Multiscale reactor modelling of the influence of substituting natural gas with hydrogen in a direct reduced iron (DRI) plant

Tata Steel IJmuiden

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# Preface

The thesis "Multiscale reactor modelling of the influence of substituting natural gas with hydrogen in a direct reduced iron (DRI) plant." is executed at Tata Steel in IJmuiden, to obtain the degree of Master of Science at the Delft University of Technology. The research is carried out from November 2021 until September 2022.

Tata Steel faces an enormous challenge in the following years to become  $CO_2$  neutral. Implementing a direct reduced iron plant to produce green steel is one major change required to meet this challenge. Contributing to a sustainability project of such a large scale motivated me to work on this thesis. In addition, I enjoyed the challenges that came with the complexity of the process.

During my research, I have had support from many peoples. I want to thank Eli Elderkamp and Michiel van der Wees from Tata Steel for their daily supervision. I am very grateful for all the feedback they gave me during my thesis. Moreover, I would like to thank Wiebren de Jong from the TU Delft for his supervision. He was always available to help me out with problems. At last, I would like to thank Mathieu Pourquie for his support on the CFD problems I encountered.

I wish you lots of reading pleasure.

Sven Grolleman Amsterdam, September 2022

# Abstract

At the moment, Tata Steel emits  $12.6 \text{ Mt CO}_2$  per year while producing 7.2 Mt steel per year. To reduce these emissions, Tata Steel has decided to replace the blast furnaces with direct reduced iron (DRI) plants in combination with reducing electrical furnaces. The DRI plants will first operate with a 100% natural gas feed. Whenever green hydrogen becomes available on the market, the natural gas will gradually be substituted with green hydrogen, reducing direct CO<sub>2</sub> emissions. Producing steel using 100% green hydrogen as the reducing gas, called green steel, comes along with an awkward problem regarding the carbon content of the DRI. Green steel has a carbon content of 0%, while carbon is essential for multiple aspects of the production process. Furthermore, the metallization of the DRI is a critical parameter in the production process. Thus, the following research question is established: "What is the influence of the ratio of hydrogen to natural gas inserted in the direct reduced iron plant on the performance of the reactor?"

To answer this research question, an extensive literature review is performed to gain knowledge of the reduction process, reduction technologies, and the existing mathematical models of the DRI plant. Furthermore, a multiscale mathematical model is made of the shaft furnace of the MIDREX plant. This model uses a grain-based pellet model, which incorporates the morphological structure of the pellets during the reduction process. The shaft furnace is modelled as a 1D model with multiple zones, in which the local energy, mass, and momentum equations are solved. However, due to the time restrictions of the thesis period, only the two reduction zones of the shaft furnace are incorporated. Hence, the shaft furnace model lacks the transition and cooling zones.

The shaft furnace model is compared to a real operating MIDREX plant named "Gilmore". The simulation results are validated against the simulation results from literature and the real plant data. The average relative error of the simulation results compared to the Gilmore plant is 14.4%. The most significant error can be attributed to the carbon weight fraction in the solid. This is the result of the missing transition and cooling zones, as most of the carburization occurs inside the transition zone. Neglecting the carbon weight fraction, the average relative error is 9.2%.

Increasing the ratio  $H_2/CH_4$  in the feed of the MIDREX plant results in an increasing  $H_2/CO$  ratio of the reducing gas entering the shaft furnace. Five cases with different  $H_2/CO$  ratios are simulated to answer the research question. The metallization of the DRI is affected by two different phenomena. First, increasing the  $H_2/CO$  ratio results in a larger gas input mole flow for the same input pressure, which is the effect of a smaller pressure drop over the shaft furnace. Subsequently, a larger gas input mole flow results in better metallization, which is the effect of more heat input and a lower gas oxidation degree in the shaft furnace. Second, as the hydrogen content increases, the temperature decreases as a result of more endothermic reduction. The thermodynamics and kinetics of reduction by hydrogen are favourable at higher temperatures, which results in a slow-down of the reduction. At lower temperatures, the thermodynamics of reduction by carbon monoxide is more favourable, realizing more reduction and increasing the temperature. This second phenomenon is predominant for equal input mole flow, resulting in worse metallization for a higher  $H_2/CO$  ratio, as confirmed by literature. Consequently, to achieve equal metallization for a higher  $H_2/CO$  ratio, the process gas compressors of the MIDREX plant will consume more electrical energy. To conclude, substituting natural gas with hydrogen does have its disadvantages, but it is highly necessary to become  $CO_2$  neutral in the future.

For further research, the addition of transition and cooling zones to the shaft furnace model is recommended, allowing investigation of the carburization of the DRI. Furthermore, the shaft furnace model is extremely useful for implementation in a complete MIDREX plant model. Such a model could be used to investigate the total  $CO_2$ , energy, and material balance of the plant for different  $H_2/CH_4$  ratios of the feed of the plant.

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# List of Abbreviations

| Abbroviation | Magning  |
|--------------|--|
| Appreviation | wearing  |
| AISI         | American Iron and Steel Institute  |
| BOD          | Basis Of Design  |
| CCUS         | Carbon Capture, Utilization and Storage  |
| CDRI         | Cold Direct Reduced Iron   |
| CFD          | Computational Fluid Dynamics   |
| COURSE50     | CO <sub>2</sub> Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 2050 |
| DRI          | Direct Reduced Iron  |
| DRP          | Direct Reduction Plant   |
| EAF          | Electrical Arc Furnace   |
| GBM          | Grain Based Model  |
| GOD          | Gas Oxidation Degree   |
| HBI          | Hot Briquetted Iron  |
| HDRI         | Hot Direct Reduced Iron  |
| PACs         | Polycyclic Aromatic Hydrocarbons   |
| POSCO        | Pohang Iron and Steel Company  |
| REF          | Reducing Electrical Furnace  |
| TSN          | Tata Steel the Netherlands   |
| ULCOS        | Ultra Low CO <sub>2</sub> Steelmaking  |
| USCM         | Unreacted Shrinking Core Model   |
| ZR           | Zero Reformer  |

