe^{2+} accumulates in Fe_3O_4 and migrates with electrons to the oxide/oxide interface; a similar scheme describes FeO formation at the magnetite/wüstite interface. Generally, it is reported that the FeO–Fe step is kinetically rate-limiting.⁶³

This evidence lies in the morphological changes occurring at elevated temperatures. Dense γFe shells form by sintering or partial melting, blocking microporosity and shifting control to solid state diffusion.⁶⁴ Under solid state diffusion, oxygen diffuses from the wüstite/Fe interface through the metal lattice to the surface where H_2 is present.⁶⁵ From another perspective, lattice oxygen removal creates vacancies and defects as well as unit-cell rearrangements that enhance reactivity.⁶⁶

Chemically, the reaction network does not differ significantly between hydrogen and carbon monoxide, but it becomes more complex in the case of mixtures of reducing gases, as occurs, for example, in the MIDREX process, where a precise percentage of syngas is used. Table 1.5 shows the complete reactive network of the reduction process, with the enthalpies calculated at a potential operating temperature (i.e., 800 °C) in the simultaneous presence of H_2 and CO.

As shown, the reduction with CO at 800 °C is overall exothermic, while the reduction with H_2 at the same temperature is overall endothermic. Therefore, if only hydrogen is used as the reductant, additional energy must be supplied to the system to maintain a sufficiently high operating temperature.⁶⁷

To carefully evaluate the thermodynamics of the complex reactive network and to facilitate understanding of the reduction phenomenon in the presence of H_2 or CO, the Chaudron diagram—also known as the Baur–Glässner diagram—is useful.

⁶² J. O. Edstrom, 'The mechanism of reduction of iron oxides.', *J. Iron Steel Inst.*, 175/289 (1953).

⁶³ A. Heidari, N. Niknahad, M. Iljana, and T. Fabritius, 'A review on the kinetics of iron ore reduction by hydrogen', (2021).

⁶⁴ D. Spreitzer and J. Schenk, 'Fluidization behavior and reducibility of iron ore fines during hydrogen-induced fluidized bed reduction', *Particuology*, 52 (2020), 36–46.

⁶⁵ R. J. Fruehan, Y. Li, L. Brabie, and E. Kim, 'Final stage of reduction of iron ores by hydrogen', *Scandinavian Journal of Metallurgy*, 34/3 (2005), 205–12.

⁶⁶ Y. Watanabe, S. Takemura, Y. Kashiwaya, and K. Ishii, 'Reduction of haematite to magnetite induced by hydrogen ion implantation', *Journal of Physics D: Applied Physics*, 29/1 (1996), 8–13.

⁶⁷ O. Hessling, J. B. Fogelström, N. Kojola, and D. Sichen, 'The Effect of the Endothermic Reaction Nature on the Iron Ore Pellet Reduction Using Hydrogen', *Metallurgical and Materials Transactions B*, 53/2 (2022), 1258–68.

The diagram in Figure 1.6 displays the equilibrium curves of reactions 1–9 and allows determination of the stability ranges of the different solid species.⁴⁸

Table 1.5 Reaction network in the presence of H₂ or/and CO and reaction enthalpies (FactSage 8.2).⁴⁸

	Reductions/reactions	$\Delta H_r^{800^\circ\text{C}}$ [kJ/mol Fe]
(1)	$3\text{Fe}_2\text{O}_{3(s)} + \text{H}_{2(g)} \rightleftharpoons 2\text{Fe}_3\text{O}_{4(s)} + \text{H}_2\text{O}_{(g)}$	–1
(2)	$\text{Fe}_3\text{O}_{4(s)} + \text{H}_{2(g)} \rightleftharpoons 3\text{FeO}_{(s)} + \text{H}_2\text{O}_{(g)}$	+17
(3)	$\text{FeO}_{(s)} + \text{H}_{2(g)} \rightleftharpoons \text{Fe}_{(s)} + \text{H}_2\text{O}_{(g)}$	+16
(4) *	$\text{Fe}_3\text{O}_{4(s)} + 4\text{H}_{2(g)} \rightleftharpoons 3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)}$	+33
(5)	$3\text{Fe}_2\text{O}_{3(s)} + \text{CO}_{(g)} \rightleftharpoons 2\text{Fe}_3\text{O}_{4(s)} + \text{CO}_{2(g)}$	–7
(6)	$\text{Fe}_3\text{O}_{4(s)} + \text{CO}_{(g)} \rightleftharpoons 3\text{FeO}_{(s)} + \text{CO}_{2(g)}$	+6
(7)	$\text{FeO}_{(s)} + \text{CO}_{(g)} \rightleftharpoons \text{Fe}_{(s)} + \text{CO}_{2(g)}$	–18
(8) *	$\text{Fe}_3\text{O}_{4(s)} + 4\text{CO}_{(g)} \rightleftharpoons 3\text{Fe}_{(s)} + 4\text{CO}_{2(g)}$	–5
(9) **	$2\text{CO}_{(g)} \rightleftharpoons \text{C}_{(s)} + \text{CO}_{2(g)}$	–85
(10) ***	$3\text{Fe}_{(s)} + \text{C}_{(s)} \rightleftharpoons \text{Fe}_3\text{C}_{(s)}$	+7
(11) ***	$3\text{Fe}_{(s)} + \text{CO}_{(g)} \rightleftharpoons \text{Fe}_3\text{C}_{(s)} + \text{CO}_{2(g)}$	–50
(12) ***	$3\text{FeO}_{(s)} + 5\text{CO}_{(g)} \rightleftharpoons \text{Fe}_3\text{C}_{(s)} + 4\text{CO}_{2(g)}$	–68
(13) ***	$\text{Fe}_3\text{C}_{(s)} + 2\text{FeO}_{(s)} \rightleftharpoons 5\text{Fe} + \text{CO}_{2(g)}$	–7
(14)	$\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_{2(g)}$	–34
(15)	$\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{H}_{2(g)} + \text{CO}_{(g)}$	+136
(16)	$3\text{Fe}_{(s)} + \text{H}_{2(g)} + \text{CO}_{(g)} \rightleftharpoons \text{Fe}_3\text{C}_{(s)} + \text{H}_2\text{O}_{(g)}$	–111
(17)	$\text{CO}_{(g)} + 3\text{H}_{2(g)} \rightleftharpoons \text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)}$	–226
(18)	$2\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_{4(g)} + \text{CO}_{2(g)}$	–130
(19)	$\text{Fe}_2\text{O}_{3(s)} + 3\text{CH}_{4(g)} \rightleftharpoons 2\text{Fe}_{(s)} + 6\text{H}_{2(g)} + 3\text{CO}_{(g)}$	+737
(20)	$3\text{Fe}_{(s)} + \text{CH}_{4(g)} \rightleftharpoons \text{Fe}_3\text{C}_{(s)} + 2\text{H}_{2(g)}$	+37

* Replacement reaction of the two previous steps: direct reduction of Fe₃O₄ to Fe, $T < 570^\circ\text{C}$

** Secondary reaction: reverse Boudouard reaction, suggested enthalpy values are in kJ/mol C

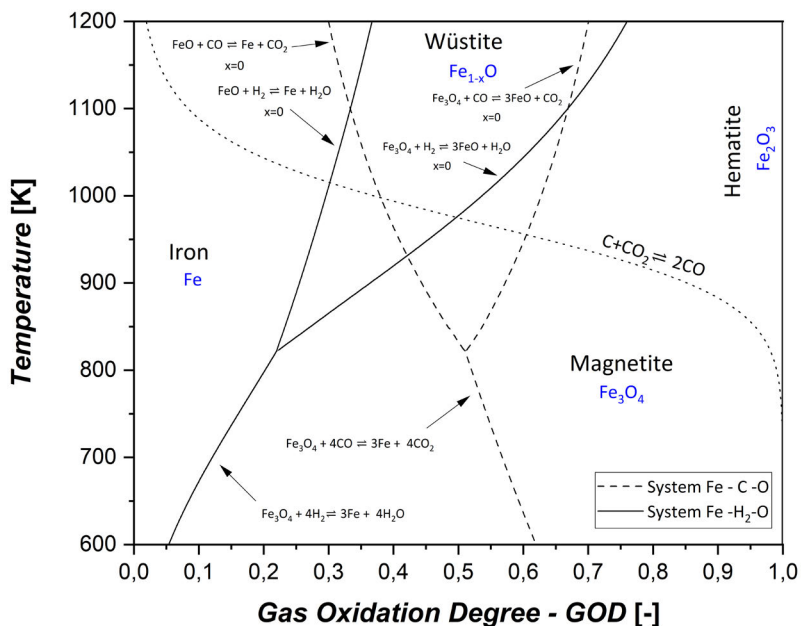


Figure 1.6 Chaudron (Baur-Glässner) thermodynamic diagram (FactSage 8.2).⁴⁸

These curves are derived from the equilibrium compositions of the reductant/oxidant mixture at the operating temperature. The abscissa represents the Gas Oxidation Degree (GOD), defined as the molar ratio of the oxidizing species to the sum of the oxidizing and reducing agents in the mixture; in the simple $\text{H}_2\text{-H}_2\text{O}$ or CO-CO_2 case (with no inert), this equals the molar fraction of H_2O or CO_2 . GOD thus represents the gas in contact with the solid—the thermodynamic driving force: $\text{GOD} = 1$ indicates no reduction, while $\text{GOD} = 0$ implies strongly reducing conditions.

Notably, the Fe_2O_3 stability field is essentially absent with H_2 or CO (its curve is nearly vertical at $\text{GOD} \approx 1$), implying that hematite tends to reduce to magnetite even with minimal reductant present. Analysis of the Fe_3O_4 and FeO regions shows that below approximately 800°C , CO requires less reductant for full conversion; at around 800°C , H_2 and CO behave similarly; above this temperature, H_2 becomes thermodynamically favored due to the distinct monotonicity of the FeO-Fe equilibria and the expansion of the Fe stability range.

The Baur–Glässner diagram also includes the reverse Boudouard equilibrium reaction, catalyzed by both iron and iron oxides (9).⁶⁸ This reaction leads to carbon deposition and subsequently to the formation of cementite (Fe_3C) via reactions 10–12. These reactions are industrially relevant because carbon incorporation into the lattice imparts the desired mechanical properties to the final product. However, this can also influence the kinetic rate due to steric hindrance between the unreacted oxide and the gas.⁶⁹

In the DR process, using CO-H_2 mixtures offers energetic synergy—the endothermic H_2 reduction is balanced by the exothermic CO reduction. In this case, a key reaction is the water–gas shift reaction (WGSR) (14), which occurs without changing the overall GOD. WGSR is also promoted by iron oxides but not by hematite.⁷⁰ Additional reactions include carbon gasification (15), which removes deposited carbon, and carburization to Fe_3C (16). Inverse reforming (17) and (18) generate CH_4 , which can further reduce (19) or carburize (20).⁷¹

1.5 Challenges in describing H_2 -based reduction kinetics

Although more than sixty years have passed since the first studies appeared in the literature on the reduction of iron oxides by hydrogen, a remarkable increase in the number of published articles has recently been observed (Article I). This new wave is undoubtedly linked to the ecological drive supported, as discussed in previous sections, by industries as well as by entities such as the European Union.

What emerges, however, is the complexity of the multiple phenomena that occur and can be keys to interpreting the results. The fundamental steps involved in gas–solid interactions are well known in this research field. These stages range from the mass transport of reactants and products through the external stagnant film and within the pores of the solid, to their arrival at the active sites that promote the reaction—similar to what occurs in heterogeneous catalysis, though with necessary differences.

⁶⁸ N. Bost, M. R. Ammar, M. L. Bouchetou, and J. Poirier, ‘The catalytic effect of iron oxides on the formation of nano-carbon by the Boudouard reaction in refractories’, *Journal of the European Ceramic Society*, 36/8 (2016), 2133–42.

⁶⁹ N. Towhidi and J. Szekeely, ‘The influence of carbon deposition on the reduction kinetics of commercial grade hematite pellets with CO , H_2 , and N_2 ’, *Metallurgical Transactions B*, 14/3 (1983), 359–67.

⁷⁰ H. Ono-Nakazato, T. Yonezawa, and T. Usui, ‘Effect of Water-Gas Shift Reaction on Reduction of Iron Oxide Powder Packed Bed with H_2 - CO Mixtures’, *ISIJ International*, 43/10 (2003), 1502–11.

⁷¹ D. Ghosh, A. K. Roy, and A. Ghosh, ‘Reduction of ferric oxide pellets with methane.’, *Transactions of the Iron and Steel Institute of Japan*, 26/3 (1986), 186–93.

In solid-state reactive processes—specifically those involving the reduction of iron oxides—both external and, more importantly, internal diffusive phenomena are considered, the latter being associated with a solid matrix that changes over time, spatially rearranging the atoms in the lattice and consequently modifying vacancies and reactivity,⁷² as well as the porosity.⁷³ To this must be added the phenomena linked to thermodynamic aspects (cf. Figure 1.6), which change as the reaction proceeds, in some cases also influencing the chemical and morphological characteristics of the solids.⁷⁴

A cornerstone of any reactive process is chemical kinetics, understood purely as the study of the reaction rate, which is a function—among the most relevant—of reactant concentrations, contact surface, and temperature.⁷⁵ The nature and morpho-structural properties of the initial solid and of the transient phases during reaction also require careful attention, as they affect all the previously discussed aspects.

Particularly from a mathematical modelling perspective, the need to introduce key assumptions useful for simplifying the system under examination must necessarily be filtered through the structural reality of the reacting solids. For this reason, the possibility of examining solids using advanced qualitative techniques enables the investigation of new key features and kinetic aspects of the process.

Several analytical techniques can be used to acquire such information, including scanning electron microscopy (SEM) with energy dispersive X-ray (EDX),⁷⁶ X-ray diffraction (XRD),⁷⁷ X-ray fluorescence (XRF),⁷⁸ and physical adsorption.⁷⁹

⁷² M. H. Abd Elhamid, M. M. Khader, A. E. Mahgoub, B. E. El Anadouli, and B. G. Ateya, 'Autocatalytic Reduction of Hematite with Hydrogen under Conditions of Surface Control: A Vacancy-Based Mechanism', *Journal of Solid State Chemistry*, 123/2 (1996), 249–54.

⁷³ A. A. El-Geassy, M. I. Nasr, and M. M. Hessien, 'Effect of Reducing Gas on the Volume Change during Reduction of Iron Oxide Compacts', *ISIJ International*, 36/6 (1996), 640–49.

⁷⁴ A. M. Soodmand, A. Heidari, S. K. Azadi, M. Iljana, A. Heikkilä, M. K. Ghosalya, S. Urpelainen, P. Cavaliere, L. Dijon, V. Morais, and T. Fabritius, 'Effect of Water Vapor on the Reduction and Carburization of Iron Ore Pellets: Theoretical and Experimental Approaches', *Metallurgical and Materials Transactions B*, 56/5 (2025), 4552–70.

⁷⁵ A. Zare Ghadi, M. S. Valipour, S. M. Vahedi, and H. Y. Sohn, 'A Review on the Modeling of Gaseous Reduction of Iron Oxide Pellets', (2020).

⁷⁶ M. Elzohiery, H. Y. Sohn, and Y. Mohassab, 'Kinetics of Hydrogen Reduction of Magnetite Concentrate Particles in Solid State Relevant to Flash Ironmaking', *Steel Research International*, 88/2 (2017), 290–303.

⁷⁷ N. Thüns, B. M. Krooss, Q. Zhang, and H. Stanjek, 'The effect of H₂ pressure on the reduction kinetics of hematite at low temperatures', *International Journal of Hydrogen Energy*, 44/50 (2019), 27615–25.

⁷⁸ A. H. A. El-Geassy, 'Rate Controlling Step in the Reduction of Iron Oxides; Kinetics and Mechanism of Wüstite-Iron Step in H₂, CO and H₂/CO Gas Mixtures', IOP Conference Series: Materials Science and Engineering, (Institute of Physics Publishing, 2017).

⁷⁹ C. J. M. Hessels, T. A. M. Homan, N. G. Deen, and Y. Tang, 'Reduction kinetics of combusted iron powder using hydrogen', *Powder Technology*, 407 (2022).

In the complex dynamics of phenomenological interpretations, correlation with the experimental data is, as in every research field, crucial. A major contribution to these aspects is certainly linked to the experimental reduction conditions, which determine the operational variability (e.g., solid quantity, volumetric flow rate, and temperature), as well as the characteristics of the experimental setup itself, such as the reactor type, as well as the precision and nature of data acquired.

The literature reports the use of various experimental systems, ranging from those classically employed to evaluate sample weight loss, such as thermogravimetric analysis (TGA),⁸⁰ and temperature-programmed reduction (TPR),⁸¹ to systems based on gaseous effluent analysis, including fluidized bed reactors (FB),⁸² and drop tube reactors.⁸³

A combination of all these elements, from design of experiments to solid characterization, can help clarify the complex task of processing, evaluating, and understanding the nature of the experimental data and its potential. Many studies in literature highlight different critical aspects.

Using thermogravimetric analysis in experiments conducted at constant temperatures between 800 °C and 1100 °C, with 30 mol% H₂ and a flow rate of 20 mL/min, Lyu et al.⁸⁴ demonstrated that the overall reduction of the material reaches almost 100% at temperatures above 900 °C. The reason lies in the cracking of the material at high temperatures, which increases solid porosity and promotes faster reduction. TPR experiments performed by the same group showed that the choice of heating rate is relevant due to morphological changes in the material, indicating the formation of dense, uniformly distributed iron layers.

Pattison et al.⁸⁵ studied iron ore pellets subjected to reduction at constant temperature in a thermobalance with a flow rate of 2 L/min and 40 vol% H₂.

⁸⁰ S. K. El-Rahaiby and Y. K. Rao, 'The kinetics of reduction of iron oxides at moderate temperatures', *Metallurgical Transactions B*, 10/2 (1979), 257–69.

⁸¹ G. Munteanu, L. Ilieva, and D. Andreeva, 'Kinetic parameters obtained from TPR data for α -Fe₂O₃ and systems', *Thermochimica Acta*, 291/1–2 (1997), 171–77.

⁸² A. Jess and H. Depner, 'Reduction and carburization of iron-ore in a fluidized bed by CO, H₂ and CH₄', *Steel Research*, 69/3 (1998), 77–84.

⁸³ D. Guo, M. Hu, C. Pu, B. Xiao, Z. Hu, S. Liu, X. Wang, and X. Zhu, 'Kinetics and mechanisms of direct reduction of iron ore-biomass composite pellets with hydrogen gas', *International Journal of Hydrogen Energy*, 40/14 (2015), 4733–40.

⁸⁴ B. Lyu, G. Wang, F. Yang, H. Zuo, Q. Xue, and J. Wang, 'Kinetic Analysis of Isothermal and Non-Isothermal Reduction of Iron Ore Fines in Hydrogen Atmosphere', *Metals*, 12/10 (2022), 1754.

⁸⁵ Patisson, Mirgaux, and Birat, 'Hydrogen steelmaking. Part 1: Physical chemistry and process metallurgy'.

Varying the temperature, the results showed that complete reduction was achieved through different dynamics, with the reaction rate decreasing sharply between 950 °C and 1000 °C. In this case, dense iron layers promoted the transition from mixed chemical reaction and intergranular diffusion to solid-state diffusion.

Many authors have also investigated the thermodynamics of reduction as a function of temperature to optimize the experimental conditions for the reduction process with H₂.⁸⁶ Pineau et al.^{87–88} studied the reduction kinetics of Fe₂O₃ at low temperatures, detecting FeO using XRD analysis during the Fe₂O₃ to Fe₃O₄ step at 415 °C, despite its theoretical instability below 570 °C.

As can be seen, temperature plays a considerable role in the interpretation of emerging phenomena. While effects such as the composition of the reducing gas⁸⁹ and the linear velocity of the gas⁹⁰ are more straightforward, this is not the case in reduction studies that take into account particle size⁹¹ and gangue content.⁹² In these latter cases, the increased phenomenological complexity due to the growth of the solid dimension (from powders to pellets) and the uncertain influence of impurities, respectively, are still under investigation by many authors.

1.6 Modelling approaches

The development of mathematical models primarily begins with assumptions based on experimental evidence, which simplify the system by neglecting certain factors and phenomena. Central to this process is the precise definition of the data's emergent properties, from which assumptions about pivotal or rate-limiting steps are deduced, supported by multiple cross-validated experimental

⁸⁶ S. Li, H. Gu, A. Huang, Y. Zou, S. Yang, and L. Fu, 'Thermodynamic analysis and experimental verification of the direct reduction of iron ores with hydrogen at elevated temperature', *Journal of Materials Science*, 57/43 (2022), 20419–34.

⁸⁷ A. Pineau, N. Kanari, and I. Gaballah, 'Kinetics of reduction of iron oxides by H₂. Part I: Low temperature reduction of hematite', *Thermochimica Acta*, 447/1 (2006), 89–100.

⁸⁸ A. Pineau, N. Kanari, and I. Gaballah, 'Kinetics of reduction of iron oxides by H₂. Part II: Low temperature reduction of hematite', *Thermochimica Acta*, 456 (2006), 75–88.

⁸⁹ M. N. Abu Tahari, F. Salleh, T. S. Tengku Saharuddin, N. Dzakaria, A. Samsuri, M. W. Mohamed Hisham, and M. A. Yarmo, 'Influence of hydrogen and various carbon monoxide concentrations on reduction behavior of iron oxide at low temperature', *International Journal of Hydrogen Energy*, 44/37 (2019), 20751–59.

⁹⁰ H. Kang, Q. Xu, Z. Cao, X. Lu, J. Shi, B. Chen, and L. Guo, 'Influence of hydrogen flow rate on multistep kinetics of hematite reduction', *International Journal of Hydrogen Energy*, 49 (2024), 1255–68.

⁹¹ E. T. Turkdogan and J. V. Vinters, 'Gaseous reduction of iron oxides: Part I. Reduction of hematite in hydrogen', *Metallurgical Transactions*, 2/11 (1971), 3175–88.

⁹² E. T. Turkdogan and J. V. Vinters, 'Reducibility of iron ore pellets and effect of additions', *Canadian Metallurgical Quarterly*, 12/1 (1973), 9–21.

evidence. Such simplifications, and consequently strong assumptions, are often necessary to facilitate numerical and mathematical computation.

In the context of mathematical modelling of iron oxide reduction processes, and more generally in the study of solid-state kinetics, numerous models have been proposed in the literature, with complexities varying considerably depending on the number of phenomena and steps considered. Therefore, depending on the experimental approach, the selection of computational methods must be carefully considered. Figure 1.7 presents a diagram of the modelling approaches used to describe solid–gas reactive systems employed over the last half-century.⁹³

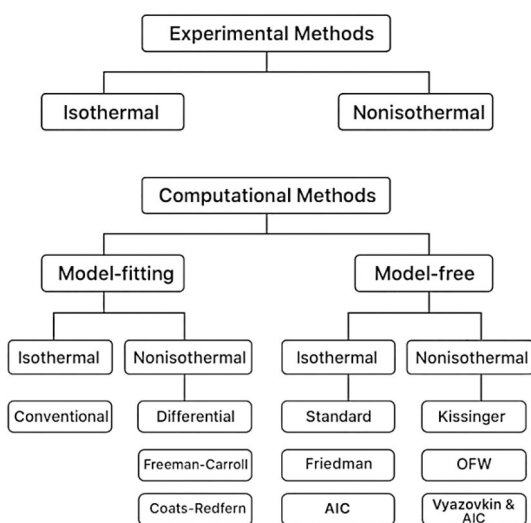


Figure 1.7 Different computational methods for the description of solid-gas reactive systems.⁹⁵

Kinetic analysis can be conducted through model-fitting or model-free approaches. In the former, experimental data are fitted to a chosen kinetic model to identify the reaction mechanism and estimate its parameters. In the latter, no specific model form is assumed, and the activation energy is derived using isoconversional methods, allowing the process behavior to be described without imposing mechanistic constraints. For example, in an isothermal process, the

⁹³ A. Khawam and D. R. Flanagan, 'Basics and applications of solid-state kinetics: A pharmaceutical perspective', (2006).

rate of the reductive solid–gas process is defined by the degree of conversion X , calculated by thermogravimetric measurements

$$\frac{dX}{dt} = k(T)f(X) = A \exp\left(-\frac{E_a}{R_g T}\right) f(X) \quad \left[\frac{-}{s}\right] = \text{depending on the mechanism} \quad (1)$$

$$X = \frac{m^0 - m}{m^0 - m^f} \quad [-] = \left[\frac{g}{g}\right] \quad (2)$$

where A is the preexponential factor, T is the temperature, R_g is the gas constant, E_a is the activation energy of the reaction, while $f(X)$ represents the function describing the reaction mechanism. The dimensionless reduction degree is defined starting from m^0 , the initial weight of the sample, m^f is the final weight, and m is the weight at a given time (t). A common approach is to use these models to evaluate which of the various fitting models best describes the experimental data, thus formally defining the mechanism and the rate-limiting step of the reduction process. Among the most used models, the Avrami model is often applied in studies of heterogeneous reactive processes to simplify nucleation and growth dynamics. More comprehensive models include the Shrinking Core Model (SCM), the grain model, and the random pore model.

Table 1.6 lists the main mechanism used for solid-state reactions (Article I).⁹⁴ A common approach is to use these models to evaluate which of the various fitting models best describes the experimental data, thus formally defining the mechanism and the rate-limiting step of the reduction process. Among the most used models, the Avrami model is often applied in studies of heterogeneous reactive processes to simplify nucleation and growth dynamics.⁹⁵ More

⁹⁴ A. Khawam and D. R. Flanagan, 'Solid-state kinetic models: Basics and mathematical fundamentals', *Journal of Physical Chemistry B*, 110/35 (2006), 17315–28.

⁹⁵ K. Piotrowski, K. Mondal, T. Wiltowski, P. Dydo, and G. Rizig, 'Topochemical approach of kinetics of the reduction of hematite to wüstite', *Chemical Engineering Journal*, 131/1–3 (2007), 73–82.

comprehensive models include the Shrinking Core Model (SCM),⁹⁶ the grain model,^{97 98} and the random pore model.^{99 100}

Table 1.6 Fitting approaches: Solid state models.

Model Family	Factors	Differential form $f(\alpha) = \frac{1}{k} \frac{dX}{dt}$
Order based	Reaction order	
	$n = 0$	1
	$n = 1$	$(1 - X)$
	$n \geq 2$	$(1 - X)^n$
Nucleation and growth	Power Law	
	$n = (\gamma + \lambda) *$	$nX^{\left(\frac{n-1}{n}\right)}$
	Avrami-Erofe'ev	
	$n = (\gamma + \lambda) *$	$n(1 - X)[- \ln(1 - X)]^{\left(\frac{n-1}{n}\right)}$
Diffusion	Dimension	
	1 (1-D)	$\frac{1}{2X}$
	2 (2-D)	$[- \ln(1 - X)]^{-1}$
	3 (3-D Jander)	$\frac{3}{2}(1 - X)^{\frac{2}{3}} \left[1 - (1 - X)^{\frac{1}{3}} \right]^{-1}$
	3 (3-D Ginstling-Brounshtein)	$\frac{3}{2} \left[(1 - X)^{-\frac{1}{3}} - 1 \right]$
Phase Boundary	Dimension	
	1 (Infinite Slab)	1
	2 (Contracting Cylinder)	$2(1 - X)^{\frac{1}{2}}$
	3 (Contracting Sphere)	$3(1 - X)^{\frac{1}{3}}$

* γ successive events necessary to form the growth nucleus

* λ nucleus growth dimensions ($\lambda = 1, 2$ or 3)

At pilot-plant or furnace scale, Computational Fluid Dynamics (CFD) models enable detailed fluid dynamic analysis and the exploration of theoretical alternatives to conventional processes that could drive future industrial

⁹⁶ Y. Hara and S. Kondō, 'Kinetics of Reduction of Iron Oxide Pellets with Hydrogen at Low Temperatures', *Transactions of the Iron and Steel Institute of Japan*, 8/5 (1968), 300–310.

⁹⁷ A. Z. Ghadi, M. S. Valipour, and M. Biglari, 'Mathematical modelling of wustite pellet reduction: grain model in comparison with USCM', *Ironmaking and Steelmaking*, 43/6 (2016), 418–25.

⁹⁸ S. M. M. Nouri, H. Ale Ebrahim, and E. Jamshidi, 'Simulation of direct reduction reactor by the grain model', *Chemical Engineering Journal*, 166/2 (2011), 704–9.

⁹⁹ M. Hosseinzadeh, N. Kasiri, and M. Rezaei, 'Random pore model insights into structural and operational parameters for hydrogen-based iron oxide reduction', *Process Safety and Environmental Protection*, 190 (2024), 464–80.

¹⁰⁰ J. J. Wong, D. Iruretagoyena, N. Shah, and P. S. Fennell, 'A three-interface random pore model: the reduction of iron oxide in chemical looping and green steel technologies', *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 479/2278 (2023).

development.^{101 102} Nevertheless, statistical analyses of the variability of kinetic parameters estimated by many authors using these modelling approaches reveal a consistent scatter as shown in Figure 1.8 (Article I).

This is a remarkable scatter in the estimated activation energies for all possible H₂-based reductions, which can be attributed to significant experimental and modelling variability and is observed across all modelling approaches (Article I). These variations highlight the need to deepen analysis in this area, from molecular and microscopic phenomena up to scale-up at furnace level.

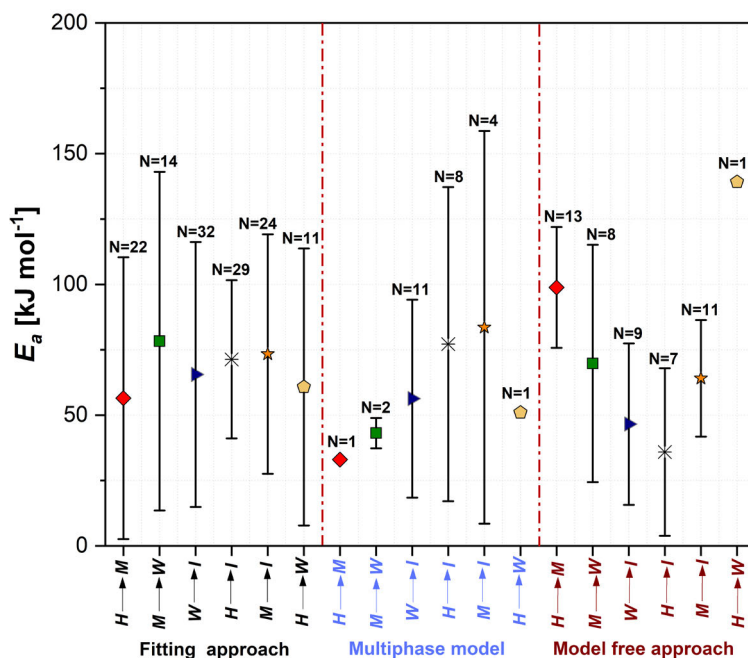


Figure 1.8 Statistical activation energies analysis H₂-based reduction with H, M, W and I indicating hematite, magnetite, wüstite and metallic iron, respectively (Article I).

¹⁰¹ D. Q. Fan, H. Y. Sohn, and M. Elzohiery, 'Analysis of the Reduction Rate of Hematite Concentrate Particles in the Solid State by H₂ or CO in a Drop-Tube Reactor Through CFD Modeling', *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 48/5 (2017), 2677–84.

¹⁰² Y. Zhuo, Z. Hu, and Y. Shen, 'CFD study of hydrogen injection through tuyeres into ironmaking blast furnaces', *Fuel*, 302 (2021).

1.7 Aim of the thesis

The main objective of the research is to develop accurate models of the reduction kinetics of iron oxides for use in process-model studies of hydrogen-based processes. The rate limiting step lies in the identification of a model structure that can, with sufficient accuracy, describe the reduction behavior of iron oxide fines, with particular attention to the partially overlapping reduction steps of hematite–magnetite, magnetite–wüstite, and wüstite–metallic iron.

The present research first focused on an extensive and critical review of the scientific literature, highlighting the wide variety of modeling and experimental approaches previously adopted to describe this gas–solid reduction system.

Building upon these findings, an extensive joint effort of mathematical modeling and reduction experiments was subsequently carried out, whose interdependence proved to be crucial for an accurate interpretation of the structural phenomena governing the reduction process.

The experiments were conducted in a continuous fixed-bed reactor under isothermal conditions, varying different operating parameters. Thin-layer tests were mainly performed to isolate and study the intrinsic kinetics of iron oxide reduction, minimizing the effects of mass transfer phenomena and thermodynamic constraints. This allows for obtaining more reliable data and helps determine fundamental kinetic parameters such as activation energy and kinetic constants.

Bed experiments were also conducted to evaluate the reliability of the parameter estimation. Furthermore, in support of the modelling assumptions, the evolution of the iron oxide properties was evaluated through several analytical techniques to provide proper morphological characterization of the initial, transient, and final samples.

Finally, an innovative methodological and modelling approach was developed. This method accurately evaluates the thermal conductivity of the outlet gases from the reactor observed during the reduction experiments and indirectly determines the overall degree of reduction. This represents a crucial step in developing accurate models that will support the future technological evolution of new green hydrogen-based direct reduction processes.

Notation

Abbreviations

BF	Blast Furnace
BOF	Basic Oxygen Furnace
CFD	Computational Fluid Dynamic
EAF	Electric Arc Furnace
EDX	Energy Dispersive X-ray
FB	Fluidized Bed
GOD	Gas Oxidant Degree
DR	Direct Reduction
DRI	Direct Reduction Iron
SCM	Shrinking core model
SEM	Scanning Electron Microscopy
SF	Shaft Furnace
SSD	Solid-State Diffusion
TCD	Thermal conductivity detector
TGA	Thermogravimetric Analysis
TPR	Temperature-Programmed Reduction
ULCOS	Ultra-Low CO ₂ Steelmaking
WGSR	Water–Gas Shift Reaction
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Symbols

A	Pre-exponential factor
E_a	Activation energy [J/mol]
f	Reaction mechanism
m	Sample weight [g]
n	Main model factor [-]
R_g	Gas constant [J/(mol K)]
t	Time [s]
T	Temperature [K]

X	Degree of conversion [-]
γ	Successive events necessary to form the growth nucleus [-]
λ	Nucleus growth dimensions [-]

Superscripts

0	Index of initial condition
f	Index of final condition

Chapter 2 – Experimental approach and model development (II, III, IV)

*“The true challenge lies in shaping models whose assumptions reflect the
fundamental processes that produce the emergent nature of dynamic phenomena,
without yielding to logical fallacies or mathematical coercion.”*

S. Mazzoleni

2.1 Solid and gas reactants

The solid samples used for the reduction experiments were purchased from Sigma-Aldrich. Specifically, hematite (Fe_2O_3) (CAS: 1309-37-1) has a purity ≥ 96 %, a density of 5.25 g cm^{-3} , while magnetite (Fe_3O_4) (CAS: 1317-61-9) has a purity ≥ 95 %, a density ranging between 4.8 and 5.1 g cm^{-3} . The particle sizes of both materials are below $5 \text{ }\mu\text{m}$. As for the gaseous phase, hydrogen (> 99.999 %) was used as the sole reducing agent, and argon (Ar) (> 99.9 %) was employed as an inert carrier gas, both supplied by Woikoski Oy.

2.2 Reactor configurations

In this work, two experimental setups were used. From an operational perspective related to the reduction processes, the two systems are highly similar, with the main difference being the reactor size. Additional differences relevant from a practical standpoint include the type of reducing species — since only one configuration allows the use of carbon monoxide and hydrogen (CO/H_2) mixtures — and the type of detector used for analyzing the gaseous effluents. Specifically, the first configuration, a Micromeritics Autochem 2910 (cf. Analytical methods), typically used for qualitative and quantitative chemisorption analyses of catalysts, is equipped with a thermal conductivity detector (TCD). The second configuration, a custom-built laboratory reactor, uses an Agilent 990 Micro-GC (cf. Analytical methods), which enables online monitoring of the outlet gas. A schematic representation of both experimental configurations is shown in Figure 2.1.

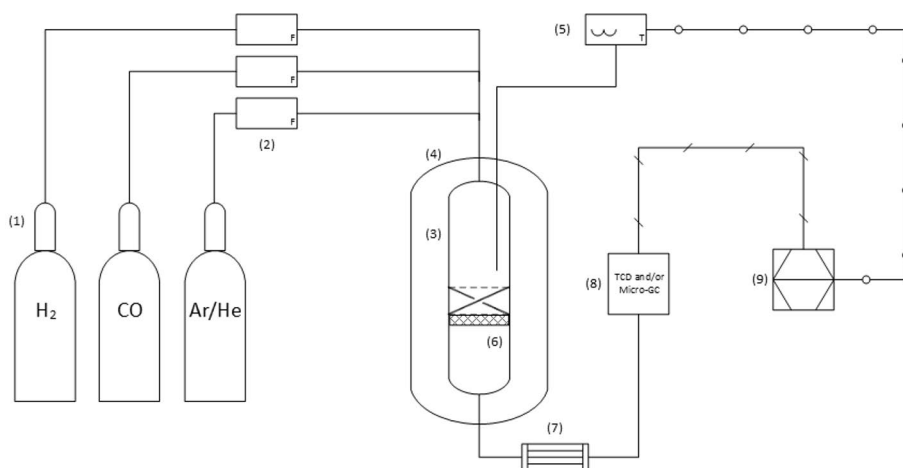


Figure 2.1 General reactor configurations scheme (Article III).

High-purity gases stored in cylinders (1) are supplied at controlled flow rates via flowmeters (2) and mixed before entering the reactor. The glass reactor (3) has a tubular geometry: the first configuration has a length (L) of 193 mm and a radius (R_r) of 9.5 mm, while for the second $L = 1$ m and $R = 15$ mm. Unlike the first configuration, the second reactor is also equipped with an external quartz jacket. An additional nitrogen (N_2) line flows through this jacket to prevent potential leakage of reducing gases, thereby improving the overall safety of the experimental setup.

Both reactors are housed in a furnace (4), which ensures precise temperature control monitored by a Type-K thermocouple (5) positioned at the reactor center near the fixed bed. All samples were heated to the operating temperature at a constant rate of 10 °C/min. The fine solid powder is loaded into the reactor and placed on a quartz disk resting on a layer of quartz wool (6). These porous layers protect the detectors (8) from possible entrainment of solid particles by the gas stream and ensure a horizontally uniform bed geometry, minimizing non-uniform gas–solid interactions along the axial direction.

Only the second configuration is equipped with a condensation system for removing the water vapor generated during the reaction (7). This feature is necessary because the Micro-GC columns are extremely sensitive to the presence of vapor (H_2O), which can negatively affect both the quantification of water and that of other gaseous effluents. For this reason, a cold trap filled with dry ice was installed between the reactor and the detector to remove all water produced during the reduction process.

Temperature (T) and signal data are continuously recorded and extracted (9).

A series of isothermal experiments was carried out by varying T , sample mass (m), total gas flow rate (Q), and reductant molar fraction (y) to assess their effects on the reaction kinetics and on the morphological evolution of the samples. Samples with $m \approx 0.010$ g (i.e., thin-layer experiments) were used for kinetic parameter estimation, while experiments with sample masses of $m \geq 0.100$ g (i.e., bed experiments) were performed for validation of the kinetic parameters.

To characterize the fluid dynamic behavior of the reactor systems used, residence time distribution (RTD) experiments were conducted. These experiments enabled the evaluation of the Peclet number (Pe), allowing for

identification of axial dispersion phenomena in both reactor configurations. It was therefore necessary to account for the dilution of the feed gas into the inert stream during the initial stages of the reaction (i.e., after the valve opening phase). The results of this analysis are reported in the dedicated section (cf. Section 3.1.2).

2.3 Analytical methods

As discussed extensively in the previous sections, analytical techniques are essential tools for investigating the phenomena that govern a given dynamic process. They contribute not only to fundamental understanding but also to an appropriate use of experimental data and the formulation of assumptions required for the mathematical development of descriptive models.

Accordingly, several techniques were employed for the analysis of gaseous effluents leaving the reactor systems and for the characterization of the solid phases subjected to reduction. To support structural hypotheses regarding the reaction mechanism and to enhance the understanding of the emerging phenomena, a comprehensive qualitative analysis was performed on the initial and final solids, as well as on intermediate (transient) samples collected during the process.

2.4 Quantitative methods

The Micromeritics Autochem 2910 unit, widely used for the characterization of materials and catalysts (e.g., in Temperature-Programmed Reduction (TPR), analyses), is equipped with a TCD that enables continuous monitoring of the outlet gas composition.

The TCD operates on a Wheatstone bridge configuration consisting of four electrically heated filaments housed within a thermally controlled cell. When gases with different thermal conductivities pass through the detector, they alter the temperature of one or more filaments, thereby changing their electrical resistance. This variation is detected and recorded as an electrical signal.

The TCD response reflects the change in the thermal conductivity of the gas mixture and is recorded approximately every 0.05 minutes, allowing for high-frequency tracking of the reaction progress. The difference in thermal conductivity between the reference gas—argon in this case—and the reactor

effluent mixture (Ar, H₂, and H₂O) provides insight into the gas composition and, consequently, the reaction evolution.

In particular, the thermal conductivity of H₂ differs by more than an order of magnitude from that of Ar and H₂O, making the TCD signal primarily sensitive to the hydrogen concentration in the outlet gas. Thus, the raw TCD signal can be directly correlated with the amount of H₂ leaving the reactor, providing crucial information on the reaction course. The interpretation and quantitative treatment of these data are further discussed in Section 2.5.

Gas-phase analysis was also performed using an Agilent 990 Micro-GC. Owing to its modular configuration with interchangeable columns and detectors, this instrument can analyze a wide range of gaseous species with high temporal resolution. The columns used are capillary-type, containing either solid or liquid stationary phases depending on the required separation characteristics. They are typically 10 m in length and 0.1 mm in internal diameter — shorter than those used in conventional gas chromatographs — to allow rapid analysis.

Two columns were used in this study: a Molecular Sieve 5Å column, employing a crystalline zeolite stationary phase with 5 Å pore size, and a PoraPlot U column, a Porous Layer Open Tubular column based on a divinylbenzene stationary phase.

The combination of these columns enables the detection of a broad spectrum of gaseous species, including H₂, CO, N₂, CO₂, and H₂O. The analysis of the reaction gases was performed through periodic injections into the Micro-GC, typically every 80 seconds.

2.5 Qualitative methods

X-ray diffraction (XRD) was used to investigate the evolution of chemical species involved in the reduction of both pure iron oxides. Diffraction patterns in the 2θ range of 20–80° were collected using a Panalytical Empyrean diffractometer equipped with a PIXcel 3D detector and CuK α radiation ($\lambda = 1.5418$ Å) as the source. The diffraction data were analyzed using HighScore Plus software and the ICDD Powder Diffraction File 2024 (PDF5+2024) database.

Particle size distribution was measured by light scattering (LS) using a Malvern Panalytical Mastersizer 3000.

Nitrogen physisorption measurements were conducted using a Micromeritics 3Flex-3500 instrument to characterize porosity and surface properties. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method, while the pore size distribution was obtained using the Non-Local Density Functional Theory model.

The morphological characteristics and surface topography of the materials were examined by scanning electron microscopy (SEM) using a NovaNanoSEM 450 equipped with a through-the-lens detector, enabling high-resolution imaging and compositional contrast.

Thermogravimetric and differential scanning calorimetric analyses coupled with mass spectrometry (TGA/DSC-MS) were performed using a Netzsch STA 449F instrument to investigate thermal behavior, identify phase transitions, and assess the moisture content of the samples.

The thickness of the solid fixed bed used during the experiments was estimated from digital photographs acquired with a Canon EOS 600D DSLR camera. The images were processed with specialized image analysis software, facilitating an accurate dimensional evaluation based on calibrated reference markers.

Further details regarding the monitoring of solid-state transformations during reduction, as well as the comparison between pure and commercial materials, are available in the works of D'Angelo et al.^{103 104}

2.6 Mathematical and physical interpretation of TCD signals

The signal obtained from the TCD is a function of both the composition of the gas mixture leaving the reactor and the thermal conductivity of the chemical species involved. As the thermal conductivity of H₂ is much higher than that of H₂O and Ar, the TCD signal approximately reflects the fraction of hydrogen in the gas stream leaving the reactor. However, simulating this signal can be particularly challenging because it is also influenced by the physical and structural properties of the Wheatstone bridge itself.¹⁰⁵

¹⁰³ A. D'Angelo, E. Salucci, V. Russo, H. Grénman, and H. Saxén, 'Hydrogen Reduction of Iron Oxide Powder in Thin Layers', *Industrial & Engineering Chemistry Research*, 64/1 (2025), 158–70.

¹⁰⁴ A. D'Angelo, E. Salucci, V. Russo, H. Grénman, and H. Saxén, 'Reduction kinetics of pure and industrial hematite samples with hydrogen in a small fixed bed system', *Chemical Engineering Journal*, 519 (2025), 165117.

¹⁰⁵ S. S. Miljanic and B. B. Radak, 'Gas Analysis - An improved mathematical model of thermal conductivity detectors', *Bulletin de la société chimique Beograd*, 49/3 (1983), 123–27.

As an illustrative example, Figure 2.2 presents the experimental results of hematite bed reduction at different operating temperatures, showing the normalized TCD signal as a function of time.

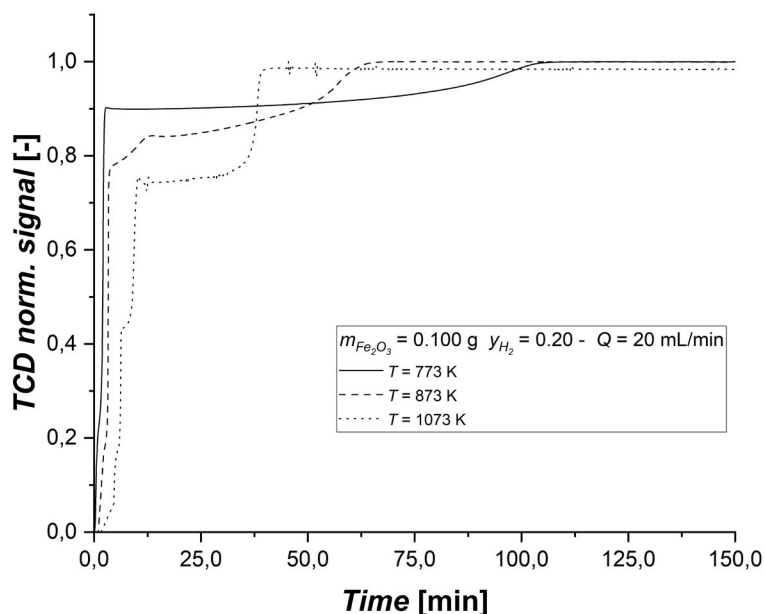


Figure 2.2 Examples of normalized TCD signals during hematite reduction at different operating temperatures.

As shown, the signal rapidly increases within a few seconds. This behavior results from the amount of unreacted hydrogen reaching the detector. The increase in the signal upon feeding H_2 is due to its higher thermal conductivity compared to the reference gas (i.e., Ar). Moreover, the signals exhibit different trends and slope variations that clearly depend on the kinetics, thermodynamics, and the number of reactions simultaneously involved as the temperature changes. As an example, the reduction at 773 K should not proceed via the FeO intermediate, which justifies its simpler form compared to the other two cases, while the form of the signal obtained at 1073 K appears to be an accelerated version of the reaction at 873 K. These slope transitions can thus be interpreted as indicators of shifts between kinetic and thermodynamic regimes, caused by the depletion of solid phases that previously dominated the reaction. In general, the reaction can be considered complete when the signal stabilizes at a normalized value of 1 (i.e., no consumption of H_2).

Initially, the approach chosen for kinetic parameter estimation consisted of comparing the normalized experimental TCD signal with a simulated signal reconstructed from the composition of the outlet gases (Article II). However, the high stiffness of the signal profiles prompted a change in methodology due to severe mathematical challenges in closing the elemental balances. An innovative approach was developed to correlate the experimental TCD data with an indirect estimation of the solid reduction degree (Articles III and IV). The numerical processing steps are illustrated in Figure 2.3.

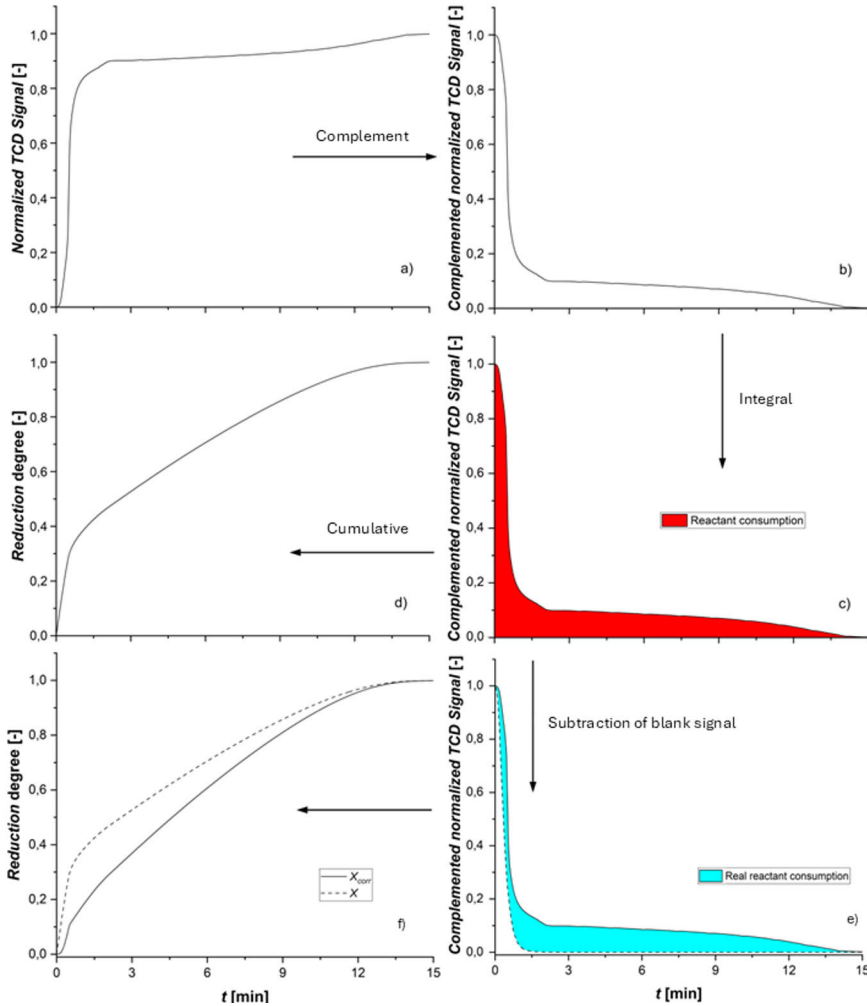


Figure 2.3 Numerical processing of raw TCD data: (a) normalized TCD signal; (b) complement of the normalized signal; (c) integration of the complement; (d) cumulative reduction degree; (e) difference between blank and reduction experiments (blue region); and (f) apparent (dashed line) and corrected (solid line) reduction degrees.