# Nomenclature

- Activity [-] а Pre-exponential factor of the Arhenius equation  $[m s^{-1}]$ Α Specific surface area of the solid pellets[m<sup>-1</sup>]  $a_s$ Gas concentration [mol m<sup>-3</sup>] С Ratio atoms carbon / atoms iron [-] С Heat capacity [J mol<sup>-1</sup> K<sup>-1</sup>]  $C_p$ Total gas concentration [mol m<sup>-3</sup>]  $c_t$ Diameter [m] d Diffusion coefficient [m<sup>2</sup> s<sup>-1</sup>] D Activation energy  $[J mol^{-1}]$  $E_a$ Shape factor of the grains [-]  $F_{g}$ Gibbs free energy  $[kJ mol^{-1}]$ G Heat transfer coefficient [kW m<sup>-2</sup> K<sup>-1</sup>] h Enthalpy [kJ mol<sup>-1</sup>] Η Η Height [m] Reaction rate constant  $[mol m^{-3} s^{-1}]$ k Permeability coefficient  $[kg m^{-3} s^{-1}]$ Κ Equilibrium constant K<sub>ea</sub> External mass transfer coefficient [m s<sup>-1</sup>]  $k_{g}$ Boltzmann constant  $[m^2 kg s^{-2} K^{-1}]$  $k_T$ Mass [kg] т Molecular weight  $[kg mol^{-1}]$ М Moles [mol] п Avogadro's number  $[mo1^{-1}]$  $N_A$ Nusselt number [-] Nu Pressure [Pa] р Peclet number [-] Ре Prandtl number [-] PrReaction rate  $[mol m^{-3} s^{-1}]$ r r Radius [m] Gas constant [J K<sup>-1</sup> mol<sup>-1</sup>] R Reynolds number [-] Re Entropy  $[J mol^{-1} K^{-1}]$ S Source term [mol m<sup>-3</sup> s<sup>-1</sup>] S Schmidt number [-] Sc Sh Sherwood number [-] Time [s] t Т Temperature [K] Velocity  $[m s^{-1}]$ u Mass fraction [-] W
- *x* Mole fraction [-]
- X Conversion [-]
- y Dimensionless position in the pellet of the grain based model [-]

| $ \begin{array}{l} \Gamma \\ \Delta_r H \\ \epsilon \\ \epsilon \end{array} $ | Tortuosity [-]<br>Heat of reaction $[kJ mol^{-1}]$<br>Lennard-Jones potential describing the intermolecular force $[m^2 kg s^{-2}]$<br>Porosity [-]<br>Relative error [-] |
|---|---|
| $\Delta_r H$<br>$\epsilon$<br>$\epsilon$                                      | Heat of reaction $[kJ mol^{-1}]$<br>Lennard-Jones potential describing the intermolecular force $[m^2 kg s^{-2}]$<br>Porosity [-]<br>Relative error [-]                   |
| $\epsilon$<br>$\epsilon$  | Lennard-Jones potential describing the intermolecular force $[m^2 kg s^{-2}]$<br>Porosity [-]<br>Relative error [-]   |
| $\epsilon$  | Porosity [-]<br>Relative error [-]  |
|   | Relative error [-]  |
| ε   |   |
| λ   | I hermal conductivity $[kW m^{-1} K^{-1}]$  |
| μ   | Viscosity [Pas]   |
| ν   | Stoichiometric coefficient of solid reactant [-]  |
| ρ   | Density $[kg m^{-3}]$   |
| $	ilde{ ho}$  | Apparent molar density [mol m <sup>-3</sup> ]   |
| σ   | Characteristic length of the intermolecular force law [m]   |
| τ   | Characteristic reaction time [s]  |
| $\Omega_D$  | Dimensionless collision integral of diffusion [-]   |
|   |   |
| Subscript   |   |
| axial   | In the axial direction of the shaft furnace   |
| bed   | Refers to the bed of the pellets  |
| C   | Catalyst  |
| chem  | Refers to chemical reactions  |
| crist   | Refers to the crystals inside the pellet  |
| diff<br>- ff  | Diffusion   |
| еп  |   |
| eq  | Equilibrium   |
| ext   | External  |
| g   | Refers to the gas phase   |
| gram  | Constituente  |
| l<br>ini  |   |
| interc  | Initial<br>Inter crystallite  |
| intera  | Inter crystallite   |
| interg  | Intra crystallite   |
| intrad  | Intra organilar   |
| k   | Refers to either carbon monoxide or hydrogen  |
| mixture   | Refers to the das mixture   |
| 0   | Refers to the outer pellet  |
| 0X  |   |
| n   | Pellet  |
| r   | Refers to reaction  |
| S   | Refers to the solid phase   |
| shaft   | Refers to the shaft furnace   |
| solid   | Refers to the solid   |
| UC  | Refers to the unreacted core  |
| 00  | Refers to the composition in the bulk gas flow  |
|   | ······································  |

## Superscript

| 0 | Standard                                     |
|---|--|
| ~ | Refers to the initial apparent molar density |
| - | Average value                                |
| • | Flow   |

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## Introduction

Currently, the steel industry accounts for 7 to 9% of the world's total direct carbon dioxide ( $CO_2$ ) emissions released by fossil fuels [95]. The majority of the carbon dioxide comes from the chemical reactions of making steel. To prevent the world from global warming by 2 °C, the emission of greenhouse gases must be cut by 80-95% compared to 1990, before 2050 [22]. The iron and steel industry must change its production processes to reduce these greenhouse gases. As a matter of fact, 73% of all steel in the world is still produced by the  $CO_2$  intensive blast furnace–basic oxygen furnace production route [95].

Tata Steel the Netherlands (TSN) is one of the world's most  $CO_2$  efficient steel producers. On the other hand, it produces  $12.6 \text{ Mt} CO_2$  per year, making it the largest industrial contributor of  $CO_2$  in the Netherlands [65]. Furthermore, the plant site of TSN is close to the village Wijk aan Zee which suffers from nuisances, dust, and hazardous emissions such as Polycyclic Aromatic Hydrocarbons (PACs) and lead. Consequently, TSN has received a lot of negative political and societal attention and has been forced to change drastically. Therefore, on September 15, 2021, TSN announced to switch to the gas-based Direct Reduced Iron (DRI) – technology [65]. The current production process is first explained simplistically to understand the switch to this technology.

At the moment, TSN produces 7.2 Mt steel per year while using the blast furnace–basic oxygen furnace production route, as can be seen in Figure 1.1 [65]. TSN has two coke plants, three sinter plants, one pellet plant, two blast furnaces, and three basic oxygen furnaces in the upstream liquid steel production process. Coke is produced by coal in the coke plants, which produce  $1.6 \text{ Mt CO}_2$  per year. Iron ores are processed into sinters or pellets. These processes emit 0.72 Mt and  $0.07 \text{ Mt CO}_2$  per year, respectively [65]. The produced cokes, sinter, and pellets, together with some iron ores in the form of powder and hot air, are implemented in the blast furnaces. Coke is used for thermal energy and the reduction of iron ores. Since iron ores only in the form of powder would extinguish the fire, sinters and pellets are added. In the blast furnace, the iron ores are reduced to iron while the remaining materials and impurities form slag. At the bottom of the blast furnace, the molten iron and slag are separated. The slag is sold to the cement industry. The blast furnaces emit  $9.9 \text{ Mt CO}_2$  per year.

The molten iron leaving the blast furnaces, called "hot metal", is transported to the basic oxygen furnace. In the basic oxygen furnace, oxygen is blown in to react highly exothermic with carbon to lower the amount of carbon and nitrogen in the iron. Moreover, scrap is added to the basic oxygen furnace to maintain the temperature and for recycling purposes. Whenever the amount of carbon in the iron is low enough, it is called steel. The basic oxygen furnace runs batch processes, in which the operating conditions of each run are changed to meet the desired steel quality of the customer. This process emits  $0.2 \text{ Mt } CO_2$  per year. Subsequently, the produced steel is cast into slabs and thus ready for the downstream processing steps. In the downstream process, the slabs will be hot/cold rolled, which emits  $0.4 \text{ Mt } CO_2$  per year. Note, that the sum of the total  $CO_2$  emissions deviates from the earlier mentioned  $12.6 \text{ Mt } CO_2$  per year, due to rounding errors.



Figure 1.1: Simplified current steel production process at TSN (in Dutch) [65].

To reduce the  $CO_2$  and hazardous emissions, TSN will replace the blast furnace technology with a Direct Reduction Plant (DRP) in combination with a Reducing Electrical Furnace (REF). The chosen gas-based DRI-technology is a production technology which makes use of either carbon monoxide (CO), hydrogen (H<sub>2</sub>), or a combination of both (called reducing gas) to reduce the iron ore in the form of pellets in a shaft furnace, as depicted in Figure 1.2. The reducing gas enters the shaft furnace just below the reduction zone (which is called the transition zone) and leaves at the top. The iron ore pellets enter the shaft furnace at the top and leave at the bottom, resulting in a counter-current flow. The cooling zone can be used to cool down the DRI. The reducing gas is produced by reforming natural gas. The reforming occurs either in the shaft furnace (in-situ) or in an external reformer, depending on the production process, as will be further explained in Paragraph 2.2. Using natural gas in this process is a proven technology and is widely applied in industry. The reduction occurs in a shaft furnace at relatively low temperatures, typically around 900 °C [43]. Hence, the reduced iron leaving the shaft furnace, called DRI, is in the solid-state. The DRI is typically 90 to 95% metallized [20].



Figure 1.2: Schematic presentation of the gas based direct reduction shaft furnace [8].

To further reduce the DRI and melt it using electrical energy, TSN will use a REF. After the REF, the iron will have similar quality as the hot metal leaving the blast furnace, so it is ready to go to the basic oxygen furnace. Most steel producers use the DRP in combination with an Electrical Arc Furnace (EAF) without a subsequent basic oxygen furnace. In fact, combining the DRP with a REF instead of with an EAF is an innovative development that has not yet been applied in the industry. Both the REF and the EAF are types of electrical furnaces, schematically shown in Figure 1.3, that use electrical energy to melt the produced DRI. However, in the REF a reducing environment exists, whereas in the EAF an oxidizing environment exists. This oxidizing environment is created by blowing in oxygen (similar to the basic oxygen furnace) to reduce the carbon content, hence producing steel. In the REF, the carbon mainly reacts with the unreduced iron ores, further reducing them.



Figure 1.3: Schematic presentation of an electrical furnace [77].

TSN decided to use a REF instead of an EAF based on the following arguments:

- Since the iron formed by the DRP in combination with the REF will have similar quality as the hot
  metal leaving the blast furnace, the basic oxygen process can continue operating in the same
  manner, and limited concessions need to be made on the product's behalf.
- In the REF further reduction of the DRI occurs, increasing the production capacity of steel.
- Both in the EAF and the REF slag is formed. Due to the differences in densities, the slag is separated easily, purifying the iron. However, the slag formed in the EAF will contain iron oxides that have not been reduced, making the economic value worthless. The slag formed in the REF is similar to the blast furnace, which can be sold to the cement industry.
- The production route using a DRP in combination with a REF and a basic oxygen furnace can handle iron ore with a lower quality than the production route using a DRP in combination with an EAF. Therefore, TSN gains a favourable position in the iron ore market.