The data analysis method developed to improve the interpretation of the reduction process leads to a crucial key point: establishing a robust correlation between the raw thermal conductivity signal and the extent of solid phase conversion in heterogeneous gas–solid reactions. The response of the gas phase detector was quantitatively correlated with the overall degree of reduction of the solid sample. The data processing procedure in detail is a) normalization to isolate gas conductivity changes (s'); b) signal complement to allow numerical integration ($\tilde{s}$); c) cumulative integration using the trapezoidal rule; d) the final processed curve. Below, the specific mathematical procedure used starting from a signal (s) obtained through the thermal conductivity detector is described.

$$s'(t) = \frac{s(t)}{\max(s(t))} \quad (\text{Step A}) \quad [-] \quad (3)$$

$$\tilde{s}(t) = 1 - s'(t) \quad (\text{Step B}) \quad [-] \quad (4)$$

$$S = \int_0^t \tilde{s}(t) dt \quad (\text{Step C}) \quad [-] \quad (5)$$

The integration of the signal ($\tilde{s}$) thus obtained represents the hydrogen consumption occurring during the reaction, which is closely correlated with the solid conversion. Cumulative integration therefore provides an indirect evaluation of the state of the reactive solid and represents an apparent reduction degree (X) curve.

The mathematical formalization of this last procedure is expressed as follows, where $\tilde{s}(t)$ denotes the modified TCD signal (i.e., complement of the normalized TCD signal) while m represents the number of datapoints.

$$X(t) = \left(\int_0^{t^1} \tilde{s}(t) dt, \int_0^{t^2} \tilde{s}(t) dt, \dots, \int_0^{t^m} \tilde{s}(t) dt \right) \quad (\text{Step D}) \quad [-] \quad (6)$$

Hence, a vector of cumulative elements is obtained, each representing the progressive area of the complemented signal up to each time step.

This mathematical procedure is particularly innovative both in the metallurgical and in the chemical engineering fields, as it correlates a highly precise and high-frequency signal—associated with the consumption of the reducing gas—to the actual progress of the solid-state reaction.

Nevertheless, it was necessary to apply a further correction to account for gas dilution phenomena, such as axial dispersion, which prevent the system from exhibiting ideal plug-flow behavior once the hydrogen valve is opened (Section 3.1.2). The hydrogen reaching the detector during the first few minutes of the reaction corresponds only to a portion of the incoming flow of unreacted H₂ due to the initial dispersion of the fluid elements. This causes an overestimation of the conversion degree, especially during the initial reaction stages—precisely the most critical ones, considering that the reduction of hematite proceeds extremely rapidly and is nearly complete within the first few minutes. Such an error would result in an incorrect evaluation of both the reaction kinetics and dynamics.

To correct the incorrect interpretation of the previous reduction degree, a specific procedure was adopted. The same mathematical procedure (steps a–d applied to a blank signal $b \rightarrow b' \rightarrow \tilde{b}$) was applied to a blank experiment dataset, i.e., a test in the absence of the solid sample conducted under the same operating conditions as the reduction tests. The subsequent step involves subtracting the cumulative blank signal integral ($\tilde{b}$) from that of the reduction experiment, isolating the actual amount of hydrogen consumed during the reaction. Step e in Figure 2.3 displays the exact region between the two curves used for the evaluation of the final reduction degree.

The final mathematical procedure is displayed below.

$$X_{corr}(t) = \left(\int_0^{t^1} \tilde{s}(t)dt - \int_0^{t^1} \tilde{b}(t)dt, \dots, \int_0^{t^m} \tilde{s}(t)dt - \int_0^{t^m} \tilde{b}(t)dt \right) \text{ (Step E)} \quad [-] \quad (7)$$

The resulting difference is illustrated in Step f of Figure 2.3, showing both the original and corrected reduction degrees.

It is important to note that the corrected reduction rate is much lower in the first few minutes than originally due to the dispersion of the reducing agent. The change in the slope of the reduction rate curve, which corresponds to the first significant change in the slope of the TCD signal, occurs when an overall reduction rate of 0.11 is reached. This value corresponds to the percentage reduction of hematite alone. This confirms the validity of the mathematical analysis, as will be shown in the following sections, given the correlation between the predominant reducing species in the reactive network and the signal.

Furthermore, valuable insights can be extracted from this numerical manipulation. By avoiding cumulative integration and instead plotting only the integral value calculated for each successive time interval, the integral represents the instantaneous amount of hydrogen consumed, which is proportional to the actual overall reduction rate. In particular, Figure 2.4 displays the normalized integrated signal (i.e., non-cumulative $\int_t^{t+dt} \bar{s}(t)dt$) derived from the same experimental data mathematically processed in Figure 2.3, directly representing the instantaneous reduction rate. Comparable results have been reported by some authors.¹⁰⁶ The initial peak is therefore correlated with the high reaction rate of the Fe_2O_3 reduction step to Fe_3O_4 , while its subsequent drop coincides with a conversion of approximately 0.11. As will be discussed in the sections dedicated to the model-based interpretation of the experimental results (cf. Section 3.8), the other regions of the curve are associated with the overlapping of the two remaining reduction steps, which are strongly influenced by the solid phase that is kinetically and thermodynamically dominant under given conditions.

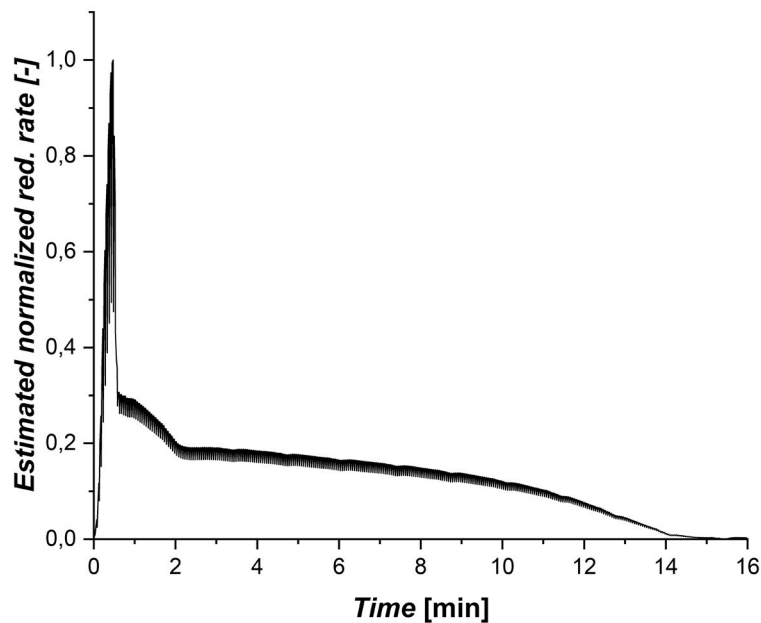


Figure 2.4 Estimated normalized reduction rate.

¹⁰⁶ P. Garg, X. Hu, Y. Li, K. Li, S. Nag, and J. Zhang, 'Kinetics of Iron Oxide Reduction in H₂/H₂O Gas Mixture: Global and Stepwise Reduction', *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 53/3 (2022), 1759–74.

Moreover, the estimated instantaneous reduction rate shows a trend that closely resembles the temporal evolution of the H_2O produced during the reaction, further confirming the reliability of this analytical approach.

2.7 Mathematical development

One of the most common mathematical approaches used to describe heterogeneous non-catalytic gas–solid reactions is the Shrinking Core Model (SCM). SCM has been widely used to describe medium-sized iron oxide pellets, typically in the millimeter-to-centimeter range, due to its ability to capture the key features of reduction kinetics with notable accuracy, even under the simplifying assumptions inherent in the approach (discussed below). In particular, the SCM accounts for the dominant diffusion and reaction phenomena that govern the overall reduction dynamics.

A key innovation of the present work is the extension of the SCM to finer granulometric systems, in which the reactive bed is decomposed into individual grains and each grain is evaluated independently within the SCM framework. This grain-resolved methodology enables an accurate representation of the experimental data and reveals the pronounced thermodynamic dependencies observed even for powders of pure iron oxides (Articles III and IV).

The main explicit assumption of this model is that the reaction occurs exclusively at the surface separating two distinct regions within the solid: an unreacted core and a reacted outer layer. As the reaction progresses and the core is gradually consumed, the surface area of this reaction front decreases accordingly.

This framework allows the definition of a radius, r , representing the instantaneous position of the moving reaction front. It is also assumed that the external particle radius, r_0 , remains constant throughout the process. However, this simplification relies on a series of implicit structural assumptions concerning different phenomena which also take into consideration the geometry and morphology of the reacting solid.

As an illustrative case, the SCM can be developed for a spherical particle undergoing a single reversible reaction, characterized by the progression of a single reaction front within the solid.

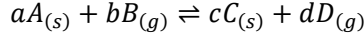


Figure 2.5 schematically illustrates the heterogeneous reaction process and the advancement of this front.

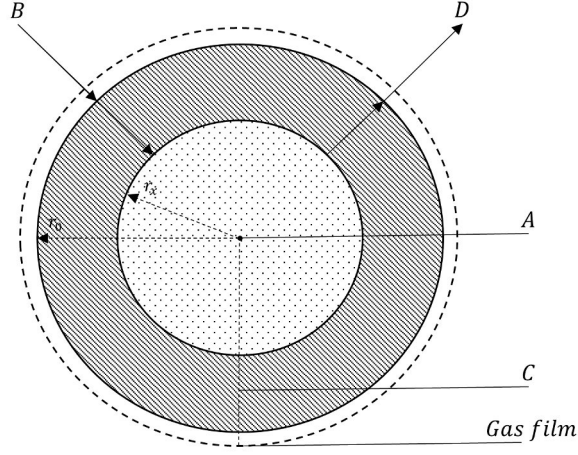


Figure 2.5 Single reaction front scheme in the SCM.

The superficial reaction rate, R , can be generally defined as a function of the local gas-phase concentrations of reactant and product at the reaction interface (i.e., c_B and c_D). The surface reaction rate correlation can be defined by the following expression

$$R = k \left(c_B(r) - \frac{c_D(r)}{K} \right) \quad \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] - \frac{\left[\frac{\text{mol}}{\text{m}^3} \right]}{[-]} \right) \quad (8)$$

where k and K are the kinetic and the thermodynamic equilibrium constants, respectively.

The degree of conversion, X , is defined as the ratio between the moles of solid reactant consumed and the initial moles present, $n(0)$.

$$X(t) = \frac{n(0) - n(t)}{n(0)} \quad [-] = \frac{[\text{mol}] - [\text{mol}]}{[\text{mol}]} \quad (9)$$

Assuming that the unreacted solid is confined within the spherical core of radius r , the number of unreacted moles decreases over time as the front moves inward and can be calculated using the following expression

$$n(t) = \frac{\rho_p}{M} \cdot V_p(t) \quad [\text{mol}] = \frac{\left[\frac{\text{g}}{\text{m}^3}\right]}{\left[\frac{\text{g}}{\text{mol}}\right]} \cdot [\text{m}^3] \quad (10)$$

where ρ_p represents the solid density, M the molecular weight and V_p represents the volume of the particle, which may also refer to the inner core depending on the stage of the reduction process.

It is possible to express the conversion in terms of the core radius considering the initial particle radius r_0 .

$$X(t) = \frac{\frac{\rho_p}{M} \cdot V_p(0) - \frac{\rho_p}{M} \cdot V_p(t)}{\frac{\rho_p}{M} \cdot V_p(0)} \quad [-] = \frac{[\text{mol}] - [\text{mol}]}{[\text{mol}]} \quad (11)$$

$$X(t) = 1 - \left(\frac{r(t)}{r_0}\right)^3 \quad V_p = \frac{4\pi r^3}{3} \quad [-] = [-] - \left(\frac{[\text{m}]}{[\text{m}]}\right)^3 \quad (12)$$

$$r(t) = r_0(1 - X(t))^{\frac{1}{3}} \quad [\text{m}] \quad (13)$$

This derivation is geometrically and conceptually equivalent to that of the contracting sphere model used in fitting model approaches (cf. Section 1.6). Consequently, the progress of the chemical reaction can be directly described through the motion of the spherical reaction front.

The gas-phase mass balance through the product layer formed during the reaction involves only transport phenomena and can be expressed as

$$\frac{\partial \varepsilon c_i}{\partial t} = -\frac{1}{r^2} \cdot \frac{\partial}{\partial r} (r^2 (x_i N + J_i)) \quad [-] \left[\frac{\text{mol}}{\text{m}^3 \text{s}}\right] = -\left[\frac{1}{\text{m}^2}\right] \cdot \left[\frac{1}{\text{m}}\right] \left([\text{m}^2] \left([-] \left[\frac{\text{mol}}{\text{m}^2 \text{s}}\right] + \left[\frac{\text{mol}}{\text{m}^2 \text{s}}\right]\right)\right) \quad (14)$$

$$\frac{\partial \varepsilon c_t}{\partial t} = -\frac{1}{r^2} \cdot \frac{\partial}{\partial r} (r^2 N) \quad [-] \left[\frac{\text{mol}}{\text{m}^3 \text{s}}\right] = -\left[\frac{1}{\text{m}^2}\right] \cdot \left[\frac{1}{\text{m}}\right] \left([\text{m}^2] \left[\frac{\text{mol}}{\text{m}^2 \text{s}}\right]\right) \quad (15)$$

On the left-hand side of the equations, c_i denotes the concentration of the i -th gaseous species (for example, H_2 or H_2O), c_t represents the total gas concentration, while ε corresponds to the particle porosity within the product layer. On the right-hand side, N indicates the total molar flux, x_i the mole fraction of the i -th species in the gas stream, and J_i the molar diffusive flux.

These mass balances require boundary conditions (BC) defined at two key interfaces — the reaction front (r) and the external surface of the particle (r_0).

$$x_i N + J_i = \pm \nu_i \cdot R(c_i(r)) \quad \left[- \right] \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] + \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left[- \right] \cdot \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] \quad (16)$$

$$x_i N + J_i = h_i c_t (x_i(r_0) - x_{i,\text{Bulk}}) \quad \left[- \right] \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] + \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \left(\left[- \right] \right) \quad (17)$$

$$N = (d - b) \cdot R(c_i(r)) \quad \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left(\left[- \right] \right) \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] \quad (18)$$

$$N = h_B c_t (x_B(r_0) - x_{B,\text{Bulk}}) + h_D c_t (x_D(r_0) - x_{D,\text{Bulk}}) \quad \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \left(\left[- \right] \right) \quad (19)$$

At the reaction front, the molar flux of each gas component is related to its stoichiometric coefficient, ν_i , and to the superficial reaction rate. In this case, equality between the reactive and transport contributions is observed. At the external surface, the molar flux depends on the external mass transfer coefficient, h_i , and the diffusive driving force related to the composition of the bulk gas ($x_{i,\text{Bulk}}$).

As for the BCs associated with the total gas mass balance, they simply result from the combination of the boundary conditions applied to each individual gas species. In the case of equimolar gas–solid reactions, the overall molar flux at the external interface becomes negligible, further simplifying the BCs.

The solid-phase mass balances refer to the entire particle and are traditionally defined with respect to the geometry of the reacting solid, given the initial particle volume $V_p(0)$ and the surface area of the reacting core $S = 4\pi r^2$.

$$\frac{\partial C_k}{\partial t} = \pm \nu_k \frac{S}{V_p(0)} \cdot R(c_B(r), c_D(r)) = \pm \nu_k \frac{3r^2}{r_0^3} \cdot R(c_B(r), c_D(r)) \quad \left[\frac{\text{mol}}{\text{m}^3 \text{s}} \right] = \left[- \right] \left[\frac{\text{m}^2}{\text{m}^3} \right] \cdot \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] \quad (20)$$

C_k denotes the overall concentration of the k -th solid species within the particle, while ν_k is the corresponding stoichiometric coefficient. This equation can be rearranged into a dimensionless form by expressing it in terms of the time derivative of the conversion degree.

$$\frac{\partial X}{\partial t} = \frac{a}{C_{A0}} \cdot \frac{3r^2}{r_0^3} \cdot k \left(c_B(r) - \frac{c_D(r)}{K} \right) \quad \left[\frac{-}{\text{s}} \right] = \left[\frac{-}{\left[\frac{\text{mol}}{\text{m}^3} \right]} \right] \cdot \left[\frac{\text{m}^2}{\text{m}^3} \right] \cdot \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] - \frac{\left[\frac{\text{mol}}{\text{m}^3} \right]}{\left[- \right]} \right) \quad (21)$$

In this context, assumptions can be introduced to simplify the governing equations, whether differential or not—and to reduce the number of mass balances to be solved. If radially homogeneous porosity within the particle is assumed, even during the reaction, ε can be removed from the time derivative in

the gas-phase mass balances. Furthermore, if temperature and pressure inside the particle are also considered homogeneous, the total gas concentration remains constant throughout the solid (i.e., $\frac{\partial c_t}{\partial t} = 0$). This implies that the molar flux can be calculated using

$$N(r) = \frac{r^2 \cdot (d - b) \cdot R(c_B(r), c_D(r))}{r_0^2} \quad \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \frac{[\text{m}^2][-] \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right]}{[\text{m}^2]} \quad (22)$$

The same assumptions also affect the term related to the diffusive flux, J . In particular, for a binary gas mixture where no variation in the total gas concentration is observed, Fick's law can be applied. Furthermore, if the particle morphology is assumed to be radially uniform, as previously stated, the effective diffusion coefficient, D_e , can be calculated from the molecular binary diffusion coefficient, D , by accounting for the particle porosity and tortuosity τ . The final expression can therefore be written as

$$J_i = -D_e \cdot \frac{\partial c_i}{\partial r} = -D \cdot \frac{\varepsilon}{\tau} \cdot \frac{\partial c_i}{\partial r} \quad \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (23)$$

Another assumption concerns the solid-phase mass balance. Specifically, if the gas concentration profiles change much more rapidly than the movement of the reaction front and the associated solid transformation, the gas-phase mass balances can be solved under steady-state conditions.

On the gas side, the mass balance therefore takes the form

$$\frac{D_e}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) = 0 \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \left[\frac{1}{\text{m}} \right] \left(\left[\text{m}^2 \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (24)$$

Based on the previous assumptions, the corresponding BCs can be modified by introducing the superficial reaction rate

$$D_e \cdot \frac{\partial c_i}{\partial r} = \pm v_i \cdot k \left(c_B(r) - \frac{c_D(r)}{K} \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \left[\frac{\text{mol}}{\text{m}^3} \right] = [-] \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] - \frac{\left[\frac{\text{mol}}{\text{m}^3} \right]}{[-]} \right) \quad (25)$$

$$D_e \cdot \frac{\partial c_i}{\partial r} = h_i \left(c_{i,Bulk} - c_i(r_0) \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \left[\frac{\text{mol}}{\text{m}^3} \right] = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (26)$$

To resolve these integrals, auxiliary functions can be introduced to define the concentrations c_i

$$c_i(t) = -\frac{A_I}{r} + B_I \quad \left[\frac{\text{mol}}{\text{m}^3} \right] = \frac{\left[\frac{\text{mol}}{\text{m}^2} \right]}{\left[\text{m} \right]} + \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (27)$$

where $I = 1, 2$ when $i = B, D$, respectively. By substituting these expressions into the boundary conditions, the following relationships are obtained

$$D_e \cdot \frac{A_I}{r^2} = \pm v \cdot k \left(-\frac{A_1}{r} + B_1 - \frac{1}{K} \left(-\frac{A_2}{r} + B_2 \right) \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \frac{\left[\frac{\text{mol}}{\text{m}^2} \right]}{\left[\text{m}^2 \right]} = \left[- \right] \cdot \left(\left[\frac{\text{mol}}{\text{m}^3} \right] - \left[- \right] \cdot \left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (28)$$

$$D_e \cdot \frac{A_I}{r_0^2} = h_i c_{i,\text{Bulk}} - h_i \left(-\frac{A_I}{r} + B_I \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \frac{\left[\frac{\text{mol}}{\text{m}^2} \right]}{\left[\text{m}^2 \right]} = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] - \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (29)$$

Using the four derived boundary conditions, a linear system can be formulated to determine the unknown parameters A_I and B_I .

$$\begin{pmatrix} \left(\frac{D_e}{r^2} + \frac{bk}{r} \right) & (-bk) & \left(-\frac{bk}{Kr} \right) & \left(\frac{bk}{K} \right) \\ \left(-\frac{dk}{r} \right) & (dk) & \left(\frac{D_e}{r^2} + \frac{dk}{Kr} \right) & \left(-\frac{dk}{K} \right) \\ \left(\frac{D_e}{r_0^2} - \frac{h_B}{r_0} \right) & (h_B) & 0 & 0 \\ 0 & 0 & \left(\frac{D_e}{r_0^2} - \frac{h_D}{r_0} \right) & (h_D) \end{pmatrix} \cdot \begin{pmatrix} A_1 \\ B_1 \\ A_2 \\ B_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ b \cdot h_B c_{B,\text{Bulk}} \\ d \cdot h_D c_{B,\text{Bulk}} \end{pmatrix} \quad (30)$$

By solving this linear system and applying the equation that relates the solid conversion to the radius of the reacting core, the solid-phase mass balance can be rewritten as

$$\begin{aligned} \frac{\partial X}{\partial t} &= \frac{a}{C_{A0}} \cdot \frac{3r^2}{r_0^3} \cdot \frac{c_{B,\text{Bulk}} - \frac{c_{D,\text{Bulk}}}{K}}{\frac{1}{k} + \frac{r_i}{D_e} \cdot \left(\frac{d}{K} + b \right) \left(1 - \frac{r}{r_0} \right) + \frac{r^2}{r_0^2} \left(\frac{d}{Kh_D} + \frac{b}{h_B} \right)} \Rightarrow \\ \Rightarrow \frac{\partial X}{\partial t} &= \frac{a}{C_{A0}} \cdot \frac{3}{r_0} \cdot \frac{c_{B,\text{Bulk}}}{\underbrace{\frac{1}{k} \cdot \frac{1}{(1-X(t))^{\frac{2}{3}}}}_{\text{kinetic resistance}} + \underbrace{\frac{r_0}{D_e} \cdot \left(\frac{d}{K} + b \right) \frac{1 - (1-X(t))^{\frac{1}{3}}}{(1-X(t))^{\frac{1}{3}}}}_{\text{internal diffusion resistance}} + \underbrace{\left(\frac{d}{Kh_D} + \frac{b}{h_B} \right)}_{\text{external diffusion resistance}}} \end{aligned} \quad (31)$$

This formulation represents the classical method of expressing the SCM balance equation, where the denominator identifies the different resistances: kinetic,

internal diffusion, and external diffusion. From this balance, it is possible to derive the characteristic times associated with reaction kinetics and mass transfer and consequently evaluate the controlling regime of the heterogeneous reaction process using the dimensionless Damköhler and Biot numbers.

2.8 Dynamic multiple shrinking core model

In the case of multiple consecutive reactions, the mathematical procedure described in the previous section can be easily extended by applying the same assumptions and introducing continuity equations between the different product layers that form during the process.

The reactive network consists of three reversible reactions in series

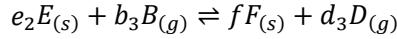
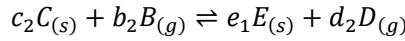
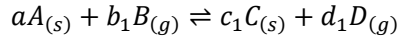


Figure 2.6 illustrates the heterogeneous reactive process and the progression of the three distinct reaction fronts.

The key assumption remains that the reactions occur exclusively at the reaction fronts, identified by different radii r_j , where index j denotes the specific reaction front.

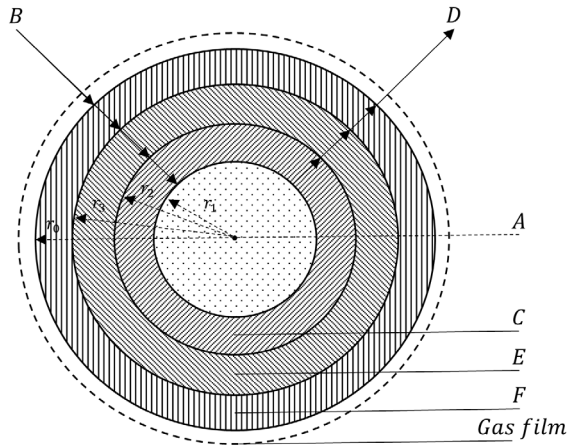


Figure 2.6 Triple reaction front scheme in the SCM.

The reaction rate at the j -th front can be calculated by considering the geometry of the corresponding core and evaluating its reactive surface area S_j .

The reaction rate can then be calculated in the same way as for the single front, i.e.,

$$R_j = \frac{S_j}{V_p} k_j \left(c_B(r_j) - \frac{c_D(r_j)}{K_j} \right) = 3 \frac{r_j^2}{r_0^3} k_j \left(c_B(r_j) - \frac{c_D(r_j)}{K_j} \right) \quad \left[\frac{\text{mol}}{\text{m}^3 \text{s}} \right] = \left[\frac{\text{m}^2}{\text{m}^3} \right] \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \left[\frac{\text{m}^2}{\text{s}} \right] \quad (32)$$

The solid-phase mass balance can be expressed in terms of the total composition of the solid species within the particle, considering only the chemical reactions in which each solid species is involved.

$$\frac{dC_A}{dt} = -aR_1 \quad (33)$$

$$\frac{dC_C}{dt} = c_1R_1 - c_2R_2 \quad \left[\frac{\text{mol}}{\text{m}^3 \text{s}} \right] \quad (34)$$

$$\frac{dC_E}{dt} = e_1R_2 - e_2R_3 \quad (35)$$

The positions of the different reaction fronts can be evaluated as functions of the overall composition of the reacted solid at each step, taking into account the stoichiometric contributions of the various reactions.

$$r_1(t) = r_0 \left(\frac{C_A(t)}{C_{A0}} \right)^{\frac{1}{3}} \quad (36)$$

$$r_2(t) = r_0 \left(\frac{C_A(t) + \frac{c_1}{a} C_C(t)}{C_{A0}} \right)^{\frac{1}{3}} \quad [m] = [m] \frac{\left[\frac{\text{mol}}{\text{m}^3} \right]}{\left[\frac{\text{mol}}{\text{m}^3} \right]} \quad (37)$$

$$r_3(t) = r_0 \left(\frac{C_A(t) + \frac{c_1}{a} C_C(t) + \frac{c_1 e_1}{a c_2} C_E(t)}{C_{A0}} \right)^{\frac{1}{3}} \quad (38)$$

In addition to applying the same assumptions regarding temperature, pressure, and total gas composition, it is also necessary to define the different porosities within the various layers. Assuming that morphology remains radially uniform

for each solid species, different effective diffusion coefficients can be assigned to the gaseous components in each layer.

$$\frac{D_{e,i}^C}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) = 0 \quad r_1 \leq r \leq r_2 \quad (39)$$

$$\frac{D_{e,i}^E}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) = 0 \quad r_2 \leq r \leq r_3 \quad \left[\frac{\text{m}^2}{\text{s}} \right] \cdot \left[\frac{1}{\text{m}} \right] \left(\left[\text{m}^2 \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (40)$$

$$\frac{D_{e,i}^F}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_i}{\partial r} \right) = 0 \quad r_3 \leq r \leq r_0 \quad (41)$$

where $D_{e,i}^C$, $D_{e,i}^E$ and $D_{e,i}^F$ represent the effective diffusivity of the i -th component in each distinct product layer. The gas-phase boundary conditions are defined analogously to the single-front case

$$D_{e,i}^C \frac{\partial c_i}{\partial r} = \pm v_{i,j} k_1 \left(c_B(r_1) - \frac{c_D(r_1)}{K_1} \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^2} \right] = [-] \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (42)$$

$$D_{e,i}^E \left(\frac{\partial c_i}{\partial r} \right)^+ = D_{e,i}^C \left(\frac{\partial c_i}{\partial r} \right)^- + b_2 k_2 \left(c_B(r_2) - \frac{c_D(r_2)}{K_2} \right) \quad (43)$$

$$D_{e,i}^F \left(\frac{\partial c_i}{\partial r} \right)^+ = D_{e,i}^E \left(\frac{\partial c_i}{\partial r} \right)^- + b_3 k_3 \left(c_B(r_3) - \frac{c_D(r_3)}{K_3} \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] = \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \pm [-] \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (44)$$

$$D_{e,i}^F \frac{\partial c_i}{\partial r} = h_i \left(c_{i,\text{Bulk}} - c_i(r_0) \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (45)$$

To solve the complex system of integrals, auxiliary functions can again be introduced to express the gas concentrations. This leads to a set of equations for each gas component, depending on the layer in which the concentration is evaluated

$$c_i(t) = \begin{cases} -\frac{A_{I,J}}{r} + B_{I,J} & r_1 \leq r \leq r_2 \\ -\frac{A_{I,J}}{r} + B_{I,J} & r_2 \leq r \leq r_3 \\ -\frac{A_{I,J}}{r} + B_{I,J} & r_3 \leq r \leq r_0 \end{cases} \quad \left[\frac{\text{mol}}{\text{m}^3} \right] = \left[\frac{\text{mol}}{\text{m}^3} \right] + \left[\frac{\text{mol}}{\text{m}^3} \right] \quad (46)$$

where $I = 1,2$ when $i = B,D$ while $J = 1,2,3$ when $j = C,E,F$, respectively. By substituting these concentrations into the boundary conditions, an initial set of eight equations is obtained

$$D_{e,i}^C \frac{A_{I,1}}{r_1^2} = \pm v_{i,j} k_1 \left(-\frac{A_{11}}{r_1} + B_{11} - \frac{1}{K_1} \left(-\frac{A_{21}}{r_1} + B_{21} \right) \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\frac{\text{mol}}{\text{m}^2}}{\frac{\text{mol}}{\text{m}^2}} \right] = [-] \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (47)$$

$$D_{e,i}^E \frac{A_{I,2}}{r_2^2} = D_{e,i}^C \frac{A_{I,1}}{r_2^2} \pm v_{i,j} k_2 \left(-\frac{A_{12}}{r_2} + B_{12} - \frac{1}{K_2} \left(-\frac{A_{22}}{r_2} + B_{22} \right) \right) \quad \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\frac{\text{mol}}{\text{m}^3}}{\frac{\text{mol}}{\text{m}^3}} \right] = \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\frac{\text{mol}}{\text{m}^3}}{\frac{\text{mol}}{\text{m}^3}} \right] \quad (48)$$

$$D_{e,i}^F \frac{A_{I,3}}{r_3^2} = D_{e,i}^E \frac{A_{I,2}}{r_3^2} \pm v_{i,j} k_3 \left(-\frac{A_{13}}{r_3} + B_{13} - \frac{1}{K_3} \left(-\frac{A_{23}}{r_3} + B_{23} \right) \right) \quad \pm [-] \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \quad (49)$$

$$D_{e,i}^F \frac{A_{I,3}}{r_0^2} = h_i c_{i,\text{Bulk}} - h_i \left(-\frac{A_{I,3}}{r_0} + B_{I,3} \right) \quad \begin{aligned} & \left[\frac{\text{m}^2}{\text{s}} \right] \left[\frac{\frac{\text{mol}}{\text{m}^2}}{\frac{\text{mol}}{\text{m}^2}} \right] \\ & = \left[\frac{\text{m}}{\text{s}} \right] \left[\frac{\frac{\text{mol}}{\text{m}^3}}{\frac{\text{mol}}{\text{m}^3}} \right] - \left[\frac{\text{m}}{\text{s}} \right] \left(\left[\frac{\text{mol}}{\text{m}^3} \right] \right) \end{aligned} \quad (50)$$

Additional four continuity equations (i.e., $T r = r_2$ and $r = r_3$) are introduced at the layer interfaces, enabling the complete resolution of the linear system

$$-\frac{A_{I,1}}{r_2} + B_{I,1} = -\frac{A_{I,2}}{r_2} + B_{I,2} \quad (51)$$

$$-\frac{A_{I,2}}{r_3} + B_{I,2} = -\frac{A_{I,3}}{r_3} + B_{I,3} \quad \begin{aligned} & \left[\frac{\frac{\text{mol}}{\text{m}^2}}{\frac{\text{mol}}{\text{m}^2}} \right] + \left[\frac{\frac{\text{mol}}{\text{m}^2}}{\frac{\text{mol}}{\text{m}^3}} \right] = \left[\frac{\frac{\text{mol}}{\text{m}^2}}{\frac{\text{mol}}{\text{m}^2}} \right] + \left[\frac{\frac{\text{mol}}{\text{mol}}}{\frac{\text{mol}}{\text{m}^3}} \right] \end{aligned} \quad (52)$$

The new linear system is presented below

$$\begin{pmatrix}
D_{eD}^C + \frac{b_1 k_1}{r_1^2} & (-b_1 k_1) & 0 & 0 & 0 & 0 & \left(-\frac{b_1 k_1}{K_1 r_1}\right) & \left(\frac{b_1 k_1}{K_1}\right) & 0 & 0 & 0 & 0 \\
\left(-\frac{d_1 k_1}{r_1}\right) & (d_1 k_1) & 0 & 0 & 0 & 0 & \left(\frac{D_{eD}^C}{r_1^2} + \frac{d_1 k_1}{K_1 r_1}\right) & \left(-\frac{d_1 k_1}{K_1}\right) & 0 & 0 & 0 & 0 \\
\left(-\frac{D_{eB}^C}{r_2^2}\right) & 0 & \left(\frac{D_{eB}^C}{r_2^2} + \frac{b_2 k_2}{r_2}\right) & (-b_2 k_2) & 0 & 0 & 0 & 0 & \left(-\frac{b_2 k_2}{K_2 r_2}\right) & \left(\frac{b_2 k_2}{K_2}\right) & 0 & 0 \\
0 & 0 & \left(-\frac{d_2 k_2}{r_2}\right) & (d_2 k_2) & 0 & 0 & \left(-\frac{D_{eD}^C}{r_2^2}\right) & 0 & \left(\frac{D_{eD}^C}{r_2^2} + \frac{d_2 k_2}{K_2 r_2}\right) & \left(-\frac{d_2 k_2}{K_2}\right) & 0 & 0 \\
0 & 0 & \left(-\frac{D_{eB}^C}{r_3^2}\right) & 0 & \left(\frac{D_{eB}^C}{r_3^2} + \frac{b_3 k_3}{r_3}\right) & (-b_3 k_3) & 0 & 0 & \left(-\frac{b_3 k_3}{K_3 r_3}\right) & \left(\frac{b_3 k_3}{K_3}\right) & 0 & 0 \\
0 & 0 & 0 & 0 & \left(-\frac{d_3 k_3}{r_3}\right) & (d_3 k_3) & 0 & 0 & \left(\frac{D_{eD}^C}{r_3^2} + \frac{d_3 k_3}{K_3 r_3}\right) & \left(-\frac{d_3 k_3}{K_3}\right) & 0 & 0 \\
0 & 0 & 0 & 0 & \left(-\frac{D_{eB}^C}{r_0^2} - \frac{h_B}{r_0}\right) & (h_B) & 0 & 0 & 0 & 0 & \left(\frac{D_{eD}^C}{r_0^2} - \frac{h_D}{r_0}\right) & (h_D) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\left(-\frac{1}{r_2}\right) & 1 & \left(\frac{1}{r_2}\right) & -1 & 0 & 0 & \left(-\frac{1}{r_2}\right) & 1 & \left(\frac{1}{r_2}\right) & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \left(-\frac{1}{r_3}\right) & 1 & \left(-\frac{1}{r_3}\right) & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix} \cdot \begin{pmatrix} A_{11} \\ B_{11} \\ A_{12} \\ B_{12} \\ A_{13} \\ B_{13} \\ A_{21} \\ B_{21} \\ A_{22} \\ B_{22} \\ A_{23} \\ B_{23} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ b \cdot h_B c_{B,Bulk} \\ d \cdot h_D c_{D,Bulk} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

To further simplify the solution, it is possible to assume uniform external mass transfer coefficients (i.e., $h_i = h$) and effective diffusion coefficients (i.e., $D_{e,i}^C = D_{e,1}$; $D_{e,i}^E = D_{e,2}$; $D_{e,i}^F = D_{e,3}$) across all layers, independent of the gaseous species.

Moreover, when the chemical reactions share identical stoichiometric coefficients for both gaseous reactants and products — as in the reduction of iron oxides — the system becomes particularly straightforward to handle (i.e., $b_1 = b_2 = b_3 = d_1 = d_2 = d_3 = 1$).

Under these assumptions, the solution of the linear system can be expressed through a set of coefficients, denoted as A_j , B_j , and F , which represent the kinetic, internal diffusion, and external diffusion resistances, respectively.

$$A_1(t) = \frac{r_0^2}{r_1^2 k_1 \left(1 + \frac{1}{K_1}\right)} = \frac{1}{(1 - X_1(t))^{\frac{2}{3}}} \cdot \frac{1}{k_1 \left(1 + \frac{1}{K_1}\right)} \quad (53)$$

$$A_2(t) = \frac{r_2^2}{r_2^2 k_2 \left(1 + \frac{1}{K_2}\right)} = \frac{1}{(1 - X_2(t))^{\frac{2}{3}}} \cdot \frac{1}{k_2 \left(1 + \frac{1}{K_2}\right)} \quad \left[\frac{s}{m}\right] = \frac{\left[\frac{m^2}{m}\right]}{\left[\frac{m^2}{s}\right] \left[-\right]} = \frac{\left[-\right]}{\left[-\right]} \frac{\left[-\right]}{\left[\frac{m}{s}\right] \left[-\right]} \quad (54)$$

$$A_3(t) = \frac{r_0^2}{r_3^2 k_3 \left(1 + \frac{1}{K_3}\right)} = \frac{1}{(1 - X_3(t))^{\frac{2}{3}}} \cdot \frac{1}{k_3 \left(1 + \frac{1}{K_3}\right)} \quad (55)$$

$$B_1(t) = \frac{r_2 - r_1}{r_1 r_2} \cdot \frac{r_0^2}{D_{e,1}} = \frac{(1 - X_2(t))^{\frac{1}{3}} - (1 - X_1(t))^{\frac{1}{3}}}{(1 - X_1(t))^{\frac{1}{3}} \cdot (1 - X_2(t))^{\frac{1}{3}}} \cdot \frac{r_0}{D_{e,1}} \quad (56)$$

$$B_2(t) = \frac{r_3 - r_2}{r_2 r_3} \cdot \frac{r_0^2}{D_{e,2}} = \frac{(1 - X_3(t))^{\frac{1}{3}} - (1 - X_2(t))^{\frac{1}{3}}}{(1 - X_2(t))^{\frac{1}{3}} \cdot (1 - X_3(t))^{\frac{1}{3}}} \cdot \frac{r_0}{D_{e,2}} \quad \left[\frac{s}{m}\right] = \frac{\left[\frac{m}{m}\right] \left[\frac{m^2}{m}\right]}{\left[\frac{m^2}{s}\right]} = \frac{\left[-\right] \left[\frac{m}{m}\right]}{\left[-\right] \left[\frac{m^2}{s}\right]} \quad (57)$$

$$B_3(t) = \frac{r_0 - r_3}{r_3} \cdot \frac{r_0}{D_{e,3}} = \frac{1 - (1 - X_3(t))^{\frac{1}{3}}}{(1 - X_3(t))^{\frac{1}{3}}} \cdot \frac{r_0}{D_{e,3}} \quad (58)$$

$$F = \frac{1}{h} \quad \left[\frac{s}{m}\right] = \frac{\left[-\right]}{\left[\frac{m}{s}\right]} \quad (59)$$

This formulation constitutes a direct extension of the single-front model, providing a comparable description of the potentially rate-limiting processes, but evaluated at each individual reaction front and in every product layer.

A crucial aspect in the description of such a reactive system lies in identifying the times at which the particle, initially composed entirely of reactant A, begins to form subsequent solid phases that can further react. This requires determining the number of active reaction fronts present at a given time. The evaluation of the degree of conversion defined by solid species can assist in this determination. At each timestep of the simulation, the composition of the solid phase is assessed to identify the number of active reaction fronts, which may vary between three and zero.

To manage the transition from one to multiple reaction fronts, the same approach can be applied as for the case of two equilibrium reactions and two corresponding fronts. The resulting mathematical framework, consisting of analytical equations, describes a dynamic multi-front reduction process.

To achieve this, boundary conditions must be defined to determine the number of active reaction fronts. A new parameter can be defined, denoted as φ , which in turn specifies the number of the accessible mathematical fronts associated with the corresponding degrees of conversion

$$\varphi = \begin{cases} 1, j = 1 & \text{if } X_1(t, z_2) = 0 \\ 2, j = 1, 2 & \text{if } X_1(t, z_2) < 1 \wedge X_2(t, z_2) = 0 \\ 3, j = 1, 2, 3 & \text{if } X_1(t, z_2) < 1 \wedge X_2(t, z_2) < 1 \wedge X_3(t, z_2) < 1 \\ 2, j = 2, 3 & \text{if } X_1(t, z_2) = 1 \wedge X_2(t, z_2) < 1 \wedge X_3(t, z_2) < 1 \\ 1, j = 3 & \text{if } X_1(t, z_2) = 1 \wedge X_2(t, z_2) = 1 \wedge X_3(t, z_2) < 1 \\ 0, & \text{if } X_1(t, z_2) = 1 \wedge X_2(t, z_2) = 1 \wedge X_3(t, z_2) = 1 \end{cases} \quad (60)$$

From this, a general expression for the reaction rate can be derived as a function of both the front index j and the number of available fronts φ

$$R_j(t)|_{\varphi} = \frac{3}{r_0} \frac{1}{W(t, A_j|_{\varphi}, B_j|_{\varphi}, F)} \cdot N_j(t, A_j|_{\varphi}, B_j|_{\varphi}, F, c_B) \quad \left[\frac{\text{mol}}{\text{m}^3 \text{s}} \right] = \left[\frac{1}{\text{m}} \right] \cdot \frac{1}{\left[\frac{\text{s}^f}{\text{m}^f} \right]} \cdot \left[\frac{\text{s}^{f-1}}{\text{m}^{f-1}} \cdot \frac{\text{mol}}{\text{m}^3} \right] \quad (61)$$

In this formulation, the term N_j represents the effective contribution of each individual reaction, while W_j denotes the total system resistance. Both quantities are defined based on the individual resistances identified in the model and vary according to the number of simultaneous reactions involved in the process.

2.9 Gas and solid mass balance

The reactor system used in this study consists of a fixed bed of iron oxide fines through which a reducing gas flows continuously.

The evaluation of the gas composition was significantly refined during this doctoral research. Initially, the gas composition was estimated using an axial dispersion model for fixed beds, considering only the reactive portion of the solid phase (Article II). Subsequently, a more accurate analysis based on RTD experiments demonstrated the necessity of also accounting for the empty reactor section above the solid bed (Section 3.1.2).

For this reason, the final formulation of the gas-phase mass balance was divided into two zones: a non-reactive region ($l = 1$) and a reactive fixed-bed region ($l = 2$), each characterized by dimensionless spatial coordinates z_1 and z_2 , respectively

$$\frac{\partial c_i(t, z_l)}{\partial t} = \begin{cases} -\frac{u}{L - \delta} \cdot \frac{\partial c_i(t, z_1)}{\partial z_1} + \frac{D_z}{(L - \delta)^2} \cdot \frac{\partial^2 c_i(t, z_1)}{\partial z_1^2} \\ -\frac{u}{\delta} \cdot \frac{\partial c_i(t, z_2)}{\partial z_2} + \frac{\partial^2 c_i(t, z_2)}{\partial z_2^2} + (1 - \varepsilon) \cdot \sum_{j|f}^3 v_{i,j} \cdot R_j(t, z_2) \end{cases} \quad (62)$$

In the governing equations, c_i represents the concentration of gas species i (H_2 or H_2O), and $v_{i,j}$ denotes the stoichiometric coefficient associated with reaction j . The main hydrodynamic parameters include the bed height h , linear gas velocity u , and axial dispersion coefficient D_z . The bed porosity, ε , was determined through physisorption measurements (Section 3.1.1). The local reduction rate, R_j is expressed as a weighted sum over the different particle size classes and can be written in general form as

$$\begin{aligned} R_j(t, z_2) &= \sum_{n=1}^N x_n \cdot R_{j,n}(t, z_2, r_n^0) \\ &= \sum_{n=1}^N x_n \cdot \frac{P}{R_g T} \frac{3}{r_n^0} \frac{1}{A_j(t, z_2, r_n^0)|_\varphi} \cdot \left(\frac{N_j(t, z_2, r_n^0)|_\varphi}{W(t, z_2, r_n^0)|_\varphi} - y_{H_2,j,eq}(t, z_2) \right) \end{aligned} \quad \begin{aligned} &\left[\frac{\text{mol}_O}{\text{m}^3 \text{s}} \right] = \\ &\frac{\left[\frac{\text{N}}{\text{m}^2} \right]}{\left[\frac{\text{J}}{\text{mol K}} \right] \left[\text{K} \right]} \frac{1}{\left[\text{m} \right]} \frac{1}{\left[\frac{\text{s}}{\text{m}} \right]} \\ &\cdot \left(\frac{\left[\frac{\text{s}^{f-1}}{\text{m}^{f-1}} \right]}{\left[\frac{\text{s}^{f-1}}{\text{m}^{f-1}} \right]} - [-] \right) \end{aligned} \quad (63)$$

Here, R_g is the universal gas constant, P is the pressure, and $y_{H_2,j,eq}$ is the equilibrium hydrogen mole fraction derived based on local gas composition and the reaction-specific equilibrium constant. The global reduction rate is then

aggregated over all particle size classes by weighing each rate by the respective initial radius r_n^0 and weight fraction x_n , thus capturing the influence of particle size distribution on the overall conversion.

The solid-side mass balance describes the dynamic of the degree of conversion X_j using the ordinary differential equation along the axial coordinate z_2 of the bed. The equation is formulated as

$$\frac{\partial X_j(t, z_2)}{\partial t} = (1 - \varepsilon) \frac{R_j(t, z_2)}{n_0 \cdot a_j} \quad \left[\frac{1}{s} \right] = [-] \frac{\left[\frac{\text{mol}_0}{\text{m}^3 s} \right]}{\left[\frac{\text{mol}_0}{\text{m}^3} \right] \cdot [-]} \quad (64)$$

where n_0 represents the initial molar oxygen content of the sample, calculated from the mass and molecular weight of the starting oxide (e.g., $n_0 = 3m/M$), while a_j denotes the fraction of oxygen contained in the specific iron oxide phase.

These parameters strongly depend on the starting material and the number of accessible reactions, which are themselves determined by the operating temperature (cf. Figure 1.6). As can be observed, both the gas- and solid-phase balances focus on the reactive region corresponding to the solid portion of the bed. In cases where the interparticle porosity changes during the reaction — supported by structural evidence obtained from qualitative analysis of transient solid samples — it becomes necessary to implement a dedicated porosity balance.

Such an approach is crucial, as solid morphology plays a determining role in accurately describing the reaction kinetics of the reduction process.

2.10 Reaction front control

In heterogeneous gas–solid systems, particularly in sequential reactions described by the SCM, certain combinations of kinetic parameters may lead to physically or chemically unrealistic outcomes, such as front crossing, where an outer reaction front progresses faster than an inner one and potentially overtakes it.

During parameter estimation, it is therefore necessary to prevent combinations of parameters that reproduce experimental data but result in such physically inconsistent behavior.

To address this issue, a mathematical control algorithm was implemented. At each integration step, the model computes the hypothetical reduction degree for

the next step using the trapezoidal method. If the estimated reduction degree of an outer front exceeds that of the adjacent inner front, the algorithm enforces equality of the corresponding derivatives. In other terms, if a faster external front tends to overtake a slower inner one, it is instead constrained to advance at the same rate as the slowest front.

This front control condition can be expressed as follows

$$X_j(t + \Delta t, z_2) = X_{j+1}(t + \Delta t, z_2) \quad \text{if} \quad X_{j-1}(t + \Delta t, z_2) < X_j(t + \Delta t, z_2) \quad (65)$$

2.11 Criterion and numerical solutions

The particle size distribution, refined through LS measurements, provided a precise estimation of the mean particle diameter and its distribution. This information was essential to assess the extent of possible external mass transfer limitations under the adopted experimental conditions. Based on these results, the external mass transfer coefficient, h , was estimated using established correlations involving the Sherwood number, the Reynolds number, and the molecular diffusivity of the gaseous species (Article III). The resulting values indicated that the characteristic times associated with external diffusion were significantly small. Consequently, external diffusion resistances could be safely neglected in kinetic analysis.

Analysis of thermal gradients within the particles confirmed that intraparticle temperature differences were negligible, with maximum deviations below 1 K (Article II).

The models were implemented in MATLAB. Spatial discretization of the partial differential equations was performed using the finite difference method, with a backward differentiation scheme for first-order derivatives and a central difference scheme for second-order derivatives. The resulting system of ordinary differential equations was integrated over time using the *ode15s* solver, which employs variable time steps and orders (1–5) based on numerical differentiation formulas (Articles II–IV).