TSN has planned to implement the proposed production route in steps. The first step is to close one of the blast furnaces and to build one DRP together with a REF with a production capacity of 2.5 Mt per year before 2030, as shown in Figure 1.4 [65]. Consequently, one of the coke plants can also be closed. This will reduce the  $CO_2$  emissions by 3.1 Mt per year when the DRP operates with natural gas. The second step is to close the second blast furnace. This will be replaced by either one or two DRPs and REFs (depending on the technological development of the capacity of the technologies) with a total production capacity of 3.5 Mt per year. In that case, the second coke plant and all sinter plants can be closed. The second step will reduce the  $CO_2$  emissions by another 4.4 Mt per year when operating with natural gas. To minimise the  $CO_2$  emissions further, in the last step, natural gas must gradually be substituted with hydrogen, or CCUS (Carbon Capture Utilization and Storage) must be realized. The use of hydrogen is preferable but highly depends on the availability of hydrogen on the market.



Figure 1.4: Energy transition steps of TSN towards green steel production (in Dutch) [65].

Producing steel using only green hydrogen as the reducing gas is called green steel, according to the World Steel Association [95]. This method will drastically reduce the production process's direct  $CO_2$  emissions. However, the hydrogen required for the DRP must be produced. In fact, only when the electricity used for the production of hydrogen (by electrolysis) is produced in a manner that it emits less than  $120 \text{ gCO}_2/\text{kWh}$ , switching to green steel emits less  $CO_2$  in total [63].

Currently, the only commercialized direct reducing technology using pure hydrogen as the reducing gas uses a two-stage fluidized bed process named CIRCORED [55]. However, the technical and economical optimal production capacity of this technology is only 1.25 Mt pear year [39]. Thus, this technology cannot reach the required production capacity of TSN of 2.5 Mt per year. Therefore, TSN decided to switch to the gas-based direct reduction technology using a shaft furnace. Currently, the shaft furnace-based DRPs of HYL/ENERGIRON and MIDREX are able to operate with a production capacity of 2.5 Mt per year [48, 80]. Hence, this study will focus on these technologies.



Figure 1.5: Iron-Carbon phase diagram [88].

Producing green steel comes along with an awkward problem regarding the carbon content of the DRI. In fact, DRI produced by 100% hydrogen results in a carbon content of 0% instead of 2-4% when produced by natural gas [57]. This carbon is important for multiple aspects of the production process:

• The basic oxygen furnace requires carbon for its main process. Whenever the carbon content of the iron arriving at the basic oxygen furnace is too low, this process must be changed, and choices must be made on the product's behalf.

- In the REF, carbon is required to reduce the iron oxides further. Adding carbon inside the REF might be possible, but this has not been proven in industry. Moreover, the carbon added in the DRP is embedded in the iron structure, resulting in a better reduction of the iron oxides in the REF.
- A lower carbon content in the iron results in a higher melting temperature, as shown in the ironcarbon phase diagram of Figure 1.5. Hence, a lower carbon content in the REF requires more electrical energy to melt the iron.

To conclude, producing iron using a DRP and REF is an innovative development introduced by TSN. To reduce the  $CO_2$  emissions as much as possible, the natural gas feed of the DRP must be completely substituted with green hydrogen. However, this results in 0% carbon in the DRI. Arguments are given concerning the need for carbon in iron and the benefits of adding this in the DRP instead of in the REF. Seeing that, it is extremely interesting to investigate what would happen if TSN would not completely switch to 100% hydrogen but would also use some natural gas in the DRP. Even though this would result in direct  $CO_2$  emissions, adding carbon could be more beneficial than operating with only hydrogen. Besides that, to become  $CO_2$  neutral, bio natural gas could be used instead of regular natural gas. The composition of the feed of the DRP will influence operating conditions such as the metallization and carburization of the DRI leaving the reactor and will also influence the total  $CO_2$ , energy, and material balance of the DRP. However, this thesis will only focus on the performance of the reactor of the DRP only. Hence, the following research question is established:

## What is the influence of the ratio of hydrogen to natural gas inserted in the direct reduced iron plant on the performance of the reactor?

To investigate this influence, a mathematical model of the reactor of the DRP is required for simulations. To make such a model, it is necessary to understand the processes involved in the DRP fully. Thus, the next chapter first gives an in-depth review of the literature regarding these processes. Then, this chapter investigates the models already made by researchers. The third chapter consists of the basis of design of the reactor and further explains the scope of the thesis. The fourth chapter is dedicated to all the modelling details of the reactor and validates the model. The fifth chapter consists of a sensitivity analysis using the created model, including the interpretation of the results. The last chapter concludes the thesis and provides recommendations for further research.

# $\sum$

## Literature review

To reduce the  $CO_2$  emissions of the steel industry, various programs have been launched all over the world [35]. In Europe, the Ultra Low  $CO_2$  Steelmaking (ULCOS) program was established in 2004 to reduce the  $CO_2$  emissions per ton of steel by 50% from its current best levels before 2050. In total, 48 companies from 15 European countries are members of ULCOS, including Tata Steel Europe. In Japan,  $CO_2$  Ultimate Reduction in Steelmaking process by innovative technology for cool Earth2050 (COURSE50) was launched in 2008. In South Korea, Pohang Iron and Steel Company (POSCO) have developed clean mechanism programs and innovative technologies to reduce greenhouse gases. The program was established in 2006. In the United States of America, the American Iron and Steel Institute (AISI) in collaboration with top universities in the field of metallurgy, have developed several technologies to reduce the  $CO_2$  emissions. Of all the programs, ULCOS is the most extensive.

As described above, lots of attention have been paid to reduce the  $CO_2$  emissions of the steel industry. In the last 100 years, various direct reduction technologies, which are able to reduce these emissions, have been developed [7]. Technologies differ in reducing agent, reactor type, capacity, and purpose. However, the focus of this study will be the gas-based shaft furnace direct technology. Multiple projects have been launched focusing on the development of making green steel using a shaft furnace. Hydrogen Breakthrough Ironmaking Technology (HYBRIT), Salzgitter Low  $CO_2$  Steelmaking (SALCOS) and earlier mentioned ULCOS are examples of these projects. Besides that, thousands of papers have been published about the reduction of iron oxides [57]. These papers cover the mechanisms, kinetics, and the influence of the reduction conditions on the reduction process. Moreover, lots of papers regarding the modelling of the DRP have been published. This chapter will give an in-depth review of the most relevant papers.

This chapter will first dive into the reduction process of iron ores. Second, the shaft furnace reduction technologies of HYL/ENERGIRON and MIDREX will be discussed. Then, the modelling of the DRP is divided into three scales: the pellet scale, the shaft furnace scale, and the plant scale. Each scale will be discussed in a separate paragraph. As explained earlier, this thesis will only focus on the modelling of the reactor. The modelling information of the total plant scale is included in the literature review to obtain a better understanding of how the reactor model could fit in a total plant model.

## 2.1. The reduction process

The composition of iron ores highly depends on the type of ore. It mainly consists of hematite ( $Fe_2O_3$ ) and a bit less of magnetite ( $Fe_3O_4$ ). Besides that, small amounts of limonite ( $2Fe_2O_3 \cdot 3H_2O$ ), siderite ( $FeCO_3$ ), and pyrite ( $FeS_2$ ) are found [52]. The mass percentages of iron in these components are 70%, 72.4%, 60%, 48.3%, and 46.6%, respectively. Moreover, iron ores always contain some gangue, which mainly exists in oxides of silicon, calcium, magnesium, and aluminium [91]. Ores are categorized by the overall mass percentage of iron. More specifically, high-grade ores have a mass percentage above 65%, medium-grade ores between 62-64%, and low-grade ores below 58% [52].

In general, the reduction of  $Fe_2O_3$  does not result directly in metallic iron (Fe), as shown in Figure 2.1. At temperatures above 570 °C,  $Fe_2O_3$  reduces to  $Fe_3O_4$ , which subsequently reduces to wüstite ( $Fe_{(1-x)}O$ ) followed by metallic iron. Wüstite is only thermodynamically stable at temperatures above 570 °C. Below this temperature it decomposes into Fe and  $Fe_3O_4$ . Wüstite is a complex non-stoichiometric oxide of iron. The stability area expands whenever the temperature increases. This is because not all places in the lattice are occupied by iron ions [94]. Therefore, the value of (1 - x) depends on the vacancies in the iron lattice. Moreover, iron can exist either in the oxidation state  $Fe^{2+}$  or  $Fe^{3+}$  in wüstite. Using a scanning electron microscope, Wagner [89] was able to identify that the wüstite grains have the composition of  $Fe_{0.95}O$  just before it reduces to iron. Moreover, this composition is widely applied in literature [31, 58, 62, 73, 74]. The reduction of iron oxide in the shaft furnace of a DRP is either by CO or H<sub>2</sub> at typical temperatures of 900 °C according to the following heterogeneous reaction equations [30, 42]:

$$3 \operatorname{Fe}_{2}O_{3}(s) + H_{2}(g) \longrightarrow 2 \operatorname{Fe}_{3}O_{4}(s) + H_{2}O(g)$$

$$\Delta H_{900^{\circ}C} = -6.5 \operatorname{kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = -106 \operatorname{kJ mol}^{-1}$$
(2.1)

$$Fe_{3}O_{4}(s) + \frac{16}{19}H_{2}(g) \longrightarrow \frac{60}{19}Fe_{0.95}O(s) + \frac{16}{19}H_{2}O(g)$$
(2.2)  

$$AH_{access} = 48 \text{ kJ mol}^{-1}$$

$$\Delta G_{900^\circ C} = -30.7 \,\mathrm{kJ}\,\mathrm{mol}^{-1}$$

$$Fe_{0.95}O(s) + H_{2}(g) \longrightarrow 0.95 Fe(s) + H_{2}O(g)$$

$$\Delta H_{900^{\circ}C} = 17 \text{ kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = 5.31 \text{ kJ mol}^{-1}$$
(2.3)

$$3 \operatorname{Fe}_{2} \operatorname{O}_{3}(s) + \operatorname{CO}(g) \longrightarrow 2 \operatorname{Fe}_{3} \operatorname{O}_{4}(s) + \operatorname{CO}_{2}(g)$$

$$\Delta H_{900^{\circ}C} = -41 \operatorname{kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = -104 \operatorname{kJ mol}^{-1}$$
(2.4)

$$Fe_{3}O_{4}(s) + \frac{16}{19}CO(g) \longrightarrow \frac{60}{19}Fe_{0.95}O(s) + \frac{16}{19}CO_{2}(g)$$
(2.5)  

$$\Delta H_{900^{\circ}C} = 20 \text{ kJ mol}^{-1}$$
  

$$\Delta G_{900^{\circ}C} = -28.4 \text{ kJ mol}^{-1}$$

$$Fe_{0.95}O(s) + CO(g) \longrightarrow 0.95 Fe(s) + CO_2(g)$$

$$\Delta H_{900^{\circ}C} = -17 \text{ kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = 7.67 \text{ kJ mol}^{-1}$$
(2.6)

As can be inferred from the above equations, the total reduction from hematite to metallic iron by  $H_2$  is endothermic and exothermic in the case of reduction by CO:

$$Fe_{2}O_{3}(s) + 3 H_{2}(g) \longrightarrow 2 Fe(s) + 3 H_{2}O(g)$$

$$\Delta H_{900^{\circ}C} = 65 \text{ kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = -134 \text{ kJ mol}^{-1}$$

$$Fe_{2}O_{3}(s) + 3 CO(g) \longrightarrow 2 Fe(s) + 3 CO_{2}(g)$$

$$\Delta H_{900^{\circ}C} = -36 \text{ kJ mol}^{-1}$$

$$\Delta G_{900^{\circ}C} = -112 \text{ kJ mol}^{-1}$$
(2.7)



Figure 2.1: Binary Fe-O stability system [72].