Parameter estimation (Article III) was carried out using *patternsearch*, a direct, derivative-free optimization algorithm suitable for nonlinear, non-smooth objective function

Notation

Abbreviations

BC	Boundary Conditions
BET	Brunauer–Emmett–Teller
CO	Carbon Monoxide
DSC–MS	Differential Scanning Calorimetric coupled with Mass Spectrometry
LS	Light scattering
RTD	Residence Time Distribution
SCM	Shrinking Core Model
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TGA	Thermogravimetric analysis
TPR	Temperature-Programmed Reduction
XRD	X-ray diffraction

Symbols

a	Stoichiometric coefficient solid species A [-]
a_j	Solid oxygen fraction [-]
A_j	Kinetic resistance coefficient [s/m]
A_I	First factor auxiliary functions [mol/m ²]
$A_{I,j}$	First factor auxiliary functions of i -th gas species in j -th product layer [mol/m ²]
b	Blank TCD signal [mV]
b'	Normalized blank signal [-]
$\tilde{b}$	Complement to 1 blank signal [-]
b_j	Stoichiometric coefficient gas species B j -th front reaction [-]
B	Stoichiometric coefficient gas species B [-]
B_j	Internal diffusion resistance coefficient [s/m]
B_I	Second factor auxiliary functions [mol/m ³]
$B_{I,j}$	Second factor auxiliary functions of i -th gas species in j -th product layer [mol/m ³]
c	Stoichiometric coefficient solid species C [-]
c_1	First stoichiometric coefficient solid species C [-]
c_2	Second stoichiometric coefficient solid species C [-]
$c_{B,Bulk}$	Bulk concentrations of B [mol/m ³]

$c_{D,Bulk}$	Bulk concentrations of D [mol/m ³]
c_i	Concentrations of i -th gas compound [mol/m ³]
C_k	Concentration of k -th solid compound [mol/m ³]
C_{A0}	Initial A concentration [mol/m ³]
d	Stoichiometric coefficient gas species D [-]
d_j	Stoichiometric coefficient gas species D j -th front reaction [-]
D	Molecular binary diffusion coefficient [m ² /s]
D_e	Effective diffusion coefficient [m ² /s]
$D_{e,i}^k$	Effective diffusion coefficient of i -th gas species in solid k -th [m ² /s]
D_z	Axial dispersion coefficient [m ² /s]
e_1	First stoichiometric coefficient solid species E [-]
e_2	Second stoichiometric coefficient solid species E [-]
f	Stoichiometric coefficient solid species F [-]
$f(X)$	Solid state reaction mechanism
F	External diffusion resistance coefficient [s/m]
h_B	External B mass transfer coefficient [m/s]
h_D	External D mass transfer coefficient [m/s]
h_i	External mass transfer coefficient [m/s]
J_i	Molar diffusive flux [mol/(m ² s)]
k	Kinetic constant [m/s]
k_j	Kinetic constant j -th reaction front [m/s]
K	Thermodynamic constant [-]
K_j	Thermodynamic constant j -th reaction front [-]
L	Reactor length [m]
m	Sample mass [g]
M	Molecular Weight [g/mol]
n	Moles of reactant [mol]
N	Total molar flux [mol/(m ² s)]
P	Pressure [N/m ²]
Pe	Peclet Number [-]
Q	Total gas flow rate [mL/min]
r	Generic core radius [m]
r_0	Initial particle radius [m]

r_j	Radius j -th front reaction [m]
r_n^0	Initial weighted radius [m]
R	Single front superficial reaction rate [mol/(m ² s)]
R_g	Gas constant [J/(mol K)]
R_j	Global local reduction rate [mol/(m ³ s)]
$R_{j,n}$	Local weighted reduction rate [mol/(m ³ s)]
R_r	Reactor radius [m]
s	Experimental TCD signal [mV]
s'	Normalized TCD signal [-]
$\tilde{s}$	Complement to 1 TCD signal [-]
S	Core surface area [m ²]
$\tilde{S}$	Signal integral [-]
S_j	Surface area j -th reaction front [m ²]
t	Time [s]
T	Temperature [K]
u	Linear gas velocity [m/s]
V_p	Particle volume [m ³]
x_n	Weight granulometric distribution [-]
$x_{i,Bulk}$	molar fraction gas phase [-]
X	Reduction degree [-]
X_j	Reduction degree of j -th reaction front [-]
y	Reductant molar fraction [-]
$y_{H_2,j,eq}$	Equilibrium hydrogen mole fraction [-]
z_l	Reactor axial coordinate [-]
δ	Reactive bed height [m]
Δt	Integration step [s]
ε	Porosity [-]
ν_i	Single front reaction i -th gas stoichiometric coefficient [-]
$\nu_{i,j}$	Single front reaction i -th, j -th stoichiometric coefficient [-]
ν_k	Single front reaction k -th solid stoichiometric coefficient [-]
ρ_p	Particle density [g/m ³]
τ	Tortuosity [-]

Subscripts

A	Solid species A
B	Gas species B
C	Solid species C
D	Gas species D
E	Solid species E
i	i -th gas species
I	Index gas species auxiliary equation
j	j -th reaction front
J	Index product layer auxiliary equation
k	k -th solid species
l	Reactor spatial domains
n	Index of granulometric family's distribution
p	Solid phase
t	total gas species
φ	Index of available reaction fronts

Superscripts

0	Index of initial condition [-]
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Chapter 3– Results (II, III, IV)

*“With no relation to social status, class, background,
whether it suits them or not, people yearn for a dream.
Sustained by a dream, hurt by a dream, revived by a dream, killed by a dream.”*

K. Miura

3.1 Characterization (III and IV)

The study of pure solids subjected to reduction began with thermogravimetric and differential scanning calorimetry (TGA/DSC) coupled with mass spectrometry (MS). This analysis enabled simultaneous characterization of the physicochemical transformations of a solid sample and identification of the evolved gases during the heating ramp. The thermal conversion in TGA was carried out in an inert atmosphere (N_2) starting from 10 mg of solid, with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and a total volumetric flow rate of $20\text{ mL}/\text{min}$.

Figure 3.1 displays the heat flow, sample mass weight, and MS signal over time for a sample of pure hematite powder.

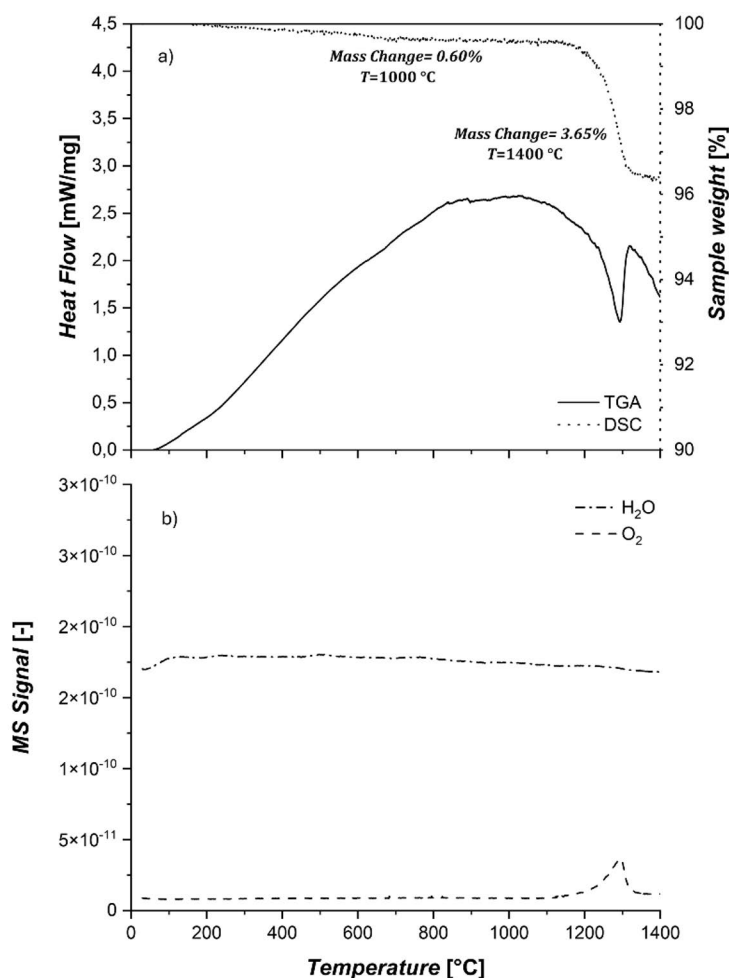


Figure 3.1 TGA/DSC (a) and MS (b) analysis results for pure hematite.

A total mass loss of about 2.6% was detected near 1000 °C for pure hematite, indicating the presence of both adsorbed and lattice-bound water. A subsequent weight decrease occurred due to the transformation of hematite into magnetite, accompanied by oxygen release.

To monitor the progress of the chemical reaction over time, a detailed analysis of the intrinsic properties of the solid samples was conducted using stop tests in the first experimental setup (Section 2.2). The same reduction experiment was repeated multiple times under identical operating conditions, with the reaction interrupted at different times and corresponding samples collected. This approach provided insight into the transient states of the system and, from a mathematical perspective, offered findings about emerging phenomena to be incorporated into the descriptive model or information that can be used to introduce simplifying assumptions in the model.

For the reduction of iron oxides with hydrogen, the experimental conditions for the stop tests were hematite mass $m_{\text{Fe}_2\text{O}_3} = 300$ g, temperature $T = 600$ °C, hydrogen molar fraction $y = 0.20$ and total gas volume flow rate $Q = 20$ mL/min. Compared to thin-layer reduction experiments ($m_{\text{Fe}_2\text{O}_3} = 0.010$ g), the reduction of a bed of pure hematite exhibited much sharper and more pronounced slope variations in the thermal conductivity detector (TCD) signal. Figure 3.2 displays the normalized TCD signal over time for a set of reduction experiments, indicating the points of the selected stops by dashed vertical lines.

Stop tests conducted after 5 min, 10 min, 50 min and 150 min were selected based on the overall behavior of the TCD signal to capture the reactor immediately before and after the main slope transitions.

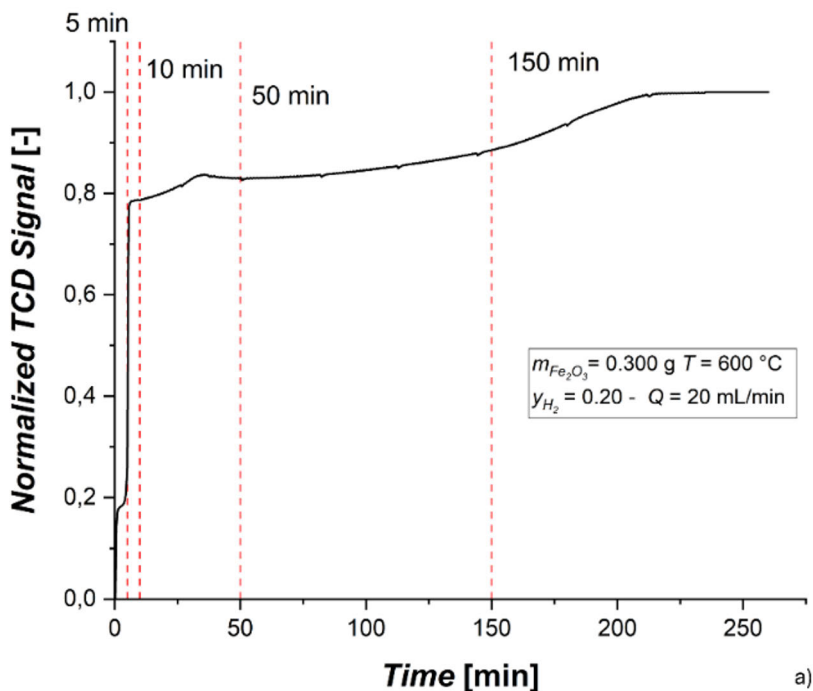


Figure 3.2 Normalized TCD signal with marked stop points.

3.1.1 Solid properties and evolution (III and IV)

The analysis of solid evolution began with the evaluation of the chemical composition of the reactive bed. Figure 3.3 presents the X-ray diffraction (XRD) reflections obtained for the samples in the process.

The analysis of solid evolution began with the evaluation of the chemical composition of the reactive bed. Starting from Fe_2O_3 , Fe_3O_4 was observed immediately, which is natural since, from a thermodynamic perspective, the first reaction step is not limited by the amount of water produced as long as there is some hydrogen left in the gas phase. Hematite was almost fully depleted within the first 10 minutes. Before 50 minutes, another change in slope occurred, and the corresponding stop test revealed the complete disappearance of Fe_2O_3 and the formation of FeO .

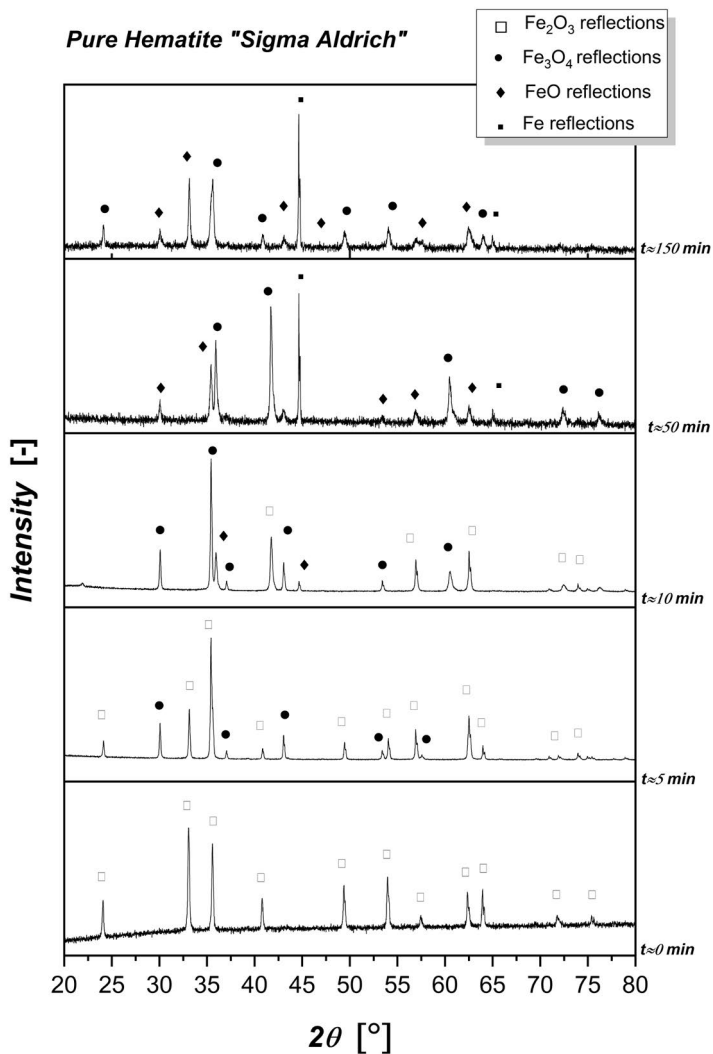


Figure 3.3 XRD diffractograms of stop-test samples (cf. Figure 3.2).

Additionally, peaks associated with metallic iron began to appear. After 150 minutes of reaction, wüstite became the dominant phase, promoting the final formation of metallic iron. After approximately 250 minutes (i.e., when the signal reached unity), the analysis showed only Fe reflections. These results confirm the strong correlation between the slope changes of the reduction curve and the shifts in the kinetically and thermodynamically dominant chemical species.

Scanning Electron Microscopy (SEM) analysis provided significant morphological and topographical information. Some of the results of the SEM analysis are displayed in Figure 3.4.

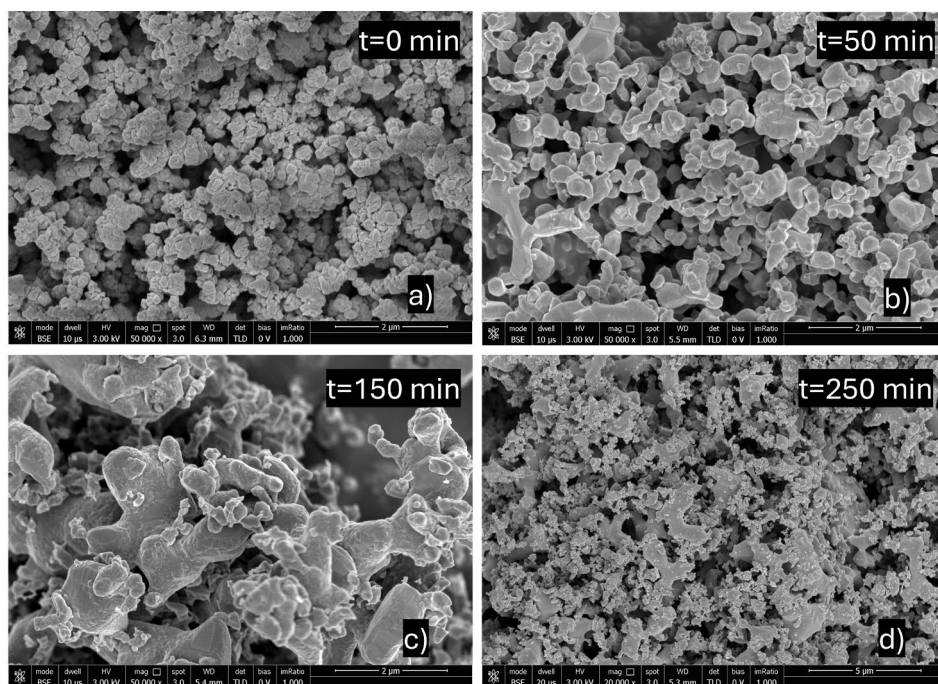


Figure 3.4 SEM images of samples collected at different times (cf. Figure 3.2).

The images show that pure hematite powder tended to agglomerate while maintaining its characteristic rhombohedral structure (a). As the reaction progressed, sintering and coalescence of iron oxide particles became evident, particularly after 50 min and 150 minutes (b and c), corresponding to the initial presence of FeO and Fe. The final SEM observations confirmed the coalescence phenomena in the fully reduced iron after 250 minutes (d). This morphological evolution highlighted that particle size distribution may vary during reduction due to aggregation mechanisms.

For this reason, the particle size distributions of the initial and final samples were determined using light scattering (LS) technique. Figure 3.5 displays the particle volume fractions for the initial hematite and iron after reduction and

their cumulative distribution curve calculated versus $\log_{10}(2r_n^0)$ ($\log_{10}(2r_n^0) = 1$ define an order of magnitude of 10^{-6} m).

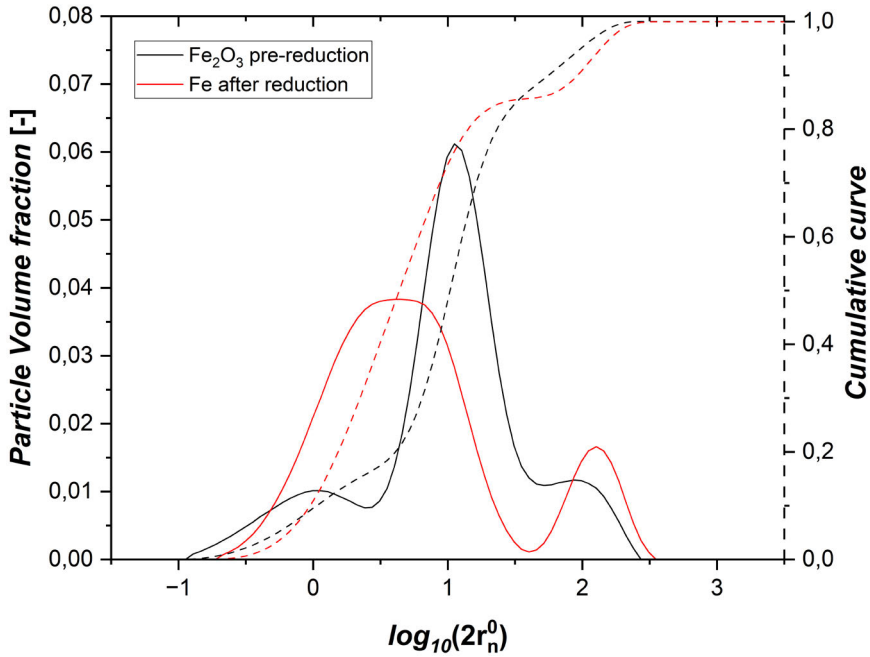


Figure 3.5 Granulometric distribution the initial sample and the sample after full conversion.

As expected, the LS analysis confirmed the coalescence phenomenon but, at the same time, demonstrated that the overall changes were minor. As can be seen, the two main granulometric families of Fe_2O_3 merged into a larger group having the average diameter nearly unchanged. The cumulative curves display a very similar behavior showing that the granulometric differences between the two samples are similar. Based on these observations, the system was modelled by assuming that the granulometric distribution of the initial material stays unchanged during the reduction process. This assumption proved to be crucial, as it allowed the simulations to accurately reproduce the experimental data (Section 3.6 considering the important influence that the particle radius has in the model (Article II).

It was also necessary to decide whether the bed porosity should be considered constant over time. This question was justified by the observed coalescence

phenomena and the contrasting evidence reported in the literature. For this reason, physical adsorption analyses were carried out to assess the temporal variation of the surface area and porosity of the solid bed through the stop tests (Articles III and IV).

The results indicated thermal activation of the solid during the initial heating ramp at 10 °C/min. At this stage, a porosity of 0.1 and a surface area of approximately 7 m²/g were measured. As soon as reduction began, the surface area initially increased and then decreased within the first 10 minutes, while porosity exhibited an opposite trend. These variations can be attributed to the competition between sintering, coalescence of the crystalline structure and the generation of new vacancies due to oxygen removal, depending on the rate of the reaction. Nevertheless, the variations in both variables remained limited compared to the initial values (after heating). The final porosity increased by about 20% (i.e., $\varepsilon = 0.12$), while surface area decreased by about 25%. Because of these modest changes, the bed porosity was assumed constant throughout the reaction.

3.1.2 Reactor fluid dynamics (III and IV)

To achieve an accurate characterization of the reactor, residence time distribution (RTD) and axial dispersion effects were evaluated. Under standard conditions ($T = 600$ °C, $Q = 20$ mL/min), the mean residence time (τ) of the elements of fluid (i.e., H₂ in Ar) was evaluated to be 3.68 min. The axial Peclet number (Pe), expressing the ratio between convective and diffusive transport, was derived from pulse-response experiments and fitted using an unsteady-state mass balance with open–open boundary conditions. An example of model fitting at $T = 600$ °C is shown in Figure 3.6 displaying the residence time distribution function (i.e., $E(t)$ density function) over the dimensionless time θ .

Values of $Pe \approx 12$ were consistently obtained for all tested flow rates, and operating temperature, indicating deviation from ideal plug flow and the necessity of developing a model that accounts for axial dispersion phenomena.

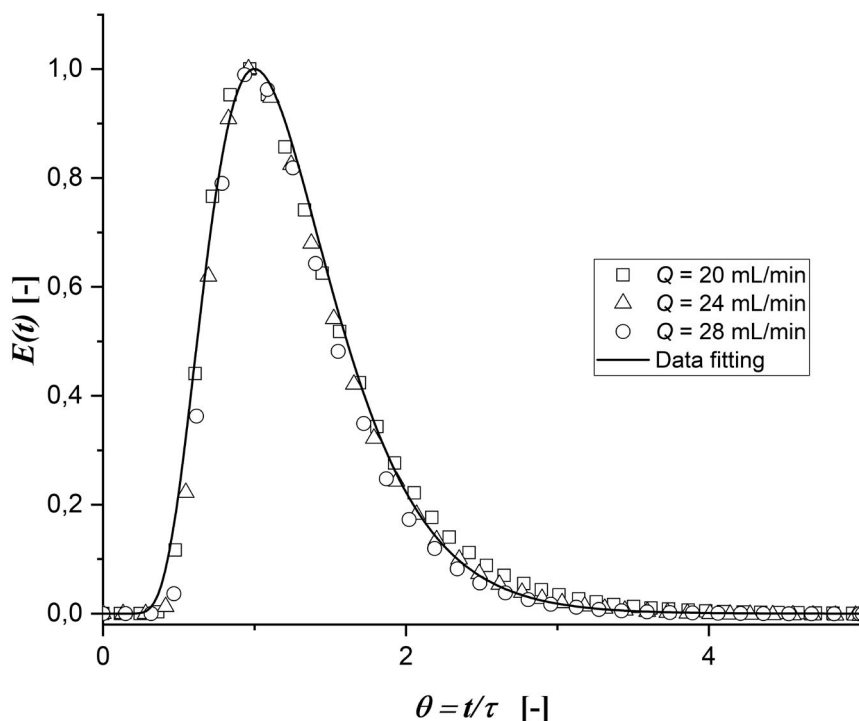


Figure 3.6 Pulse experiment fitting at $T = 600\text{ }^{\circ}\text{C}$.

3.2 Experimental results (III and IV)

The kinetic study of iron oxide reduction under various operating conditions was conducted to evaluate the kinetic parameters of the individual reduction steps and to determine the control regimes of the process. The experimental investigations were performed by varying temperature, reductant concentration, total volumetric flow rate, and sample mass.

Figure 3.7 incorporates the normalized TCD signal in a series of reduction experiments conducted with hematite powder at different temperatures and the Baur–Glässner Diagram highlighting the significant thermodynamic differences associated with the operating temperature.

These results emphasize the complexity of the reduction process since the shape and slope of the curves are directly related to the predominant chemical reaction, to the controlling regime, and thermodynamics. In particular, thermodynamic

influence, as will be discussed later, becomes a key aspect in the interpretations enabled by the mathematical model (cf. Section 3.8).

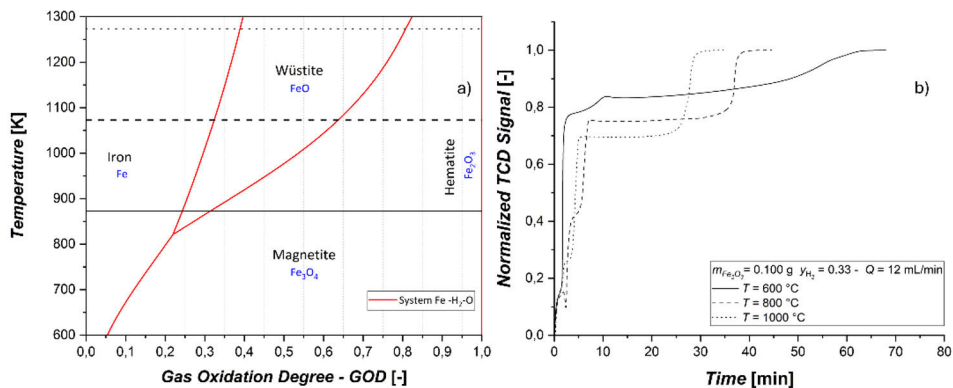


Figure 3.7 a) Baur-Glässner Diagram with operating temperatures, b) Examples of normalized TCD signal in Fe_2O_3 reduction experiments at different temperatures.

By using the data analysis method developed in this doctoral work, it was possible to correlate the information on the reductant composition— through the TCD signal— with the corresponding global degree of reduction of the solid sample (cf. Section 2.6). As an example, Figure 3.8 displays the final interpretation of the TCD signals shown in Figure 3.7b as the evolution of the total reduction degree of the solid sample.

As can be observed, the developed integration method preserves the distinct differences between experiments conducted at the different operating temperatures. This approach not only simplifies the modelling description— eliminating the need to simulate the TCD signal— but also retains all the key information of the reduction process, such as slope transitions, which play a fundamental role in the interpretation of the experimental results.

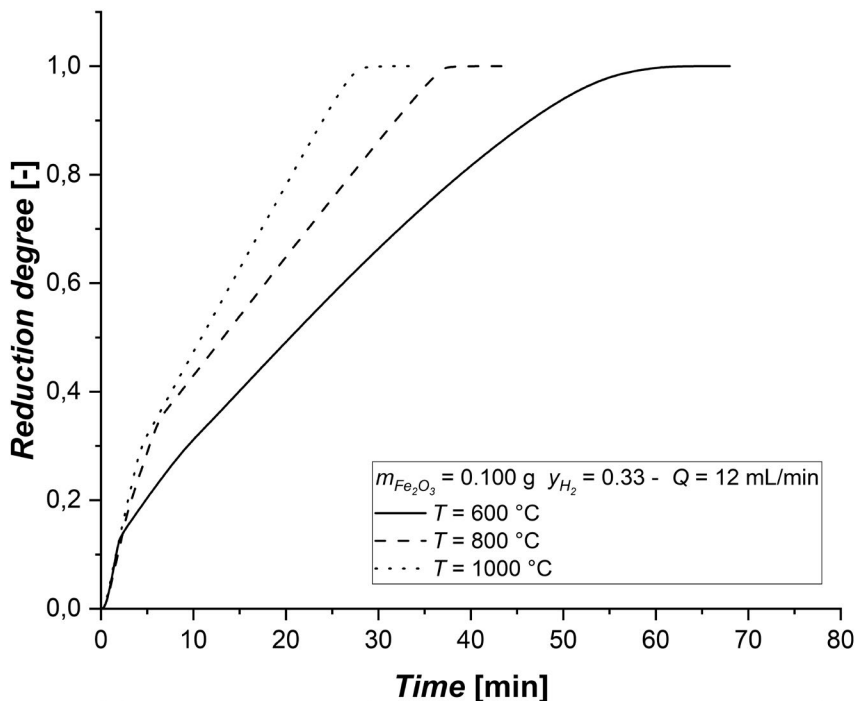


Figure 3.8 Examples of reduction degree in Fe_2O_3 reconstructed from the TCD signal of reduction experiments at three different temperatures (cf. Figure 3.7).

3.2.1 Isothermal hydrogen reduction experiments

To accurately determine the kinetics of iron oxide reduction by H_2 , a series of thin-layer isothermal experiments was performed under different operating conditions using argon as inert gas. The effects of temperature, total volumetric gas flow rate, and hydrogen molar fraction were investigated. Table 3.1 provides an overview of the experimental tests carried out in the Autochem 2910 setup (cf. Section 2.2) using pure hematite and magnetite powders.

This dataset was specifically chosen to minimize overlapping phenomena that could affect the parameter estimation. The use of a very thin reactive bed allows for neglect of diffusion-related effects and prevents severe compaction of fine materials at high temperatures. Finally, this experimental approach can minimize local thermodynamic limitations caused by water generated during the reaction.

Table 3.1 Experimental conditions used for thin layer hematite and magnetite reduction.

Species	Test	T [°C]	Q [mL/min]	y_{H_2} [–]	m [g]
Fe ₂ O ₃	1	600	20	0.15	0.0158
Fe ₃ O ₄					0.0136
Fe ₂ O ₃	2	600	20	0.20	0.0133
Fe ₃ O ₄					0.0153
Fe ₂ O ₃	3	600	20	0.25	0.0144
Fe ₃ O ₄					0.0131
Fe ₂ O ₃	4	700	20	0.20	0.0133
Fe ₃ O ₄					0.0139
Fe ₂ O ₃	5	800	20	0.20	0.0158
Fe ₃ O ₄					0.0102
Fe ₂ O ₃	6	600	18	0.20	0.0129
Fe ₃ O ₄					0.0129
Fe ₂ O ₃	7	600	24	0.20	0.0145
Fe ₃ O ₄					0.0116
Fe ₂ O ₃	8	600	28	0.20	0.0138
Fe ₃ O ₄					0.0133
Fe ₂ O ₃	9	1000	20	0.20	0.0129

As an example, the effect of feed gas composition was studied by varying the hydrogen molar fraction, thereby modifying the driving force of the reaction. Figure 3.9 displays the reduction behavior of pure hematite and magnetite.

As expected, increasing the hydrogen content significantly reduced the overall time required to complete the reduction process. A higher hydrogen availability enhances the reaction driving force, increasing the reduction rate at each step. The results showed that Fe₂O₃ is reduced consistently faster than Fe₃O₄. This can be attributed to the larger particle size of magnetite, as observed in the LS analysis.

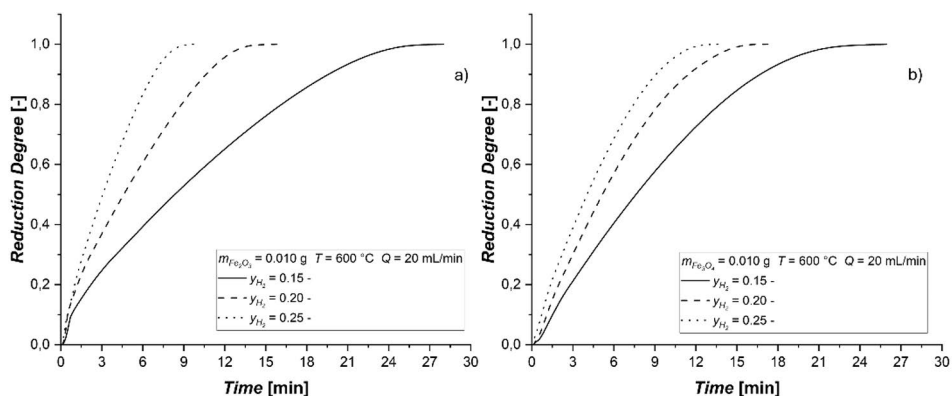


Figure 3.9 Effect of feed gas hydrogen content in thin layer bed: a) Fe_2O_3 and b) Fe_3O_4 .

Regarding the other operating conditions, the effects of temperature and total volumetric flow rate are straightforward: increasing temperature or flow rate reduces the overall reduction time. A comparison between the two datasets shows that the influence of operating parameters becomes less significant when larger particles are involved.

The reason lies in phenomena that largely depend on the particle size, particularly reaction kinetics and mass-transfer processes. In the first case, the reaction rate is strongly affected by the available surface area and, consequently, by the specific area (i.e., the ratio between particle surface and volume), which decreases with increasing particle radius (as for a sphere is $3/R$). The same applies to transport phenomena since the characteristic times of both internal and external diffusion increase with particle size. Therefore, regardless of the controlling regime, an increase in particle radius always results in a decrease in the overall reaction rate.

Based on the kinetic parameters determined from the thin-layer experiments, validation was carried out using systems of increasing complexity. These tests were performed with solid masses at least an order of magnitude larger. The design of these experiments aimed to reveal potential phenomena such as hydrogen starvation and thermodynamic driving-force limitations within the different layers of the solid bed.

The bed can be conceptually divided into multiple thin layers, each corresponding to a thin-sample region, with the main distinction that the gas composition evolves along the bed height. From this perspective, the mass of solid samples introduced into the reactor determines not only the total amount of reducible oxide but, more importantly, how bed height influences kinetics and thermodynamics. The deeper layers of the bed encounter a gas mixture that is progressively depleted in hydrogen and enriched in water vapor, imposing thermodynamic limitations on the magnetite and wüstite reductions.

Validation or bed-scale experiments were conducted using the same setup, with only pure hematite powder and a wide range of operating conditions. Figure 3.10 displays the effect of solid mass on the reduction behavior. The first set of experiments was conducted at $T = 600\text{ }^{\circ}\text{C}$ (a), while the second was at $T = 800\text{ }^{\circ}\text{C}$ (b). Both sets used a fixed flow rate of $Q = 0.20\text{ mL/min}$ and reductant molar fraction $y_{H_2} = 0.20$.

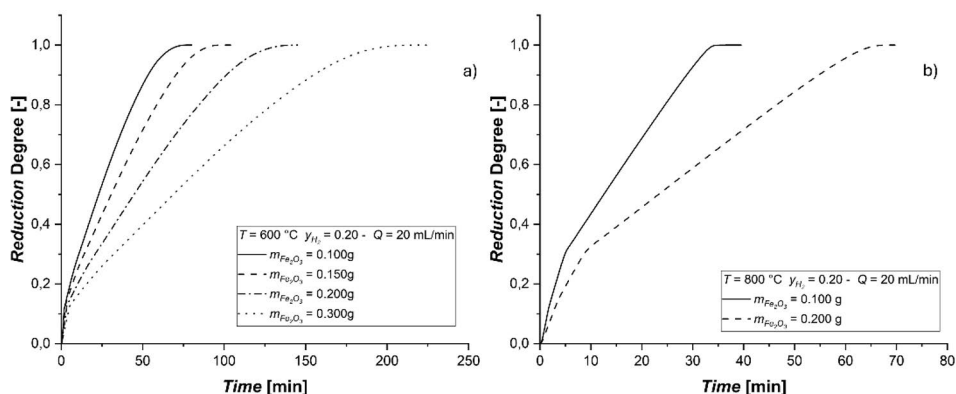


Figure 3.10 Effect of solid mass on Fe_2O_3 bed reduction at a fixed $Q = 0.20\text{ mL/min}$ and $y_{H_2} = 0.20$ for: a) $T = 600\text{ }^{\circ}\text{C}$, and b) $T = 800\text{ }^{\circ}\text{C}$.

As observed, the total reduction time naturally increases with the solid sample mass, showing a nearly linear relationship. Observing the results, the curves tend to display increasingly linear trends as the operating conditions of temperature and mass increase. As will be shown in the following sections, the interpretation of this linearity is related to how strongly the reduction depends not only on the dominant kinetics but, above all, on thermodynamics (cf. Section 3.8).

Probe experiments using CO and CO/H₂ mixtures as reducing agents were carried out and are described in the section *Ideas for Future Work* (Section 4.2).

3.3 Modelling results

The development of the complete mathematical model, presented in Section 2.7, required a series of improvements based on the characterization results of both the solids and the reactor system, but above all from continuous interaction and collaboration with the experimental campaign. The model-experiment dichotomy is crucial both for revising phenomena considered in the model to properly describe the data and for experimentally exploring specific operating conditions suggested by intriguing simulation outcomes. For this reason, the mathematical model exhibits slight differences across the versions developed over time. Nonetheless, the foundations of the model, constituted by the key assumptions, remain essentially unchanged throughout the work.

The main differences between the model versions lie in how the particles were considered. In the first part of the work, a single particle size was assumed for the solid phase while the latest version of the model considered a particle size distribution, achieving a more realistic behavior of the reaction fronts.

Another improvement is a detailed description of the gas-phase fluid dynamics. This was achieved by introducing two distinct spatial domains, initially treated as one. This subdivision was necessary to accurately describe the empty volume of the reactor upstream of the reactive bed and to capture the axial dispersion phenomena evaluated through RTD experiments (cf. Section 3.1.2).

The mathematical model combines a classical axial dispersion approach with a dynamic shrinking-core model that includes the product-layer formulation. The model also increased its rigor in describing the solid bed. The fixed bed, discretized into several layers, reacts sequentially from a single reaction front to multiple (up to three) and back to a single front. The model dynamically assesses the solid-state evolution within each layer, capturing a broad range of coupled phenomena, including reaction kinetics, thermodynamics, and both external and internal mass-transfer resistances.

3.4 First model approach and results (II)

Initially, the model was presented and applied to a probe experiment to test its interpretative capability for experimental outcomes, as well as its numerical and mathematical coherence and flexibility. This was accomplished by obtaining diffusional, kinetic, and thermodynamic parameters from the literature and then simulating the thermal conductivity signal based on the compositions of the off gases.

Figure 3.11 shows one of the main results of this model, reporting the molar fractions of solid (x) and gaseous components in the bed as a function of the axial coordinate of the reactor over time. The simulation in question used the following operating conditions, identical to the probe experiment: 0.1 g bed of pure hematite at 873 K, a total gas flow of 20 mL/min, and a H_2 molar fraction of 0.20.

The simulations show that hematite (a) reacts very rapidly, promoting the complete formation of magnetite within the first 5 minutes, in line also with XRD observations. Magnetite (b) and wüstite (c) display very similar axial profiles, driven mainly by the same underlying phenomenon. Focusing on the differences in concentration profiles at the boundary conditions (reactor inlet $z = 0$ and outlet $z = 1$), several conclusions were drawn. Near the inlet, Fe_3O_4 is completely converted within a few minutes into FeO due to the constant supply of fresh H_2 (e) while the H_2O (f) locally produced during reduction is diluted and transported downwards. The same result is observed for FeO, with the expected differences in reaction rate. The upper portion of the bed is not affected by equilibrium constraints. The dynamics change markedly as the outlet is approached. The consumption of intermediates in the lower bed is significantly slowed by hydrogen starvation and by the presence of H_2O produced and transported from the upper regions of the reactor. This is evident in the molar fractions of H_2 and H_2O approaching the outlet. This leads to a limited driving force that affects Fe_3O_4 reduction and, particularly, the FeO-to-Fe (d) step.

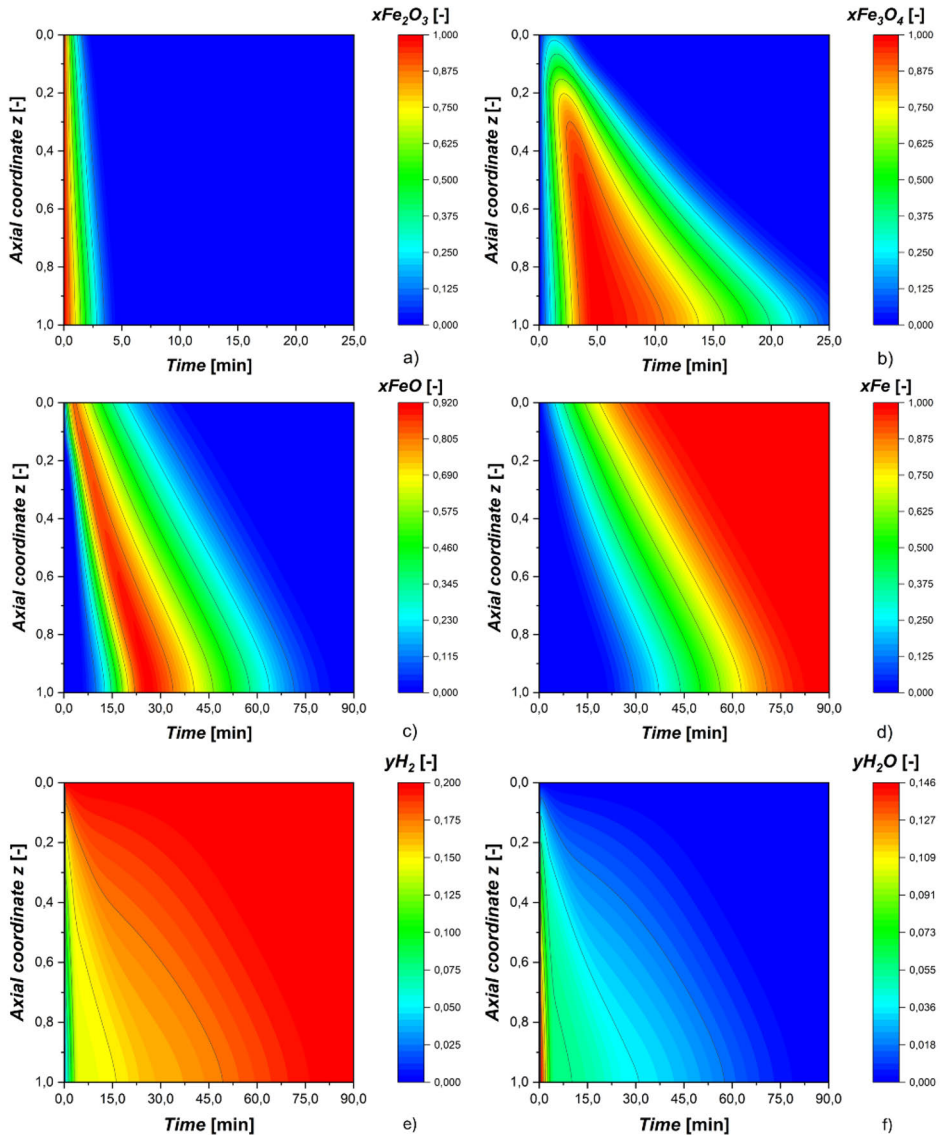


Figure 3.11 Axial bed profiles over time of the iron and iron oxides: (a) Fe_2O_3 , (b) Fe_3O_4 , (c) FeO , (d) Fe , H_2 (e) and H_2O (f). Note the different time scales of the panels.

To simulate the TCD signal, temperature-dependent equations were introduced to evaluate the contribution of the thermal conductivity (λ) of the gases involved in the chemical reaction (Argon included). The relationships and parameters used were taken from CHEMCAD ¹⁰⁷

$$\lambda_i = \frac{g_{1,i} \cdot (T/K)^{g_{2,i}}}{1 + \frac{g_{3,i}}{(T/K)} + \frac{g_{4,i}}{(T/K)^2}} \quad \left[\frac{W}{m \cdot K} \right] = \frac{\left[\frac{W}{m \cdot K} \right] \cdot [-]}{[-] + [-] + [-]} \quad (1)$$

where $g_{d,i}$ represents the parameters ($d = 1..4$) of the empirical equation for each i -th gas species. A first comparison using literature kinetic parameter between probe data and the simulated TCD signal from the off-gas composition is shown in Figure 3.12.

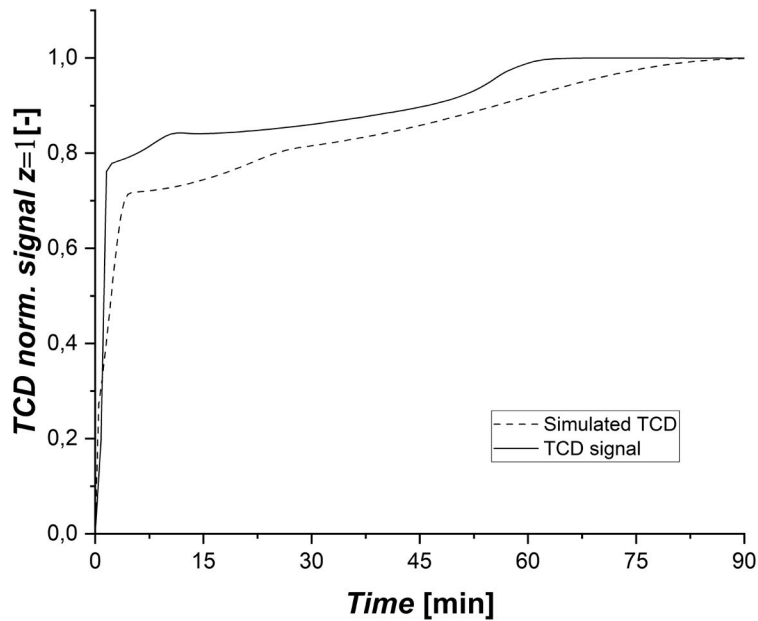


Figure 3.12 Comparison between TCD signal and simulated TCD signal. Probe experiment operating conditions: 0.1 g bed of hematite, reductant percentage (H_2) of 20%, temperature of 873 K and volumetric flow rate of 20 mL/min.

This simulated signal is qualitatively very similar to its experimental counterpart, even though no adjustment of the kinetic parameters had been

¹⁰⁷ Chemstations, 'CHEMCAD v. 7.0', (2020).

undertaken. Therefore, it may be concluded that the model provides essential information about the course of the chemical reactions, since the different slopes reflect the three stages of the reduction.

A good fit to the experimental data was obtained by modifying the kinetic constants of the first and third reactive steps. Figure 3.13 displays that the simulated TCD signal is in good agreement with the experimental one, as the model accurately reproduced the experimental behavior, including the positions of the slope changes in the signal. These holds promise for a more extensive future parameter estimation based on a large bulk of experimental data.

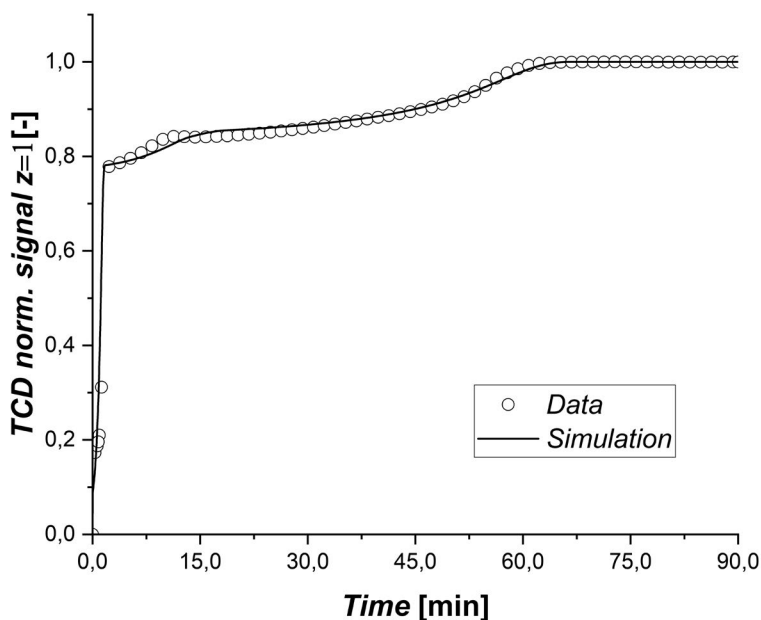


Figure 3.13 First comparison attempts between experimental data and simulation.

The design of the thin-layer experiments arose directly from the exploratory insights provided by the initial mathematical model. This dataset should have minimal influence from interparticle diffusive phenomena, particularly those related to water dynamics. The selection of operating parameters was also crucial: pushing some parameters too far would have resulted in excessively rapid chemical reactions, increasing the number of concomitant phenomena

within short time intervals and potentially complicating, or even making the estimation of reduction kinetic parameters impossible.

3.5 Parametric investigation (II)

To assess the predictive capability and performance of the model, several simulations were conducted to evaluate its response to parametric perturbations. In this theoretical study, starting from a base simulation– defined by a set of structural parameters– systematic perturbations were introduced around their nominal values. These perturbations were applied individually to isolate their specific effects.

Among the operational parameters, the model's responses were analyzed with respect to temperature, solid mass, feed gas composition, and average particle radius of the powder. Additional parameters investigated included the three reference kinetic constants and the axial dispersion coefficient.

As representative examples, some of the most relevant results from this parametric study are presented below. The standard conditions used correspond to those adopted in the previous simulation (cf. Figure 3.11 and Figure 3.12).

The operating temperature is of primary importance because it simultaneously affects intraparticle diffusion, chemical kinetics, and thermodynamic equilibria. This is also consistent with the significant variability observed experimentally when changing temperature (cf. Section 3.2.1). Figure 3.14 shows the simulated TCD curves for the off gas during hematite reduction at different temperatures.

The simulation results are qualitatively consistent with the preliminary experimental data (cf. Figure 3.8) obtained under similar operating conditions. The slope changes in the curves, which correspond to changes in the amount of hydrogen consumed, are particularly informative. As an example, the point of complete magnetite reduction (green circles) becomes more evident at higher temperature, manifested as a pronounced change in the curve slope.

The simulated signals become progressively sharper as temperature increases because of the growing difference between the kinetic parameters associated with Fe_3O_4 and FeO reduction. The closer these values (and their corresponding reaction rates) are, the more difficult it becomes to distinguish when the magnetite reduction is approaching completion.

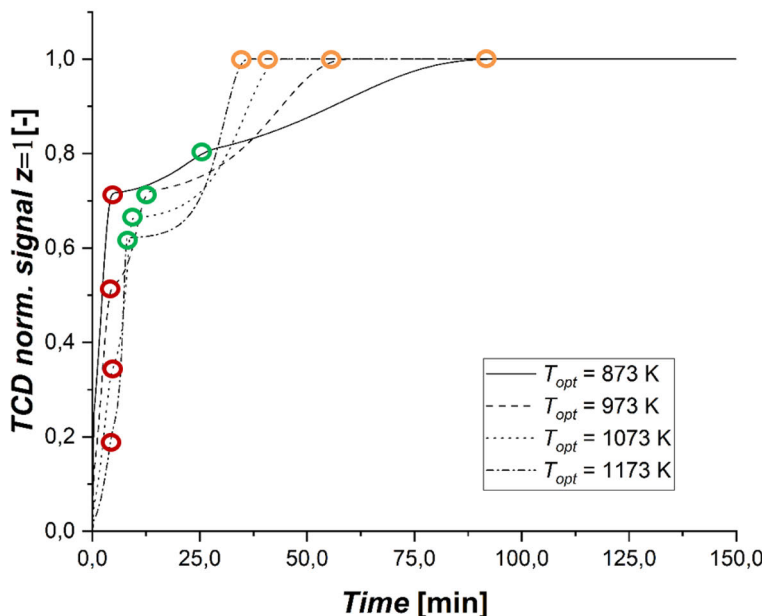


Figure 3.14 Temperature effect on simulated TCD signals over time. Red, green, and orange circles represent the almost complete reduction of Fe_2O_3 , Fe_3O_4 and FeO , respectively.