#### 2.1.1. Thermodynamics

To describe the thermodynamics of the reduction of iron oxides by  $H_2$  and CO, the Baur-Glässner diagram is useful, as shown in Figure 2.2. The diagram describes the thermodynamic stability areas of iron oxides based on the temperature and the Gas Oxidation Degree (GOD), which is defined as:

$$GOD_{H_2} = \frac{H_2O}{H_2O + H_2}; \qquad \qquad \text{for hydrogen}$$
(2.9)

$$GOD_{CO} = \frac{CO_2}{CO_2 + CO};$$
 for carbon monoxide (2.10)

The gas oxidation degree represents the reduction force of the gas composition. A lower gas oxidation degree results in a higher reduction force. The figure shows that at temperatures below 570 °C, wüstite is thermodynamically unstable. For the reduction of any iron oxide by hydrogen, it is always thermodynamically favourable to reduce at the highest possible temperature. In the case of reduction by carbon monoxide, reducing magnetite to wüstite (above 570 °C) is thermodynamically favourable at higher temperatures. However, the reduction of wüstite towards metallic iron is thermodynamically favourable at lower temperatures. Comparing the thermodynamics of hydrogen and carbon monoxide, at temperatures higher than 810 °C, the reduction potential of hydrogen is larger. Below 810 °C, carbon monoxide has a larger reduction potential.



Figure 2.2: Baur-Glässner diagram for the  $Fe-O-H_2$  and Fe-O-C system including the Boudouard equilibrium for 1 bar and a carbon activity of 1 [72].

The figure also gives the Boudouard equilibrium line at 1 bar with a carbon activity of 1. The Boudouard reaction is given below [30]. In fact, this line depends on the pressure and carbon activity. The carbon in this reaction can either be in the form of soot or cementite ( $Fe_3C$ ), which will be further explained in Paragraph 2.2. For a gas mixture containing CO and CO<sub>2</sub>, the Boudouard equilibrium line separates the diagram into two areas. Below the line, carbon deposition occurs, which may impede the reduction process. Towhidi and Szekely [85] have found that carbon deposition by the Boudouard reaction does not occur at temperatures above 900 °C and that the maximum deposition occurs at temperatures from 500 to 600 °C. Moreover, carbon deposition is catalysed by metallic iron. Looking at the reduction by carbon monoxide in Figure 2.2, the Boudouard equilibrium line crosses the wüstite-iron reduction line at 700 °C and the magnetite-wüstite reduction line at 650 °C. Thermodynamically, this means that reducing wüstite to iron below 700 °C is impossible because carbon monoxide reacts to carbon and carbon dioxide. Similarly, the reduction of magnetite to wüstite is thermodynamically impossible below 650 °C. However, the kinetics of the Boudouard reaction is slow compared to the kinetics of the reduction reactions, which makes reduction below these temperatures possible in reality [30].

$$2 \operatorname{CO}(g) \longleftrightarrow \operatorname{C}(s) + \operatorname{CO}_2(g) \qquad \qquad \Delta H_{900^\circ C} = -135 \, \text{kJ mol}^{-1} \qquad (2.11)$$

#### 2.1.2. Kinetics

The iron ore pellets reduced in the shaft furnace consist of multiple small grains. The small grains consist mainly of hematite. The pellets are approximately spherical and generally have a diameter of 7 to 15 mm [8]. Zhang et al. [100] have experimentally concluded that the size of the grains is on the scale of microns and are irregular shaped. The typical size of a grain, reported in literature, is  $20 \,\mu\text{m}$  [8, 60]. Assuming the temperature is higher than 570 °C, each of the pellets is reduced in three steps. Gas-solid reactions enable the reduction. The kinetics involved depends on various transport phenomena steps [12, 24, 29, 41]:

- 1. Mass transfer of the gaseous reactants (H<sub>2</sub> and CO) from the bulk gas stream through the gas film to the outer surface of the solid pellet.
- 2. Diffusion of the gaseous reactants through the pores of the pellet.
- 3. Adsorption on the reaction surface of the pellet.

- 4. Chemical reaction, removing oxygen from the iron oxide to form either  $H_2O$  or  $CO_2$ .
- 5. Simultaneously desorption of gaseous products from the pellets' surface and solid-state diffusion of solid reaction products. These solid products nucleate and grow nuclei.
- 6. Diffusion of the gaseous products through the pores towards the outer surface of the pellet.
- 7. Mass transfer of the gaseous reactants through the gas film back into the bulk gas stream.

The slowest transport phenomenon is called the rate-limiting step and depends on many variables. The three most common ratelimiting steps are graphically explained in Figure 2.3, as a function of the concentration of the gaseous reactant  $C_A$  along the radius of the pellet.  $C_{Ag}$  represents the concentration of the gaseous reactant in the bulk gas flow.  $C_{As}$  is equal to the concentration of gaseous reactant on the exterior surface of the pellet.  $C_{Ac}$  is used to describe the equilibrium concentration of the reaction. Note that Figure 2.3 depicts the pellet according to the Unreacted Shrinking Core Model (USCM), which is explained in Paragraph 4.2.

In situation (a), the mass transfer through the laminar gas film is the rate-limiting step. Fick's law of diffusion describes the driving force for mass transfer depending on the concentration difference between the bulk flow and the reaction surface [72].

In situation (b), mass transfer by diffusion through the pores of the pellet is the rate-limiting step. This occurs whenever the outer surface of the iron ore pellet gets reduced and forms a porous iron layer. In the case of slow diffusion of the gaseous reactant through this porous layer, the overall reaction is rate-limited by the diffusion through the pores.

Situation (c) describes the chemical reaction rate-limited situation. This occurs whenever the chemical reaction rate is slower than the mass transfer rates. The reaction rate depends on the type of iron oxide, the interface of the reaction, the temperature, and the concentration of the reducing gas [72].

Situations (a) and (b) are both mass transfer limited, whereas (c) is chemical reaction limited. Whenever the total reaction is mass transfer limited, the chemical reaction rate occurs faster than the transfer of reactants and products. The rate of chemical reactions increases exponentially with temperature. On the other hand, mass transfer only slightly depends on temperature. Hence, in general, mass transfer is only the rate-limiting step at high temperatures [28].

The above-described transport phenomena steps are accompanied by external convective heat transfer between the gas stream and the surface of the solid pellet. Moreover, inside the pellet, heat is mainly transported by conduction. Valipour [86] mathematical studied the isothermal and non-isothermal reduction of hematite pellets by hydrogen, carbon monoxide, and a mixture of both. He concluded that no radial temperature distribution inside the pellet exists during the reduction process. Hence, heat transfer inside the pellet is very fast due to the high conductivity of the material. The external convective heat transfer is also very efficient due to the high gas velocity at which the shaft furnace operates [30]. Thus, heat transfer will not limit the reduction process of the pellets.



Figure 2.3: Graphical presentation of the possible rate-limiting steps of the reduction of hematite. a) limited by mass transfer through the gas film, b) limited by pore diffusion, c) limited by chemical reaction [41].



Figure 2.4: Time required to attain a certain degree of reduction for different reducing gas compositions at 800 °C and 1 atm total pressure. (a), (b), (c), (d) shows 40, 50, 60, 75% total reduction degree, respectively [76].

Figure 2.5: Reduction ratio of the reduction rate by a mixture of  $H_2$  / CO to the rate of reduction by pure CO at different temperatures [84].

The reduction kinetics depend on various conditions like temperature, pressure, reduction degree, gas composition, and morphology. Hence, the rate-limiting step changes along the reduction process. In the beginning, the reactions occur at the pellet's outer surface, resulting in a chemical reaction rate-limited situation. As the reduction proceeds towards the centre of the pellet, pore-diffusion gets more and more important and eventually becomes the rate-limiting step. Towidi and Szekely [84] experimentally studied the reduction rate of hematite pellets by pure hydrogen and a mixture of hydrogen and carbon monoxide at a temperature range of 600–1234 °C. They concluded that for conversions lower than 50%, the chemical reaction is the rate-limiting step. For conversions of 50–90%, pore diffusion becomes the rate-limiting step. However, the exact values depended on the temperature, pellet size, and gas composition. Therefore, the reduction is generally mixed rate-limited [33].

Various researchers have also investigated which reduction step from hematite to iron is the slowest step [57]. Reduction parameters such as temperature, gas composition, and raw material determine the type of iron formed. Whenever wüstite reduces (above 570 °C) and forms a dense iron layer, the gaseous reactants must diffuse through the dense iron layer. This result in much slower kinetics. Hence, the reduction from wüstite to iron is the slowest step.

The thermodynamics of this slowest reduction step, from wüstite to iron, is favourable at higher and lower temperatures by hydrogen and carbon monoxide, respectively. On the other hand, the kinetics of the reduction process is always faster at higher temperatures. Thus, reduction by hydrogen is always the most favourable at higher temperatures. In the case of carbon monoxide, it is a battle between thermodynamics and kinetics. In addition, the diffusion of carbon monoxide is slower than hydrogen as a consequence of higher viscosity and larger molecule size [72]. Many papers conclude that hydrogen reduction is faster than carbon monoxide, as shown in Figures 2.4. Even though thermodynamics at 800 °C favours reduction by carbon monoxide, the reduction time while using more hydrogen is lower in all cases because hydrogen diffusion is much faster than carbon monoxide. This implies that the diffusion rate is more important than the thermodynamic driving force [76, 102]. Towhidi and Szekely [84] also concluded in their research that at temperatures below 780 °C, the reduction by pure hydrogen is 2 to 3 times faster than by pure carbon monoxide. At temperatures above 780 °C, the reduction is 8 to 10 times faster, as shown in Figure 2.5.

Researchers also investigated the effect of pressure on the reduction rate. They concluded that the absolute pressure does not affect the reduction rate when maintaining the partial pressure of the reducing gas constant (constant molar flow) [29, 37]. However, when increasing the absolute pressure in conjunction with the partial pressure of the reducing gas, the reduction rate increases [67].

Various studies have investigated the influence of grain size and particle size on the reducibility. When having larger grains, the pore diffusion distance increases, resulting in a more significant diffusion time and consequently a longer reduction time. This is confirmed by Teplov [82], during an experiment on the reduction of magnetite with hydrogen at temperatures between 300-570 °C with grain sizes between 1 and 160  $\mu$ m. Whenever the particle size increases, the specific area decreases. Hence, the reduction time increases because reduction starts at the outer area and the diffusion distance to the centre of the pellet increases [99]. Corbari and Fruehan [14] investigated the reduction of iron oxides to wüstite using a mixture of CO/CO<sub>2</sub> at 1000 °C. They investigated pellets in the range of 110  $\mu$ m to 3 mm. The reduction rates of pellets between 110 and 508  $\mu$ m are similar, which implies that gas diffusion through the pores is fast enough and not the rate-limiting step for this situation. The reduction rate decreases at pellets larger than 500  $\mu$ m.