Conversely, the greater the difference in reaction rates, the more evident the transition from one predominant reaction to the next. The same applies to the transition from predominant reduction of hematite to magnetite, where an increased temperature makes the point where the hematite reduction approaches its end indistinguishable.

Moreover, the TCD signal becomes progressively flatter during the initial stage of wüstite reduction, indicating that at 1173 K the reaction consumes a nearly constant amount of hydrogen. This effect is correlated with the large amount of H_2O produced, which reduces the driving force of the final reaction, particularly in the lower sections of the bed, where equilibrium conditions are approached.

As with temperature, another crucial operational parameter is the average particle radius of the powder forming the solid bed. The particle radius is a key factor in evaluating resistance to external and intraparticle transport and in determining the reaction rate, as it directly influences the reactive surface area. Figure 3.15 shows the model response to changes in particle radius.

As the particle radius decreases, mass transfer resistance and surface per volume decrease, leading to faster reaction rates and shorter overall reduction times (cf. Section 2.7). This parameter mainly affects the last two reduction steps, revealing thermodynamic constraints related to the faster production of water.

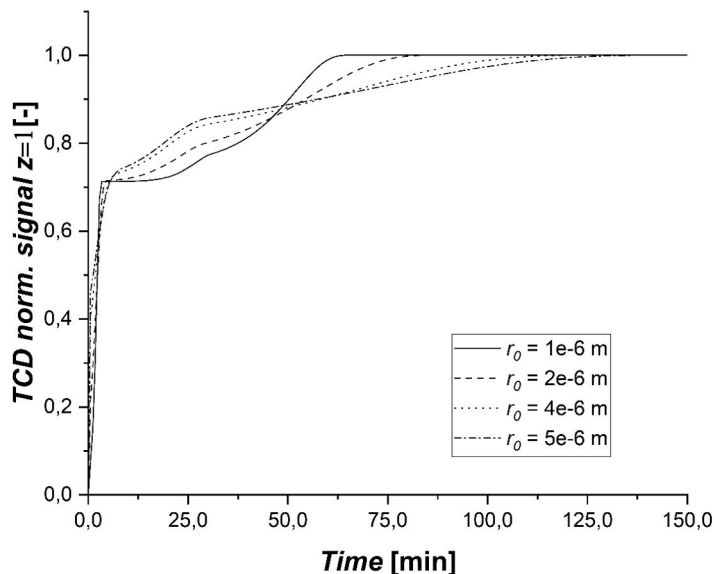


Figure 3.15 Particle radius effect on simulated TCD signals over time.

To assess globally the responsiveness of the mathematical model, a local sensitivity analysis was performed. The sensitivity was evaluated through the sensitivity index

$$SSE_{m,\Delta} = \sqrt{\frac{1}{t_v \cdot z_v} \sum_{\chi=1}^5 \sum_{l=1}^{z_v} \sum_{t=1}^{t_v} \left(\frac{C_{t,l}^{\chi}(p_1, \dots, p_m \pm \Delta, \dots, p_n) - C_{t,l}^{\chi}(p_1, \dots, p_n)}{C_{t,l}^{\chi}(p_1, \dots, p_n)|_{\max} - C_{t,l}^{\chi}(p_1, \dots, p_n)|_{\min}} \right)^2} \quad (2)$$

Each parameter of interest (p_m) was independently perturbed, over the number n of parameters studied, by either $\pm 10\%$ or $\pm 50\%$ ($\pm \Delta$). The sensitivity index quantifies the normalized elemental effect of each parameter across all parameters included in the analysis: the reference kinetic constants, the axial dispersion coefficient, the particle radius, the total solid mass, the inlet hydrogen molar fraction, and the total gas flow rate. This index was computed for all state variables considered in the model (Article 2) ($C_{s,l}^{\chi}$), including the gas-phase

compositions and the solid-phase reduction degrees, for a total of five variables. The sensitivity is performed by comparing all values of the state variables in time and space of the system (indices t and s , respectively), where z_v represents the number of grid points of the dimensionless axial coordinate of the reactor while t_v is the number of simulated time points. Considering the higher level of uncertainty associated with the kinetic constants, the pre-exponential factors were perturbed by $\pm 50\%$ relative to their nominal values, whereas all other parameters were varied within a narrower range of $\pm 10\%$. The results of the sensitivity analysis are illustrated in Figure 3.16.

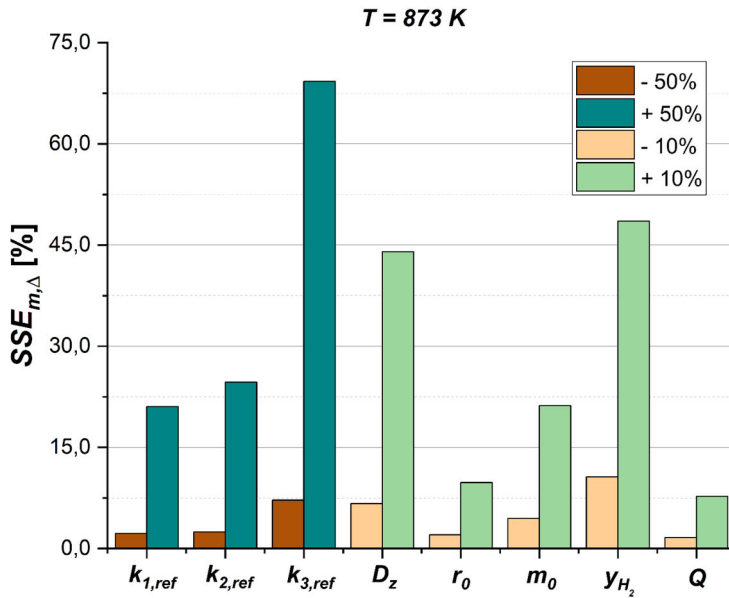


Figure 3.16 Results of local sensitivity analysis: first, second and third reference kinetic constants ($k_{1,ref}$, $k_{2,ref}$, $k_{3,ref}$) axial dispersion coefficient (D_z), particle radius (r_0), initial sample mass (m_0), hydrogen feeding molar fraction (y_{H_2}) and volumetric flowrate (Q).

It is obvious that some parameters exert a markedly greater influence on the model predictions, particularly when their values are increased. Among these, the reference kinetic constant of the third reduction step, the axial dispersion coefficient, and the inlet hydrogen molar fraction consistently emerge as the most influential. In particular, the kinetic constant of the third reaction exhibits a sensitivity index approaching 70%. An increase in the axial dispersion coefficient significantly accelerates the overall reduction process, emphasizing

the necessity of employing an accurate evaluation of RTD. A comparable sensitivity associated with the hydrogen molar fraction further demonstrates the crucial effect of hydrogen concentration in the gas phase on the global reduction kinetics.

3.6 Estimation of kinetic parameters (III)

Based on the mathematical model described in Section 2.9 and the experimental reduction data for thin layers of pure hematite and magnetite, an extensive estimation of the kinetic parameters was performed using the objective function

$$O = \sum_s^S \left(\frac{X_{\text{meas},s} - \bar{X}_{\text{sim},s}}{X_{\text{meas},s}} \right)^2 \quad (1)$$

where the experimental conversion $X_{\text{meas},s}$, obtained from numerical processing of the TCD signal, was compared with the simulated average conversion of the solid $\bar{X}_{\text{sim},s}$. The rate constants, k , of each individual reduction step were estimated using the final version of the mathematical model. During this procedure, the experimental data were grouped by operating temperature and starting material, distinguishing between pure hematite and magnetite powders, due to their markedly different initial particle-size distributions.

The kinetic coefficients related to the reduction process — namely, the activation energy (E_a) and the reference kinetic constant (k_{ref}) — were calculated from the linearized Arrhenius plots.

Figure 3.17 presents the linearized Arrhenius plots, while Table 3.2 reports the corresponding activation energies and reference rate constants, together with the regression errors.

The Arrhenius plots display a consistent trend in the rate constants, with low uncertainties in both activation energies and pre-exponential factors. The relative errors for E_a and k_{ref} remain below 11% and 15%, respectively, confirming the reliability of the fitting procedure.

The resulting activation energies fall within the range reported in the literature and are in good agreement with the average values obtained for each specific reaction step (Article I). From a kinetic-control perspective, the activation energy provides a qualitative numerical indication: all reduction steps are chemically

controlled except for the first one, which is governed by a mixed regime of internal diffusion and chemical control.

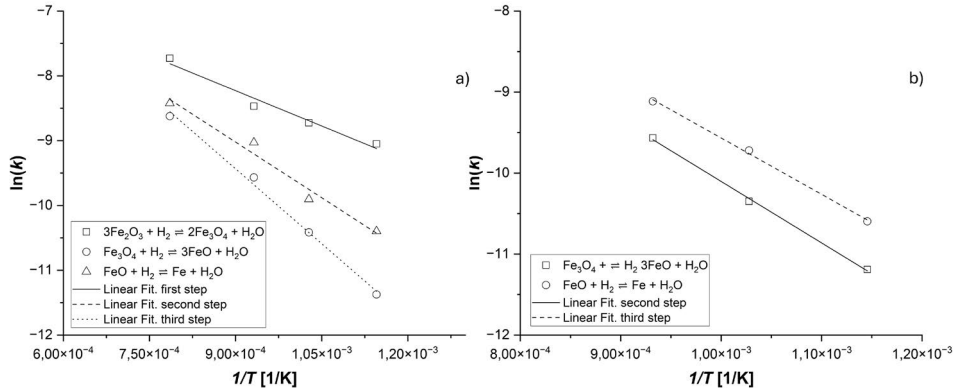


Figure 3.17 Arrhenius plots for a) Fe_2O_3 and b) Fe_3O_4 reduction.

Table 3.2 Estimated parameters in the reaction rate expressions.

Starting material	Reactions	E_a [kJ/mol]	k_{ref}
Fe_2O_3	$\text{Fe}_2\text{O}_3 \rightleftharpoons \text{Fe}_3\text{O}_4$	30 ± 4	$7 \cdot 10^{-3} \pm 6 \cdot 10^{-4}$
Fe_2O_3	$\text{Fe}_3\text{O}_4 \rightleftharpoons \text{FeO}$	64 ± 3	$8 \cdot 10^{-2} \pm 1 \cdot 10^{-2}$
Fe_2O_3	$\text{FeO} \rightleftharpoons \text{Fe}$	48 ± 5	$2 \cdot 10^{-2} \pm 3 \cdot 10^{-3}$
Fe_3O_4	$\text{Fe}_3\text{O}_4 \rightleftharpoons \text{FeO}$	64 ± 2	$8 \cdot 10^{-2} \pm 9 \cdot 10^{-3}$
Fe_3O_4	$\text{FeO} \rightleftharpoons \text{Fe}$	58 ± 23	$7 \cdot 10^{-2} \pm 9 \cdot 10^{-3}$

A comparison between activation energies for corresponding reactions for the two starting materials is also interesting. While the values for magnetite-to-wüstite are nearly identical, indicating that the hematite reduction proceeds almost independently of magnetite, the discrepancy in the last (wüstite-to-iron) reaction step can be attributed to the differences in granulometry, which may further increase along with coalescence phenomena (cf. Section 3.4).

All experimental curves under varying operating conditions were accurately described using the same set of kinetic parameters for both starting materials.

For example, Figure 3.18 compares experimental and simulated reduction-degree trends over time for tests conducted at different operating temperatures.

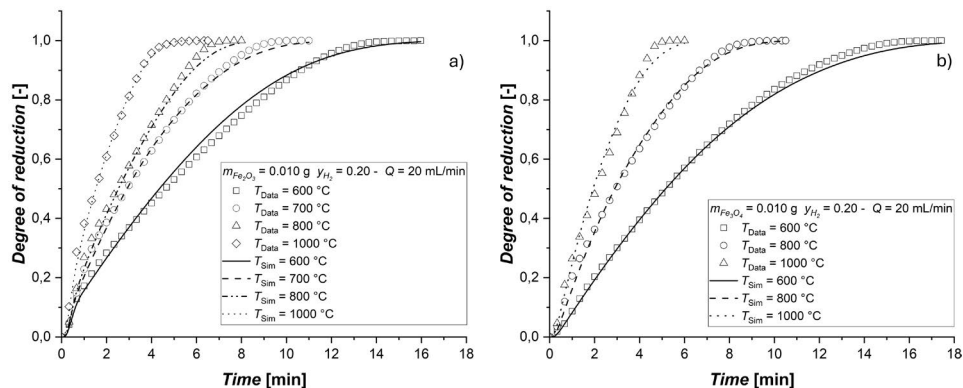


Figure 3.18 Effect of temperature on a) Fe_2O_3 and b) Fe_3O_4 with $y_{H_2} = 0.20$ and $Q = 20$ mL/min. Experimental results indicated by markers, simulated results by solid, dash, dash-dotted and dotted lines.

These results confirm the assumptions derived from the transient characterization of the solids, namely the absence of significant morphological or structural changes in the lattice with temperature, thus validating the hypothesis of constant porosity after the sample-heating stage.

Similarly, experiments under different reducing-gas fractions and total gas flow rates were accurately reproduced by the model. Globally, all these results are summarized in Figure 3.19, which presents a parity plots for all thin-layer experiments of hematite (a) and magnetite (b). As shown in the plots, and supported by the calculated R^2 values, the agreement between experimental and simulated data lies within a variability of $\pm 10\%$, which must be considered encouraging.

To gain deeper insight into the reduction process, the simulation was further exploited to its full potential. This approach not only clarifies mechanistic aspects but also validates the internal consistency of the model assumptions with the literature data. Figure 3.20 illustrates the evolution of individual reduction degrees for each solid species, along with the overall reduction progress in thin-layer experiments.

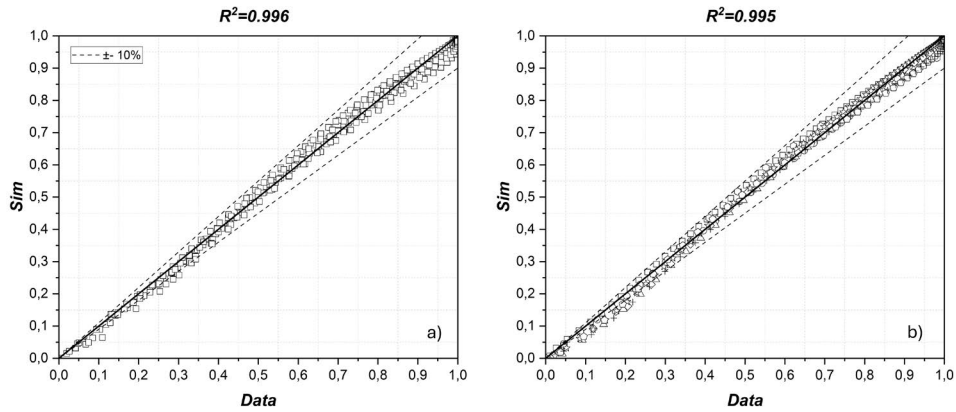


Figure 3.19 Reduction degree parity plots: Experiments vs. simulations H_2 -based reduction of thin layer of a) Fe_2O_3 and b) Fe_3O_4 .

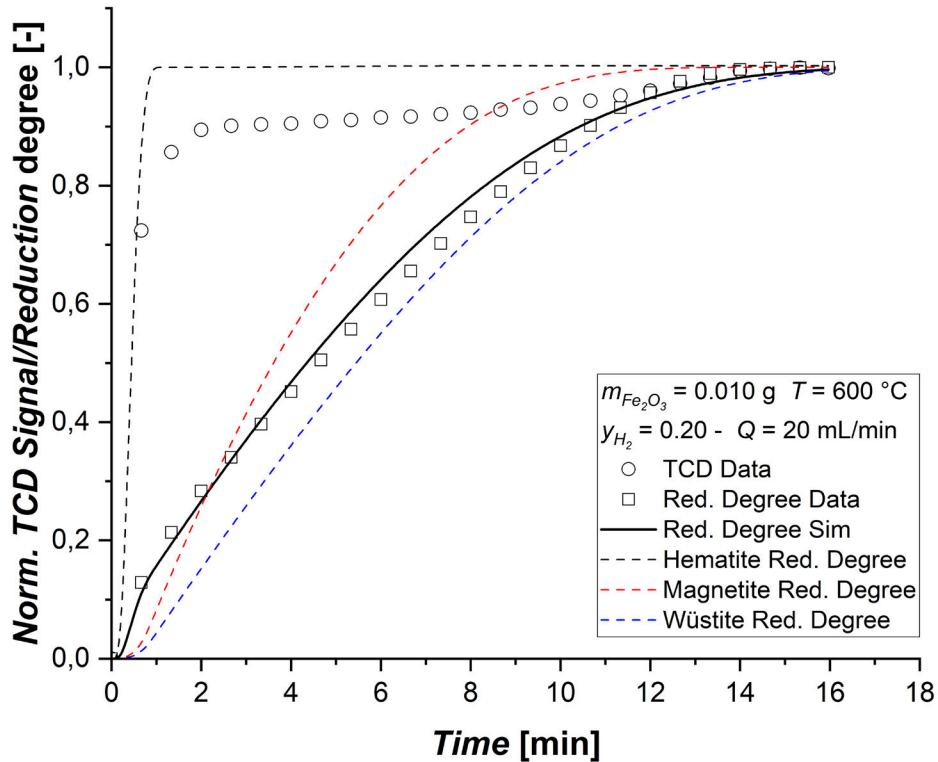


Figure 3.20 Experimental and simulation results of reduction of thin layers of hematite under the experimental conditions $m_{\text{Fe}_2\text{O}_3} = 0.010 \text{ g}$, $T = 600 \text{ }^\circ\text{C}$, $y_{\text{H}_2} = 0.20$, $Q = 20 \text{ mL/min}$.

This experimental–simulation comparison confirms that hematite is fully converted within the first minute, with minimal overlap with the subsequent step. In later stages, magnetite and wüstite reductions proceed almost concurrently, sustained by the high driving force since water accumulation is negligible. The chosen low gas-flow rate prevents excessively fast reactions, allowing accurate observation of transient behavior and enabling reliable kinetic-parameter validation through simulation.

The adoption of a rigorous and innovative experimental methodology, combined with a flexible mathematical model, provided a coherent interpretation of the reduction behavior. The estimated kinetic parameters enable the model to accurately reproduce all experimental datasets, demonstrating its robustness and predictive capability across the investigated conditions.

Although no water vapor is introduced in the feed gas, the experiments still provide valuable information on the role of H_2O in the reduction process. Water is continuously generated within the reactive bed as a by-product of iron oxide reduction, and under the low-flow conditions adopted, it can locally accumulate. Consequently, the influence of water vapor on reaction kinetics and equilibrium can be indirectly assessed through the model (cf. Section 3.8).

3.7 Kinetic parameter validation (IV)

To examine the effect of bed height on the reduction of pure iron oxide powders, a wide dataset of operating conditions was designed. The approach involved increasing the complexity of the reactive system to establish a new benchmark for the kinetic parameters estimated for each reduction step.

A dedicated experimental campaign was designed to challenge both the experimental apparatus and the mathematical model. The mathematical model clearly showed that vertical stratification in the upper beds has a significant impact on the global evaluation of the reductive process, significantly influencing the efficiency of the process. (Article II).

Model accuracy across all 17 experiments is summarized in the parity plot of Figure 3.21, where the markers align closely with the diagonal, yielding a high R^2 , indicating that all experimental data under different operating conditions are

accurately described using the same kinetic parameters obtained starting from thin layer experiments.

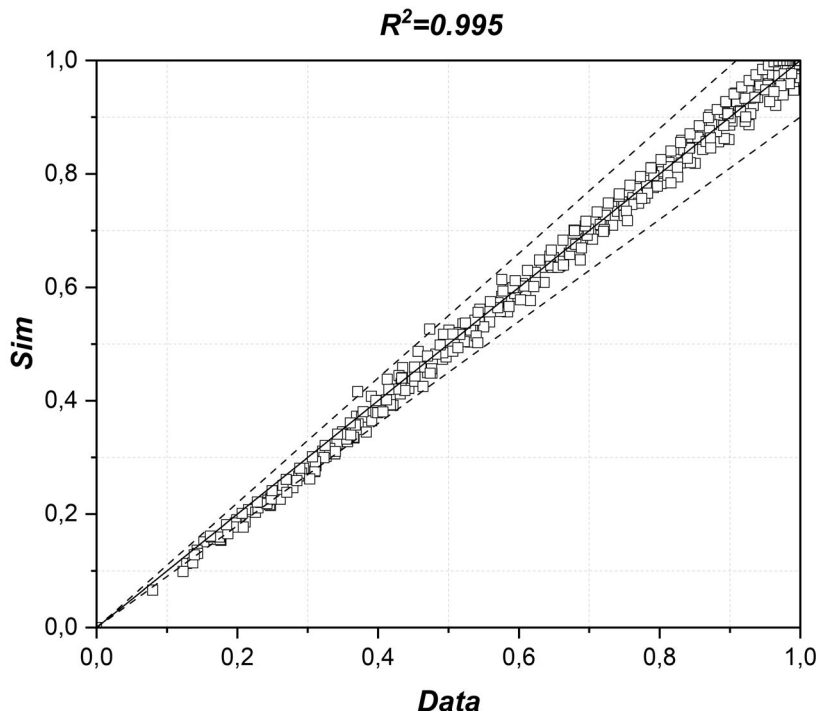


Figure 3.21 Reduction degree parity plots for H₂-based reduction of Fe₂O₃ in a bed.

The comparison of this large experimental data set with model simulations validates the model's ability to capture the governing phenomena of the process. Moreover, the increased system complexity did not alter the identified control regimes (Article III), confirming that the adopted mechanisms and simplifying assumptions (e.g., constant bed porosity, initial particle size distribution) remain appropriate.

An example of a comparison between experiments and simulation is presented in Figure 3.22 displaying the reduction-degree trends over time for tests conducted at three temperatures and two hydrogen molar ratios of the feed gas.

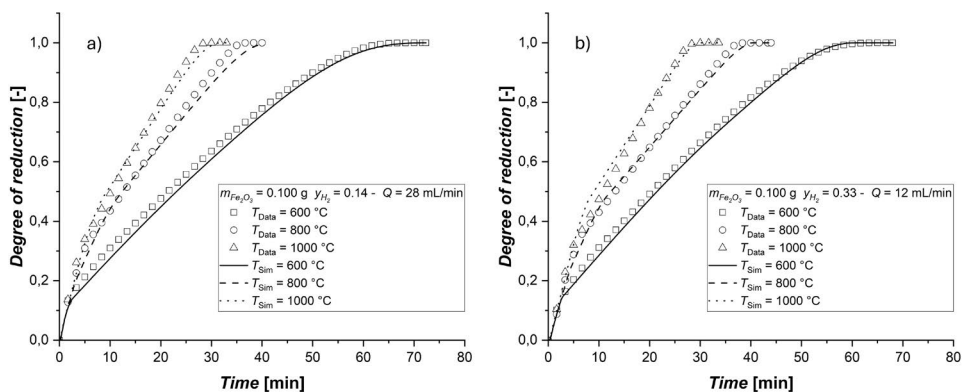


Figure 3.22 Effect of temperature on Fe_2O_3 reduction in a bed for $m_{Fe_2O_3} = 0.100$ g with a) $y_{H_2} = 0.14$ and $Q = 28$ mL/min b) $y_{H_2} = 0.33$ and $Q = 12$ mL/min. Experimental results are indicated by symbols, simulated results by solid, dash-dotted, and dotted lines.

The most distinct and well-described slope change corresponds to the point of hematite exhaustion, occurring at a conversion slightly above 0.11. This is due to partial magnetite reduction overlapping with the first step in the upper bed, where the driving force remains strong throughout the experiments. For the subsequent two reduction steps, the thermodynamic limitations observed at higher temperatures in the corresponding TCD signals (i.e., flat signal regions, Figure 3.8) are accurately captured by the model. In particular, the degree of reduction shows a linear conversion, indicating an approximately constant rate during the final step.

The temperature effect exhibits additional nuances compared to thin-layer experiments. In powder beds, high temperatures may promote not only kinetic and thermodynamic variations but also more relevant morphological and structural evolution. Bed compaction and coalescence can hinder the diffusion of reducing species through the lattice, thereby slowing the reactions. However, in this work, temperature did not emerge as a dominant factor for changes in the structure of the solid phase.

Given the importance of the driving force in hematite-bed reduction systems, a comparison between model and experimental data as a function of the feed-gas composition is justified. Figure 3.23 illustrates the influence of hydrogen molar

fraction on the overall reduction degree of hematite beds for two flow rates, 20 mL/min and 28 mL/min.

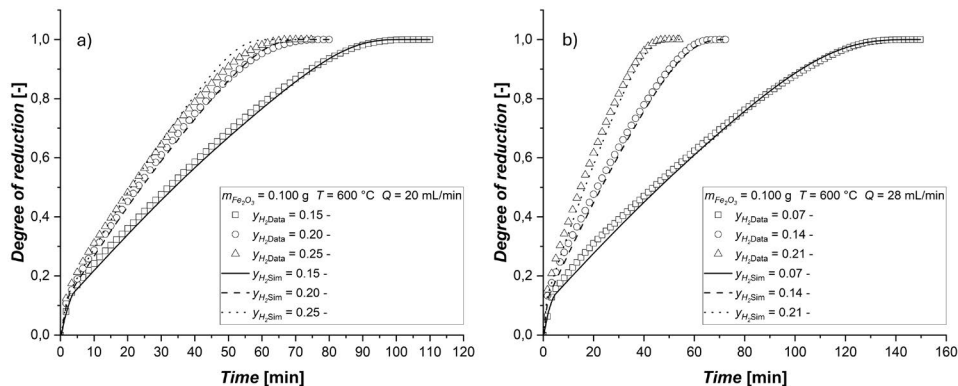


Figure 3.23 Effect of hydrogen mole fraction on Fe_2O_3 reduction in a bed for $m = 0.100$ g and $T = 600$ °C with a) $Q = 20$ mL/min b) $Q = 28$ mL/min. Experimental results are indicated by symbols, simulated results by solid, dash-dotted, and dotted lines.

Increasing the hydrogen content accelerates the reduction and shortens the overall reaction time, influencing the thermodynamic behavior and producing a nonlinear decrease in total reduction time. The reduction curves for $y_{H_2} = 0.20$ and 0.25 almost overlap at $Q = 20$ mL/min due to the substantial formation of water vapor, which drastically reduces the driving force in the lower bed regions. At the higher flow rate (b), the impact of hydrogen concentration becomes more pronounced because the increased gas throughput mitigates hydrogen starvation and effectively displaces locally produced water.

As shown, the mathematical model reproduces all these details accurately, capturing phenomena essential for understanding the intrinsic mechanisms of the reduction process.

The last two operating conditions investigated (not shown here but described in Article IV), i.e., the gas volume flow rate and the initial mass of the solid loaded into the reactor, were also well described by the model. The latter is particularly important, as it determines bed height and consequently the degree of stratification and thermodynamic effects.

3.8 Modeling results interpretation (IV)

To further explore interparticle dynamics, simulation-based case studies were performed under variable operating conditions, particularly temperature. The aim of this analysis was to extract key information about the reduction process by comparing the high-frequency normalized TCD signal with the gas- and solid-phase data provided by the model.

Errore. L'origine riferimento non è stata trovata. and Figure 3.24 show the simulated kinetic (a) and thermodynamic profiles (a-b) of two experiments conducted with $m = 0.100$ g, $y_{H_2} = 0.14$, and $Q = 28$ mL/min at 600 °C and 800 °C, respectively, together with the corresponding simulated TCD signals and reduction-degree curves. The GOD, calculated from the evaluation of the gas composition leaving the reactor, is shown as solid black lines in panel b. The experimental TCD curve is represented by solid blue lines, while the experimental reduction degree is shown as a solid red line.

At 600 °C (**Errore. L'origine riferimento non è stata trovata.**), the initial GOD peak reflects the complete conversion of hydrogen to water vapor during the beginning of Fe_2O_3 reduction, which is not thermodynamically limited and completes within approximately 4 minutes. At this stage, GOD decreases, enabling (thermodynamically) magnetite reduction followed by FeO formation in the lower layers. These steps proceed more slowly under strong thermodynamic constraints. The FeO stability region is narrow, and the simulated GOD stabilizes precisely within this range during magnetite reduction. The final FeO-to-Fe step is the slowest, requiring nearly one hour due to the low driving force.

Raising the temperature to 800 °C (Figure 3.24) markedly accelerates the reduction process. While the initial Fe_2O_3 reduction rate remains comparable to that at 600 °C, the magnetite reduction rate increases significantly. This results in simultaneous hydrogen consumption by Fe_2O_3 and Fe_3O_4 , intensifying kinetic competition among the layers. Consequently, hematite reaches complete reduction in a time comparable to 600 °C, while magnetite is reduced much faster. These transitions are clearly visible in the experimental TCD signal, where the slope changes correspond to the dominant reaction stages.

In the final stage of the magnetite reduction, GOD begins to decrease, triggering the onset of the wüstite reduction step. As can be seen in Figure 3.24a the FeO stability range expands, allowing for its formation at higher water concentrations. In this stage of the reduction process, the TCD signal first increases and then decreases again, entering a plateau region. This behavior corresponds to the transition in predominant thermodynamics from Fe_3O_4 reduction to FeO reduction.

During the plateau phase, where the reaction rate remains constant due to steady hydrogen consumption, the simulated GOD shows that reduction proceeds exclusively along the thermodynamic FeO/Fe equilibrium curve. This observation significantly helps the interpretations of the reductive process and is perfectly consistent not only with experimental evidence for thermodynamic constraints but also with characteristics of solids.

Overall, the modelling results demonstrate that thermodynamics plays a decisive role in shaping the reduction dynamics and potential structural evolution, particularly in thicker beds or iron ore pellets.

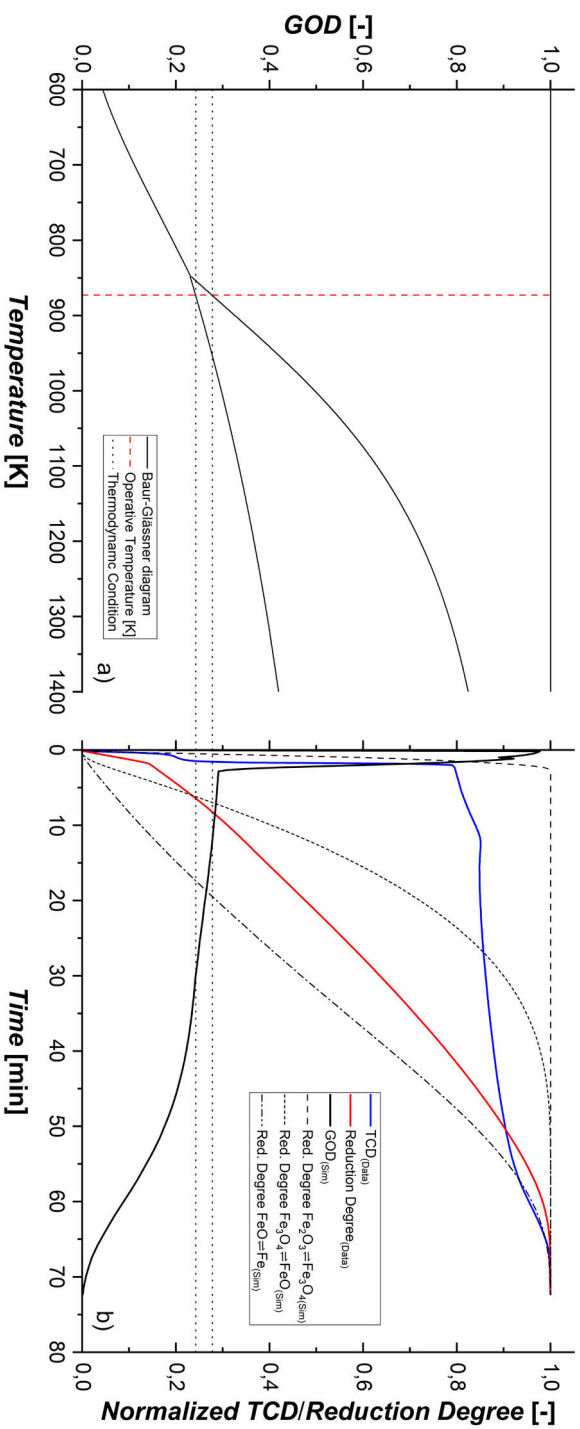


Figure 3.24 Interpretation of Fe_2O_3 bed reduction experiments at 600°C under the conditions $m = 0.100 \text{ g}$, $\gamma_{\text{H}_2} = 0.14$ and $Q = 28 \text{ mL/min}$. a) thermodynamic interpretation, and b) kinetic data and simulation results. Panel b) shows the simulated GOD (solid black line), the experimental TCD curve (solid blue line), and the experimental reduction degree (solid red line).

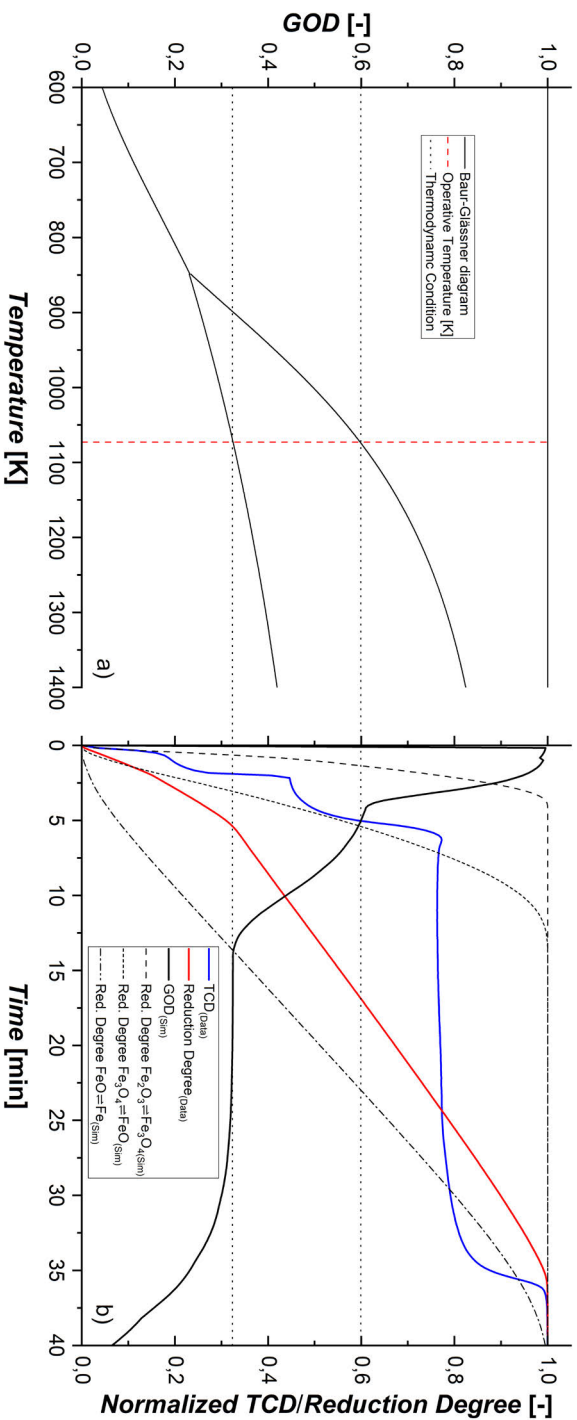


Figure 3.24 Interpretation of Fe_2O_3 bed reduction experiments at 800°C under the conditions $m = 0.100$ g, $\gamma_{\text{H}_2} = 0.14$ and $Q = 28$ mL/min. a) thermodynamic interpretation, and b) kinetic data and simulation results. Panel b) shows the simulated GOD (solid black line), the experimental TCD curve (solid blue line), and the experimental reduction degree (solid red line).

Notation

Abbreviations

GOD	Gas Oxidation Degree
MS	Mass Spectrometry
RTD	Residence Time Distribution
SCM	Shrinking Core Model
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TGA- DSC	Thermogravimetric analysis coupled with Differential Scanning Calorimetric
XRD	X-ray diffraction

Symbols

$C_{s,l}^x$	Model variable state [-]
$E(t)$	Density function [-]
E_a	Reaction activation energy [kJ/mol]
k	Kinetic constant [m/s]
k_{ref}	Reference kinetic constant [m/s]
m	Sample mass [g]
O	Objective function [-]
p_m	Perturbed parameter
Pe	Peclet Number [-]
Q	Total gas flow rate [mL/min]
R	Particle Radius [m]
$SSE_{m,\Delta}$	Local sensitivity index [-]
t	Time [s]
t_v	Number of time points [-]
T	Temperature [K]
T_0	Initial ramp temperature [K]
x	Solid molar fraction [-]
$X_{mean,s}$	Global reduction degree [-]
$\bar{X}_{SIM,s}$	Mean simulated reduction degree [-]
y	Gas mole fraction [-]
y_{H_2}	Hydrogen mole fraction [-]

z	Reactor axial coordinate [-]
z_v	Number of spatial grid points [-]
Δ	Parametric perturbation
ε	Porosity [-]
θ	Dimensionless time [-]
λ_i	Gas thermal conductivity [W/(m K)]
τ	Mean resident time [min]

Subscripts

0	Index of initial condition [-]
i	i-th gas species
l	Index in space vector
n	Index number of parameter
s	Index of dataset vector
t	Index in time vector
v	Space or time vector length

Superscripts

χ	Index of state variables [-]
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Chapter 4– Conclusions

*“Within every success lies the seed of failure,
and within every failure lies the seed of success.”*

K. Torishima and N. Hill

4.1 Conclusions

Scientific research on the reduction of iron oxides has advanced over several decades, yet the process remains complex due to the interplay of kinetic, diffusive, and thermodynamic phenomena, as well as the structural evolution of the solid phases. The literature review conducted in this work revealed considerable variability in the reported kinetic parameters, highlighting inconsistencies in activation energies and reaction mechanisms. This variability underscores the need for comprehensive experimental analyses that can distinguish intrinsic kinetic behavior from transport and morphological effects, and for mathematical models that explicitly account for these interrelated aspects.

The research addressed these challenges by combining systematic experiments with advanced mathematical modelling. A dynamic multi-interface shrinking-core model, coupled with an axial dispersion description of the gas phase, was developed in order to describe reduction experiments performed on hematite and magnetite powders under controlled conditions. The model, designed for robustness and flexibility, accurately reproduced experimental trends obtained through thermal-conductivity-based gas analysis, demonstrating its reliability across different operating conditions.

This work presents a significant methodological advancement by extending the application of the SCM beyond its traditional scope. Although SCM has typically been used to describe the reduction behavior of medium-sized iron-oxide pellets (i.e., millimeters to centimeters), its application to fine-grained systems has not been reported in the literature. In this study, the reactive bed was divided into individual grain families, with each grain analyzed separately within the SCM framework. This grain-level approach allows a detailed representation of the reduction process that explicitly incorporates the particle-size distribution of the powders.

A comparative analysis was conducted between the experimental results of thin-layer reduction tests and the corresponding model simulations. To enable this comparison, an innovative numerical approach was developed that correlates the evolution of the thermal conductivity of the exhaust gases with the overall reduction degree of the solids. By integrating granulometric data obtained from

sample characterization, the model provided a precise determination of the kinetic parameters for each reaction step in the reduction sequence. This methodology represents a novel contribution, as it combines gas-phase monitoring with particle-size distribution analysis to achieve a highly accurate description of the reduction process—an approach not previously reported in the literature.

These approaches allowed estimation and validation of the kinetic parameters for each reduction step, confirming their physical consistency and agreement with literature data. The combined experimental–modelling approach revealed that hematite reduction proceeds extremely rapidly under mixed kinetic–diffusion control, while magnetite and wüstite reductions are predominantly governed by chemical kinetics. Thermodynamic constraints become significant only under conditions of water vapor accumulation, particularly in deeper bed layers, where they reduce the local driving force. This behavior was systematically captured by the model and confirmed by experimental evidence. Increasing bed height and system complexity did not alter the underlying controlling regimes, validating the robustness and transferability of the derived kinetic parameters.

It is important to highlight that this behavior closely resembles what occurs in a shaft furnace, where the reduction potential of the gas can become locally depleted due to the accumulation of water vapor in the upper part of the reactor. The capability of the model to accurately capture this water effect makes it particularly valuable as a starting point for describing more complex systems, where similar limitations may arise under realistic process conditions.

Overall, the results demonstrate that the developed methodology – based on rigorous experimentation, detailed gas analysis, characterization of solid samples, and physically grounded modelling – provides a reliable framework for interpreting the dynamics of hydrogen-based reduction of iron oxides.

Future work should focus on the quantitative assessment of these phenomena in lattices containing impurity (i.e., commercial materials) to further support the transition to low-carbon, hydrogen-based ironmaking technologies. Special attention should be given to the role of water formation and accumulation within the reactive medium, as its presence can strongly affect the local reaction environment and cause significant morphological and structural changes in the

solid phase. This aspect becomes even more relevant when moving from fine powders to larger and more compact solids, such as pellets, where internal diffusion limitations and local temperature gradients may lead to non-uniform reduction fronts, pore evolution, or partial sintering.

Since the H_2 -based reduction process cannot be completely decoupled from a carbon source, which ultimately supplies the carbon needed for steel production, a detailed kinetic investigation of mixed H_2/CO systems is of primary importance. Accordingly, preliminary reduction tests were performed with pure CO and H_2/CO mixtures to assess, at an exploratory level, the applicability of the same experimental and modeling framework adopted for pure hydrogen, thus establishing a basis for future, more in-depth kinetic analyses.

To accurately describe such systems, it will be necessary to extend the current modelling framework by introducing additional levels of physical complexity. Specifically, the development of a coupled mass and energy balance model would allow the mutual interactions between chemical kinetics, heat transfer, and evolving solid morphology to be captured. The experimental and modelling foundations established in this doctoral work provide a robust basis for this next step in complexity, enabling future investigation of realistic pellet-scale systems under dynamic, water-influenced conditions representative of industrial hydrogen-based reduction processes.

The scale-up from powder to pellet form makes the description of the reductive process more complex, owing to the increased number of phenomena that must be considered (e.g., intraparticle temperature gradients) and to the structural modifications occurring in the solid, which may prevent the direct application of the Shrinking Core Model. Some simplifying assumptions—such as homogeneous radial porosity and uniform temperature and pressure within the particle—may no longer hold. This could affect the evaluation of gaseous components within the solid phase.

For this reason, it becomes necessary to increase the level of model complexity, for instance by employing a pellet-grain model, in which the reduction process of the individual grains is still described by the shrinking core. Such an approach, however, must be supported by complementary experimental evidence capable of validating its structural and kinetic assumptions.

4.2 Ideas for future work

This doctoral research also included preliminary works and ideas on new in-depth investigation of other reduction processes that differ from those previously described in terms of reducing agent used and on the application of a programmed temperature ramp.

Specifically, regarding the variability of the reducing agent, probe experiments were conducted both in the presence of carbon monoxide and using mixed H_2/CO reducing atmospheres.

The first case study is a starting point to evaluate, similarly to hydrogen, the intrinsic kinetics of the three reduction steps, also assessing the impact of the reverse Boudouard reaction on the overall carbon mass balance and the potential formation of cementite.

In the second case study, using H_2/CO mixtures, the total number of accessible reactions increases significantly (cf. Table 1.5), resulting in greater complexity in both experimental data interpretation and kinetic parameter estimation. As an example, the presence of the water–gas shift reaction (WGSR) can play a critical role in the system by altering the equilibrium of individual reduction reactions—either increasing or decreasing the amount of one reductant in favor of the other— while simultaneously producing the opposite oxidant species. The interplay of these effects requires a detailed prior understanding of the individual reduction kinetics to properly evaluate the impact of both WGSR and carbon deposition, as both reactions are catalyzed by iron oxides or metallic iron, each exhibiting different catalytic activities (cf. Section 1.4).

The third and final case study involved a kinetic investigation of hydrogen-based hematite reduction under non-isothermal conditions using a temperature-programmed reduction (TPR) approach. These experiments are particularly valuable because, under controlled conditions, they allow for effective separation of different reactions, enabling the evaluation of kinetic parameters that are directly comparable to those derived from isothermal studies.

4.2.1 Isothermal reduction with CO or mixture H₂/CO

Reduction experiments in the presence of CO and mixed reductants were primarily conducted in the second experimental setup. This choice was dictated by the impossibility of using the TCD signal to monitor the reaction kinetics, due to the practically identical thermal conductivity of CO and CO₂—unlike the H₂/H₂O pair. For all these reasons, the final result is a flat TCD signal that does not provide any kinetic information.

Furthermore, when using mixed reductants, the Autochem 2910 does not permit the use of reagent/adsorbate gas mixtures, but only pure gases that are subsequently mixed with the carrier.

For this reason, the gas composition of the effluents was analyzed using an Agilent Micro GC 990 (cf. Section 2.2). Through careful instrument calibration performed on all gaseous species except water vapor – excluded to protect the chromatographic columns— it was possible to correlate the retention time of each chemical species with its molar fraction (or concentration) via peak areas, representing the residence time distribution of each component.

Due to the increased size of the new tubular reactor (length +233%, diameter +36.3%), the experimental design required a proportional increase in both the standard solid sample mass m to obtain a thin layer, and the total volumetric gas flow rate Q . The operating conditions for the baseline case were therefore set as $m = 0.15$ g, $T = 600$ °C, $y_{\text{red}} = 0.20$, $Q = 100$ mL/min.

To assess the comparative reduction performance of the new setup, additional experiments were conducted using only hydrogen, thereby generating a complete dataset under identical conditions for H₂ and CO, using helium (He) as carrier gas.

Figure 4.1 displays an example comparison under equivalent experimental conditions, where the first reaction was conducted with CO only and the second one with H₂ only. The absence of water molar fraction in the H₂-based reduction results is due to its removal by a cold trap positioned between the reactor and the detector (cf. Section 2.2).

The evolution of the reducing species is initially very similar, reflecting the fast kinetics of the hematite's reduction step, which is not thermodynamically limited

(cf. Figure 1.6). As in the hydrogen case, CO reduction also displays distinct slope changes associated with the progression of the reactive process, although these are less pronounced. Hydrogen consumption is generally more rapid, achieving complete conversion in shorter times than CO.

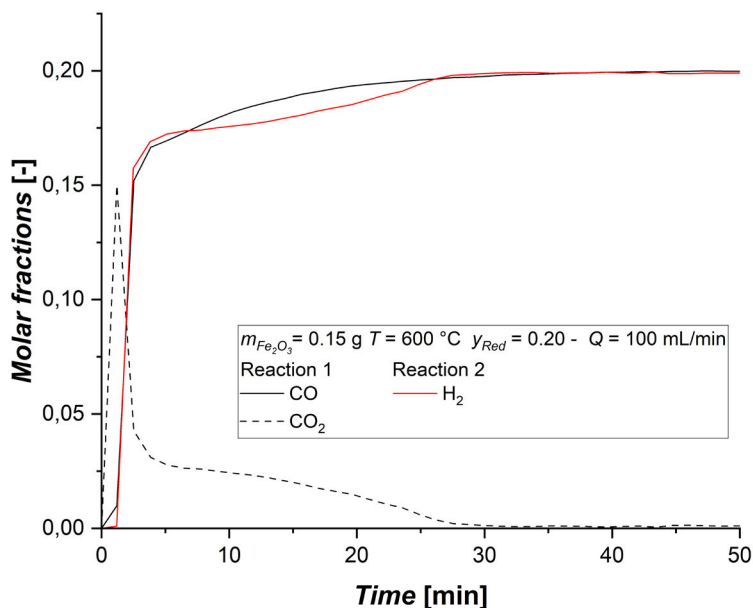


Figure 4.1 Comparative analysis of reduction processes using CO and H₂.

The results of CO-based reduction clearly show a low but continuous CO₂ evolution beyond 30 minutes of reaction. Considering the absence of carbon deposition on the sample (i.e., no reverse Boudouard reaction), this behavior suggests that the reduction was not fully completed. The final reaction stage appears significantly retarded, likely due to the different permeability of the two reducing gases through the solid, which limits the reduction.

The study of CO-based reduction processes under varying conditions did not reveal significant molar fraction changes compared to H₂-based reductions. Therefore, the data analysis method developed for TCD signals was extended to the gas chromatographic results (cf. Section 2.2). The mathematical integration approach amplifies subtle differences between curves, allowing better discrimination of kinetic behavior.

Additionally, XRD and CHNS elemental analyses of the reduced samples confirmed minimal carbon deposition, below 5 wt%, indicating that secondary reactions such as the reverse Boudouard reaction were negligible. Consequently, the integral-based calculation was considered valid for evaluating the overall reduction degree, as it incorporates the complete carbon mass balance. Figure 4.2 illustrates the effect of temperature on the CO-based reduction of hematite.

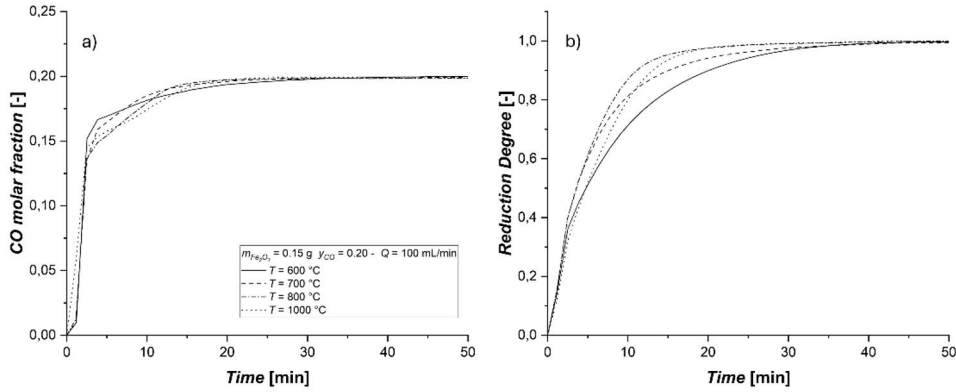


Figure 4.2 Effect of temperature in CO-based reduction of Fe_2O_3 : a) CO molar fraction and b) reduction degree.

As can be observed, the CO molar fraction curves show shape variations after 4–5 minutes, presumably corresponding to the point of almost complete reduction of hematite and magnetite. This correspondence is evident in the integrated results, which amplify the differences between the experiments.

The integrated reduction degree curves indicate enhanced reduction rates with increasing temperature, at least up to 800 °C. Beyond this point, a slowdown occurs, likely due to the formation of dense $\gamma\text{-Fe}$ layers above 912 °C, as widely reported in the literature (cf. Section 1.3), which impede gas diffusion through the lattice. Under these conditions, intraparticle diffusion becomes dominant, and in extreme cases, a solid-state diffusion regime may prevail.

For reduction experiments performed with both carbon monoxide and hydrogen, data analysis becomes more complex, particularly when attempting to evaluate the overall reduction degree, as done for the pure-gas datasets. This complexity arises from secondary reactions affecting mass balances and the individual contributions of each reducing agent— most notably the WGSR.

This reaction can also be beneficial, as in the presence of high CO and H₂O concentrations where it can promote the formation of a higher local H₂ fraction and CO₂. This can enhance the driving force of the H₂-based reduction while slightly decreasing that of CO. This dual effect can be significant, given the higher permeability, faster kinetics, and more favorable thermodynamics of hydrogen above 800 °C.

Solid characterization revealed that, under certain operating conditions, carbon deposition could reach up to 47 wt% of the final sample mass, complicating closure of the overall carbon balance. For this reason, the mathematical integration procedure could not be directly applied. Figure 4.3 provides an example of a probe experiment of hematite reduction at 600 °C with equimolar reductant fractions.

The evolution of the reducing species is generally consistent with previous cases and closely resembles the comparison between hydrogen and carbon monoxide reductions under identical operating conditions. Specifically, considering the feeding reductant percentage, the sum of the mole fractions of the reductants in mixed experiments equals the mole fraction of the individual reductants in pure experiments (cf. Figure 4.1).

Further analysis of this data is required to quantify the actual impact of secondary reactions once the intrinsic kinetic contributions of the pure reductants have been established. This would allow the actual reduction contribution of both reducing species to be evaluated retrospectively, thereby increasing our understanding of the reductive process. This step is crucial for the design and optimization of direct reduction processes.

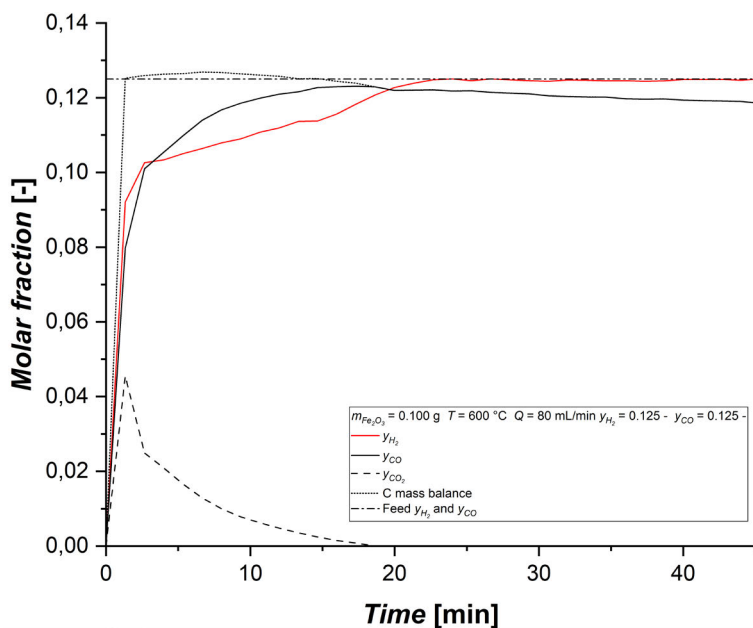


Figure 4.3 Example of reduction experiment of Fe_2O_3 in the presence of equimolar reductants.

4.2.2 Non-isothermal hydrogen reduction

Hydrogen-based reduction experiments of pure hematite were also conducted under TPR conditions to evaluate the kinetic contributions of the different reaction steps while exploiting the thermodynamics of the process. These experiments were performed using Autochem 2910 due to its high precision and reproducibility of the temperature ramp, ensuring accurate energy input to the furnace. Additionally, the high data acquisition frequency enables reliable evaluation of fast reaction kinetics. The transient analysis of the solid samples was crucial for assessing the evolution of their chemical composition and morpho structural properties.

Figure 4.4 shows the TCD signal from a TPR-based reduction experiment, used as a standard test for transient solid evaluation through stop tests, together with the corresponding temperature ramp.

To characterize the solid sample during the reduction process, as in the isothermal case, stop tests were undertaken These involved repeating the same

reduction experiment and interrupting it at different times. The reduction of 0.1 g of pure hematite powder was conducted starting from 300 °C with a heating rate (β) of 5 °C/min, using a total gas flow rate of 30 mL/min and a hydrogen molar fraction of 0.10.

As in the isothermal case, the signal evolution correlates with the progress of the chemical reaction, being directly linked to the outlet H_2 concentration. Initially, the signal displays a trough indicating considerable hydrogen consumption. Starting below the eutectoid point (300 °C), the process promotes only the hematite-to-magnetite and direct magnetite-to-iron reductions (cf. Figure 1.6). However, the latter is extremely slow due to both kinetic and thermodynamic limitations.

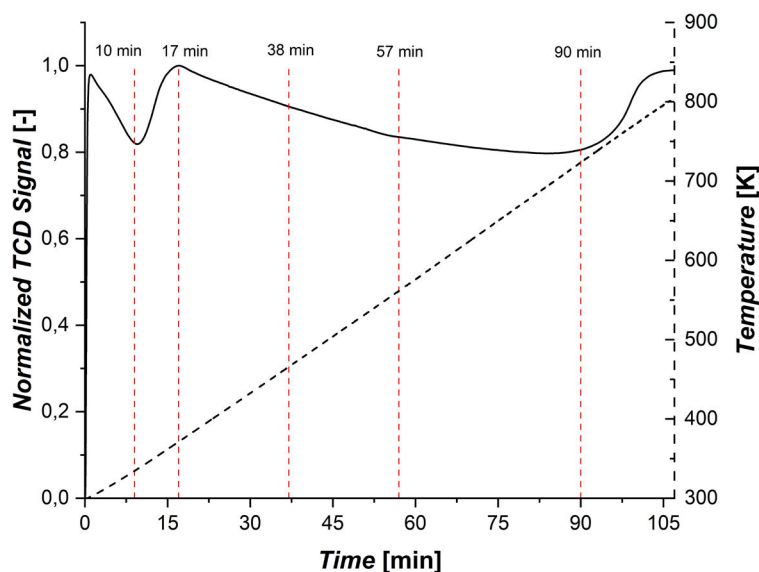


Figure 4.4 Example of TPR H_2 based reduction of Fe_2O_3 . Operating conditions: $m = 0.1$ g $\beta = 5$ °C/min $T_0 = 300$ °C $y_{H_2} = 0.1$ – and $Q = 30$ mL/min. TCD signal expressed by solid line, temperature ramp by dashed line, and stop test points by dashed red lines.

XRD reflections confirmed the presence of hematite after 10 minutes and only magnetite after 17 minutes. The first trough, related solely to the hydrogen consumed during the first step of reduction, can be accurately quantified to

determine its kinetics. After 17 minutes, the direct Fe_3O_4 -to-Fe reduction proceeds slowly, as confirmed by XRD patterns showing also the presence of metallic iron after 38 and 57 minutes.

Progressing beyond 570 °C (after about 54 minutes) causes a slight inflection in the signal due to the change in reaction kinetics and thermodynamics. At this point, the steps involving FeO formation become accessible. The last two reactions proceed in series, as confirmed by the XRD of the 90-minute sample showing Fe_3O_4 , FeO, and Fe peaks. The reaction ends when the normalized signal reaches unity, with XRD showing only reduced Fe. The knowledge gained from isothermal studies greatly facilitated probe data interpretation and the subsequent experimental design under varying heating rates, initial oxide masses, volumetric flow rates, and hydrogen fractions.

The experimental data obtained was analyzed using the same integration method as applied for the isothermal case to correlate detector response (off-gas composition) with the reduction degree of the solids.

Figure 4.5 presents a parametric study of the effect of heating rate, showing normalized TCD signals over time (a) and corresponding reduction degrees (b). As expected, increasing the heating rate enhances all reaction rates. The effect is particularly evident in the TCD signal associated with the hematite reduction trough. This indicates that the area of the four troughs, for the same mass of solid, must be equal as it represents the hydrogen consumed in the first reaction step.

Higher heating rates lead to an earlier approach to the eutectoid temperature, as indicated by the circular markers. The slope-change observed at 5 °C/min develops into a distinct peak, as shown in the zoomed region. An increase in H_2 consumption is observed, which then stabilizes after a signal increase. The reasons lie not only in the higher reduction rate of magnetite to wüstite, but also in the transition between thermodynamic equilibria. These dynamics are more pronounced at high temperatures, even in isothermal cases of H_2 -based reduction. This interpretation is further supported by the model-based analysis of the isothermal experiments (cf. Section 3.8, Figure 3.24). Forthcoming research should involve implementing a dedicated energy balance within the mathematical model to account for the temperature ramp and to estimate the kinetic parameters of the four reactions.

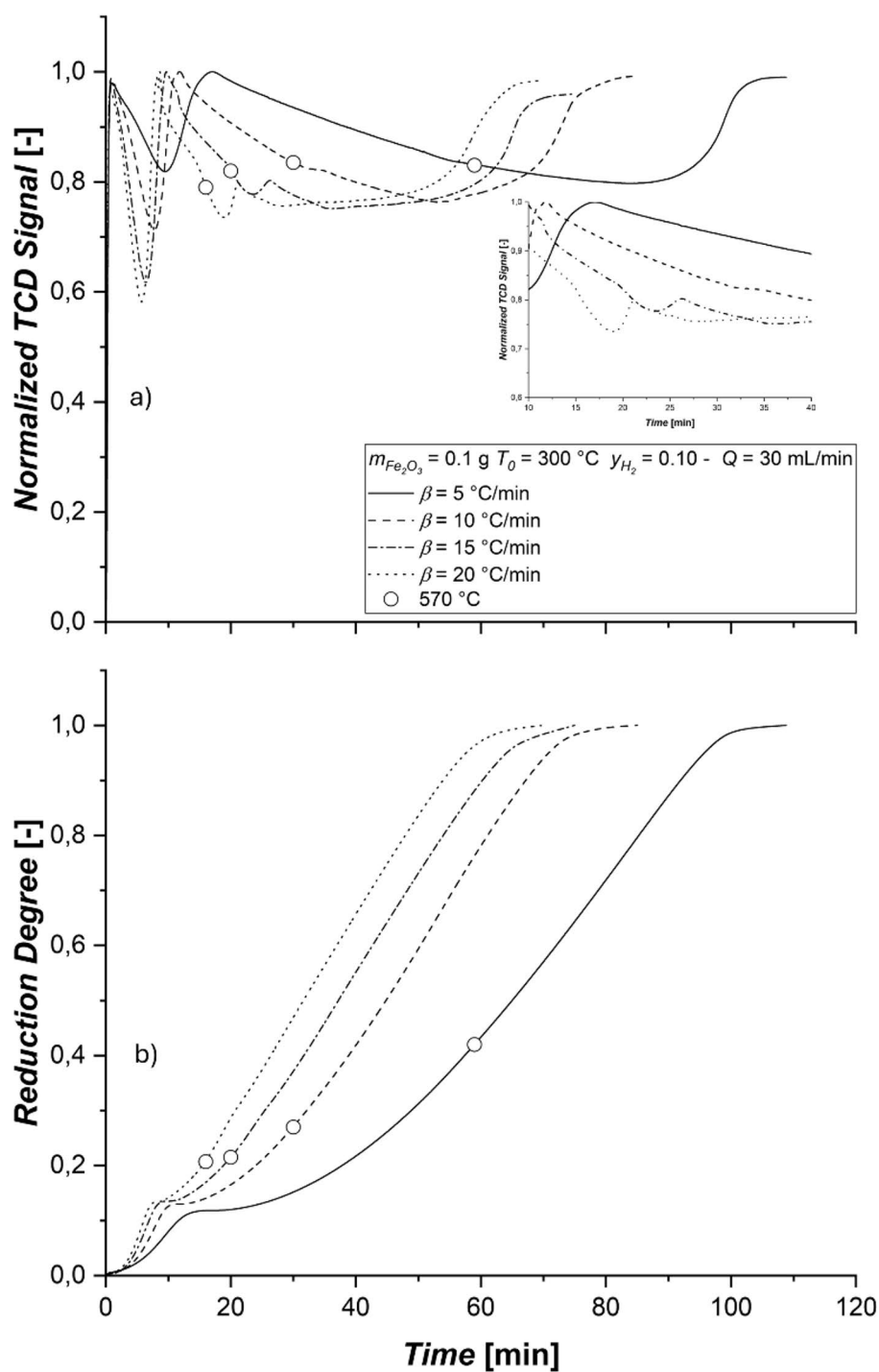


Figure 4.5 Effect of temperature in H₂-based TPR reduction of Fe₂O₃: a) Normalized TCD signal and b) reduction degree.

Notation

Abbreviations

TCD	Thermal Conductivity Detector
TPR	Temperature-Programmed Reduction
WGSR	Water-gas shift reaction
XRD	X-ray diffraction

Symbols

m	Sample mass [g]
Q	Total gas flow rate [mL/min]
T	Temperature [K]
T_0	Initial ramp temperature [K]
y_{CO}	Gas mole fraction [-]
y_{H_2}	Carbon monoxide mole fraction [-]
y_{Red}	Reductants mole fraction [-]
β	Heating rate [°C/min]

Publications

"The Beast that Shouted 愛 at the Heart of the World."

H. Anno, N.G.E.

I

Salucci E., D'Angelo A., Russo V., Grénman H., and Saxén H. *"Review on the Reduction Kinetics of Iron Oxides with Hydrogen-Rich Gas: Experimental Investigation and Modeling Approaches"* Industrial & Engineering Chemistry Research **(2025)** 64 (1), 1-35.

II

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Modelling of iron oxide reduction with hydrogen in a small fixed bed

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ABSTRACT

The need to reduce the environmental impact of the steel industry necessitates the development of new production routes that drastically reduce the emissions of carbon dioxide. A potential solution is to change the reductant from carbon monoxide to hydrogen. In the development of such new ironmaking technologies, it is important to understand the iron oxide reduction kinetics under the novel conditions. In this work, a mathematical model of a small fixed-bed reactor was developed using the key assumptions of the Shrinking Core Model to describe the kinetics of the reactive network and mass transport phenomena involved. The model was found to be robust and to perform in a consistent way when subjected to changes in the model parameters and conditions. It was demonstrated to qualitatively reproduce the results of reduction experiments in a small-scale laboratory reactor. Preliminary analysis indicated a promising potential to adapt the model quantitatively to experimental results.

1. Introduction

Steelmaking is one of the most significant contributors to global CO₂ emissions, accounting for 2.6 Gt/a, which represents approximately 8 % of the direct global emissions (Energy Agency, 2020). Traditionally, the production of iron and steel begins in the blast furnace (BF), where iron ores (i.e., iron oxides) and coke (obtained by dry distillation of metallurgical coal) are alternately charged from above, while preheated air is blown into the lower part. Partial oxidation of the coke in the lower parts of the furnace produces large amounts of CO, which acts as a reducing agent in the gas. The reactions that occur in series in the furnace due to the presence of CO gradually remove oxygen from the iron oxides, which eventually, due to the high temperatures yield molten iron and slag (as a by-product), and a partially oxidized gas (Hutny et al., 1991). The molten iron, also called hot metal, is tapped out in the lower part of the furnace together with slag and is converted into steel in the downstream basic oxygen furnace process, while the gases leave the furnace at the top. It should be noted that the blast furnace cannot operate without coke as this burden material provides permeability to the bed and acts as a support in the lower part of the BF, where the ores have melted.

As an alternative to the BF, the Midrex direct reduction process was introduced 40 years ago, utilizing natural gas instead of coal. Syngas, produced by reforming natural gas, is used as a reducing gas mixture of primarily H₂ and CO. Under these conditions, Direct Reduced Iron (DRI)

is produced by gas–solid reactions (Atsushi et al., 2010). Some of the advantages of this process over the BF are the lower operating temperatures and the absence of molten phases. However, the DRI produced must be melted in a separate vessel, traditionally an electric arc furnace. To decarbonize the iron and steel industry, an option is to use green hydrogen H₂ in the reducing gases in the DR furnace, eliminating the carbonaceous sources (Patisson et al., 2021) and green electricity in the melter.

Over the past 60 years, the scientific community has largely focused on studying the reduction of iron oxides by CO or CO–H₂ mixtures (Jess and Depner, 1998, Rahmatmand et al., 2023). The reason is obvious: in the BF, which still today represents the dominant ironmaking technology in the world, the reduction gas is primarily CO with smaller concentrations of H₂. More recently, because of the pressing need to reduce CO₂ emissions in iron and steelmaking, hydrogen reduction has attracted more attention (Spreitzer & Schenk, 2019). The reduction behavior of iron oxides in hydrogen-containing gases is still not sufficiently known, and more detailed studies of the kinetics should be undertaken. From a thermodynamic point of view, both the reduction in the presence of CO and in the presence of H₂ can be analyzed using the well-known Baur–Glässner or Chaudron diagram in Fig. 1, in which the temperature is shown on the ordinate and the Gas Oxidation Degree (GOD) on the abscissa (Bale et al., 2016 FactSage 8.2).

The GOD represents the ratio between the oxidizing species (CO₂ or H₂O) and the sum of the gaseous components (oxidant and reductant), i.

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Notation			
Abbreviations		N_j	Effective reaction SCM term ($f = 1 [-]$, $f = 2 [s^2/m^2]$, $f = 3 [s^3/m^3]$)
BF	Blast Furnace	n	Number of parameters [-]
CFD	Computational Fluid Dynamic	n_O	Initial concentration of oxygen [mol/m ³]
GOD	Gas Oxidant Degree	P	Operating pressure [N/m ²]
DRI	Direct Reduction Iron	R	Ideal gas constant [J/(K mol)]
SCM	Shrinking core model	r_0	Iron oxide particle radius [m]
Symbols		r_j	Reduction rate SCM [mol/(m ³ s)]
A_j	Kinetic reaction resistance [s/m]	T	Operating temperature [K]
a_j	Proportional oxygen content parameter [-]	t	Time [s]
B_j	Intraparticle diffusion resistance [s/m]	t_v	Number of time points [-]
C	Model variable state ($X_j [-]$ or c_i [mol/m ³])	u	Gas velocity [m/s]
c_i	Concentration i th gas in the reactor [mol/m ³]	W	Total resistance ($f = 1 [-]$) ($f = 2 [s^2/m^2]$) ($f = 3 [s^3/m^3]$)
$c_{i,in}$	Feed i th gas concentration [mol/m ³]	X_j	Reduction degree j th reaction front [-]
D_z	Axial dispersion coefficient [m ² /s]	$y_{i,j}$	Gas molar fraction i th species of j th reaction front [-]
D_j	Intraparticle diffusion coefficient j th reaction front [m ² /s]	$d_{H_2,j,eq}$	Equilibrium molar fraction of H ₂ of j th reaction front [-]
$d_{1,j}$	First coefficient empirical interparticle diffusion equation [m ² /s]	z	Reactor axial coordinate [-]
$d_{2,j}$	Second coefficient empirical interparticle diffusion equation [-]	z_v	Number of spatial grid points [-]
$d_{3,j}$	Third coefficient empirical interparticle diffusion equation [K]	Δ	Parametric perturbation
$E_{a,j}$	Activation energy j th reaction front [J/mol]	ΔG_j	Gibbs free energy changes j th reaction front [J/mol]
F	External diffusion resistance [s/m]	ΔH_j	Enthalpy changes j th reaction front [J/mol]
$g_{1,i}$	First coefficient in empirical thermal conductivity equation [W/(m K)]	ΔS_j	Entropy changes j th reaction front [J/mol]
$g_{2,i}$	Second coefficient in empirical thermal conductivity equation [-]	Δt	Maximum integration step
$g_{3,i}$	Third coefficient in empirical thermal conductivity equation [-]	ε	Bed void degree [-]
$g_{4,i}$	Fourth coefficient in empirical thermal conductivity [-]	λ_i	Gas thermal conductivity [W/(m K)]
H	External diffusion coefficient [m/s]	$\nu_{i,j}$	Stoichiometric matrix [-]
h	Height of the solid bed [m]	Subscripts	
K_j	Equilibrium constant j th reaction front [-]	f	Number of available reaction fronts
k_j	Kinetic constant j th reaction front [m/s]	i	Gas species
$k_{j,ref}$	Pre-exponential kinetic factor j th reaction front [m/s]	j	Reaction fronts
m_O	Iron oxide initial mass [g]	l	Index in space vector
		m	Index in parameter vector
		p	Model parameter
		s	Index in time vector
		v	Space or time vector length
		Superscripts	
		χ	Index of state variables [-]

e., it indicates the mole fraction of the oxidation agent in the system for each individual reaction. The crucial information that can be obtained from the diagram relates to the stability ranges of the different iron oxides at different operating temperatures in relation to the reduction driving forces. In the presence of CO, H₂, or both, at temperatures above 843 K, the reduction process undergoes three reversible reactions in series. Starting from the reduction of hematite (Fe₂O₃), the most abundant iron ore in nature, it passes through magnetite (Fe₃O₄) and wüstite (FeO) eventually producing metallic iron (Fe). In case of operating temperatures below 843 K, the reaction to FeO does not occur due to its instability, so the magnetite converts directly to iron (Zhang et al., 2013).

The main experimental approaches to study this reduction use thermogravimetric systems (Oh & Noh, 2017) or packed oxide beds (Chen et al., 2018) in contact with H₂ evaluating the reaction in terms of sample weight loss or analysis of the composition of the exhaust gases. The most commonly studied operating parameters for reduction kinetics are temperature (El-Geassy et al., 1996, Bernasowski, 2014), reducing gas composition (molar ratio of H₂ and inert gas) (Wei et al., 2018), and its volumetric flow rate (Hou et al., 2012). The study of the morphology and composition of the solid material to evaluate the state of the initial material (composition, structure, etc.) and the products as well as the

different reaction steps are important elements (Gao et al., 1993). Many authors have evaluated the dependence of the reaction progress on the size and geometry of the mineral (e.g., minerals in brick or spherical shape) (Hou et al., 2012, Bonalde et al., 2005) or on its porosity (El-Geassy & Nasr, 1988). The main mathematical model used to describe the reduction process and estimate the kinetic parameters has been the *Avrami* model, but it has significant limitations (Piotrowski et al., 2005). Many other modeling approaches have been reported in the literature, such as the Shrinking Core Model (Zuo et al., 2015), the Grain Model (Bonalde et al., 2005), or the Random Pore Model (Szekely & Evans, 1970). Mathematical models have also been developed to address the study of reduction supported by the fluid dynamic analysis of the gas/solid system using Computational Fluid Dynamics modeling (CFD) at both laboratory scale (Kazemi et al., 2017) and furnace scale (Mauret et al., 2023). However, the findings are inconclusive since many different rate-limiting steps have been reported, including intraparticle diffusion, kinetics, or mixed counterparts depending on the experimental conditions or the reduction steps studied (Lin et al., 2003). Furthermore, the experimental and theoretical approaches have resulted in a large scattering of kinetic coefficients. For instance, reported activation energy values estimated for all individual reactions or for the whole reduction process vary widely between 18 kJ/mol and 246 kJ/

mol (Pineau et al., 2006). The main reason for this lies in the different experimental approaches (Hammam et al., 2021), and in the key properties of the solid and the reducing gases. In several works, the sample used for the evaluation of the kinetic parameters contained a high proportion of gangue (Chen et al., 2015) while it in other studies was prepared in situ in the laboratory with high purity (Jozwiak et al., 2007). The shape and dimensions of the particles as well as their physical properties, including porosity and density, also varied (El-Geassy & Nasr, 1988) making the assessment of the accuracy of the reported activation energies difficult. For this reason, it is not possible to determine the parameters of the intrinsic kinetics based on what has been reported in the literature (Spreitzer & Schenk, 2019). In order to provide a solid framework for a systematic study of the reduction kinetics of iron oxides with H_2 , this work proposes a mathematical model capable of describing the system in its complexity by evaluating both kinetic and mass transfer phenomena of the reduction of iron oxides in a small fixed bed. The goal of the model is to act as a tool by which kinetic parameters can be estimated based on results from small-scale reduction experiments, which is a prerequisite for a model-based analysis of new direct reduction processes of iron ore using hydrogen.

2. Materials and methods

2.1. Mathematical model

The mathematical model developed in this study includes the description of the reaction network for the reduction of iron oxide in the presence of H_2 . The reactor system studied consists of a fixed bed of iron oxide fines through which a reducing gas flow. The operating conditions imply the need to evaluate the kinetic, thermodynamic, and diffusive intra- and interparticle phenomena. Table 1 shows the system of reversible chemical reactions relevant in the system.

The reactive and diffusive intraparticle phenomena can be described in detail by the Shrinking Core Model (Hara et al., 1974), which is based on a series of implicit assumptions:

Table 1

Reaction network. Enthalpy values taken from (Zhang et al., 2013).

Reaction fronts (j)	Reduction reaction	ΔH^0 [kJ/mol]
1	$3Fe_2O_3 + H_2 \rightleftharpoons 2Fe_3O_4 + H_2O$	-2
2	$Fe_3O_4 + H_2 \rightleftharpoons 3FeO + H_2O$	+ 89
3	$FeO + H_2 \rightleftharpoons Fe + H_2O$	+ 25
4*	$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$	+ 38

* Reaction 4 replaces reactions 2 and 3 if the operating temperature is lower than 843 K.

- solid structure and porosity of the different solid layers are radially homogeneous;
- constant total gas concentration inside the particle (if the temperature and pressure of the gas in the particle are uniform);
- diffusion flux described by Fick's law with constant effective diffusivity;
- quasi-stationary state of the gas (i.e., no accumulation of gas species).

The main explicit assumption of the SCM is that the reaction occurs exclusively at surfaces that characterize the separation between distinct zones of the solid, an unreacted core and a reacted outer layer. The surface area of this reaction front decreases as the reaction progresses (i.e., as the core is consumed). Given the reactive network studied in this work, it is necessary to account for three different reaction fronts. Fig. 2 provides a schematic description of the reactor system and the proposed three-front reaction SCM model.

2.2. Solid mass balance

To describe the degree of reduction of different oxides, differential mass balance equations were implemented in the model over time (t) and along the axial coordinate of the reactor (z)

$$\frac{\partial X_j(t, z)}{\partial t} = \frac{r_j(t, z)}{n_0 \cdot a_j} \quad (1)$$

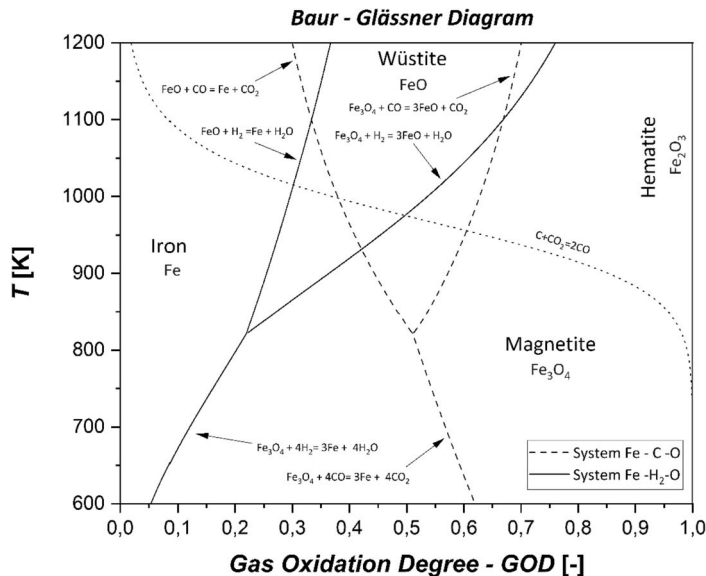


Fig. 1. Baur-Glässner/Chaudron thermodynamic diagram (Bale et al., 2016 FactSage 8.2).

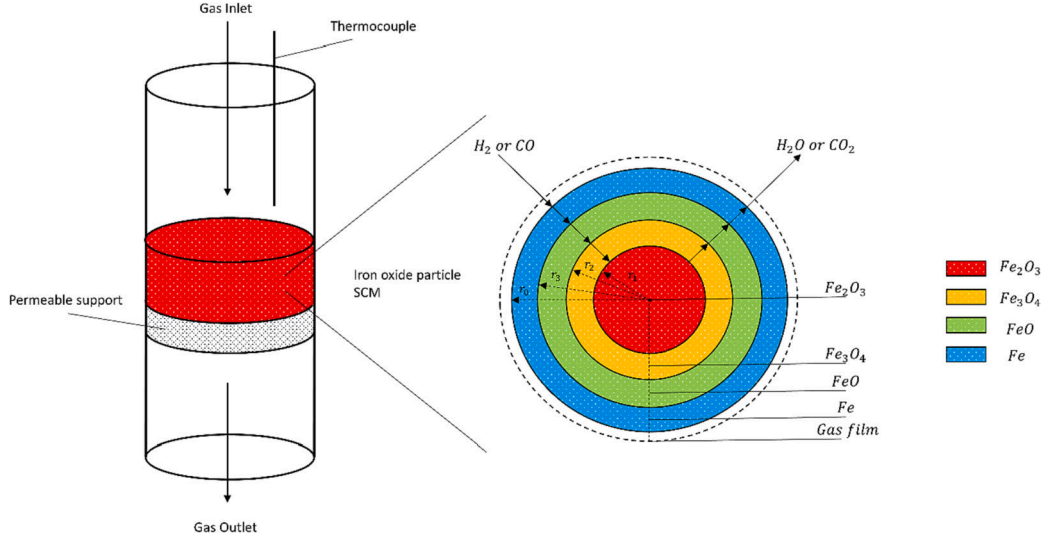


Fig. 2. Fixed bed reactor scheme and three-interface shrinking core model, with SCM transient reduction of hematite particle.

where X_j represents the degree of j -th reaction front (Fe_2O_3 reduction, etc.), $n_0 = 3m_0/M_{\text{Fe}_2\text{O}_3}$ is the initial oxygen content calculated from the initial mass, m_0 ,

$$r_j(t, z) = \frac{P}{RT} \frac{3}{r_0} \frac{1}{A_j(t, z)} \left|_f \left(\frac{N_j(t, z)}{W(t, z)} \right) - y_{\text{H}_2, j, \text{eq}}(t, z) \right) \quad (2)$$

where R is the gas constant, r_0 is the radius of the initial particle, $y_{\text{H}_2, j, \text{eq}}$ is the equilibrium molar fraction of H_2 for the j -th reaction, while P and T are the operating pressure and temperature, respectively. $y_{\text{H}_2, j, \text{eq}}$ is calculated for each reaction front according to

$$y_{i, j, \text{eq}}(t, z) = \frac{1}{1 + K_j} (y_{\text{H}_2, j}(t, z) + y_{\text{H}_2\text{O}, j}(t, z)) \quad (3)$$

where $y_{\text{H}_2, j}$ and $y_{\text{H}_2\text{O}, j}$ represent the molar fractions of the gaseous reactant and product at a given reaction front (also taking into account the presence of inert gas), while K_j is the equilibrium constant of the j -th reaction.

Starting from the reduction of hematite, the reactive network moves from an initial phase, in which all three reaction fronts are accessible, to the next phase after the complete reduction of hematite ($X_1(t, z) = 1$) in which only two fronts are present. Similarly, when the magnetite is completely reduced ($X_2(t, z) = 1$), there is a transition to a single-front system. In general, the formulations of the coefficients A_j , W_j , and N_j that define the reduction rate must necessarily change as a function of the number of possible reductions ($A_j(t, z)|_f$, $W_j(t, z)|_f$ and $N_j(t, z)|_f$). The value of the parameter f , which is defined in the system of equations (4), indicates the number of reaction fronts at the time f and the axial coordinate z

$$\text{if } \begin{cases} X_1(t, z) < 1 & f = 3 \quad j = 1, 2, 3 \\ X_1(t, z) = 1 \wedge X_2(t, z) < 1 & f = 2 \quad j = 2, 3 \\ X_1(t, z) = 1 \wedge X_2(t, z) = 1 \wedge X_3(t, z) < 1 & f = 1 \quad j = 3 \end{cases} \quad (4)$$

N_j represents the effective reduction contribution of each reaction, while W is the total resistance of the system. Both are defined starting from the terms that respectively identify the resistances of the process: kinetic A_j ,

intraparticle diffusion B_j , and external diffusion F . The equations derived for the case of a triple reaction front ($f = 3$) are

$$N_1(t, z)|_3 = (A_1 A_2 A_3) \cdot y_{\text{H}_2, 1} + [A_1 A_2 (B_3 + F)] \cdot y_{\text{H}_2, 3, \text{eq}} + [A_1 A_3 B_2 + A_1 A_3 (B_3 + F) + A_1 B_2 (B_3 + F)] \cdot y_{\text{H}_2, 2, \text{eq}} + [A_3 B_1 (A_2 + B_2) + A_3 B_1 (A_2 + B_2) + B_1 (A_2 + B_2) (B_3 + F) + A_2 A_3 B_2 + A_2 A_3 (B_3 + F) + A_2 B_2 (B_3 + F)] \cdot y_{\text{H}_2, 1, \text{eq}} \quad (5)$$

$$N_2(t, z)|_3 = [A_2 A_3 (A_1 + B_1)] \cdot y_{\text{H}_2, 2} + [A_2 (A_1 + B_1) (B_3 + F)] \cdot y_{\text{H}_2, 3, \text{eq}} + [A_3 (A_1 + B_1) (B_3 + F) + B_2 (A_1 + B_1) (B_3 + F) + A_3 B_2 (A_1 + B_1)] \cdot y_{\text{H}_2, 2, \text{eq}} + [A_2 A_3 B_2 + A_2 A_3 B_2 + A_2 B_2 (B_3 + F) + A_2 A_3 (B_3 + F)] \cdot y_{\text{H}_2, 1, \text{eq}} \quad (6)$$

$$N_3(t, z)|_3 = [A_3 (A_1 + B_1) (A_2 + B_2) + A_2 A_3 B_2] \cdot y_{\text{H}_2, 3} + [(A_1 + B_1) (A_2 + B_2) (B_3 + F) + A_2 B_2 (B_3 + F)] \cdot y_{\text{H}_2, 3, \text{eq}} + [A_3 (A_1 + B_1) (B_3 + F)] \cdot y_{\text{H}_2, 2, \text{eq}} + [A_2 A_3 (B_3 + F)] \cdot y_{\text{H}_2, 1, \text{eq}} \quad (7)$$

$$W(t, z)|_3 = \{ (A_1 + B_1) \cdot [A_3 (A_2 + B_2 + B_3 + F) + (A_2 + B_2) \cdot (B_3 + F)] + A_2 [A_3 (B_2 + B_3 + F) + B_2 (B_3 + F)] \} \cdot y_{\text{H}_2, 1, \text{eq}} \quad (8)$$

The corresponding equations for calculating the contributions in the case of a double reaction front ($f = 2$) are

$$N_2(t, z)|_2 = (A_2 A_3) \cdot y_{\text{H}_2, 2} + [A_2 (B_3 + F)] \cdot y_{\text{H}_2, 3, \text{eq}} + [A_2 B_1 + (A_3 + B_2) (B_3 + F)] \cdot y_{\text{H}_2, 2, \text{eq}} \quad (9)$$

$$N_3(t, z)|_2 = A_3 (A_2 + B_2) \cdot y_{\text{H}_2, 2} + [(A_2 + B_2) (B_3 + F)] \cdot y_{\text{H}_2, 3, \text{eq}} + [A_3 (B_3 + F)] \cdot y_{\text{H}_2, 2, \text{eq}} \quad (10)$$

$$W(t, z)|_2 = A_3 (A_2 + B_2 + B_3 + F) + (A_2 + B_2) \cdot (B_3 + F) \quad (11)$$

while the system for the case of a single reaction front ($f = 1$) is

$$N_3(t, z)|_1 = y_{H_2,3}(t, z) - y_{H_2,3,eq}(t, z) \quad (12)$$

$$W(t, z)|_1 = \frac{A_3 + B_3 + F}{A_3} \quad (13)$$

This modeling approach proves particularly useful because it also allows for evaluation of the potential reduction of the other two iron oxides. The evaluations of the A_j , B_j and F terms are

$$A_j(t, z)|_f = \frac{1}{(1 - X_j(t, z))^{\frac{1}{2}} k_j \left(1 + \frac{1}{k_j}\right)} \quad (14)$$

$$B_j(t, z)|_f = \frac{(1 - X_{j+1}(t, z))^{\frac{1}{2}} - (1 - X_j(t, z))^{\frac{1}{2}}}{(1 - X_j(t, z))^{\frac{1}{2}} (1 - X_{j+1}(t, z))^{\frac{1}{2}}} D_j r_0 \quad (15)$$

$$F = \frac{1}{H} \quad (16)$$

where k_j is the kinetic constant of the j :th reaction front, D_j is the intraparticle diffusion coefficient, which depends on the morphological properties of the oxide, while H is the external diffusion coefficient. As for the external diffusion phenomena, the resistance to the transport of gases outside the particles is negligible in the present case because the packed bed consists of iron oxide fines ($r_0 < 5\mu\text{m}$), so H is very high. The kinetic (Chu et al. 2005), thermodynamic (Zhang et al., 2013), and diffusion (Takahashi et al., 1971) parameters used in the model are calculated using values reported in the literature, based on the formulas (cf. Tables 2 and 3)

$$k_j = k_{j,ref} \cdot \exp\left[\left(-\frac{E_{a,j}}{R}\right) \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (17)$$

$$K_j = \exp\left(-\frac{\Delta G_j}{RT}\right) = \exp\left(-\frac{\Delta H_j - T\Delta S_j}{RT}\right) \quad (18)$$

$$D_j = d_{1,j} \cdot \exp\left(d_{2,j} - \frac{d_{3,j}}{T}\right) \quad (19)$$

In the equations, $k_{j,ref}$ and $E_{a,j}$ are the pre-exponential factor and activation energy, respectively, of the j :th reduction used in the modified Arrhenius equation, T_{ref} is the reference temperature (here 600 °C), ΔH_j and ΔS_j represent the enthalpy and entropy changes of the reaction by which the Gibbs free energy changes (ΔG_j) can be determined, while the terms $d_{1,j}$, $d_{2,j}$ and $d_{3,j}$ are coefficients of the empirical equation

Table 2
Fixed model parameters.

Parameter	Value	Unit	Parameter	Value	Unit
$d_{1,1}^*$	$1 \cdot 10^{-4}$	$\text{m}^2 \text{s}^{-1}$	$g_{1,2}^{**}$	$7 \cdot 10^{-5}$	$\text{W m}^{-1} \text{K}^{-1}$
$d_{2,1}^*$	3.43	—	$g_{2,2}^{**}$	1.1	—
$d_{3,1}^*$	$4.2 \cdot 10^3$	K	$g_{3,2}^{**}$	$8.5 \cdot 10^2$	—
$d_{1,2}^*$	$1 \cdot 10^{-4}$	$\text{m}^2 \text{s}^{-1}$	$g_{4,2}^{**}$	$-1.5 \cdot 10^5$	—
$d_{2,2}^*$	5.64	—	$g_{1,3}^{**}$	3.7	$\text{W m}^{-1} \text{K}^{-1}$
$d_{3,2}^*$	$6.8 \cdot 10^3$	K	$g_{2,3}^{**}$	$-3.8 \cdot 10^1$	—
$d_{1,3}^*$	$1 \cdot 10^{-4}$	$\text{m}^2 \text{s}^{-1}$	$g_{3,3}^{**}$	$9.6 \cdot 10^2$	—
$d_{2,3}^*$	4.77	—	$g_{4,3}^{**}$	$1.9 \cdot 10^6$	—
$d_{3,3}^*$	$5.9 \cdot 10^3$	K	$E_{a,1}^{***}$	$33.4 \cdot 10^3$	J mol^{-1}
$g_{1,1}^{**}$	$2.6 \cdot 10^{-3}$	$\text{W m}^{-1} \text{K}^{-1}$	$E_{a,2}^{***}$	$58.2 \cdot 10^3$	J mol^{-1}
$g_{2,1}^{**}$	$7.4 \cdot 10^{-1}$	—	$E_{a,3}^{***}$	$57.1 \cdot 10^3$	J mol^{-1}
$g_{3,1}^{**}$	9.0	—	ϵ	0.25	—
$g_{4,1}^{**}$	0	—			

* (Takahashi et al., 1971).

** (CHEMCAD).

*** (Chu et al., 2005).

Table 3

Key coefficients of model used for parametric analysis.

Parameter	Value	Unit
T	873	K
$k_{1,ref}^*$	$5 \cdot 10^{-5}$	m s^{-1}
$k_{2,ref}^*$	$2 \cdot 10^{-4}$	m s^{-1}
$k_{3,ref}^*$	$4 \cdot 10^{-5}$	m s^{-1}
D_z	$1 \cdot 10^{-6}$	$\text{m}^2 \text{s}^{-1}$
r_0	$2.5 \cdot 10^{-6}$	m
m_0	0.1	g
y_{H_2}	0.2	—
Q	20	ml min^{-1}

* (Chu et al., 2005).

describing intraparticle diffusion. The intrinsic properties of the solid (e. g. porosity), which are considered constant under the assumptions of the shrinking core model, are implicitly expressed in the $d_{1,j}$, $d_{2,j}$ and $d_{3,j}$ coefficients. The diffusion of gaseous species in the solid is therefore mechanistically described as a molecular diffusion phenomenon.

2.3. Gas mass balance

Mass balance equations for H_2 and H_2O were formulated to describe the variation of reducing gas composition in the fixed bed by describing the interaction with the solid through the SCM

$$\frac{\partial c_i(t, z)}{\partial t} = \underbrace{-\frac{u}{h} \frac{\partial c_i(t, z)}{\partial z}}_{\text{Convection}} + \underbrace{\frac{D_z}{h^2} \frac{\partial^2 c_i(t, z)}{\partial z^2}}_{\text{Axial dispersion}} + \underbrace{\frac{1}{\epsilon} \sum_{ij} \nu_{ij} \cdot r_j(t, z)}_{\text{Reaction SCM}} \quad (20)$$

In the equation, c_i represents the concentration of the i :th species in the system, h is the fixed-bed height, u is the superficial gas velocity defined as the ratio between the volumetric flow rate of the gas and the (empty) cross-sectional area of the reactor, while D_z represents the coefficient of axial dispersion. ν_{ij} is the stoichiometric coefficient of gaseous species i in reaction j (Table 1), while ϵ is the voidage of the bed.

The boundary conditions of the system of partial differential equations were defined at the reactor inlet ($z = 0$) and outlet ($z = 1$) as

$$c_i(t, z)|_{z=0} = c_{i,in} - \frac{\partial c_i(t, z)}{\partial z} \Big|_{z=1} = 0 \quad (21)$$

In this modeling work, the energy balance of the reduction of iron oxides with H_2 was not considered, although, as indicated in Table 1, the reactive network is endothermic overall. The reason for this exclusion lies in the operating conditions of the model, which describes the reduction of small beds of very fine ore particles, where the temperature gradients can be considered negligible, and an external controlled heat source guarantees that the temperature stays constant. In order to theoretically evaluate this assumption, the criterion

$$T_j^{\text{center}} - T_j^{\text{surface}} = \frac{D_j \cdot (-\Delta H_j)}{\lambda_j} (c_{\text{H}_2}^{\text{surface}} - c_{\text{H}_2}^{\text{center}}) \quad (22)$$

was used, where λ_j represents the thermal conductivity coefficient of the reacting oxides (Akiyama et al., 1992). While the first term on the right-hand side is always less than $1 \text{ K m}^3 \text{ mol}^{-1}$ for all solids involved (in a range of $5 \cdot 10^{-2} - 1 \cdot 10^{-1} \text{ K m}^3 \text{ mol}^{-1}$), the evaluation of the second term on the right-hand side can be done using as an example the worst-case scenario in terms of concentration variations between the surface and the center of the particle. This is represented by the maximum H_2 concentration in the absence of inert at 873 K ($c_{\text{H}_2}^{\text{feed}} \approx 14 \text{ mol m}^{-3}$) assumed as the surface composition and no H_2 in the core. An intraparticle temperature variation of $-6.49 \cdot 10^{-1} \text{ K}$, 1.61 K and 1.23 K is observed for the reduction of hematite, magnetite and wustite,

respectively. This result supports the assumption of a negligible intra-particle temperature variation, which is also supported by recent experimental findings by Hessling et al. (2022) that indicate temperature differences of less than 10 K between the surface and core of much larger (12 mm) pellet particles.

2.4. Local sensitivity analysis

Sensitivity analysis of a mathematical model can provide important preliminary information for future estimation of, for example, kinetics coefficients by evaluating the response of the model to parametric perturbations. For this purpose, a local sensitivity analysis was undertaken (Morris, 1991; Norton, 2015), calculating a sensitivity index

$$SSE_{m,\Delta} = \sqrt{\frac{1}{t_v \cdot z_v} \sum_{v=1}^5 \sum_{l=1}^{z_v} \sum_{s=1}^{t_v} \left(\frac{C'_{s,l}(p_1, \dots, p_m \pm \Delta, \dots, p_n) - C'_{s,l}(p_1, \dots, p_n)}{C'_{s,l}(p_1, \dots, p_n) \big|_{\max} - C'_{s,l}(p_1, \dots, p_n) \big|_{\min}} \right)^2} \quad (23)$$

after varying each parameter of interest individually by $\pm 10\%$ or $\pm 50\%$. The sensitivity index expresses the standardized elemental effect of parameter $p_m(\pm\Delta)$ over the number n of parameters studied in the analysis (i.e., $k_{j,ref}$, D_z , r_o , m_O , y_{H_2} and Q) calculated for all state variables $C'_{s,l}$ considered (here gas composition and reduction degrees, i.e., 5) with respect to the values of the state variables calculated starting from chosen values of the p vector (i.e., the base case). The sensitivity is performed by comparing all values of the state variables in time and space of the system (indices s and l , respectively), where z_v represents the number of grid points of the dimensionless axial coordinate of the reactor while t_v is the number of simulated time points. The maximum and minimum values of the state variables used in the denominator of the index are set in relation to the overall reaction time. The sensitivity index is obtained divided the comparison by the number of samples per observed output.

2.5. Front reaction control

By definition, the kinetic terms describing the chemical reactions in the SCM do not depend on the amount of species in the solid phase, but exclusively on the compounds in the gas phase. For this reason, for certain combinations of the model parameters it is possible that an outer front in the SCM would move faster than an inner one, leading to physically infeasible states if the interfaces cross. To avoid this problem for both the local sensitivity study and future kinetic parameter estimation, a reaction front control procedure was developed. After calculating the value of $dX_j(t, z)/dt$ for time t , the future value $dX_j(t + \Delta t, z)/dt$ is estimated through the trapezoidal method, where Δt is defined as the maximum integration step of the solver of the model (cf. Section 2.6). If the new intermediate degree of reduction ($j > 1$ at $t + \Delta t$) is greater than that of the previous reaction, the equality of the derivatives over time in t are forced. Physically, this means that it is impossible for an outer front to cross an inner one, and at most it they can move with an equal rate. The key condition for controlling the front is

$$X_j(t + \Delta t, z) = X_{j+1}(t + \Delta t, z) \quad \text{if} \quad X_{j-1}(t + \Delta t, z) < X_j(t + \Delta t, z) \quad (24)$$

2.6. Numerical solution

The mathematical model was developed in Matlab 2023a by solving the system of partial differential equations, using the finite difference method (backward with respect to the first-order derivative of the space and centered with respect to the second-order derivative of the space), setting 50 grid points for the axial dimensionless coordinate of the reactor. The ordinary differential equations are solved using the ode15s function, a variable step size, variable order solver based on numerical

differentiation formulas of 1–5 orders. This, together with the front reaction control, was found to yield robust solutions for practically arbitrary parameter values in the model.

2.7. Experimental setup

Reduction experiments were performed with an Autochem2910, which is generally used for chemisorption studies on catalysts. This experimental apparatus made it possible to undertake iron oxide reduction in a fixed bed configuration by feeding the hydrogen-containing gas from above. The oxide fines charged into the glass reactor are retained by a porous support, which also allows the effluent gases to reach the Thermal Conductivity Detector (TCD) for compositional analysis. The reagent bed (diameter 8 mm) consists of hematite powder (purity 97 %, Sigma Aldrich) with a particle diameter of less than 5 μm (cf. Fig. 2). The probing experiments were performed isothermally with pre-determined H_2/Ar molar ratio (H_2 , 99.9 % purity; Ar, 99.9 % purity) and total gas flow rate. The signal obtained from the TCD is a function of the composition of the gas mixture leaving the reactor and the thermal conductivity of the chemical species involved. Since the thermal conductivity of H_2 is much higher than that of H_2O and Ar (which are very similar), the TCD signal roughly reflects the share of hydrogen in the gas leaving the reactive system. As an example, Fig. 3 shows experimental results of the reduction of a bed of 0.1 g of fine hematite (bed diameter of 8.5 mm and bed height of approximately 0.5 mm), carried out at different temperatures but at the same gas volume flow rate (20 mL/min) and molar ratio ($\text{H}_2:\text{Ar} = 1:4$), where the normalized signal of TCD is plotted over time. The normalization was done by dividing the TCD value of the outgoing gas by that of the incoming gas.

The signals show very different trends and changes in slope, which clearly depend on the number of reactions involved and their rate as the temperature changes. In general, the reaction can be said to be complete when the signal stabilizes at a value of 1, which means that no H_2 is consumed in the bed. The reduction at 773 K should not proceed via the FeO intermediate (cf. Fig. 1), which justifies its simpler form compared to the other two cases, while the form of the signal obtained at 1073 K appears to be an accelerated version of the reaction at 873 K. To better understand the observed phenomenological dynamics, a profound experimental study supported by a well-characterized mathematical model is required.

To simulate the TCD signal, equations were introduced into the mathematical model that depend on the operating temperature and serve to evaluate the contribution of the thermal conductivity of the gases involved in the chemical reaction. The relationships and parameters ($g_{1,i}$, $g_{2,i}$, $g_{3,i}$ and $g_{4,i}$) were taken from CHEMCAD.

$$\lambda_i = \frac{g_{1,i} \cdot (T/\text{K})^{g_{2,i}}}{1 + \frac{g_{3,i}}{(T/\text{K})} + \frac{g_{4,i}}{(T/\text{K})^2}} \quad (25)$$

3. Numerical results

3.1. Model simulation

A parametric study was conducted on the mathematical model describing the bed reduction of fine iron oxides particles in an isothermal fixed bed described through the theoretical assumptions of the three-interface SCM to evaluate its performance.

The study was commenced by utilizing thermodynamic and kinetic parameters reported in the literature, carefully selecting the operating conditions (T , Q , $C_{\text{H}_2,\text{in}}$, etc.) and the other structural coefficients of the model (D_z , ϵ , etc.). Table 2 and Table 3 list the values and units of all fixed parameters or key coefficients; the latter represent the base case values and form the starting point for the parametric analysis of the mathematical model.

Given the wide variation in the activation energy found in the

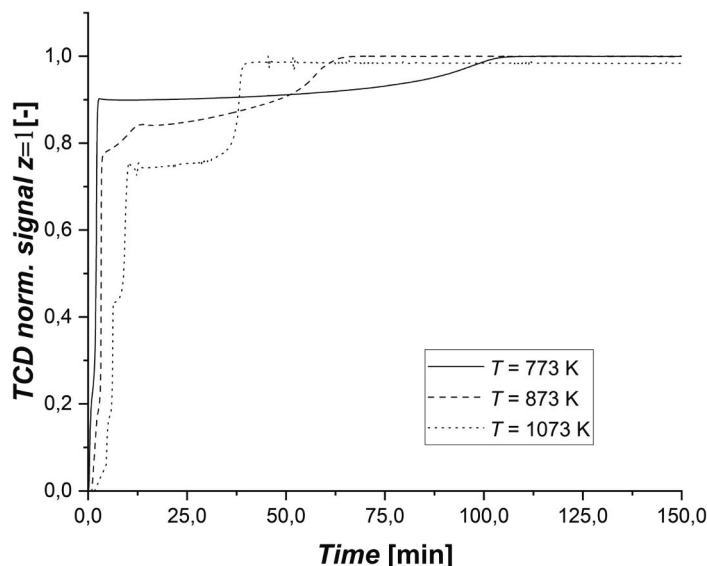


Fig. 3. Examples of experimental results relating to the reduction of hematite powder in a fixed bed reactor at different operating temperatures.

literature for each reduction, the kinetic parameters used in the model were chosen so that the different $E_{a,j}$ represent an average of those reported in the literature accompanied by the reference kinetic constants.

Figs. 4 and 5 show the main results of the model simulating the reduction of a 0.1 g (pure) hematite bed at a temperature of 873 K, a total gas volume flow of 20 mL/min, and a feed molar ratio of $H_2:Ar$ of 1:4 using the base case set of parameters, reported in Table 3.

The contour plots in Fig. 4 show the axial profiles of the mole fractions of (a) hematite, (b) magnetite, (c), wüstite and (d) iron as a function of reactor axial coordinate and reaction time. The hematite converts completely in less than 5 min, promoting the rapid production of the first intermediate. In Fig. 4b, the balance between the production and consumption of magnetite is peculiar when focusing on the difference between reactor inlet and outlet. In the beginning ($t < 5$ min), the formation of magnetite agrees with the consumption of the initial reactant and reaches mole fractions of about 0.5 throughout the reactor. However, near the reactor inlet ($z = 0$), magnetite is completely consumed within the first 5 min, promoting the formation of the second intermediate (wüstite). This is due to the constant supply of fresh hydrogen at the reactor inlet, which strongly drives the formation of products in all reactions (see also Fig. 5a). For this reason in the upper part of the bed, the amount water produced during the reduction is always lower than the amount of H_2 , so the reaction rates are not limited by equilibrium constraints. Approaching the lower end of the reactor, the dynamics of the system change radically, leading to a significant accumulation of magnetite (with a molar ratio approaching unity) in the first 10 min. The consumption of Fe_3O_4 in the lower bed is significantly slowed down by the high consumption of H_2 and the associated production of H_2O in the upper parts of the bed. The accumulation of water in the gas phase, which is increased by the resistance to inter- and intraparticle transport, thermodynamically slows down the chemical reaction. This results in a limited driving force for the reaction, so approximately 25 min is required to complete the reduction of the magnetite in the whole bed. As seen in Fig. 4c, a similar trend is observed for wüstite in the lower region of the bed: while complete reduction is observed at the top of the bed in about 30 min, it takes about 90 min to

fully convert the wüstite to metallic iron. The reaction of FeO to Fe is also kinetically the slowest among the reduction steps (Spreitzer & Schenk, 2019). The simulation results underline a very important aspect, also for the definition of a set of experimental tests, namely the need to consider the quite complex impact of the bed dynamics on the total reduction time.

Figure 5a and b show the mole fractions of H_2 and H_2O in the gas phase as a function of axial coordinate and time. The molar ratio of hydrogen in the system is always high (0.2) at the reactor entrance, but only for the initial phase of the experiment it is almost halved at the reactor end, confirming the observations of the solid phase composition plots in Fig. 4. Water naturally exhibits a mirror image pattern to hydrogen. Fig. 5c shows the temporal development of the mole fractions of the solid species in the entire reactor, indicating the time intervals at which the disappearance of some reaction intermediates can be observed. Fig. 5d shows an example of a normalized TCD signal calculated based on the simulated composition of the reactor off-gas (H_2 , H_2O , and Ar), as the sum of the mole fractions multiplied by the corresponding thermal conductivity coefficients obtained by empirical equations (24). This signal provides important information about the course of the chemical reactions, which end when the value of one is reached (which implies that the off-gas has identical composition as the feed gas). The different slopes of the TCD curve reflect the three stages of the reduction, indicating when one reaction ends and the next becomes the dominant one. Comparison between Fig. 5c and 5d confirms that the disappearance of an intermediate oxide corresponds to a particular change in the slope of the simulated signal. In this way, it is possible both to evaluate the different modeling results of the parametric study by directly comparing the simulated signals and to perform a first analysis of the quality of the model compared to the experimental data.

3.2. Parametric investigation

Several simulations were performed to evaluate the model's response to the parametric perturbation in which a parameter or operating condition is perturbed from its base-point value (cf. Table 3). In this section

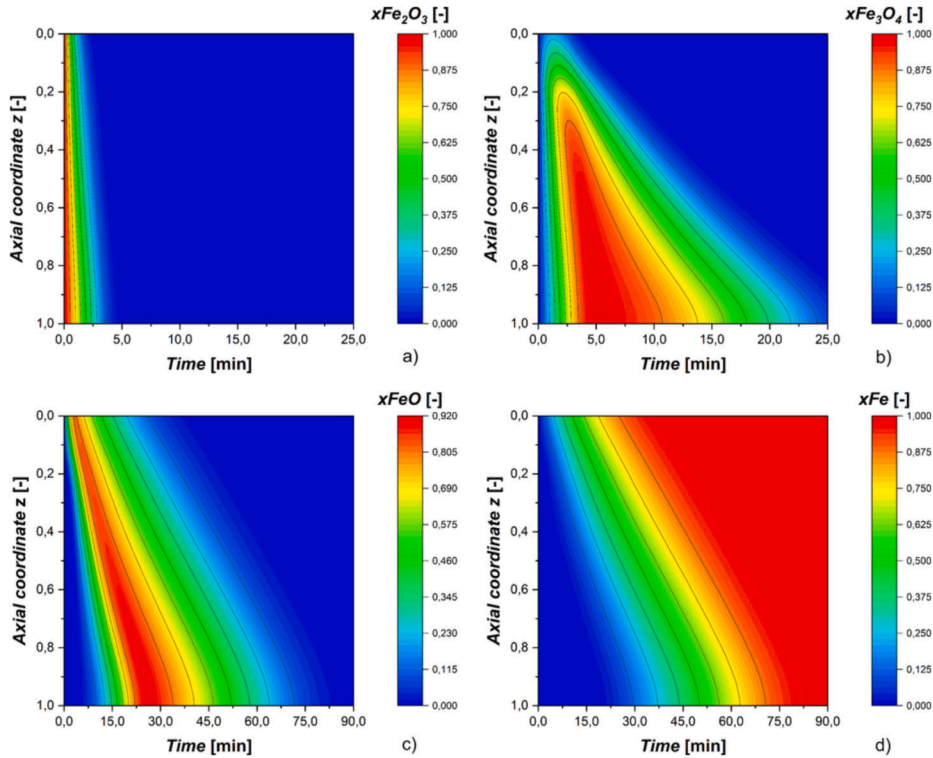


Fig. 4. Axial bed profiles over time of the iron and iron oxides: (a) Fe_2O_3 , (b) Fe_3O_4 , (c) FeO and (d) Fe , where the gas enters from above. Note the different time scales of the top and bottom panels.

we present some results of the effect of key parameters on the reduction behavior. The main purpose of this parametric study is to show how model parameters and boundary conditions affect the reduction of iron oxides. These results can be used to gain a comprehensive understanding of the system and how it would manifest in the TCD signal, which is the main information of the experimental device. This analysis is also useful for an upcoming parameter estimation where it is important to identify factors with significant effects.

3.3. Temperature

The operating temperature is one of the most important parameters of the model because it affects the intraparticle diffusion phenomena (Eq. 19) as well as the kinetics (Eq. 17) and thermodynamics (Eq. 18). It is well known that in reactions in gas/solid systems, both with heterogeneous catalysts and with reactive solids, the different dependence of diffusion and kinetic phenomena on temperature has a crucial influence on the limiting process, which is kinetics at low operative temperature and diffusion at high T . Fig. 6 shows the simulated TCD curves for the off-gas in the reduction of hematite at increasing operating temperatures.

As can be seen, the simulation results are qualitatively similar to those obtained in the experimental results illustrated in Fig. 3 under the same operating conditions. The temperature range of 873–1173 K is interesting since the formation of wüstite is suppressed below 843 K (Zhang et al., 2013), while most experimental results as reported in the

literature are for temperatures lower than 1173 K (Spreitzer & Shenk, 2019). An increased temperature shortens the overall reaction time, and at 1173 K the total time that is less than half of the time required for complete reduction at 873 K. The simulated TCD signal in the first few minutes of the reaction decreases with increasing temperature due to the rapid H_2 consumption by the hematite and magnetite reductions. For temperatures below 1073 K, the slope changes of the curves which reflect the approach of complete reduction of the hematite are clearly observed, but they are less clear beyond this temperature as the rate of the magnetite-to-wüstite reaction increases. At high temperatures, the point of complete magnetite reduction becomes more evident, seen as a large change in the slope of the curve. The trend of the TCD signal becomes progressively flatter during the initial stage of the wüstite reduction, implying that at 1173 K the reaction consumes a constant amount of H_2 for almost 10 min. Due to the high presence of H_2O produced by the oxides in the upper parts of the bed, the driving force of the reaction in the lower parts of the bed is low and may vanish if the gas reaches equilibrium conditions.

3.4. Reference kinetic constants

The pre-exponential reference kinetic constants (cf. Eq. (17)) are among the most important parameters in the model, as they affect the kinetic resistance terms A_j (cf. Eq. (14)) and thus the reaction rates of the series of reduction steps. Fig. 7 shows the results of the effect of the first ($k_{1,\text{ref}}$), second ($k_{2,\text{ref}}$), and third ($k_{3,\text{ref}}$) reference kinetic constants,

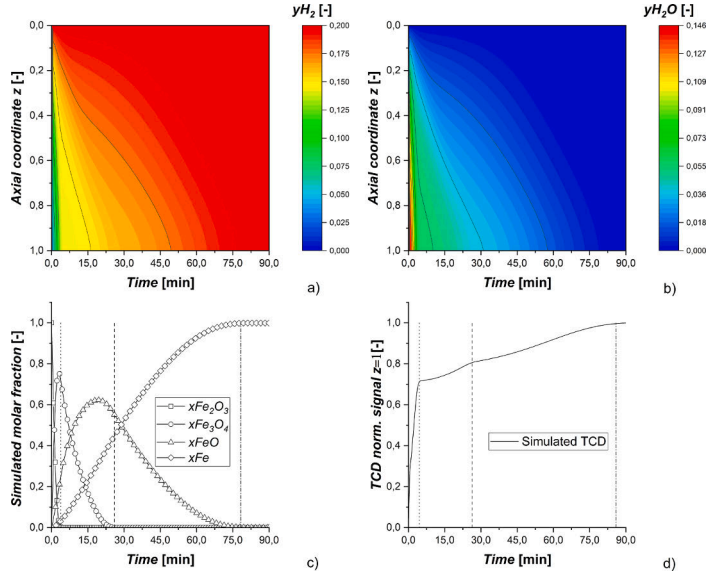


Fig. 5. Axial bed profiles over time of the gas phase: H_2 (a) and H_2O (b). Simulated TCD signal from off-gas composition (c). Dot line represents the end of the reduction of the major part of Fe_2O_3 , dashed line the end of the reduction of the major part of Fe_3O_4 , dot-dash line the end of the reduction.

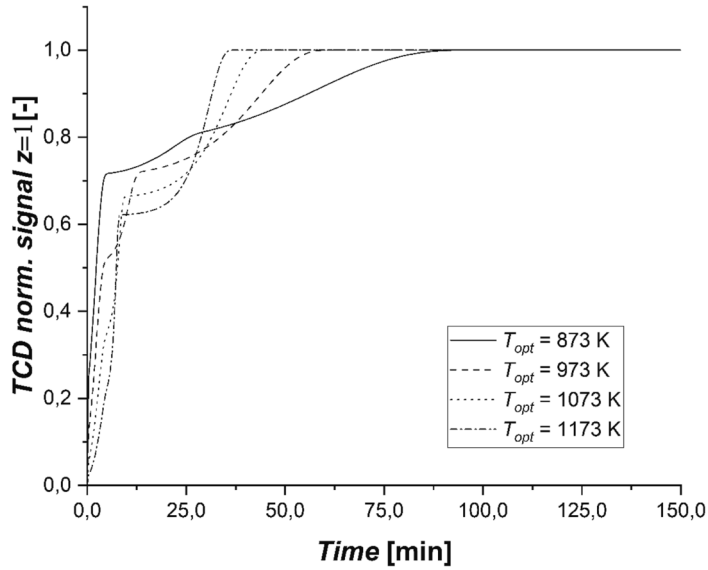


Fig. 6. Simulated TCD signals from off-gas composition over time, studying the effect of temperature.

respectively, on the simulated TCD signals of the gases leaving the reactor.

The variation of the first pre-exponential constant, $k_{1,ref}$, which is related to the reduction of hematite, mainly affects the initial phase of the reaction. Studying the variation of the parameter in an interval be-

tween $2.5 \cdot 10^{-5} \text{ m s}^{-1}$ and $1.0 \cdot 10^{-4} \text{ m s}^{-1}$, it is possible to observe the increase of the kinetic parameter promotes the first reaction, as seen in Fig. 7a, but the effect on the overall reduction is minor, since the hematite-magnetite steps is the fastest one. When the parameter assumes the maximum value, the reaction is completed in less than 5 min,

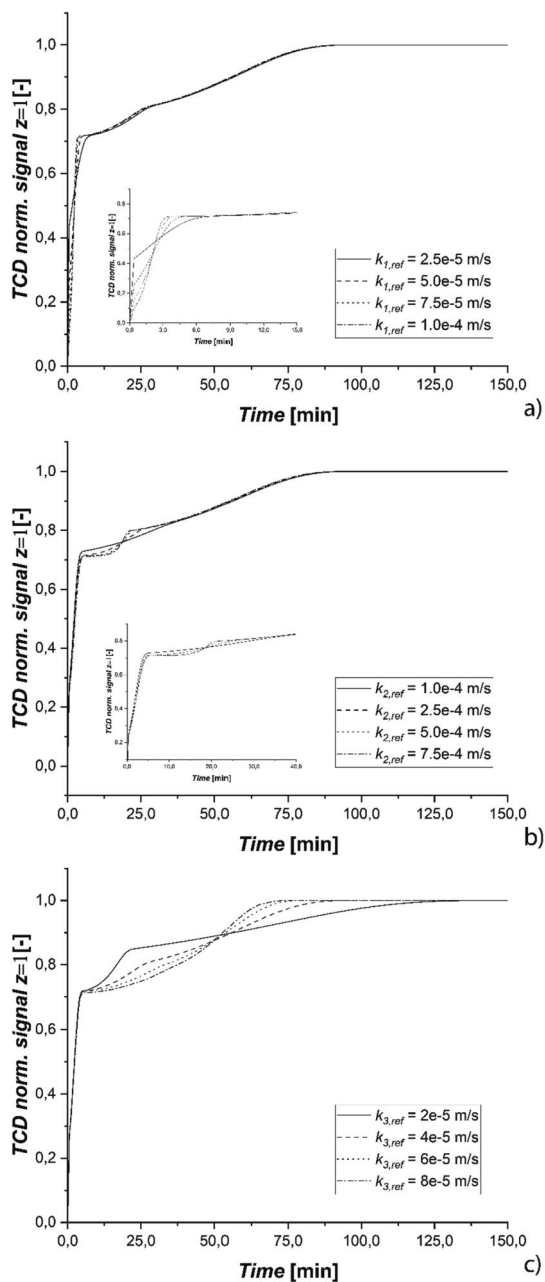


Fig. 7. Simulated TCD signals from off-gas composition over time, studying the effect of the reference kinetic constants: (a) $k_{1,ref}$, (b) $k_{2,ref}$ and (c) $k_{3,ref}$.

which is half of the time needed to complete the first reduction step if the parameter assumes its minimum value.

The second pre-exponential kinetic constant, $k_{2,ref}$, affects mainly the TCD in the middle area of the figure and very little the part of the signal where the hematite reduction is completed. By increasing this parameter from $1.0 \cdot 10^{-4} \text{ m s}^{-1}$ to $7.5 \cdot 10^{-4} \text{ m s}^{-1}$, the time of the magnetite-to-wüstite reaction step (Fe_3O_4) is reduced, although at high values the chemical reaction becomes thermodynamically limited due to the presence of H_2O produced in the first two reactions (yielding a plateau in the TCD signal). In contrast to the subsequent reactions, the reduction of hematite is never thermodynamically limited (cf. Fig. 1); this leads the system experiencing an initial phase where a water pulse propagates through the bed. If the value of $k_{2,ref}$ is decreased, the slopes become much less pronounced, and it is no longer possible to discern the end point of the second reaction in the TCD signal. At the smallest value of $k_{2,ref}$ studied, the magnetite reduction is so slow that its contribution to the TCD overlaps with that of the wüstite reduction.

As expected, the third pre-exponential kinetic constant, $k_{3,ref}$, related to wüstite reduction has the strongest influence on the model results, for both Fe_3O_4 and FeO reduction, being crucial in determining the overall reaction time. By manipulating the parameter in the range between $2 \cdot 10^{-5} \text{ m s}^{-1}$ and $8 \cdot 10^{-5} \text{ m s}^{-1}$, it is noted that the as the value of the parameter decreases, the lower H_2 consumption in the bottom regions of the bed, where more wüstite is initially present, favors a rapid reduction of unreacted magnetite in the lower bed. This is seen as an increasingly pronounced peak in the signal due to the complete reduction of Fe_3O_4 . Conversely, a high value of $k_{3,ref}$ makes the slope variation disappear, favoring greater water production and consequently leading to kinetic (i.e., low driving forces) and thermodynamic limitations. The overall reaction time changes significantly, varying from about 70 min for the maximum $k_{3,ref}$ value to 150 min for the minimum value.

3.5. Axial dispersion

The axial dispersion parameter D_z (cf. Eq. (20)) influences the gas-side mass balance through the resistance to interparticle transport thus affecting all reaction steps. Fig. 8 that depicts the results of perturbing the value of D_z between $1 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $5 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ shows that even a modest change in the parameter leads to large changes in the system. As the coefficient increases, the resistance to transport of the gaseous species through the reactor decreases, allowing them to cross the bed more efficiently, leading to enhanced reactions. For the same reason, the thermodynamic limitations due to the presence of water are

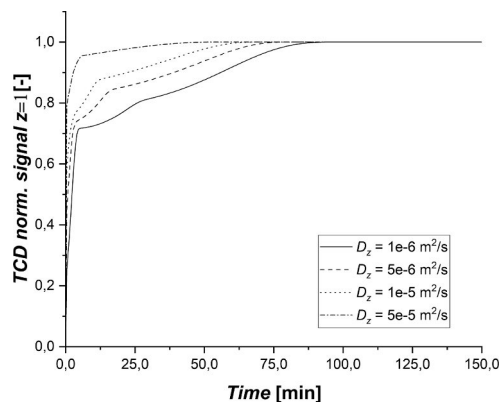


Fig. 8. Simulated TCD signals from off-gas composition over time, studying the effect of axial dispersion.

also lesser as it is more easily removed from the bed. The overall reaction time is about 50 min for the maximum value of the parameter, while it is about 90 min for the minimum value of D_z .

3.6. Particle radius

The particle radius influences the model decisively through the resistance to intraparticle transport (B_p) and the reaction rate, given the assumptions of the SCM. It also affects the surface area. Fig. 9 shows the results of varying the value of r_0 from $1 \mu\text{m}$ to $5 \mu\text{m}$, indicating that the appearance of the TCD curve changes substantially with the particle radius. As the particle radius decreases, the internal diffusion resistance become less relevant and an important increase in the reaction rate is observed for all reduction steps due to a larger surface area-to-volume ratio. Such events, with different weight significantly shortens the overall reaction time. The particle size mainly affects the reduction rates of magnetite and wüstite, as the reduction of hematite is very fast. It can be observed that as the granulometry of the solid decreases, thermodynamic limitations become more evident (plateaus in the TCD signal), which are due to the high reaction rate and the accumulation of H_2O in the lower zones of the bed.

3.7. Bed mass

The initial mass, m_0 , of the oxide to be reduced influences not only the amount of oxygen (n_0) to be removed but also the height of the fixed bed in the gas-side mass balances. Fig. 10, which depicts how m affects the simulated TCD signals, indicates that a 50 % increase in the bed mass prolongs the overall reduction time by about 30 %. The effect of the fixed bed height through the increase of the resistance of the convection and interparticle diffusion phenomena is less relevant due to the small bed heights studied.

3.8. Gas composition

The composition of the feed gas naturally represents one of the most important factors for the reactions. By increasing the molar ratio of hydrogen, y_{H_2} , in the feed gas, the reduction of the oxides can be enhanced, as seen in Fig. 11, where feed mole fractions from 10 % to 40 % (with Ar as the complement) were applied. All steps of the reaction proceed faster, reducing the overall reaction time, and thermodynamic limitations are no longer obvious, particularly not for the higher H_2 :Ar molar ratio where the driving force of the system is sufficient at all parts of the bed.

3.9. Volumetric gas flow rate

Finally, the effect of total volumetric gas flow rate, Q , of the feed, which mainly influences the convection phenomena (w) defined in the gas-side mass balance of the mathematical mode (Eq. (20)) was varied from 10 mL/min to 40 mL/min. As seen in Fig. 12, a high Q value yields a faster reduction because the reactant is supplied more quickly into the reactor, preventing hydrogen starvation.

3.10. Local sensitivity analysis

A local sensitivity analysis of a model is a useful method for evaluating and summarizing its response to perturbations of parameter values from those of a base case simulation. More importantly, it is valuable for comparing the effects emanating from different parameters, which yields important information for a subsequent parameter estimation: parameters with minor influence can be excluded from the estimation phase, reducing the complexity of the numerical problem. Fig. 13 shows the sensitivity index of key parameters of the model estimated by Eq. (22) (cf. Section 2.4) at two different operating temperatures, 873 K and 1173 K.

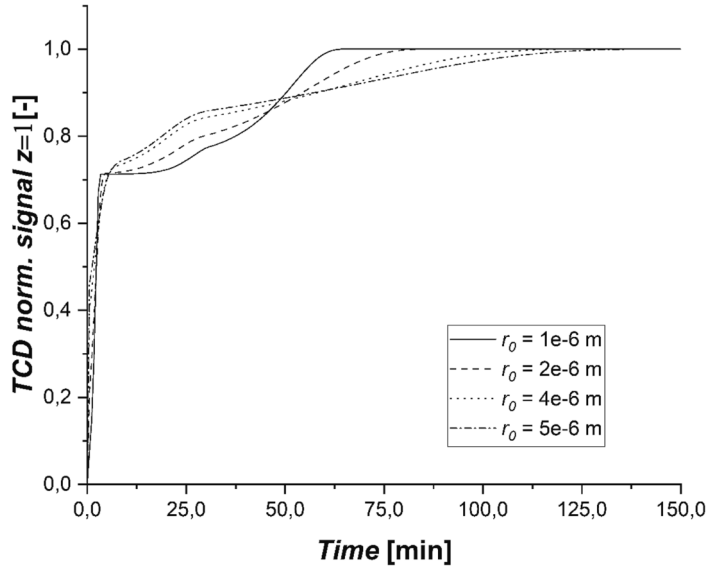


Fig. 9. Simulated TCD signals from off-gas composition over time, studying the effect of particle radius.

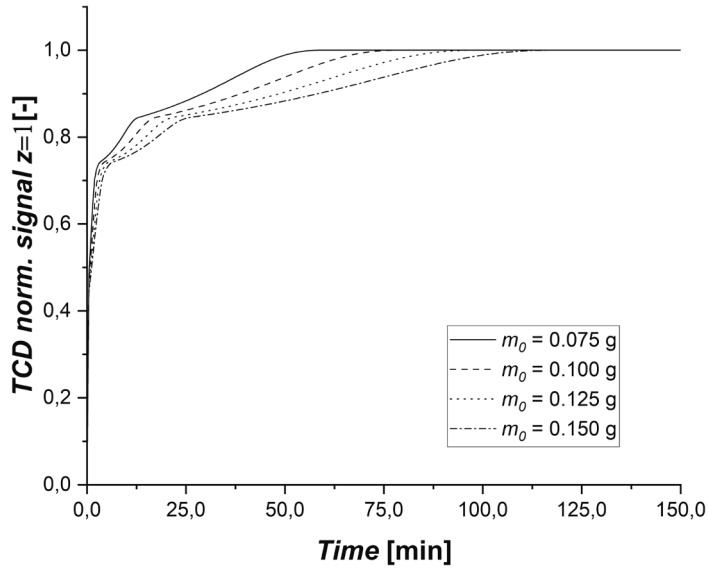


Fig. 10. Simulated TCD signals from off-gas composition over time, studying the effect of initial iron oxide mass.

Since many different phenomena described by the model depend on temperature, the local sensitivity analysis was performed by manipulating the model parameters at the different operating temperatures. Because of larger uncertainty, the pre-exponential constants were varied with respect to their base case values by $\pm 50\%$ while all other parameters were perturbed by $\pm 10\%$. The graphs of the figure show that some

coefficients, especially when increased, have a significant influence on the system behavior. In particular, $k_{3,ref}$, D_2 and y_{H_2} have always the greatest impact and, in the case of the kinetic parameter, reach a sensitivity index ($SSE_{m,\Delta}$) of almost 70 % at 873 K. This result confirms what was already observed in the earlier analysis (cf. Fig. 6c), and that $k_{3,ref}$ also affects the rate of the magnetite-to-wüstite reaction. Increasing

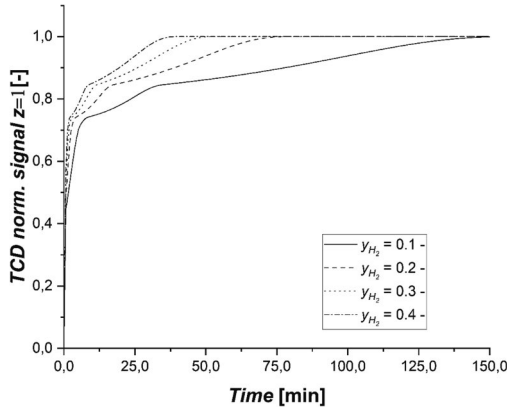


Fig. 11. Simulated TCD signals from off-gas composition over time, studying the effect of the molar ratio of hydrogen in the feed gas.

the values of D_z drastically accelerates the reduction in all steps, which stresses the need of an accurate expression for interparticle diffusion. A similar sensitivity is observed for y_{H_2} indicating the critical role played by the concentration of hydrogen in the gas. The remaining pre-exponential coefficients, together with the solid mass, form the set of parameters with medium influence on the model. The kinetic coefficients $k_{1,ref}$ and $k_{2,ref}$ have an effect mainly during the first 10–20 min of the reduction process which partially explains the lower impact of these parameters. Finally, r and Q have a smaller influence in the range of $\pm 10\%$. As for the role of temperature, the influence of changes in all the parameters tends to decrease with temperature due to the notable increase in reaction rates and the tendency to make diffusive phenomena more relevant.

3.11. Simulation and data comparison

In order to indicate the potential of the model to quantitatively explain the results of iron oxide reduction experiments undertaken (cf. Section 2.7), a preliminary attempt was made to mimic the conditions in a reduction experiment of a 0.1 g bed of fine hematite by a gas consisting of 20 % H_2 and 80 % Ar at a temperature of 873 K with a volumetric flow rate of the gas was $Q = 20\text{ mL/min}$. After adjustments of the pre-exponential constants and the axial dispersion coefficient of the model to $k_{1,ref} = 6 \cdot 10^{-5}$, $k_{2,ref} = 5 \cdot 10^{-5}$, $k_{3,ref} = 2.4 \cdot 10^{-5}$ and $D_z = 3.9 \cdot 10^{-6}$, as shown in Fig. 14, the simulated TCD signal shows a good agreement with the experimentally observed counterpart. It should be pointed out that the activation energies were not changed from their base-point values because their influence on the system in the specific case is small as the operating temperature is equal to the reference temperature (T_{ref}) of the Arrhenius equation.

As can be seen, the model describes the experimental data well, including the changes in the slope of the signal reflecting the transition from one reduction step to the next. These encouraging results indicate the flexibility of the model and hold promise for a successful parameter estimation in forthcoming work using data from a large set of experiments. To this end, the ideal approach for the future is to conduct a large number of experiments in order to reduce experimental uncertainty and limit the number of parameters to be estimated to the most influential ones based on sensitivity analysis. Finally, because of the important role of the particle size, it will be necessary to further develop the mathematical model by considering the particle size distribution of the iron oxides fines.

4. Conclusions and future perspective

This work has presented a mathematical model of a system for reduction experiments of a small bed of iron oxide fines through which a hydrogen-containing gas passes at high temperature. A three-interface shrinking core model is used to describe the phenomena at and in the small particles, which is combined with a dynamic model of the particle

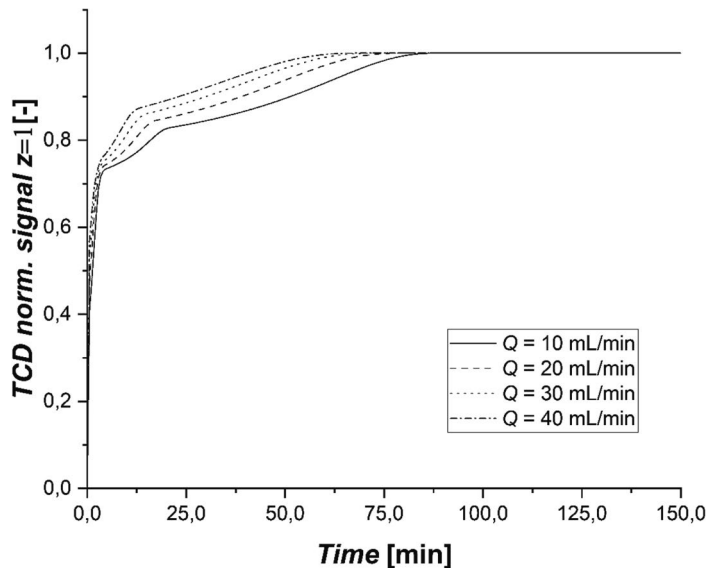


Fig. 12. Simulated TCD signals from off-gas composition over time, studying the effect of the gas flow rate.

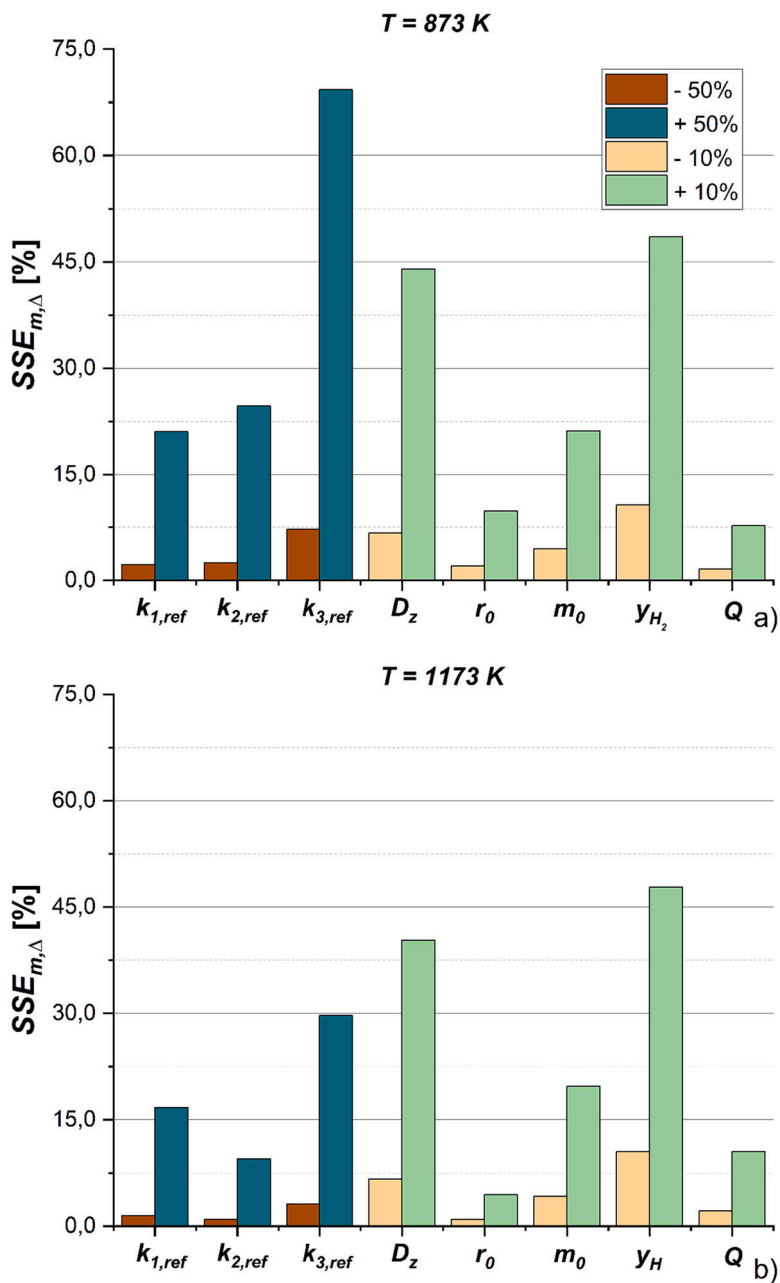


Fig. 13. Results of local sensitivity analysis: sensitivity index (cf. Eq. (22)) of key model parameters at (a) 873 K and (b) 1173 K.

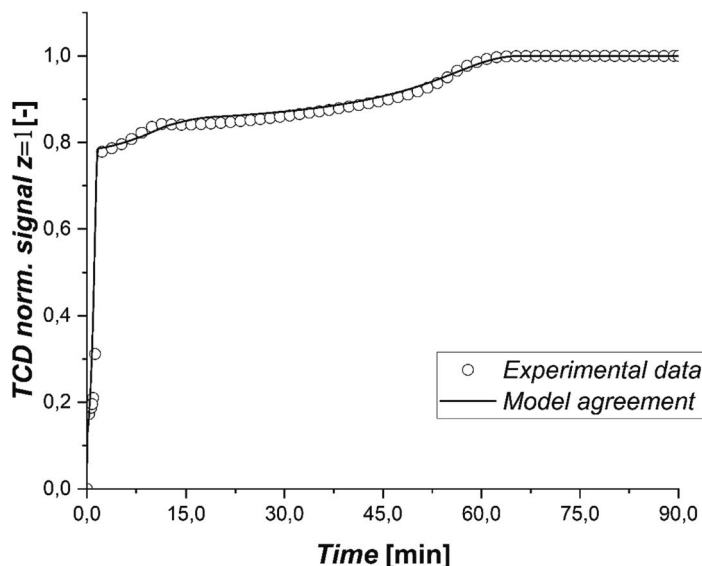


Fig. 14. Comparison between experimental data and simulation after adjustment of some model parameter values.

bed. Particular attention was paid to making the model robust so it can be executed for a wide range of model parameter values. With parameters of the kinetic and mass transfer expressions taken from the literature, the progress of the reduction reactions from hematite through magnetite and wüstite to metallic iron was simulated. A systematic analysis was undertaken to reveal the effect of different parameters and (boundary) conditions on the rate of the reduction steps. A comprehensive sensitivity study of the mathematical model was performed by analyzing its response to parametric perturbation, identifying parameters of particular importance. Finally, a preliminary attempt was made to reproduce experimental results by tuning a limited set of model parameters, and the model was demonstrated to have the flexibility to adapt to the results of the experiments quantified by the thermal conductivity of the gas leaving the bed. Based on a large set of data from systematic reduction experiments undertaken at different operating conditions, the kinetic parameters of each reaction step will be determined by the model in future work, comparing the findings with values reported in the literature. The experimental study has already been extended to analyzing the reduction kinetics of ground commercial ironmaking materials (BF and DR pellets) in the same fixed bed system. The findings will be used to evaluate the influence of the differences in the behaviour of morphology and the chemical composition on the overall behavior. Moreover, the data will be used to update the kinetic expressions in simulation models of furnaces of industrial size developed by the group and its research partners (e.g., Shao et al., 2023, Mauret et al., 2023). This effort will mark the crucial initial stages of our research establishing a solid foundation for exploring the reduction of increasingly complex systems, which will include the study of the reduction of fines of commercial materials and eventually the scale-up of the model to consider solid particles of realistic size (e.g., pellets).

CRedit authorship contribution statement

Emiliano Salucci: Writing – original draft, Validation, Software, Methodology, Formal analysis. **Antonio D'Angelo:** Investigation, Data curation. **Vincenzo Russo:** Writing – review & editing, Supervision.

Henrik Grénman: Writing – review & editing, Supervision, Project administration, Conceptualization. **Henrik Saxén:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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III

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Kinetic modeling and parameter estimation of thin-layer iron oxide reduction with hydrogen in a fixed-bed reactor

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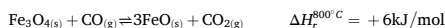
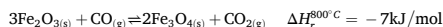
ABSTRACT

In recent years, the reduction of iron ores by hydrogen has gained increased attention, as it could significantly reduce greenhouse gas emissions from the metallurgical sector in the near future. In order to enable a rapid technological development in this direction, it is essential to start from the fundamentals of the reduction process, i.e., to investigate the intrinsic kinetics of iron oxide reduction. In this work, an in-depth kinetic investigation of the reduction of pure powdered iron oxides in a packed bed reactor-like system was carried out. The conversion of the solid reactant was followed by measuring the outlet gas composition with the help of rapidly responsive thermal conductivity, and the kinetics of the reduction were mathematically modeled. Based on the assumptions behind the shrinking core model, a mathematical model was developed for a thin fixed-bed reactor that successfully described the experimental data by accurately determining key kinetic parameters. The results show that the different reaction steps are chemically controlled, except for the first step, which is governed by a mixture of internal diffusion and chemical control.

1. Introduction

Although iron and steel have been produced for many centuries, several technical innovations in the second half of the 18th century laid the foundations for future mass production. In particular, the introduction of coke in the blast furnace (BF) proved to be decisive, as it served as a cost-effective source of heat and reducing agents [1]. Through continuous technical development, the steel industry was able to significantly increase its efficiency and has reached an annual production of almost 2000 million tons of steel, of which today 73.7% is produced in the blast furnace–basic oxygen furnace (BF–BOF) process [2]. This sector is currently the largest industrial consumer of coal, accounting for approximately 15% of global consumption [3]. Unsurprisingly, the reliance on carbon-based technologies leads to significant carbon dioxide (CO₂) emissions, estimated at around 2.6 Gt/year [4]. This makes the steel industry one of the largest contributors to greenhouse gas emissions and is responsible for around 8% of direct global industrial CO₂ emissions [2]. Across the entire complex production chain, 70% of the CO₂ emissions come from the blast furnace process, mainly due to the need for high operating temperatures and the reduction of iron ores (iron oxides) [5]. The heart of the process, part of

what is known as primary steelmaking, begins with an initial pre-treatment and agglomeration of the powder raw materials (coking and sintering/pelletizing), followed by the alternating charging of coke and the preprocessed ore into the blast furnace. At the same time, hot air enriched with oxygen (hot blast) and pulverized coal are injected through nozzles (“tuyeres”) in the lower part of the furnace [6]. The interaction between the oxygen in the blast and the coke and injected hydrocarbons leads to a partial combustion of the carbon, which not only provides energy for the operation of the furnace but also enables the formation of carbon monoxide (CO). This, in turn, enables the conversion of oxides into metallic iron through a series of chemical reactions, generally starting from hematite (Fe₂O₃), and all leading to the formation of carbon dioxide [7]:



As shown, the reversible reaction network includes two intermediate species: magnetite (Fe₃O₄) and wüstite (FeO), and the energy

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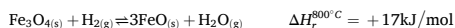
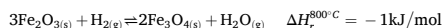
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contribution of these reactions is clearly exothermic [8]. In addition to the reactions listed above, also the reverse Boudouard reaction [9]



occurs at higher temperatures, developing CO_2 and C in the presence of CO. In the upper furnace, the reverse Boudouard reaction may occur, leading to deposition of carbon (e.g., on iron [9]). The high temperatures in the blast furnace, which can exceed 2000°C in the lower zones, favor two critical conditions for the process: improved kinetics of oxygen removal from the iron oxides and melting of the metal. In the lowest part of the furnace, i.e., the hearth, molten slag containing inorganic compounds such as silicates and aluminosilicates are separated from the molten metal due to their different densities. The role of coke is essential for three additional reasons: it maintains the gas permeability of the BF by providing coke slits in the cohesive zone (where the iron ores start to soften and finally melt) through which the gas can flow, and permeability for the gas and liquids in the lower zone [10]. The coke also supports the bed as the tiny solid species in the lower furnace, and finally ensures a sufficient carbon content in the hot metal (around 4%) in the melt, which is a prerequisite in the downstream BOF process where the carbon dissolved in the hot metal is oxidized, heating the melt as it is decarburized to obtain an alloy with desired mechanical properties [11].

This overview makes it clear that carbon is an inherent component in current ironmaking technologies, which need to be fundamentally revised as the CO_2 emissions should be substantially decreased. In particular, a chemical alternative to CO and lower operating temperatures are required. Alternative processes such as the Midrex were already proposed in the 1960s [12], utilizing natural gas as the source of energy and reductants. They are referred to as direct reduction (DR) and are based on solid-gas reactions between iron ores and a reducing agent, which is a mixture of CO and hydrogen (H_2), generally obtained by methane reforming. The reaction network is thus extended to include the following reduction reactions, which are stoichiometrically similar to those already listed:



As the chemical nature of the reactions suggests, H_2 reduction, unlike CO reduction, is generally endothermic [8]. This requires careful evaluation of the energy balance of the DR furnace to maintain optimal operating temperatures. However, these processes do not require the extreme temperatures of the BF–BOF route as no molten iron is produced at this stage. The reduced iron ore or pellets, usually referred to as direct reduced iron (DRI), are later melted in an electric arc furnace [13]. From a thermodynamic perspective, the reactions of iron oxides with CO or H_2 have been extensively studied and can be summarized in the Baur–Glässner/Chaudron diagram in Fig. 1 [8].

The diagram presents the stability regions of solid iron oxides and iron as a function of the Gas Oxidation Degree (GOD) and temperature. The GOD is the ratio between the concentration of the oxidizing species (CO_2 or H_2O) and the total concentration of the oxidizing and reducing species. In the absence of inert gasses, the GOD corresponds to the molar fraction of the oxidizing agent. The diagram indicates the existence of an eutectoid point above 570°C at which FeO is formed. In the diagram, $\text{GOD} = 1$ corresponds to no reduction potential of the gas. For Fe_2O_3 , for example, a gas with $\text{GOD} < 1$ can reduce it at any temperature, i.e., even in the presence of infinitesimal amounts of reducing agent. In the other stability ranges, there are significant differences between CO and H_2 . Due to the different monotonic trends of the FeO–Fe equilibrium curves, H_2 reduction above 800°C becomes advantageous as the stability field of iron expands, while it contracts for CO-based reduction.

To reduce the carbon footprint of the steel industry, the most

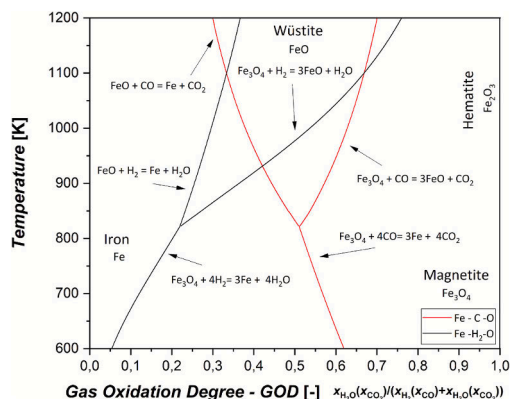


Fig. 1. Baur–Glässner/Chaudron thermodynamic diagram [8].

promising alternative today is to use green hydrogen instead of CO in the reduction steps [14]. A key factor to be explored is therefore the redox kinetics and morphological evolution of the solid material in the presence of H_2 . The scientific literature is very extensive in terms of practical and methodological aspects [15]. The most commonly used setup for reduction experiments is a thermogravimetric system [16,17], which evaluates the conversion of iron oxides to metallic iron based on the weight loss of the solid sample. An alternative is the indirect evaluation of solid metallization of the sample via the analysis of the gas composition at the outlet, using balance equations to follow the oxygen transferred from the solid to the gas phase [18,19]. Among the operating parameters, temperature plays a pivotal role due to its wide-ranging influence on kinetics [20,21], thermodynamics [22,23] (Fig. 1), fluid dynamics [24,25] and morphological changes [26,27]. Another key factor is the nature of the solid and its intrinsic properties, such as porosity [28,29] and shape [30,31]. The literature covers reduction experiments of both pure [32,33] and commercial materials [34,35] and shows considerable differences in the transient morphological evolution [36,37] especially in the case of pellet reduction where tortuosity and porosity changes can influence crucially the gas diffusion [38,39]. Furthermore, the effect of gangue remains unclear in many respects, even though various studies have attempted to identify its influence through rigorous experimental or numerical approaches [40,41]. Granulometric distribution is also of critical importance, with particle sizes ranging from nano powders [42] through grains or fines [43] to commercial pellets up to tens of millimeters in diameter [44]. For the gas used in the experiments, it is essential to properly consider the solid behavior in order to avoid limiting phenomena such as gas starvation and external diffusion. Therefore, many studies focus on variations in composition [45,46] and linear gas velocity (i.e., volumetric flow rate) [47,48]. From a modeling perspective, Avrami models are often used in studies of heterogeneous reactive processes to simplify nucleation and growth dynamics [49,50]. More comprehensive models include the Shrinking Core Model (SCM) [51,52], the grain model (GM) [53,54] or the random pore model (RPM) [55,56]. At pilot plant or furnace scale, Computational Fluid Dynamics (CFD) models enable detailed fluid dynamic analysis and the exploration of theoretical alternatives to conventional processes that could drive future industrial development [57,58].

From this broad spectrum of experimental and modeling approaches, kinetic parameters of surprising discrepancy have been reported. For example, various authors have reported activation energies between 18 and 246 kJ mol^{-1} [59], with standard deviations often reaching 80% of the average value [60]. This leads to very different conclusions about the

rate-limiting steps of the reduction process, which may be kinetic [61], diffusive [62] or shifting regimes [63]. Such inconsistencies highlight a critical gap in current kinetic modeling: the lack of systematic approaches to isolate intrinsic chemical kinetics from transport and morphological effects. To address this, the present study introduces a combined experimental and modeling framework designed to minimize these interferences and provide reliable kinetic parameters for hydrogen-based iron oxide reduction. By accurately evaluating the thermal conductivity of the outlet gases of the reactor applied in the reduction experiments, an innovative method was developed to analyze experimental data and indirectly determine the overall degree of reduction. This work proposes a stepwise approach to extract kinetic parameters under conditions as close as possible to intrinsic by coupling experiments on micron-scale powders in thin fixed beds with a mathematical model capable of capturing the complexity of the reacting system. The experimental and modeled results were validated by analyzing solid samples from the experiments using various analytical techniques. The aim is to minimize interference from external mass and heat transfer and particle coalescence. The model serves as a tool for parameter identification at small scale, which is a prerequisite for model-based analysis and design of direct reduction processes using hydrogen. Developing an overall model based on accurate intrinsic kinetic parameters and subsequently incorporating transport phenomena leads to significantly better predictive and extrapolative capability compared to models relying on lumped parameters. This aspect is particularly critical for scale-up, as errors present at small scale tend to be amplified when transitioning to larger systems. For these reasons parameters obtained for powders are intended for future integration into pellet-level models (SCM or Grain Model with evolving porosity and tortuosity) and reactor-scale simulations of countercurrent furnaces.

2. Materials and methods

2.1. Materials

The solid samples used for the reduction experiments in this work were purchased from Sigma-Aldrich. Specifically, hematite (CAS: 1309-37-1) has a purity $\geq 96\%$, a density of 5.25 g/cm^3 , and particle sizes smaller than $5 \mu\text{m}$, while magnetite (CAS: 1317-61-9) has a purity $\geq 95\%$, a density ranging between 4.8 and 5.1 g/cm^3 , and particle sizes below $5 \mu\text{m}$.

The use of powders makes it possible to minimize phenomena that influence the reduction kinetics. Based on the evaluation of specific criteria, the mass and heat transfer limitations can therefore be considered negligible. The powders were characterized from multiple perspectives to assess particle size distribution, porosity, specific surface area and initial and transient chemical composition. These analyzes confirmed the theoretical and modeling assumptions used to evaluate the reduction kinetics. As for the gas phase, hydrogen ($>99.999\%$), which was used as the sole reducing agent, and argon (Ar) ($>99.9\%$), which served as an inert carrier gas, were supplied by Wolkoski Oy.

2.2. Chemical and physical characterization

X-ray diffraction (XRD) was used to thoroughly analyze the evolution of the chemical species involved in the reduction of the pure iron oxides. Specifically, diffraction patterns in the 2θ range of $20\text{--}80^\circ$ were collected using a Panalytical Empyrean XRD instrument equipped with a PIXcel 3D detector and $\text{CuK}\alpha$ radiation ($1.5418 \text{ \AA}$) as the source. Particle size distribution analysis (i.e., Light scattering, LS) was performed using a Malvern Panalytical MASTERSIZER 3000. Nitrogen physisorption measurements were performed using a Micromeritics 3Flex-3500 system to evaluate the porosity of the material as well as its specific surface area (i.e., BET method). Further analyses, such as thermogravimetry/differential scanning calorimetry coupled with mass spectrometry (i.e., TGA/DSC-MS), are described in more detail in D'Angelo et al. [37].

2.3. Experimental setup

The reduction experiments on both solid materials were performed under different operating conditions using an Autochem 2910 device. Although this apparatus is generally used for chemisorption studies on catalysts, it has also proven to be effective for studies on heterogeneous gas-solid reactions. The experimental setup is equipped with a thermal conductivity detector (TCD) for the analysis of off-gases, which allows very frequent and precise measurements (i.e., thermal conductivity values every 0.02 s) of the gas composition. The TCD works based on a classic Wheatstone bridge configuration. The system generates a signal by detecting the temperature change - and therefore the electrical resistance - of heated filaments in contact with the gas. The TCD signal is determined by comparing the thermal conductivity between a reference gas (Ar) and the gas mixture exiting the reactor, which contains Ar, H_2 and H_2O . This approach is particularly effective for hydrogen reduction studies, as the thermal conductivity of H_2 and the other gases differ significantly. As a result, the TCD signal can be interpreted as an indicator of the amount of unreacted hydrogen at the reactor outlet. The setup of the experimental system is shown in Fig. 2.

A fixed bed reactor configuration was adopted. High purity gases stored in cylinders (1) are fed at a controlled flowrate via flowmeters (2) and mixed before entering the reactor. The glass reactor (3) has a tubular geometry with a length (L) of 193 mm and a radius (R) of 11 mm . It is housed in a small furnace (4) which allows precise temperature control, which is monitored by a Type-K thermocouple (5) located in the center of the reactor near the fixed bed. The fine solid sample is loaded into the reactor and placed on a quartz disk resting on a layer of quartz wool (6). These porous layers serve to protect the detectors (7) from possible entrainment of solid particles by the gas flow and to ensure a horizontally flatbed geometry, minimizing non-uniform gas-solid interactions along the bed. The TCD signal and temperature data are finally recorded and extracted (8). The use of the TCD in this study is motivated by its practical suitability for monitoring H_2 -based iron oxide reduction. While mass spectrometer (MS) and gas chromatography (GC) techniques provide species-specific detection, TCD offers a rapid, continuous and quantitative signal directly correlated with the reaction progress without species-dependent calibration. Its robustness under standard operating conditions and its limited sensitivity to background fluctuations make it particularly reliable. TCD is widely accessible in conventional gas-analysis setups and provides adequate sensitivity for detecting variations in H_2 concentration within $\text{H}_2/\text{H}_2\text{O}$ systems. Moreover, its intrinsic tolerance to water vapor allows direct analysis of the gas stream produced during reduction, avoiding the need for extensive pretreatment typically required when MS or GC systems are exposed to significant amounts of moisture. These advantages make TCD a practical, reliable, and efficient tool for real-time kinetic monitoring in hydrogen-driven reduction studies.

To validate the use of the TCD for evaluating the reduction of iron oxide with H_2 , an Agilent 990 Micro GC was used to evaluate the composition of the off gases. Fig. S1 (Supplementary Material) compares the TCD raw signal and Micro GC H_2 molar fraction profiles for the same experiment, illustrating consistent trends and validating the TCD-based approach.

Repeatability was verified through repeating the same experiment under identical conditions (Table 1, 2H); the comparative plot (Fig. S2) and all raw data (Figs. S3 and S4) are provided in the Supplementary Material. The repetition resulted in error bars below 1% , confirming the robustness of the measurements.

In all experiments, the solids were heated at a constant temperature ramp of 10°C/min to ensure uniform thermal evolution across all samples. To accurately determine the kinetics of iron oxide reduction by H_2 , a series of isothermal experiments were performed under different operating conditions. In particular, the effect of temperature (T), total volumetric gas flow rate (Q) and hydrogen molar fraction (y_{H_2}) was

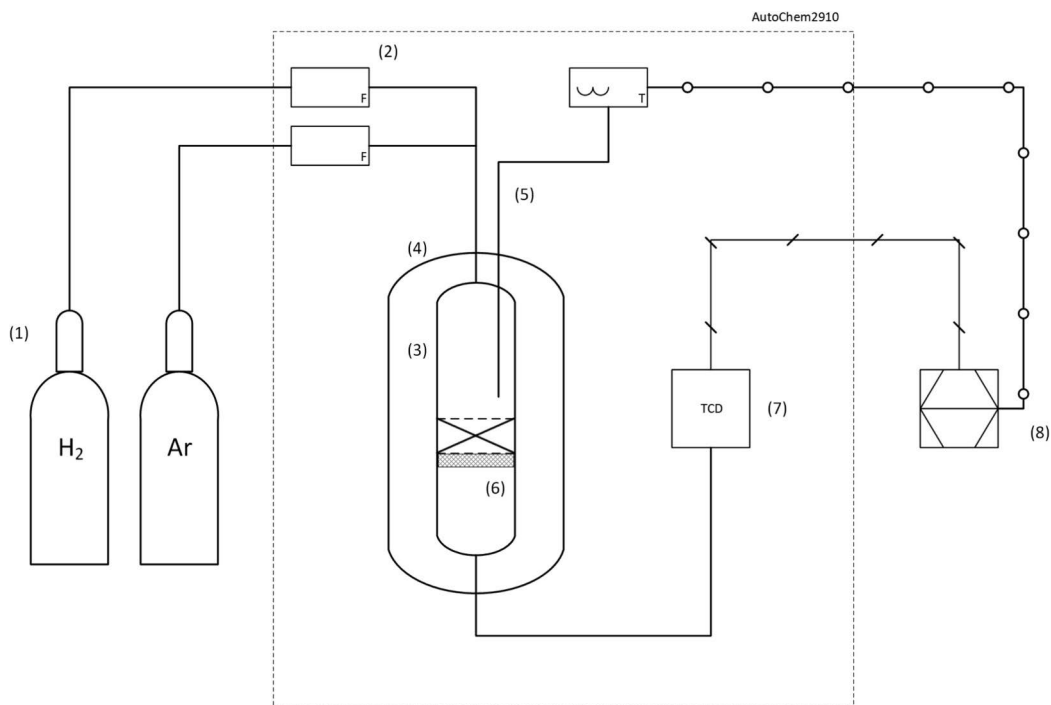


Fig. 2. Schematic of the thin solid reactor experimental setup: gases cylinders (1), flowmeters (2), reactor (3), furnace (4), thermocouple (5) inert support (6), detectors (7) and computer (8).

Table 1

Experimental conditions used for hematite and magnetite reduction.

Species	Test	T [°C]	Q_{H_2} [mL/min]	Q_{Ar} [mL/min]	Q [mL/min]	y_{H_2} [–]	mass [g]
Fe ₂ O ₃	1H	600	3	17	20	0.15	0.0158
Fe ₂ O ₃	2H	600	4	16	20	0.20	0.0133
Fe ₂ O ₃	3H	600	5	15	20	0.25	0.0144
Fe ₂ O ₃	4H	700	4	16	20	0.20	0.0133
Fe ₂ O ₃	5H	800	4	16	20	0.20	0.0158
Fe ₂ O ₃	6H	1000	4	16	20	0.20	0.0129
Fe ₂ O ₃	7H	600	3	15	18	0.20	0.0129
Fe ₂ O ₃	8H	600	5	19	24	0.20	0.0145
Fe ₂ O ₃	9H	600	6	22	28	0.20	0.0138
Fe ₃ O ₄	1M	600	3	17	20	0.15	0.0136
Fe ₃ O ₄	2M	600	4	16	20	0.20	0.0153
Fe ₃ O ₄	3M	600	5	15	20	0.25	0.0131
Fe ₃ O ₄	4M	700	4	16	20	0.20	0.0139
Fe ₃ O ₄	5M	800	4	16	20	0.20	0.0102
Fe ₃ O ₄	6M	600	3	15	18	0.20	0.0129
Fe ₃ O ₄	7M	600	5	19	24	0.20	0.0116
Fe ₃ O ₄	8M	600	6	22	28	0.20	0.0133

investigated.

2.4. Mathematical and physical interpretation of TCD signals

Analyzing the thermal conductivity signal can be particularly challenging, especially when attempting to simulate the signal itself. This is because the signal not only reflects the conductivity difference between the reference gas and the exhaust gases but is also affected by the physical and structural properties of the Wheatstone bridge [64].

Despite this complexity, the high sensitivity of the acquired data allows for a unique interpretation of the reduction process. As an example, Fig. 3 shows the original thermal conductivity signal obtained during a hematite reduction experiment at 600 °C with a total gas flow rate of 20 mL/min and a hydrogen molar fraction in the feed of $y_{H_2} = 0.2$.

As can be seen, the signal increases within a few seconds of starting the test, which is due to the higher thermal conductivity of the reducing gas compared to the reference gas (Ar). It can be expected that the changes in signal slope are correlated with the different phases of the

Table 2
Fixed model parameters. * [44], ** [68], *** [67].

Parameter	Value	Unit	Parameter	Value	Unit
$d_{1,1}^*$	$1 \cdot 10^{-4}$	$m^2 s^{-1}$	$m_{2,2}^*$	0.50	—
$d_{2,1}^*$	3.43	—	$m_{3,2}^*$	$1.26 \cdot 10^3$	—
$d_{3,1}^*$	$4.2 \cdot 10^3$	K	$m_{4,2}^*$	$-1.96 \cdot 10^5$	—
$d_{1,2}^*$	$1 \cdot 10^{-4}$	$m^2 s^{-1}$	$m_{1,3}^*$	$8.39 \cdot 10^{-7}$	Pa s
$d_{2,2}^*$	5.64	—	$m_{2,3}^*$	0.62	—
$d_{2,3}^*$	$6.8 \cdot 10^3$	K	$m_{3,3}^*$	75.38	—
$d_{1,3}^*$	$1 \cdot 10^{-4}$	$m^2 s^{-1}$	$m_{4,3}^*$	-432.5	—
$d_{2,3}^*$	4.77	—	v_1^{***}	7.07	—
$d_{3,3}^*$	$5.9 \cdot 10^3$	K	v_2^{***}	12.7	—
$m_{1,1}^*$	$1.56 \cdot 10^{-7}$	Pa s	v_3^{***}	18	—
$m_{2,1}^*$	0.71	—	ϵ	0.1	—
$m_{3,1}^*$	-5.87	—	Pe	12	—
$m_{4,1}^*$	210	—	L	0.18	m
$m_{1,2}^*$	$2.70 \cdot 10^{-6}$	Pa s	R	$5.50 \cdot 10^{-3}$	m

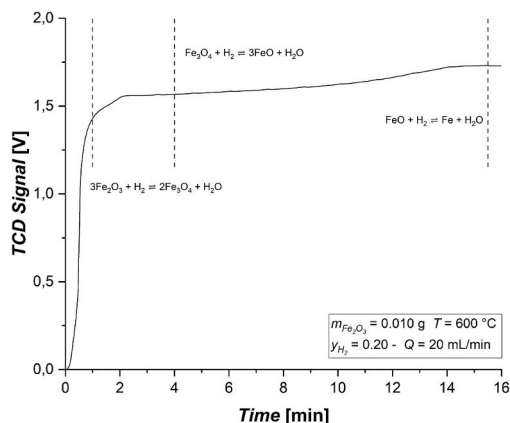


Fig. 3. Example of TCD signal; experimental conditions: $m_{Fe_2O_3} = 0.010$ g, $T = 600$ °C, $y_{H_2} = 0.20$, $Q = 20$ mL/min.

reaction and are therefore likely caused by the nature of the reactive network. These slope changes may thus indicate shifts in the kinetic or thermodynamic regime caused by the depletion of solid chemical species that previously dominated the reaction. The first major slope change, which occurs after a few minutes, can be interpreted as the almost complete reduction of Fe_2O_3 , which is known in the literature as the fastest step and is not limited by thermodynamics (Fig. 1). According to this interpretation, the subsequent changes in the slope correspond to the approach of the next reduction step or a shift in the dominant chemical species consuming H_2 , depending on its kinetics as well as diffusion and thermodynamic constraints. To verify these assumptions, stop tests were conducted under the same operating conditions, where the reaction was stopped after 5 min, 10 min, 50 min and beyond. The XRD analysis of the samples collected confirmed these assumptions and showed a direct correlation between the acquired signal and the conversion of the solids in the reactor. However, as mentioned above, the simulation of the signal itself (and not the intrinsic thermal conductivity of the exhaust gas) is complex. Since the signal is mainly influenced by hydrogen, an alternative approach was proposed, correlating the gas-derived signal with an indirect estimate of the overall sample reduction degree. To this end, several mathematical transformations were applied to the measurement. Fig. 4 illustrates the numerical processing step by step (from A to D) leading to the result.

The procedure starts with an initial normalization of the data (A); under certain conditions, the normalized signal alone can represent the thermal conductivity of the analyzed gasses [64]. This enables the second step, taking the complement (of one) of the signal (B), which is useful for integral calculation. Step C is crucial as it involves a cumulative integral of the complement signal point by point using the trapezoidal method, yielding a signal in (D) that reflects the reduction curves reported by several authors in thermogravimetric studies [65]. However, particularly in the early stages of the reaction, the hydrogen reaching the detector corresponds to the H_2 supplied due to dilution effects (i.e., axial dispersion). This leads to an overestimation of the degree of conversion, since the integral contains both the hydrogen that has reacted in the sample and the fraction that has not reached the detector due to physical effects.

As will be shown later in the Results section, the fluid dynamics of the reactor were evaluated using a residence time distribution (RTD) analysis, which revealed that the system did not behave like an ideal plug flow reactor. In order to accurately evaluate the data, the integral had to be corrected by the blank signal (i.e., from an experiment in the absence of the solid sample) under the same operating conditions. Fig. 5a shows an example of the overlap between the blank TCD signal and the result of a reduction test. The difference, highlighted in blue, is considered for producing a corrected normalized TCD signal to be treated by the procedure outlined above, yielding a significantly different estimate of the reduction degree (Fig. 5b).

The area to be considered, which represents the actual H_2 consumption by the chemical reaction, lies between the two curves (Fig. 5a). By subtracting the cumulative integrals, the corrected final result is obtained, which is no longer overestimated. Signal processing was carried out using deterministic mathematical operations – normalization, complement transformation, cumulative integration, and blank subtraction – based on the intrinsic properties of the TCD signal, without empirical filtering or arbitrary smoothing. The inherent stability of the TCD signal eliminates issues related to baseline drift or offset definition, ensuring greater robustness. Blank subtraction was synchronized with experimental timing (valve opening) to minimize alignment artefacts.

This value can then be compared with the actual global reduction degree of the solid sample and used to estimate the kinetic parameters of the multistage reduction of iron oxides. The most important innovation is the means to correlate the raw data – measured with a very accurate gas detector – with the degree of conversion of a solid in heterogeneous gas-solid reactions. This is confirmed in the present work not only by the accurate fit of the experimental data, but also by an accurate physico-chemical interpretation provided by the model of the reactive system.

2.5. Mathematical model

The mathematical model developed in this study to evaluate the reduction kinetics of pure iron oxides represents a more rigorous and detailed version of a model previously presented by the authors [66]. The main differences lie in a more detailed assessment of the mass balance of the chemical reaction, which takes into account the particle size distribution of the solid, in a more realistic behavior of the reaction fronts and in a more detailed treatment of the gas-phase fluid dynamics within the full and empty volume of the reactor. The proposed model combines a classical axial dispersion approach with a dynamic shrinking core model (SCM) that includes the product layer approach. The thin fixed bed, which is discretized vertically into a grid of 20 points in the model, reacts in each layer according to sequential reaction dynamics evolving from a single reaction front to three fronts and then back to one front in the particles. At each time step, the model dynamically evaluates the state of the solids in each layer and selects the appropriate set of equations based on the number of reaction fronts. In this way, a wide range of phenomena are taken into account, including kinetics, thermodynamics as well as external and internal diffusion effects. On the solid side, the model assumes radial homogeneity of all structural,

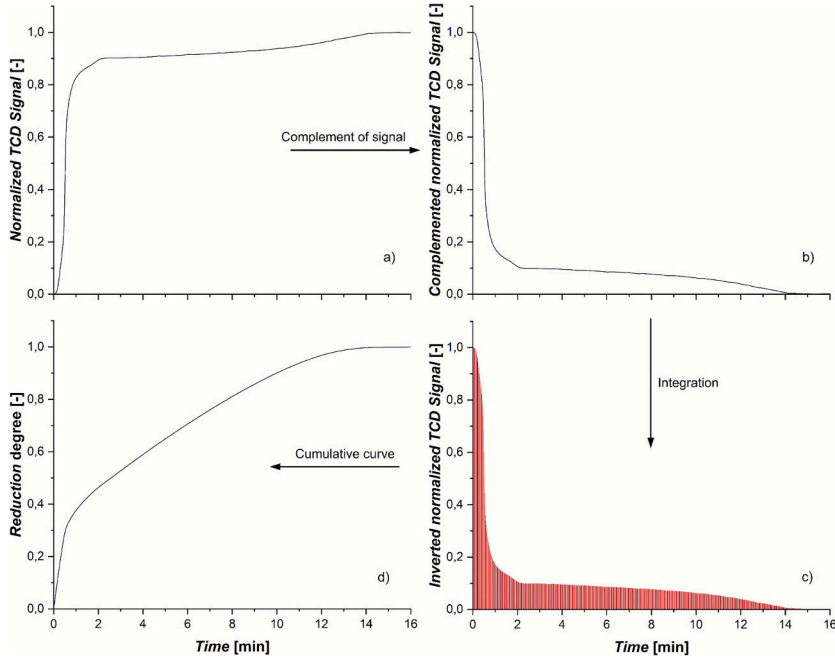


Fig. 4. Numerical elaboration of TCD signal raw data: a) Normalized TCD signal; b) Complement of normalized TCD signal; c) Integration of the complement signal; d) reduction degree obtained from cumulative integration.

compositional, and porosity-related properties of the layers. On the gas side, a constant total gas concentration within the particles at uniform temperature and pressure within the particles as well as a quasi-steady state (i.e., no accumulation of gas phase species) are assumed. In the model a reaction takes place exclusively at the interface between two distinct solid regions: an unreacted inner core and a surrounding shell of reacted material. As the core is being consumed, the surface area of the reaction front gradually decreases. The different remaining product layers are always considered in the context of intraparticle diffusion phenomena that describe the reaching the reaction front or product gases that exit. In the reaction network considered in this study, a maximum of three different reaction fronts is considered.

2.5.1. Gas mass balance

The gas-phase mass balance equations describe the evolution over time (t) of the concentrations of reducing and oxidizing agents in the reactor. The gas-phase model includes convection, axial dispersion and a reaction term that is governed by dynamic SCM. Based on the reactor length L and the height of the solid bed h , two dimensionless axial coordinates, z_1 and z_2 , are defined to identify the two reactor zones: the empty zone ($l = 1$) (convection and dispersion) and the reactive zone ($l = 2$) (gas flow and chemical reactions). In the system of differential equations, subscript i refers to the gas phase species (i.e., H_2 and H_2O), while j represents the reaction or reaction front under consideration: $j = 1$ for the first reduction (hematite to magnetite), $j = 2$ for the second (magnetite to wüstite), and $j = 3$ for the third one (wüstite to metallic iron).

$$\frac{\partial c_i(t, z_l)}{\partial t} = \begin{cases} \frac{u}{L-h} \frac{\partial c_i(t, z_1)}{\partial z_1} + \frac{D_z}{(L-h)^2} \frac{\partial^2 c_i(t, z_1)}{\partial z_1^2} & \text{for } l=1 \\ \frac{u}{h} \frac{\partial c_i(t, z_2)}{\partial z_2} + \frac{\partial^2 c_i(t, z_2)}{\partial z_2^2} + (1-\epsilon) \cdot \sum_{j=1}^3 \nu_{ij} \cdot r_j(t, z_2) & \text{for } l=2 \end{cases} \quad (1)$$

In this equation, c_i is the concentration of the i :th gas species, while ν_{ij} are the stoichiometric coefficients of the i :th gas species in reaction j . The boundary conditions of the PDE system are defined at the reactor inlet ($z_1 = 0$), at the outlet of the empty zone ($z_1 = 1$), at the inlet of the reactive bed ($z_2 = 0$) and at the system outlet ($z_2 = 1$).

$$c_i(t, z_1) \big|_{z_1=0} = c_{i,in} \quad \frac{\partial c_i(t, z_1)}{\partial z_1} \bigg|_{z_1=1} = 0 \quad (2)$$

$$c_i(t, z_2) \big|_{z_2=0} = c_i(t, z_1) \big|_{z_1=1} \quad \frac{\partial c_i(t, z_2)}{\partial z_2} \bigg|_{z_2=1} = 0 \quad (3)$$

As for the geometric and fluid dynamic parameters, h is the theoretical height of the fixed bed; u is the superficial gas velocity and D_z is the axial dispersion coefficient. These parameters are calculated using

$$h = \frac{V_s}{S} = \frac{m_s}{\rho \cdot \pi R^2} \quad (4)$$

$$u = \frac{Q}{S} = \frac{Q_0}{S} \cdot \frac{T}{T_0} \beta \quad (5)$$

$$D_z = \frac{L \cdot u}{Pe} \quad (6)$$

S is the cross-sectional area of the reactor (derived from the inner

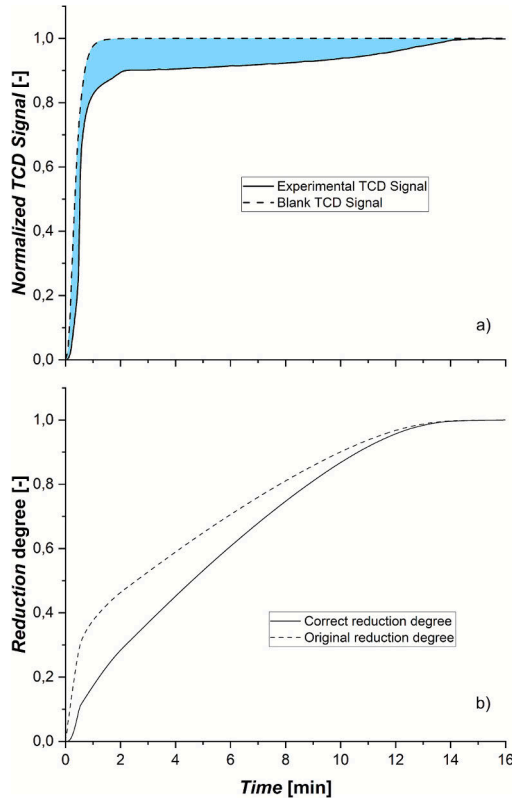


Fig. 5. Numerical correction of the reduction degree from TCD signal raw data: a) difference between the TCD signals in the blank and reduction experiments (blue region), and b) original (solid line) and corrected (dashed line) reduction degrees.

radius R), and V_s is the theoretical volume of the loaded sample obtained as the mass-to-density ratio of the iron oxide. The gas velocity is defined as the ratio of the actual volumetric flow rate Q to S , where Q is derived from the volumetric flow rate at standard conditions (Q_0), adjusted by the operating temperature T and the reference temperature $T_0 = 295$ K and converted using the factor $\beta = 10^{-6}/60$ (m^3/min)/(dm^3/s). The axial dispersion coefficient D_x is calculated based on its definition using the Peclet number (Pe). The fluid dynamics and the Peclet number were evaluated experimentally by residence time distribution (RTD) tests (see Results section). Finally, ϵ is the initial bed void fraction experimentally determined by physisorption experiments. For the reactive term, the reduction rate r_j is given by

$$r_j(t, z_2) = \sum_{n=1}^N x_n \cdot \frac{P}{R_g T} \frac{1}{r_n^0} \frac{1}{A_j(t, z_2, r_n^0)} \left(\frac{N_j(t, z_2, r_n^0)}{W(t, z_2, r_n^0)} - y_{H_2,j,eq}(t, z_2) \right) \quad (7)$$

R_g is the gas constant, P represents the operating pressure and $y_{H_2,j,eq}$ is the equilibrium molar fraction of the reducing agent for reaction j . The global reduction rate is calculated by weighing each reaction rate by the initial radius r_n^0 of each particle size class and their respective weight fraction x_n . With this approach, the contribution of the individual particle size classes to the overall reduction process can be evaluated. The

particle size distributions of the hematite and magnetite samples are presented in the Results section. To properly evaluate the driving force of each reaction front, $y_{H_2,j,eq}$ is evaluated for the j th reaction as

$$y_{H_2,j,eq}(t, z_2) = \frac{1}{1 + K_j} \left(y_{H_2,j}(t, z_2) + y_{H_2O,j}(t, z_2) \right) \quad (8)$$

where $y_{i,j}$ represents the molar fraction of the gas species over time and position within the bed while K_j is the equilibrium constant of the j th reaction.

Variables A_j , N_j and W are crucial for describing how the model dynamically describes the progress of the reduction and selects the appropriate number of analytical equations. For example, if X_j is defined as the degree of conversion of an oxide ($j = 1$ Fe₂O₃, $j = 2$ Fe₃O₄, $j = 3$ FeO) with hematite as the starting material, the interaction between the reducing gas and the solid initially defines the first and only active reaction front with $X_1(t, z_2) = 0$ ($f = 1$). If a layer satisfies both the conditions $X_1(t, z_2) < 1$ and $X_2(t, z_2) = 0$, two reaction fronts become active. A third front appears if $X_1(t, z_2) < 1$ and $X_2(t, z_2) < 1$. Conversely, the number of active fronts decreases when $X_j(t, z_2) = 1$, which indicates that the oxide in question has been completely converted in this layer. As a result, W and N_j vary depending on the number of active reaction fronts. The parameter f changes its value based on the model's self-assessment, according to the scheme

$$\text{if } \begin{cases} X_1(t, z_2) = 0 & f = 1 \quad j = 1 \\ X_1(t, z_2) < 1 \wedge X_2(t, z_2) = 0 & f = 2 \quad j = 1, 2 \\ X_1(t, z_2) < 1 \wedge X_2(t, z_2) < 1 \wedge 0 < X_3(t, z_2) < 1 & f = 3 \quad j = 1, 2, 3 \\ X_1(t, z_2) = 1 \wedge X_2(t, z_2) < 1 \wedge X_3(t, z_2) < 1 & f = 2 \quad j = 2, 3 \\ X_1(t, z_2) = 1 \wedge X_2(t, z_2) = 1 \wedge X_3(t, z_2) < 1 & f = 1 \quad j = 3 \\ X_1(t, z_2) = 1 \wedge X_2(t, z_2) = 1 \wedge X_3(t, z_2) = 1 & f = 0 \end{cases} \quad (9)$$

N_j here denotes the effective reduction rate for the j th front, while W represents the total resistance for mass transfer and reaction. These are calculated using the parameters A_j , B_j and F , which represent kinetic resistances, intraparticle diffusion resistances and external diffusion resistances, respectively, according to

$$N_1(t, z_2, r_n^0) \big|_3 = [A_1 A_2 A_3] \cdot y_{H_2,1} + [A_1 A_2 (B_3 + F)] \cdot y_{H_2,3,eq} + [A_1 A_3 B_2 + A_1 A_3 (B_3 + F) + A_1 B_2 (B_3 + F)] \cdot y_{H_2,2,eq} + [A_3 B_1 (A_2 + B_2) + A_3 B_1 (A_2 + B_2) + B_1 (A_2 + B_2) (B_3 + F) + A_2 A_3 B_2 + A_2 A_3 (B_3 + F) + A_2 B_2 (B_3 + F)] \cdot y_{H_2,1,eq} \quad (10)$$

$$N_2(t, z_2, r_n^0) \big|_3 = [A_2 A_3 (A_1 + B_1)] \cdot y_{H_2,2} + [A_2 (A_1 + B_1) (B_3 + F)] \cdot y_{H_2,3,eq} + [A_3 (A_1 + B_1) (B_3 + F) + B_2 (A_1 + B_1) (B_3 + F) + A_3 B_2 (A_1 + B_1)] \cdot y_{H_2,2,eq} + [A_2 A_3 B_2 + A_2 A_3 B_2 + A_2 B_2 (B_3 + F) + A_2 A_3 (B_3 + F)] \cdot y_{H_2,1,eq} \quad (11)$$

$$N_3(t, z_2, r_n^0) \big|_3 = [A_3 (A_1 + B_1) (A_2 + B_2) + A_2 A_3 B_2] \cdot y_{H_2,3} + [(A_1 + B_1) (A_2 + B_2) (B_3 + F) + A_2 B_2 (B_3 + F)] \cdot y_{H_2,3,eq} + [A_3 (A_1 + B_1) (B_3 + F)] \cdot y_{H_2,2,eq} + [A_2 A_3 (B_3 + F)] \cdot y_{H_2,1,eq} \quad (12)$$

$$W(t, z_2, r_n^0) \Big|_3 = \left\{ (A_1 + B_1) \cdot [A_3(A_2 + B_2 + B_3 + F) + (A_2 + B_2) \cdot (B_3 + F)] + A_2[A_3(B_2 + B_3 + F) + B_2(B_3 + F)] \right\} \cdot \gamma_{H_2,1,eq} \quad (13)$$

$$N_2(t, z_2, r_n^0) \Big|_2 = (A_2 A_3) \cdot \gamma_{H_2,2} + [A_2(B_3 + F)] \cdot \gamma_{H_2,3,eq} + [A_2 B_1 + (A_3 + B_2)(B_3 + F)] \cdot \gamma_{H_2,2,eq} \quad (14)$$

$$N_3(t, z_2, r_n^0) \Big|_2 = A_3(A_2 + B_2) \cdot \gamma_{H_2,2} + [(A_2 + B_2)(B_3 + F)] \cdot \gamma_{H_2,3,eq} + [A_3(B_3 + F)] \cdot \gamma_{H_2,2,eq} \quad (15)$$

$$W(t, z_2, r_n^0) \Big|_2 = A_3(A_2 + B_2 + B_3 + F) + (A_2 + B_2) \cdot (B_3 + F) \quad (16)$$

$$N_3(t, z_2) \Big|_1 = \gamma_{H_2,3}(t, z_2) - \gamma_{H_2,3,eq}(t, z_2) \quad (17)$$

$$W(t, z_2, r_n^0) \Big|_1 = \frac{A_3 + B_3 + F}{A_3} \quad (18)$$

The analytical expressions for these variables vary depending on the number of active fronts. For oxides other than hematite — where all three reaction fronts may occur at some point — the same modeling approach applies to experiments starting from Fe_3O_4 or FeO , with fewer maximum fronts. A_j , B_j and F are defined as

$$A_j(t, z_2) \Big|_f = \frac{1}{(1 - X_j(t, z_2))^{\frac{2}{3}} k_j} \cdot \frac{1}{\left(1 + \frac{1}{k_j}\right)} \quad (19)$$

$$B_j(t, z_2, r_n^0) \Big|_f = \frac{(1 - X_{j+1}(t, z_2))^{\frac{1}{3}} - (1 - X_j(t, z_2))^{\frac{1}{3}}}{(1 - X_j(t, z_2))^{\frac{1}{3}} \cdot (1 - X_{j+1}(t, z_2))^{\frac{1}{3}}} \cdot \frac{r_n^0}{D_j}; \quad X_{j+1}(t, z_2) = 0 \text{ if } j + 1 > \max(j) \Big|_f \quad (20)$$

$$F = \frac{1}{H} \quad (21)$$

where k_j is the kinetic constant, D_j is the intraparticle diffusion coefficient and H is the external mass transfer coefficient. The kinetic parameters were determined by fitting experimental reduction data using the linearized Arrhenius equation, while the thermodynamic [8] and diffusion parameters [44] were obtained from established theoretical and empirical expressions (Table 2).

$$k_j = k_{j,ref} \cdot \exp \left[\left(-\frac{E_{a,j}}{R} \right) \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (22)$$

$$K_j = \exp \left(-\frac{\Delta G_j}{RT} \right) \quad (23)$$

$$D_j = d_{1,j} \cdot \exp \left(d_{2,j} - \frac{d_{3,j}}{T} \right) \quad (24)$$

$k_{j,ref}$ and $E_{a,j}$ are the pre-exponential factor and the activation energy, respectively, while T_{ref} is the reference temperature (600 °C). ΔG_j is the change in Gibbs free energy calculated from the changes in enthalpy (ΔH_j) and entropy (ΔS_j) of the reactions. The terms $d_{1,j}$, $d_{2,j}$ and $d_{3,j}$ are coefficients used in the equation to describe intraparticle diffusion.

2.5.2. Solid mass balance

The solid phase mass balances of the different iron oxides are described as functions of time and position z along the axial coordinate of the reactive bed

$$\frac{\partial X_j(t, z_2)}{\partial t} = (1 - \epsilon) \frac{r_j(t, z_2)}{n_0 a_j} \quad (25)$$

where n_0 represents the initial oxygen content (e.g., $n_0 = 3m/M_{Fe_3O_4}$) of the sample, while a_j is the proportional oxygen content function of the type of iron oxide.

The overall degree of reduction of the solid is therefore calculated by

$$X(t, z_2) = \sum_j a_j \cdot X_j(t, z_2) \quad (26)$$

The average degree of reduction ($\bar{X}_s$), calculated along the z_2 , was used for comparison with the experimental data in the objective function during parameter estimation (Section 2.5.5).

2.5.3. Phenomenologies negligible by criterion

Regarding external diffusion phenomena, the particle size distribution provided by the supplier and later refined through DLS techniques suggests that such mass transport limitations can be reasonably neglected. The external mass transfer coefficient, denoted as H , was calculated under varying operating conditions and for all particle size families. It is given by

$$H = Sh \cdot \frac{D_{mol}}{2r_n^0} \quad (27)$$

where Sh is the Sherwood number and D_{mol} is the molecular diffusivity. The Sh value is estimated using classical correlations involving the

Schmidt (Sc) and Reynolds (Re) numbers, through

$$Sh = 2 + 0.6Re^{1/2}Sc^{1/3} \quad (28)$$

$$Sc = \frac{\mu_g}{\rho_g \cdot D_{mol}} \quad (29)$$

$$Re = \frac{2R_{it} \cdot \rho_g}{\mu_g} \quad (30)$$

The molecular diffusivity was calculated using the formulation proposed by Valipour et al. [67]

$$D_{mol} = \frac{1 \cdot 10^{-7} \cdot T^{1.75}}{P \cdot \left(\sum v_i^{1/3} \right)^2} \left(\sum \frac{1}{M_i} \right)^{1/2} \quad (31)$$

where v_i represent the diffusion volumes of the gas species involved (Table 2). Finally, μ_g and ρ_g represent the viscosity and density of the gas, respectively, calculated as

$$\rho_g = \frac{P \cdot \sum y_i M_i}{R_g T} \quad (32)$$

$$\mu_g = \sum y_i \mu_i; \quad \mu_i = \frac{m_{1,i} \cdot (T/K)^{m_{2,i}}}{1 + \frac{m_{3,i}}{(T/K)} + \frac{m_{4,i}}{(T/K)^2}} \quad (33)$$

coefficients m_i are derived from an empirical equation obtained via

CHEMCAD [68]. The detailed and quantitative evaluation of the mass transfer coefficient H revealed an average value of approximately 1000 m/s, confirming that the external mass transfer resistance can be neglected when compared to the other resistances considered in the SCM model. In this study, the energy balance for the reduction of iron oxides with hydrogen was not considered, although the entire reaction network is endothermic. This choice is justified by the operating conditions describing the reduction of small beds of very fine particles where temperature gradients can be considered negligible if a strong external heat source is used to keep the temperature constant. To support this assumption theoretically, a criterion was adopted

$$T_j^{\text{center}} - T_j^{\text{surface}} = \frac{D_j(-\Delta H_j)}{\lambda_j} (c_{\text{H}_2}^{\text{surface}} - c_{\text{H}_2}^{\text{center}}) \quad (34)$$

where λ_j are the thermal conductivity coefficients of the reacting oxides [69]. The first term on the right side of the equation was evaluated to be always less than $1 \text{ K m}^3 \text{ mol}^{-1}$ ($5 \cdot 10^{-2}$ to $1 \cdot 10^{-1} \text{ K m}^3 \text{ mol}^{-1}$) for all solids involved. The second term was evaluated using a worst-case scenario, assuming the highest hydrogen concentration at the surface (about 14 mol/m^3 at 873 K) and zero in the particle core. Based on this assessment, intraparticle temperature variations of -0.649 K for hematite, 1.61 K for magnetite and 1.23 K for wüstite were found. These results confirm the assumption of negligible internal temperature gradients, which is also supported by recent experimental evidence from Hesslering et al. [70] in the case of much larger pellets.

2.5.4. Reaction front control

In heterogeneous gas–solid reactions, the reaction kinetics generally depend on the composition of the gas phase, while the solid phase usually only plays an indirect role, allowing the degree of conversion to be calculated. To accurately determine the kinetic parameters governing the reduction of iron oxides, it is necessary to prevent the mathematical model from selecting combinations during parameter estimation that match the data but give theoretically incorrect results. This is the case with sequential reaction fronts, where in the SCM an outer front can progress faster than an inner front, which can lead to an overlap or, in the worst-case scenario, a crossing of the fronts — situations that are physically inadmissible. To solve this problem, a mathematical means was developed to control the reaction front. For each integration step of the model, it calculates the hypothetical value of the subsequent reduction. Based on the derivative value $dX_j(t, z)/dt$ at a certain time t , the model estimates the future term using the trapezoidal method $dX_j(t + \Delta t, z)/dt$ where Δt is the maximum integration step defined by the numerical solver of the model. If the calculated degree of reduction of the outer front at time $t + \Delta t$ exceeds that of the adjacent inner front, the code forces the derivatives to be equal. This means that if an outer front moves faster than an inner front and could potentially overtake the latter, the two fronts are instead forced to advance at the same rate.

The key condition for front control is

$$X_j(t + \Delta t, z) = X_{j+1}(t + \Delta t, z) \quad \text{if} \quad X_{j-1}(t + \Delta t, z) < X_j(t + \Delta t, z) \quad (35)$$

2.5.5. Numerical solution

The mathematical model was developed in Matlab 2024a, where the system of partial differential equations was solved using the finite difference method. The backward scheme was used for the evaluation of the first-order spatial derivative and the centered scheme for the second-order spatial derivative. The two axial coordinates of the reactor were discretized into 20 nodes each. The resulting system of ordinary differential equations was solved with the function *ode15s*, a solver of variable step size and variable order based on numerical differentiation formulas of order between 1 and 5. The parameter estimation was performed with *patternsearch*, a direct optimization algorithm belonging to the class of derivative-free methods. It is a deterministic solver based on a pattern search method in which the algorithm explores the solution space using

a grid (pattern) and adapts this grid according to the optimization progress. The objective function used to minimize the distance between experimental data and the average simulated value of the thin layer over time ($\bar{X}_s$) is the following expression.

$$O = \sum_s \left(\frac{X_{\text{meas},s} - \bar{X}_s}{X_{\text{meas},s}} \right)^2 \quad (36)$$

Finally, the values and units of all model parameters are reported in Table 2.

3. Results

3.1. Materials characterization

In order to follow the development of the chemical reaction over time, a detailed analysis of the composition of the fixed bed was conducted using stop tests. The same reduction experiment was repeated several times under identical operating conditions, whereby the reaction was stopped at different times and corresponding samples were taken. Due to the minimum sample mass required for successful XRD analysis ($> 70 \text{ mg}$), the experiments were performed with an initial solid mass of approximately 300 mg. Apart from the mass, all other operating conditions were identical to those specified in Table 1 for the standard test, which serves as a common reference point for all studies on the specific operating effects on the process (i.e., test 2H/M). The standard test was carried out at a temperature of 600°C , a hydrogen molar fraction of 0.2 (balanced with argon as inert gas) and a total flow rate of 20 mL/min. When examining the reduction of a bed of pure hematite, the normalized thermal conductivity signal shows much sharper and more pronounced slope changes compared to the thin layer counterpart. A major challenge in this analysis lies in the complex interdependence of the signal, which is influenced by overlapping compositions in different bed layers and potential thermodynamic limitations due to hydrogen starvation and high vapor concentration in certain parts of the reactive bed. For this reason, this kinetic study propose a simplified analysis for thin bed layers — assuming a homogeneous composition throughout — avoiding increased complexity related to the influence of additional phenomena on the reduction behavior. The normalized thermal conductivity signal and the XRD results of the starting material and the intermediate samples are shown in Fig. 6.

The analysis confirmed that the starting material is pure hematite with rhombohedral structure crystallizing in the $R\bar{3}c$ space group. The stop tests conducted after 5 min, 10 min, 50 min and 150 min reveal the evolution of the fixed bed composition over time. These points were selected based on the overall behavior of the TCD signal to capture the reactor state just before and after the main slope transitions as well as during the slowest phase of the reduction (i.e., 150 min). It was observed that Fe_3O_4 appears very early and that Fe_2O_3 is almost completely depleted within the first 10 min, supporting the hypothesis that the slope changes in the TCD signal are directly related to the dominant solid-phase species and its control over the reaction regime. Before 50 min, another change in slope is observed, and the test stop after this time reveals the complete disappearance of Fe_2O_3 and the formation of FeO. In addition, the peaks associated with metallic iron begin to appear. After 150 min, wüstite appears to be the dominant phase promoting the final formation of metallic iron. The presence of magnetite in this phase can be partly explained by the disproportionation reaction of FeO into magnetite and metallic iron [60] that can occur during the cooling phase of the reactor. This cooling was carried out at a moderate ramp rate for technical and safety reasons, as it is not possible to rapidly quench a glass reactor system from operating to ambient temperature. The most important result of this analysis is not only the confirmation of the sequential nature of the reduction — as widely reported in the literature — but also the correlation of the gas phase signal with the evolution of the composition in the solid phase. While the size distribution of the

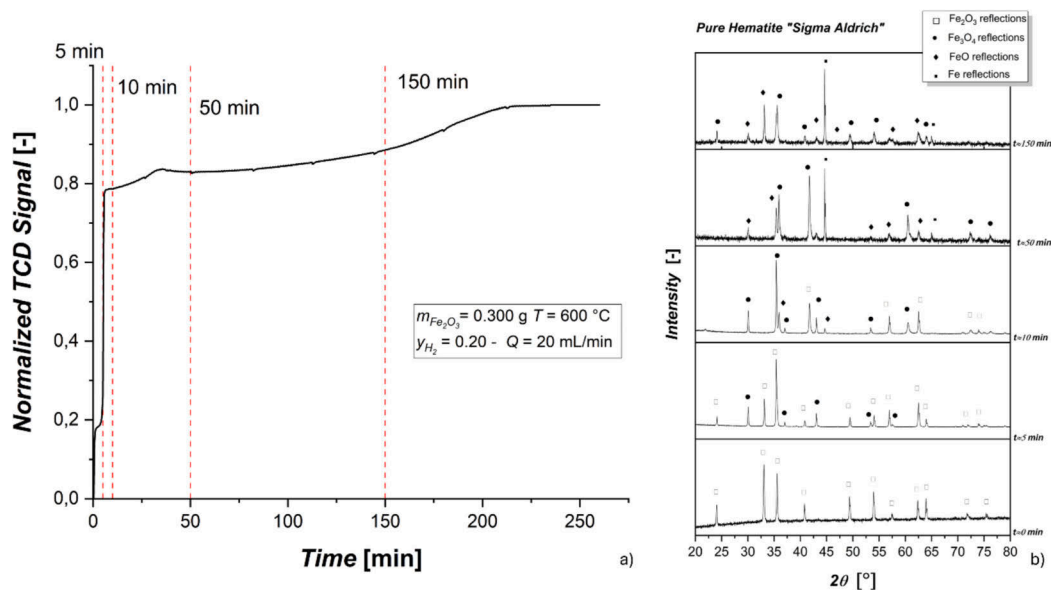


Fig. 6. a) Normalized TCD signal with marked stop points; b) XRD diffractograms of stop-test samples. Experimental conditions: $m_{\text{Fe}_2\text{O}_3} = 0.300 \text{ g}$, $T = 600^\circ \text{C}$, $y_{\text{H}_2} = 0.20$, $Q = 20 \text{ mL/min}$.

powder is usually provided by the manufacturer, a more detailed knowledge of the granulometric families is crucial to accurately evaluate the reaction rate using the dynamic SCM approach. Therefore, detailed LS analyses were performed to assess the particle size distribution. Fig. 7 shows the particle volume fractions for hematite and magnetite and cumulative distribution curve calculated based on $\log_{10}(2r_d^3)$ (order of magnitude 10^{-6} m). To evaluate the presence of phenomena such as agglomeration and coalescence of the particles, the LS technique was also used to analyze the grain size distribution of the reduced iron obtained from both hematite powder and pure magnetite. The results reported in Fig. S5 (Supplementary Material) show that in both cases the differences between the starting material and the reduced iron are negligible.

The results show significant differences. Hematite (Fig. 7a) has a narrow and well-defined size distribution with an average diameter between $1 \mu\text{m}$ and $2 \mu\text{m}$. In contrast, magnetite has a much broader distribution, which partly contradicts the particle size of $<5 \mu\text{m}$ stated by the manufacturer for both samples. Some magnetite particles reach a diameter of up to $100 \mu\text{m}$, probably due to agglomeration. This result is critical as the reaction kinetics are strongly influenced by the particle size distribution, especially for the less oxidized form of iron where mass transport limitations may occur. Nitrogen physisorption measurements on the starting materials previously heated to 600°C and evaluated using the BET method provided essential information about the surface area and porosity (ϵ). The initial porosity was found to be 0.1 for both samples [37].

3.2. Experimental results

The kinetic study of the reduction of a thin iron oxide layer under different operating conditions was carried out to evaluate the kinetic parameters of the individual reduction steps and to determine the control regimes of the process. The experimental investigations were performed by varying the operating temperature, the hydrogen content of

the reduction gas and the total volumetric flow rate. The same experimental conditions were used for both pure hematite and pure magnetite powder. The model-based results obtained by parameter estimation, together with the experimental data processed using the integration and blank test correction method (cf. Materials and Methods), demonstrate that the mathematical model can accurately describe the overall reduction behavior determined based on the thermal conductivity of the outgoing gas flow.

As previously mentioned, the TCD signal primarily reflects the hydrogen content in the outlet gas, and the slope variations in the curves are closely related to the controlling regime as well as to the thermodynamics of the chemical reactions. This behavior is particularly evident in Fig. 8, which shows how the normalized TCD signal changes in a series of experiments conducted with hematite powder at different temperatures.

The experimental results highlight critical aspects of the reduction process. The shape and slope of the curves are clearly related to the rate at which the reducing agent is consumed, with a significantly increased rate at higher temperatures, but can also be influenced by the reaction equilibria. Comparative tests with different pure and commercial solid samples with the same methodology have also shown that the morphological and structural nature of the sample plays a key role and should be taken into consideration in the interpretation of the signals.

This suggests that changes in slope can also be attributed to changes in the solid surface area accessible to the gas and its evolution during the reaction [36,37]. Given the high sampling frequency of the TCD signal, the signal was down-sampled to 20 s between the points to improve the clarity of the data representation in the figures that follow.

3.2.1. Temperature effect

Temperature is one of the most significant variables in the study of iron oxide reduction. An increased temperature improves the kinetics and efficiency of the process but also affects the equilibrium conditions. In particular, operation above the eutectoid point in the Baur–Glassner

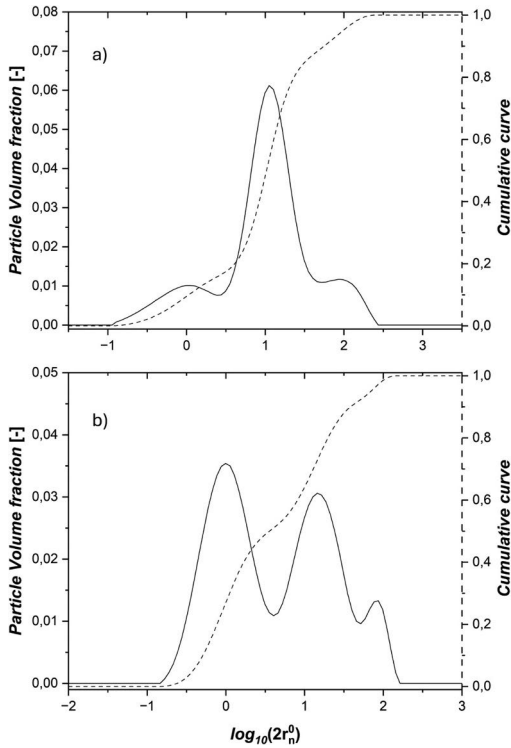


Fig. 7. Granulometric distribution of a) Fe_2O_3 Sigma A, and b) Fe_3O_4 Sigma A.

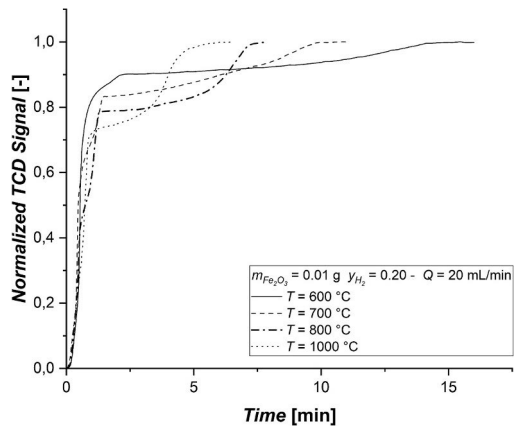


Fig. 8. Normalized TCD signal in Fe_2O_3 reduction experiments: $m_{\text{Fe}_2\text{O}_3} = 0.010$ g, $y_{\text{H}_2} = 0.20$, $Q = 20$ mL/min, $T = 600$ °C, 700 °C, 800 °C and 1000 °C.

diagram (i.e., about 570 °C) allows access to the stability region for the sequential reduction reactions from Fe_3O_4 to FeO and from FeO to Fe . As temperature increases, thermodynamics increasingly favors these two

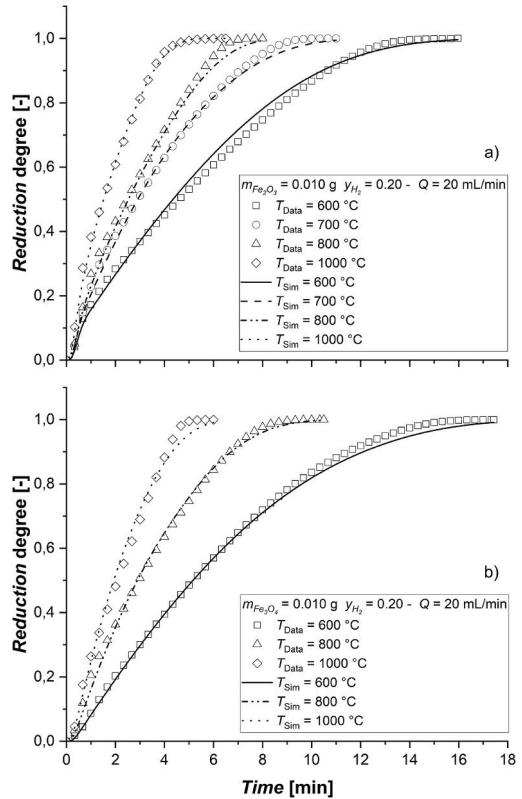


Fig. 9. Effect of temperature on a) Fe_2O_3 and b) Fe_3O_4 reduction under general experimental conditions: $m = 0.010$ g, $y_{\text{H}_2} = 0.20$, $Q = 20$ mL/min. Experimental results indicated by markers, simulated results by solid, dash-dotted and dotted lines.

reactions, significantly expanding the range of water vapor concentrations that do not inhibit the chemical process (Fig. 1). The markers in Fig. 9 show the effects of temperature on the overall degree of reduction of pure hematite and magnetite over time in the reduction experiments.

Comparing Figs. 8 and 9, which are different representations of the same experimental results, the differences between the normalized TCD signal become more pronounced through the integration procedure. In this way, important process characteristics become clear particularly in the early first part of the reaction. It is obvious that increasing the operating temperature significantly reduces the overall reduction time due to the increase in reaction rate and consequent hydrogen consumption. The results show that the complete conversion of hematite to magnetite takes place in less than one minute under all experimental conditions: a significant change in the slope can be observed at a degree of conversion of around 0.11 . This value corresponds to the completion of the first reduction step, which is fast and thermodynamically unhindered. As for the reduction of Fe_3O_4 to FeO , the slope transitions in the thin-layer experiments are less pronounced than in the fixed-bed experiments (Fig. 6a). This is due to the small mass of solids used in the experiments: the water vapor produced is removed very efficiently, which supports not only the second but also the third reduction stage. For this reason, these reduction steps can occur almost simultaneously,

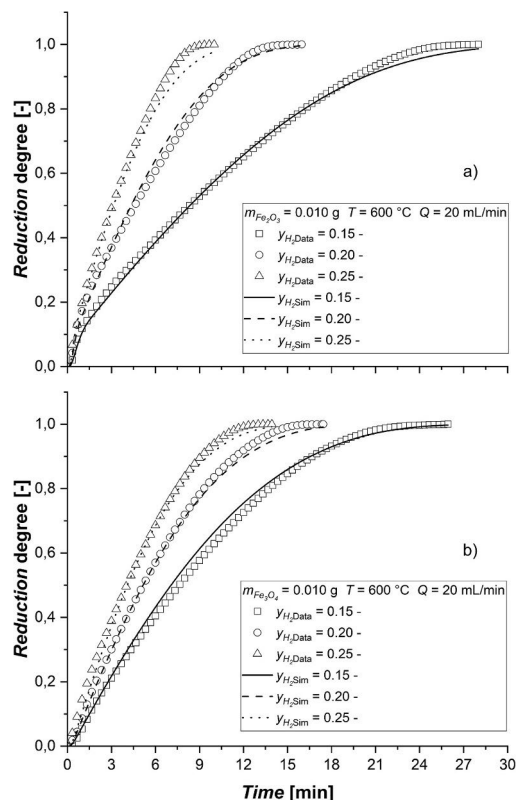


Fig. 10. Effect of feed gas hydrogen content on a) Fe_2O_3 and b) Fe_3O_4 reduction under general experimental conditions: $m = 0.010$ g, $T = 600^\circ\text{C}$, $Q = 20$ mL/min. Experimental results indicated by markers, simulated results by solid, dash-dotted, and dotted lines.

so it is difficult to distinguish between them. The reduction of magnetite cannot be considered completed at an overall conversion degree of about 0.3 as this likely includes a contribution from the FeO-to-Fe step. The final, slower step is clearly the reduction of wüstite, as widely reported in literature [15]. The differences in reduction rates between hematite and magnetite powders, especially at lower temperatures (e.g., 600°C) are mainly due to the difference in particle size distribution, which slows down the reaction for the latter case. This gap is only closed at the highest temperatures.

3.2.2. Effect of gas composition

The effect of the composition of the feed gas was studied by changing molar fraction of the hydrogen (y_{H_2}), with the balance being inert gas (Ar), affecting the driving force of the reactions, with results for hematite and magnetite sample reported in Fig. 10.

As expected, an increased hydrogen content significantly decreases the overall time required to complete the reduction process. A high availability of hydrogen enhances the driving force and reaction rates in all steps. In addition, at higher H_2 :Ar molar ratios, thermodynamic limitations are reduced or even removed. The reduction of Fe_2O_3 is consistently faster than that of Fe_3O_4 , attributed theoretically to the crystal structure of Fe_3O_4 , which has a stronger binding force for oxygen than Fe_2O_3 . In this case, the much larger particle size distribution in the

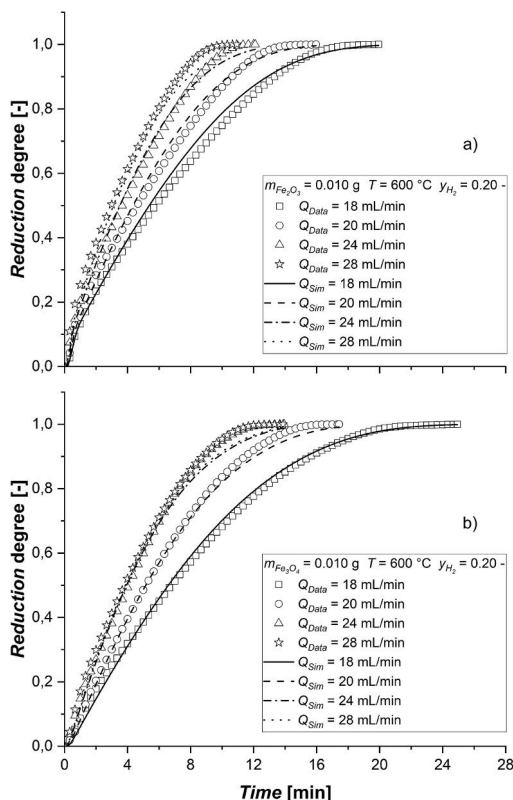


Fig. 11. Effect of volumetric flow of feed gas on a) Fe_2O_3 and b) Fe_3O_4 reduction under general experimental conditions: $m = 0.010$ g, $T = 600^\circ\text{C}$, $y_{\text{H}_2} = 0.20$. Experimental results indicated by markers, simulated results by solid, dash-dotted, and dotted lines.

magnetite sample also slows down the reaction kinetics. A comparison between the two data sets shows that the effect of the operating parameters becomes less significant when large particles are present.

3.2.3. Effect of volumetric gas flow rate

Finally, the influence of the total volumetric flow rate (Q) of the feed gas was investigated. This variable significantly influences the convection phenomena within the reactor system (Eqs. (1) and (5)). An insufficient flow rate can lead to an excessive accumulation of water vapor in the bed, limiting the reaction progress due to thermodynamic constraints. Conversely, increasing the flow rate helps to maintain a high hydrogen concentration throughout the process, which promotes the progress of the reaction in all phases. Fig. 11 illustrates the effect of the gas flow rate on the reduction behavior of pure hematite and magnetite.

Increasing the flow rate clearly reduces the overall reduction time. For pure hematite, this variable appears to have the least impact, while for magnetite it has a greater effect. The experimental data reveals that the difference between 24 mL/min and 28 mL/min is minor for hematite and practically negligible for magnetite.

3.3. Parameter estimation

In the parametric analysis, the experimental trials were separated by

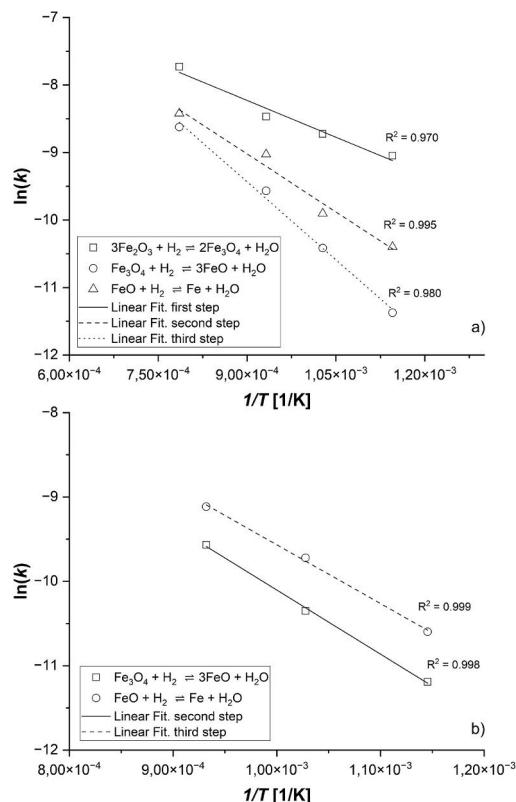


Fig. 12. Arrhenius plots for a) Fe_2O_3 and b) Fe_3O_4 reduction.

Table 3
Estimated parameters in the reaction rate expressions.

Starting material	Reactions	E_a	$k_{1,ref}$	R^2
Fe_2O_3	$\text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$	30 ± 4	$7 \cdot 10^{-3} \pm 6 \cdot 10^{-4}$	0.970
Fe_2O_3	$\text{Fe}_3\text{O}_4 = \text{FeO}$	64 ± 3	$8 \cdot 10^{-2} \pm 1 \cdot 10^{-2}$	0.995
Fe_2O_3	$\text{FeO} = \text{Fe}$	48 ± 5	$2 \cdot 10^{-2} \pm 3 \cdot 10^{-3}$	0.980
Fe_3O_4	$\text{Fe}_3\text{O}_4 = \text{FeO}$	64 ± 2	$8 \cdot 10^{-2} \pm 9 \cdot 10^{-3}$	0.999
Fe_3O_4	$\text{FeO} = \text{Fe}$	58 ± 3	$7 \cdot 10^{-2} \pm 9 \cdot 10^{-3}$	0.998

temperature and solid type. The kinetic parameters estimated in this study were determined through a simultaneous evaluation of the three reduction steps. The mathematical model developed here discretizes the solid phase and allows the coexistence of multiple reaction fronts within the same particle whenever dictated by local conditions. This formulation naturally accommodates the experimentally observed overlap of the reactions, rather than imposing strictly sequential progression. At each reaction instant, the model calculates the degrees of reduction associated with each elementary step, whose sum yields the overall degree of reduction (Eq. (26)), directly comparable to the experimental data. With this approach, the contributions of the individual reactions to the global rate enable the evaluation of distinct kinetic constants.

For each set of experimental data, the kinetic constants k_j were evaluated with respect to the available reactions. Using the linearized Arrhenius equation, the natural logarithm of the constants was plotted

against the reciprocal of the temperature. For hematite as starting material, this approach yielded four data points for each of the three reactions and for magnetite, three points for each of the two reactions. Fig. 12 shows the resulting Arrhenius plots, while Table 3 contains the calculated activation energies and reference kinetic constants together with the respective errors from the linear regression.

The Arrhenius plots in Fig. 12 show a clear and consistent trend in the calculated values of k_j . This result is supported by the low errors observed when estimating the activation energies and pre-exponential factors using the linearized Arrhenius equation. In particular, the errors for $E_{a,j}$ fall below 11% and for k_j below 15%. As far as the first reduction step is concerned, the reaction always proceeds very quickly, especially at higher temperatures. For this reason, the use of a high-precision, high-frequency measuring device was crucial. As can be seen for all the experiments, the mathematical model successfully reproduces observed conversion, as seen by the agreement between the continuous lines and the markers in Figures from 9 to 11. This can be observed especially in the case study on the temperature effect (c.f. Fig. 9). This shows that there are no significant morphological and structural changes in the solid due to temperature, especially in terms of porosity (surface area) and granulometric distribution conditions defined by the characterization techniques. One notable exception in the description of experimental data is in the gas composition effect result during the last phase of the hematite reduction where the hydrogen fraction is about 0.15 (c.f. Fig. 10). This deviation may be explained by a possible error in the small mass (10 mg) of the sample: a weighing error to the fourth decimal place could cause such a discrepancy, especially in the slower final phase of the reduction [66]. Finally, the simulation results related to the volumetric flow rate effect show excellent agreement with the experimental data at higher flow rates, while at lower flow rates a slight underestimation of the final reduction degree can be observed.

4. Discussion

Many kinetic models have been proposed for the hydrogen-based reduction of iron oxides. These models generally fall into two broad categories: phenomenological models (like Avrami-type formulations) and physicochemical models. The latter includes comprehensive approaches such as the Random Pore Model and Grain Model, which are specifically designed to capture the structural evolution and diffusion limitations occurring within the solid during reduction [60].

Models like the RPM and GM are particularly suited for analyzing the reduction kinetics of pellets or larger agglomerates, where the internal structure (porosity, tortuosity) significantly evolves and mass-transfer resistances can become dominant. Several studies show that the internal structure and solid organization can change drastically with the operating condition such as temperature [29,39] or, in the case of H_2 -based reduction, the presence of water vapor [71,72]. In stark contrast, the present study employs an experimental configuration using thin beds of pure oxide powders, intentionally designed to minimize mass-transfer effects. This methodological choice allows for the extraction of kinetic parameters that closely reflect the intrinsic chemical reactivity of the system, without the need for complex structural assumptions (e.g., pore distribution) inherent to models like the RPM or GM. The proposed Shrinking Core Model is an appropriate choice for isolating this intrinsic chemical step under our controlled conditions. The reliability of this approach is confirmed by the resulting activation energies: $74.8 \pm 49.0 \text{ kJ mol}^{-1}$ for hematite reduction, $66.0 \pm 57.2 \text{ kJ mol}^{-1}$ for magnetite reduction, and $62.0 \pm 43.9 \text{ kJ mol}^{-1}$ for the final step [60]. These values fall within the statistically expected literature ranges. The SCM, validated here, can nevertheless be extended to a grain-level or multiscale description if future analyses of commercial materials warrant the incorporation of structural factors.

The results have clearly shown that the mathematical model is capable of accurately describing the experimental data on the reduction

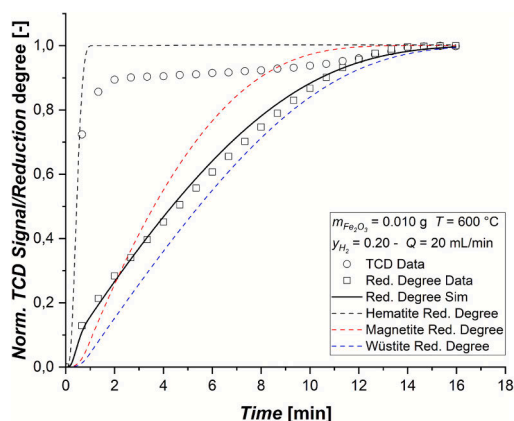


Fig. 13. Experimental and simulation results of reduction of thin layers of hematite under the experimental conditions $m_{\text{Fe}_2\text{O}_3} = 0.010 \text{ g}$, $T = 600^\circ \text{C}$, $y_{\text{H}_2} = 0.20$, $Q = 20 \text{ mL/min}$.

of hematite and magnetite in hydrogen-containing gas flows. However, in order to achieve a better understanding of the reduction process, it is necessary to utilize the simulation to its full capacity. This approach is essential not only to gain insight into key aspects of the system under investigation, but also to assess the quality and consistency of the results with theoretical model assumptions and as a comparison with data reported in the literature. Fig. 13 presents the evolution of the individual reduction degrees X_i for each solid species and the progress of the overall reduction reaction for a thin solid layer experiment. These average values are used because even in a mathematically discretized thin bed, slight variations in the reduction dynamics occur. In particular, the simulated average overall reduction degree ($\bar{X}$) — as described in the section on the numerical solution — is used to fit the experimental data. An important finding from Fig. 13 is that the reaction fronts of the different steps never overlap during the whole process. This important aspect is often neglected in modeling studies of iron oxide reduction but is crucial in heterogeneous non-catalytic reactions in the specific case of reactions in series: the conversion from one solid species to the next is not directly coupled in the mass balances, which requires careful mathematical control and validation of the adjustment of the kinetic parameters by simulation tests.

The standard test case shown (i.e., test H2) confirms that hematite is rapidly converted within the first minute under the given conditions, with minimal overlap with the subsequent reduction step. For the later steps, where the magnetite and wüstite reduction have closely following reaction fronts, a separate evaluation cannot be adopted. This can be explained by the fact that the driving force in thin iron oxide layers remains very high due to a low accumulation of water vapor. Although the reactions proceed quickly with a maximum of H_2O formation in the hematite step and the larger amount of H_2O formation in the following steps, the low height of the solid layer prevents hydrogen starvation and an accumulation of oxidizing agents. Further information provided in Fig. S6 (Supplementary Materials) shows simulation results in the form of contour plots of the dynamic evolution of solid and gas composition over time in the thin film fixed bed. Since there are practically no thermodynamic limitations — especially for FeO — the reactions can take place simultaneously and the reduction can be completed within minutes. The small amount of reducing agent and the limited flow rate were deliberately chosen in the experimental design to prevent excessively fast reactions to allow for adequate observation of the reduction dynamics. In the latter case, thermodynamics plays a pivotal role in

governing the reaction fronts. As is also shown, the evolution of the average overall reduction degree — calculated starting from the sum of the reduction degrees across all particle size classes — starts increasing with a slight delay, which is mainly due to the initial dilution of the reducing gas in the inert carrier. A significant change in the slope only occurs when the hematite reduction has been completed. The second phase is much more uniform due to the overlap of the subsequent reactions, which prevents the occurrence of a clearly dominant solid phase species responsible for hydrogen consumption. Based on these considerations, all simulations associated with the experimental data were thoroughly checked after parameter fitting to evaluate the quality of the results.

Regarding regime control, it is generally assumed that if half of the calculated activation energy is just below or equal to 20 kJ mol^{-1} , there is a mixture of internal diffusion and chemical control. From a numerical point of view, the comparison of the activation energies and the pre-exponential factors for the second reduction step shows almost identical values. This finding is consistent with the results presented in Fig. 13, which show that hematite reduction is almost completely independent of magnetite reduction in terms of hydrogen consumption. This separation of the contributions allows for a reliable estimation of the kinetic parameters for the second reaction step. In both cases, the activation energy values suggest that the controlling regime is chemical.

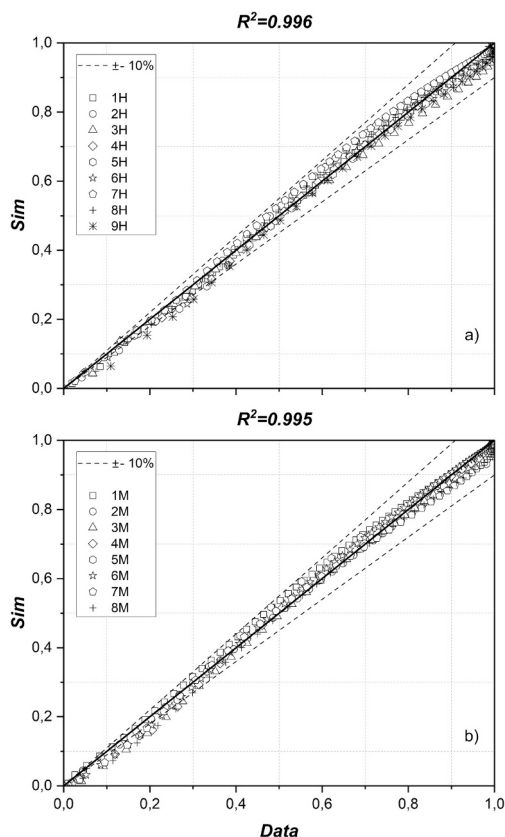


Fig. 14. Reduction degree parity plots: Experiments vs. simulations of a) Fe_2O_3 and b) Fe_3O_4 reduction in hydrogen-containing gas.

The third and final step shows slightly different activation energies for the two solids, but the controlling regime remains chemical in both cases. The discrepancies can be attributed to differences in particle size distribution. In particular, the last step of the reduction, where more water vapor is produced, is sensitive to the particle radius as an operating parameter [66]. It is interesting to compare the results obtained in this study with the values reported in the literature. The calculated activation energies are within the reported ranges but also agree well with the average values defined for each specific reaction step [60]. The wide variability in kinetic parameters reported in the literature is largely due to differences in solid sample history, purity, intrinsic properties, and post-synthesis treatments. In addition, many modeling approaches are based on simplified assumptions and kinetic parameters that often reflect apparent rather than intrinsic activation energies.

The choice of a rigorous experimental approach coupled with the use of a flexible mathematical model based on solid-phase approximations that reflect the experimental observations of intrinsic properties has thus led to consistent results, resulting in kinetic parameters in the model that successfully describes all experimental data for both data sets. A summary of the agreement between simulations and experiments is provided in the double parity plot of the reduction degrees in Fig. 14. As can be seen from the plots the comparison between experimental and simulated data, down-sampled to 30 s between the points, is largely within a variability of $\pm 10\%$. The goodness of fit is confirmed by the coefficients of determination, with $R^2 = 0.996$ for the reduction of pure hematite and $R^2 = 0.995$ for the reduction of pure magnetite and by the low root mean square errors, which are RMSE = 0.021 and RMSE = 0.020, respectively.

5. Conclusions

In this work, a comprehensive experimental and modeling investigation of a system for the reduction of thin beds of iron oxide fines with hydrogen as a reducing agent was presented. The experiments were conducted in a packed bed reactor-like system under different operating conditions, including temperature, hydrogen content, total volumetric flow rate and oxide type. Two pure powdered oxides — hematite and magnetite — were used. The experimental campaigns allowed for a detailed analysis of the reduction kinetics in the different reaction steps facilitated by an accurate analysis method based on measurements of the thermal conductivity of the outlet gas. Through rigorous mathematical data processing, the experimental signal was successfully correlated with the degree of conversion of the solid reactant. This innovative approach was further validated by combining the results of chemical and granulometric analyses of the solids with the consistent results of the developed mathematical model. A dynamic model of the shrinking core with multiple interfaces was coupled with a classical axial dispersion model to account for both particle and reactor phenomena, including gas-phase transport through the empty reactor space and the solid bed. The model was able to accurately reproduce the new experimental data. Based on a large data set of systematic reduction experiments performed under different conditions, the kinetic parameters for each individual reaction step were rigorously determined and compared with values reported in the literature. This enabled a thorough and comprehensive evaluation of the entire reduction process. An important finding of the work is the small influence of thermodynamic constraints on the reduction process, which is due to the negligible residence time of the locally generated water vapor in the solid phase in the present setup. This leads to a strong driving force of the reducing gas. The reduction of hematite to magnetite is extremely rapid and is governed by a mixture of internal diffusion and chemical regime. The subsequent reductions of magnetite and wüstite are similarly rapid and are both governed by chemical control, although a slight difference in activation energy was observed in the third reduction step depending on the type of sample (hematite vs. magnetite) used. Using micron-scale powders and thin fixed beds made it possible to determinate the intrinsic kinetics of hydrogen reduction of iron oxides under conditions that minimize

internal and external transport limitations. The kinetic parameters obtained were further validated in another study, which investigated a broader set of reduction experiments on packed beds of hematite powders, analyzing in more detail the role of emerging phenomena, including the influence of water vapor on thermodynamics and kinetics. This methodological roadmap includes extending the experiments to commercial fines obtained from BF and DRI pellets to evaluate the influence of morphology and chemistry, with dedicated structural evolution based on detailed characterization. The final step will be scaling up to full-size pellets through more complex modeling approaches (e.g., GM), integrating the phenomena and the resulting kinetic expressions into reactor-scale simulations. Generally, these results provide a valuable starting point for the evaluation of increasingly complex reduction systems, both experimentally and from a modeling perspective helping the development of future hydrogen-based technologies aimed at reducing the carbon footprint of the ironmaking sector.

Notation

Abbreviations

BF	Blast Furnace
CFD	Computational Fluid Dynamic
GM	Grain model
GOD	Gas Oxidant Degree
DRI	Direct Reduction Iron
LS	Light scattering
RMSE	Root mean square errors
RPM	Random pore model
SCM	Shrinking core model
TCD	Thermal conductivity detector

Symbols

A_j	Kinetic reaction resistance [s/m]
a_j	Proportional oxygen content parameter [–]
B_j	Intraparticle diffusion resistance [s/m]
c_i	Concentration i :th gas in the reactor [mol/m ³]
$c_{i,in}$	Feed i :th gas concentration [mol/m ³]
D_j	Intraparticle diffusion coefficient j :th reaction front [m ² /s]
D_{mol}	Molecular diffusivity coefficient [m ² /s]
D_z	Axial dispersion coefficient [m ² /s]
$d_{1,j}$	First coefficient empirical interparticle diffusion equation [m ² /s]
$d_{2,j}$	Second coefficient empirical interparticle diffusion equation [–]
$d_{3,j}$	Third coefficient empirical interparticle diffusion equation [K]
$E_{a,j}$	Activation energy j :th reaction front [J/mol]
e	Fitting parameter error
F	External diffusion resistance [s/m]
$g_{1,i}$	First coefficient in empirical thermal conductivity equation [W/(m K)]
$g_{2,i}$	Second coefficient in empirical thermal conductivity equation [–]
$g_{3,i}$	Third coefficient in empirical thermal conductivity equation [–]
$g_{4,i}$	Fourth coefficient in empirical thermal conductivity [–]
H	External diffusion coefficient [m/s]
h	Height of the solid bed [m]
K_j	Equilibrium constant j :th reaction front [–]
k_j	Kinetic constant j :th reaction front [m/s]
$k_{j,ref}$	Pre-exponential kinetic factor j :th reaction front [m/s]
L	Reactor length [m]
M	Molecular weight [g/mol]

m	Iron oxide initial mass [g]
$m_{1,i}$	First coefficient in empirical viscosity equation [Pa s]
$m_{2,i}$	Second coefficient in empirical viscosity equation [–]
$m_{3,i}$	Third coefficient in empirical viscosity equation [–]
$m_{4,i}$	Fourth coefficient in empirical viscosity equation [–]
N	Number of granulometric families [–]
N_j	Effective reaction SCM term ($f = 1$ [–], $f = 2$ [s ² /m ²], $f = 3$ [s ³ /m ³])
n_0	Initial concentration of oxygen [mol/m ³]
O	Objective function
P	Operating pressure [N/m ²]
Pe	Peclet number [–]
Q	Volume flow rate [mL/min]
R	Reactor radius [m]
R_g	Ideal gas constant [J/(K mol)]
Re	Reynolds number [–]
r_n^0	Iron oxide particle radius [m]
r_j	Reduction rate SCM [mol/(m ³ s)]
S	Reactor cross sectional area [m ²]
Sc	Schmidt number [–]
Sh	Sherwood number [–]
T	Operating temperature [K]
t	Time [s]
u	Gas velocity [m/s]
V	Solid volume [m ³]
v_i	Diffusion volumes coefficients [–]
W	Total resistance ($f = 1$ [–]) ($f = 2$ [s ² /m ²]) ($f = 3$ [s ³ /m ³])
X_j	Reduction degree j :th reaction front [–]
x_n	Weight granulometric distribution [–]
y_{ij}	Gas molar fraction i :th species of j :th reaction front [–]
$y_{H_2,j,eq}$	Equilibrium molar fraction of H ₂ of j :th reaction front [–]
z	Reactor axial coordinate [–]
β	Unit conversion term [(m ³ /min)/(dm ³ /s)]
ΔG_j	Gibbs free energy changes j :th reaction front [J/mol]
ΔH_j	Enthalpy changes j :th reaction front [J/mol]
ΔS_j	Entropy changes j :th reaction front [J/mol]
Δt	Maximum integration step
ε	Bed void degree [–]
λ_j	Solid thermal conductivity [W/(m K)]
ρ	Solid density [g/cm ³]
ρ_g	Gas density [g/cm ³]
ν_{ij}	Stoichiometric matrix [–]
μ_g	Gas viscosity [Pa s]

Subscripts

f	Number of available reaction fronts
i	Gas species
j	Reaction fronts
l	Spatial reactor domain
n	Index of granulometric family's distribution
s	Index of signal data distribution

Superscripts

0	index of initial condition [–]
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CRedit authorship contribution statement

Emiliano Salucci: Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Formal analysis, Data curation. **Antonio D'Angelo:** Methodology, Investigation, Data curation. **Vincenzo Russo:** Writing – review & editing, Conceptualization. **Henrik Grénman:** Writing – review & editing, Project administration, Conceptualization. **Henrik Saxén:** Writing – review & editing, Project

administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.172848>.

Data availability

Data will be made available on request.

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Supplementary Materials (Article III)

Kinetic modelling and parameter estimation of thin-layer iron oxide reduction with hydrogen in a fixed-bed reactor

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Supplementary Materials

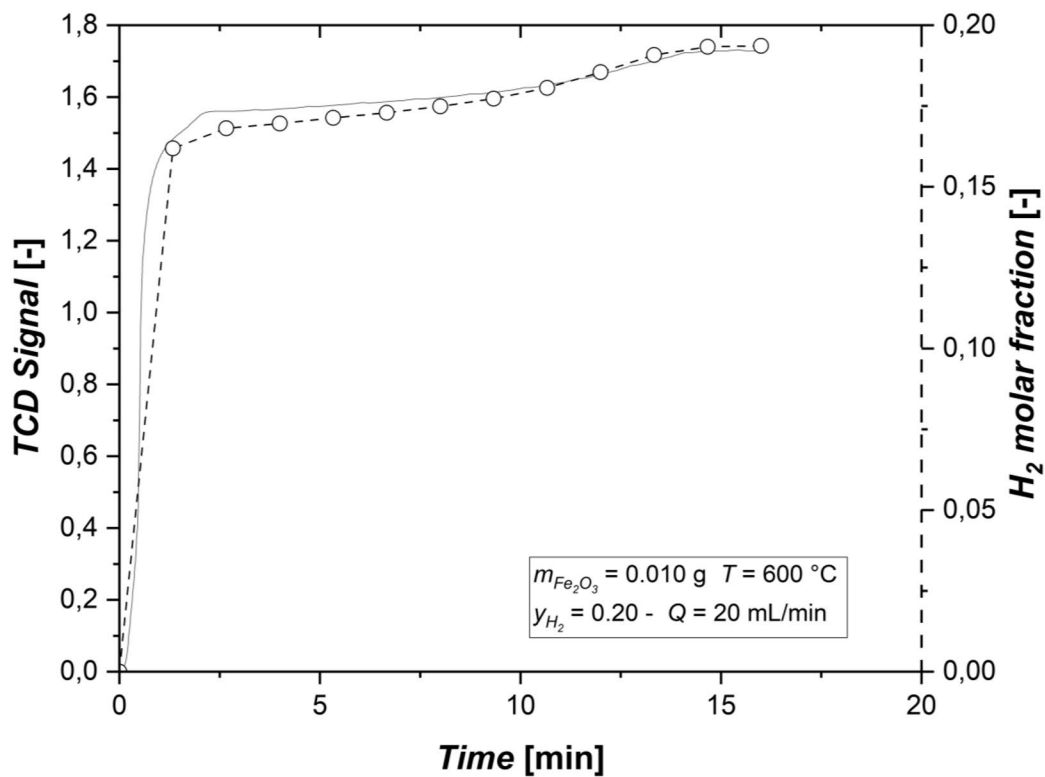


Figure S1. Comparison between the signal derived from the TCD and signal derived from Micro GC.

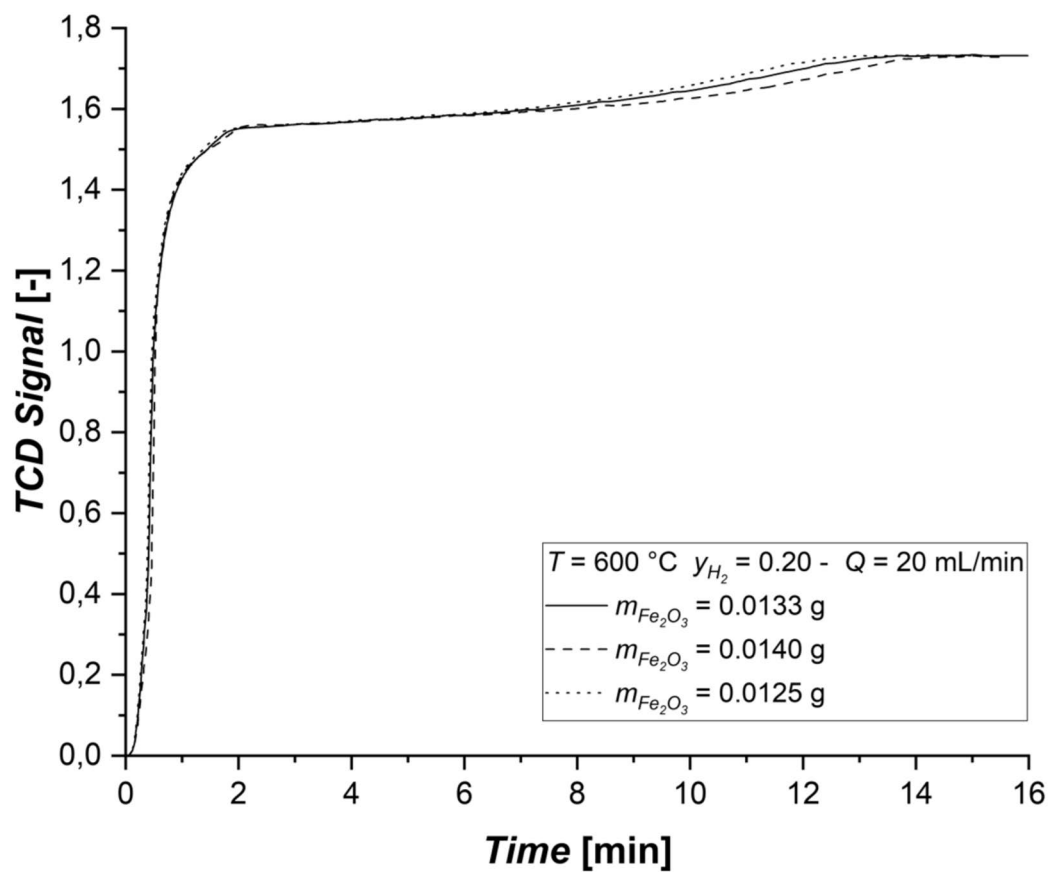


Figure S2. Repeatability test of the TCD signal for hematite powder reduction.

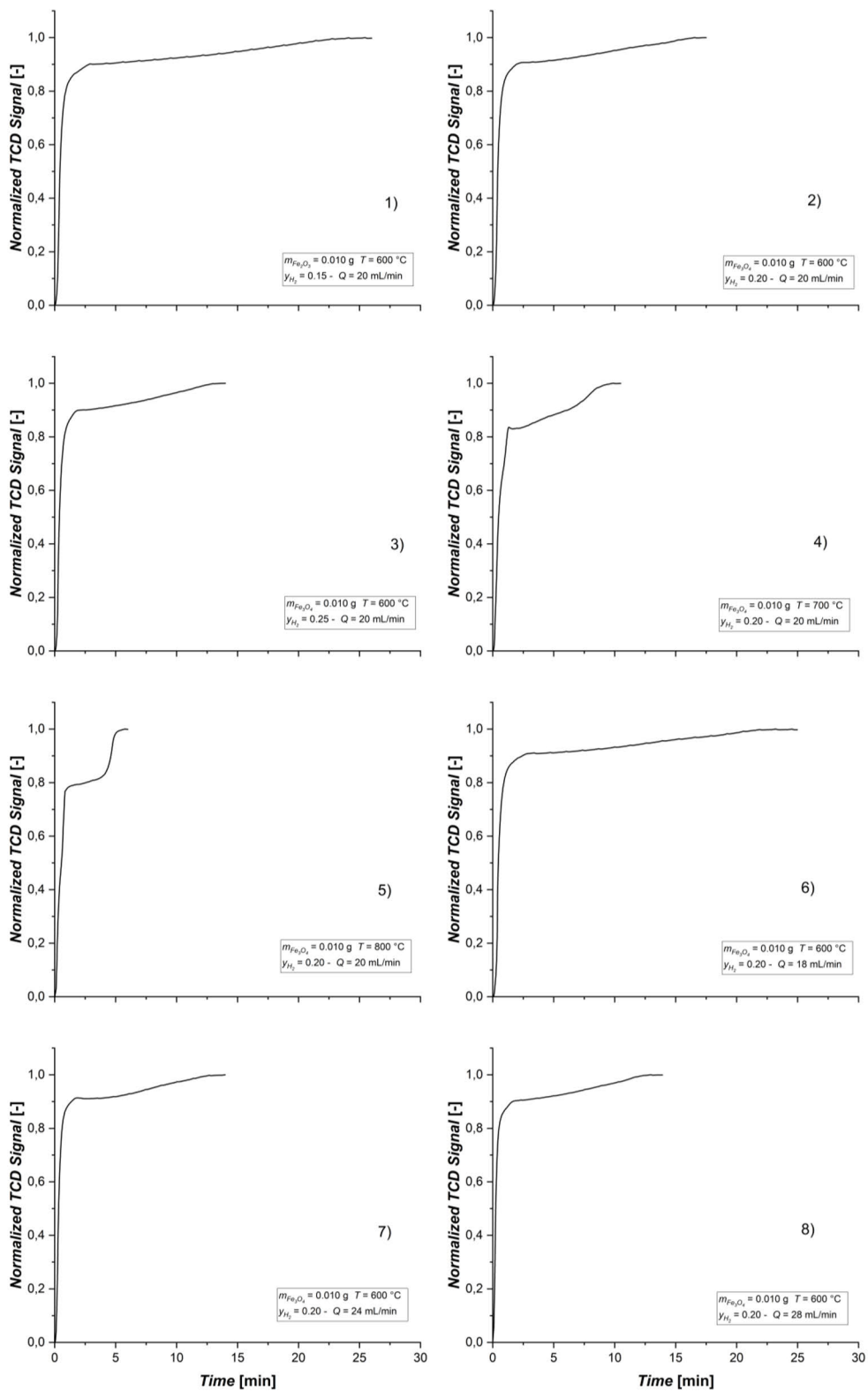


Figure S3. TCD dataset on hematite powder reduction.

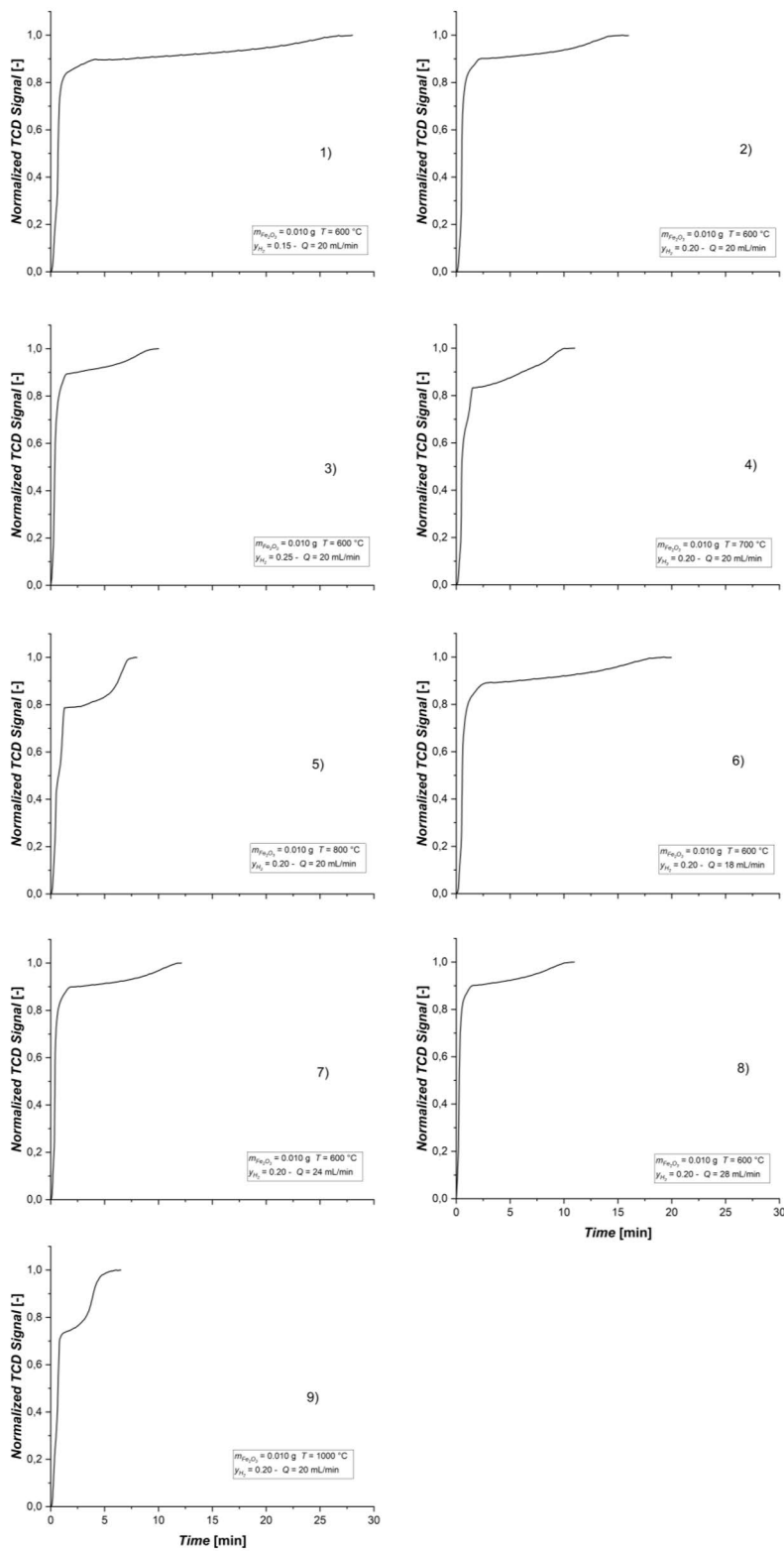


Figure S4. TCD dataset on magnetite dust reduction.

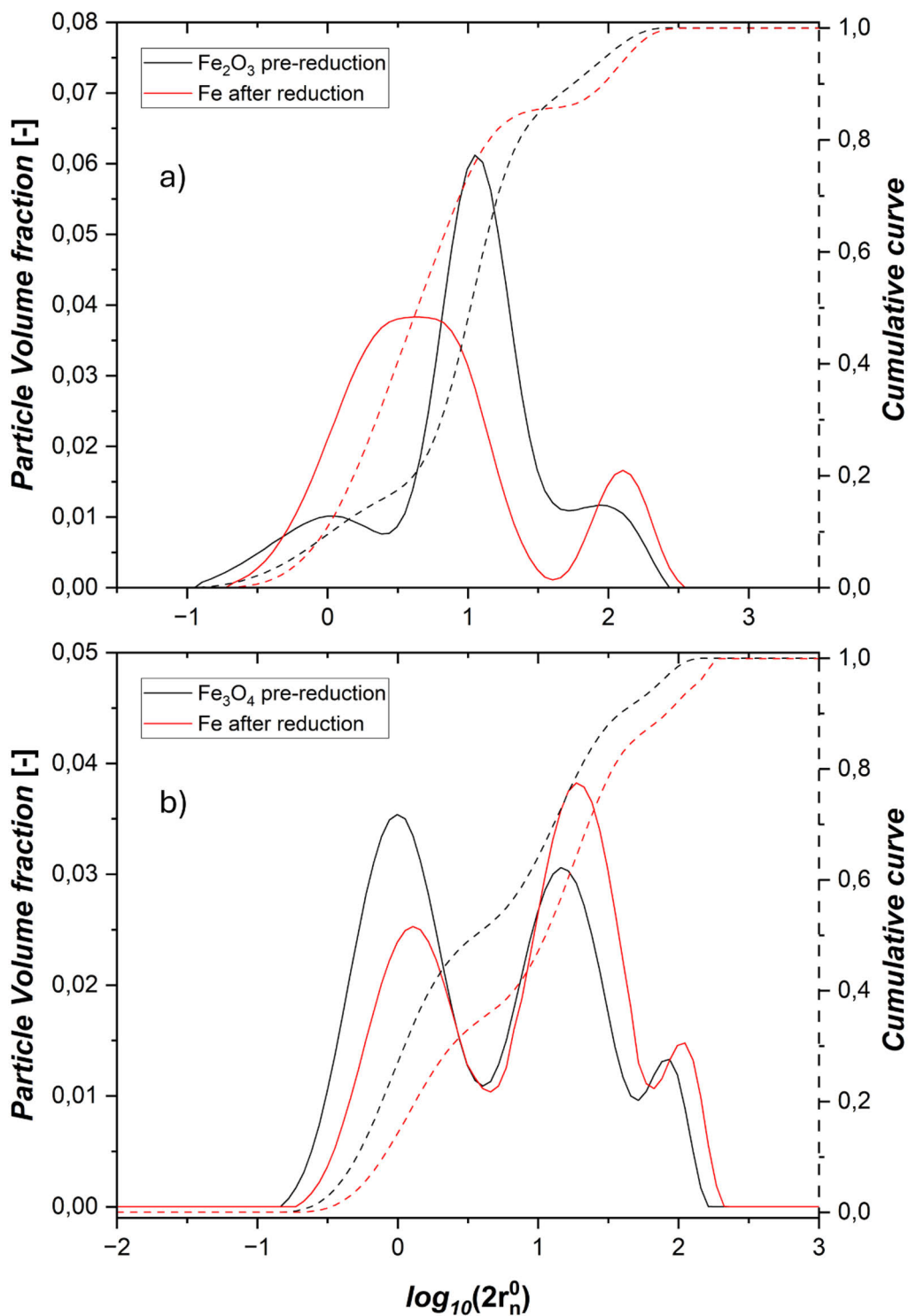


Figure S5. Granulometric distribution of a) Fe_2O_3 and Fe, and b) Fe_3O_4 and Fe.

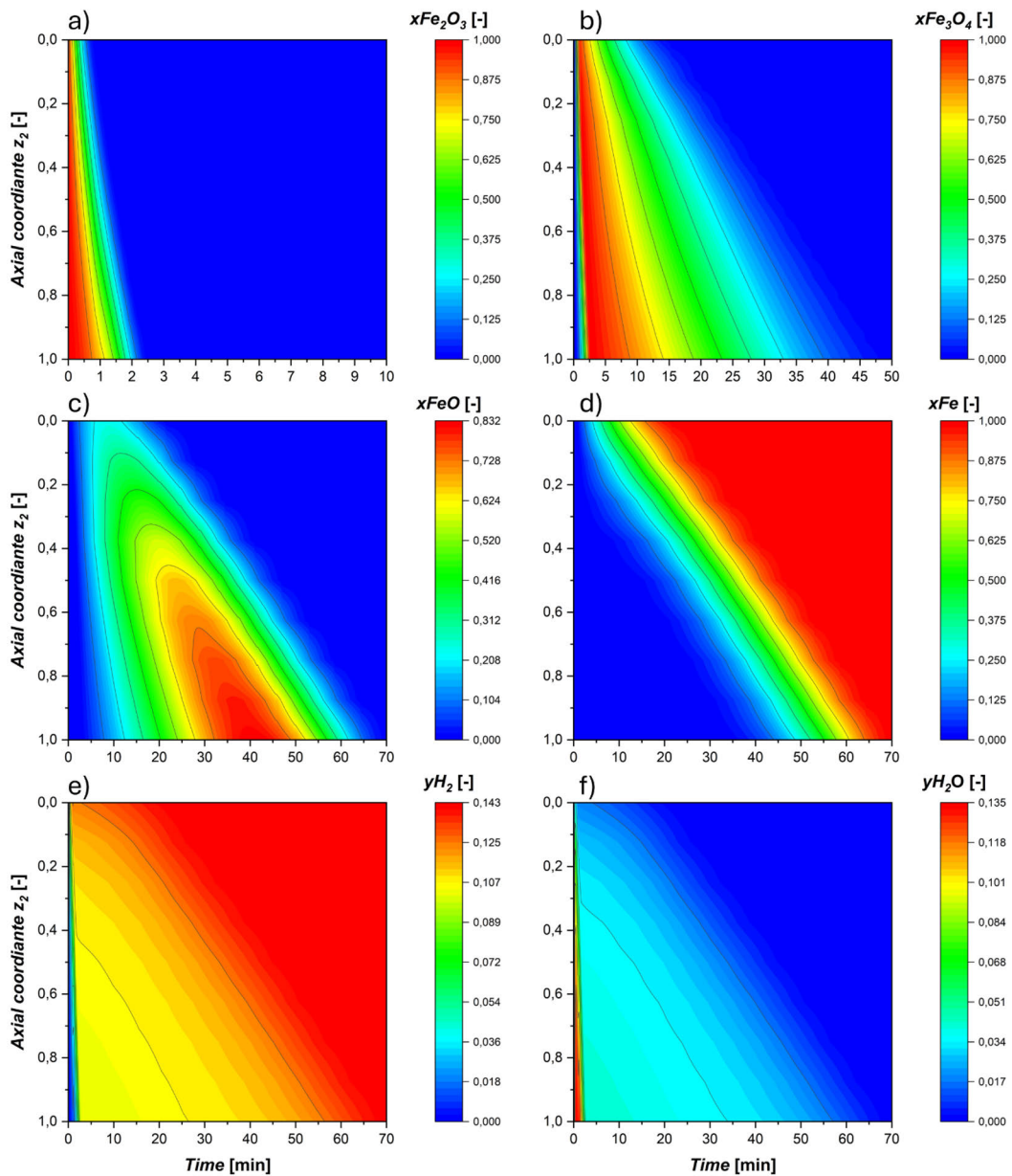


Figure S6. Contour plots axial coordinate vs Time: Thin layer hematite reduction simulation: $T = 873 \text{ K}$, $y_{\text{H}_2} = 0.2$ —, $Q = 20 \text{ mL/min}$ and $m = 0.0133 \text{ g}$. a) Fe_2O_3 solid molar fraction; b) Fe_3O_4 solid molar fraction; c) FeO solid molar fraction; d) Fe solid molar fraction; e) H_2 gas molar fraction and f) H_2O gas molar fraction.

IV

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