Besides the grain size and pellet size, the porosity also has an essential effect on the reduction time [72]. Higher porosity results in better permeability, allowing better diffusion of the reducing gas towards the reaction area. Since pore diffusion can be the rate-limiting step, porosity is an important factor for the reduction rate. Literature supports this statement. For instance, Skorianz [69] concluded that iron oxides with higher porosity showed the best reducibility.

## 2.2. Reduction technologies

At the moment, 72.4% of all DRI is produced by shaft furnaces [49]. As mentioned earlier, two direct reduction technologies using a shaft furnace are commercially available: MIDREX and HYL/ENERGIRON. MIDREX is responsible for 79.6% of all produced DRI in a shaft furnace, HYL/ENERGIRON for the remainder. These technologies can produce DRI in three different product forms: Cold Direct Reduced Iron (CDRI), Hot Briquetted Iron (HBI), and Hot Direct Reduced Iron (HDRI), as shown in Figure 2.6. CDRI is DRI cooled in the cooling zone of the shaft furnace. HBI and HDRI are both not cooled in the shaft furnace but discharged hot. HBI is afterwards pressed into dense briquettes that are much less porous and, therefore, much less likely to re-oxidize. CDRI and HBI are mostly produced to store or transport to other production sites. HDRI is transported directly to the next stage in the production process of steel making on the same production site, resulting in lower electrical energy consumption due to the sensible heat provided. Since TSN will use a REF on the same production site as the DRP, HDRI will be produced. The MIDREX and the HYL/ENERGIRON reduction technologies will be discussed in this paragraph, along with their developments and required modifications to produce green steel.



Figure 2.6: Possible process products. From left to right: CDRI, HBI, HDRI [30].

## 2.2.1. MIDREX

The MIDREX process scheme is given in Figure 2.7. As can be seen in this figure, natural gas is reformed by a MIDREX reformer. This reformer is a dry reformer using hundreds of alloy tubes filled with a nickel catalyst [30]. The reforming reaction is given by [93]:

$$CH_4(g) + CO_2(g) \longrightarrow 2CO(g) + 2H_2(g)$$
  $\Delta H_{1000^\circ C} = 258.9 \text{ kJ mol}^{-1}$  (2.12)

Since natural gas can contain some sulphur, the catalyst can be poisoned over time. After reforming, the produced hydrogen and carbon monoxide flow towards the shaft furnace. Before the gas enters

the shaft furnace, oxygen and natural gas can be injected into the combustion chamber for the partial oxidation of natural gas. This can be done to increase the temperature and to produce reducing gas, according to the reaction below [16]. To enhance carburization, natural gas can be injected with less oxygen than required for partial oxidation. The remainder of natural gas will enable reaction 2.19 as explained later.

$$CH_4(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + 2H_2(g)$$
  $\Delta H_{727^\circ C} = -22.1 \text{ kJ mol}^{-1}$  (2.13)

Figure 2.7: MIDREX process scheme with hydrogen addition [64]. Figure 2.8: MIDREX H<sub>2</sub> process scheme with pure hydrogen [64].

Afterwards, pure hydrogen can be added to reduce the production of CO<sub>2</sub>. In the shaft furnace, the reducing gas reduces the iron ore pellets, producing water and carbon dioxide, which leaves the shaft furnace at the top. The top gas mainly contains water and carbon dioxide. Since the conversion does not reach 100%, the top gas also contains hydrogen, carbon monoxide, and natural gas. The water is separated from this stream by the top gas scrubber. Afterwards, a fraction of the stream will be burned by adding air and possibly natural gas to supply the heat of the former. The remainder will be compressed and sent to the reformer, with the addition of natural gas, for another pass through the system. The MIDREX plant uses heat recovery since it preheats the streams entering the reformer by the flue gas. In fact, Figure 2.7 is not complete. In reality, the shaft furnace does have the option of cooling the reduced iron in the lower part of the shaft furnace to produce CDRI, similar to the HYL III shaft furnace shown in Figure 2.9. The cooling is mostly done by injecting cold natural gas, which also enhances carbon deposition.

The hydrogen content in the reducing gas of the MIDREX plant without adding pure hydrogen is typically 55-58% [92]. A maximum of 30 vol% of pure hydrogen can be added to the MIDREX scheme shown in Figure 2.7. At higher percentages, the MIDREX plant can be modified towards the so-called "MIDREX H<sub>2</sub> plant", shown in Figure 2.8. This plant either substitutes the reformer with a gas heater or repurposes the reformer as a gas heater. On September 16, 2019, ArcelorMittal and MIDREX announced their corporation to build the first commercialized MIDREX plant in Germany, operating with 100% hydrogen as the reducing gas [50]. This demonstration plant will produce 100,000 tons of DRI per year in the coming years.

### 2.2.2. HYL/ENERGIRON

Tenova HYL has developed several gas-based direct reduction plants with external and in-situ reforming. The HYL III is the most recent developed plant operating with an external reformer, as depicted in Figure 2.9. This external reformer uses a nickel catalyst and reforms the natural gas according to the well-known steam methane reforming reaction [30]:

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$
  $\Delta H_{900^\circ C} = 224 \text{ kJ mol}^{-1}$  (2.14)

After the reformer, the unreacted water will be separated. Subsequently, the gas will be heated in the gas heater by burning the desired fuel (most likely hydrogen or natural gas). Afterwards, the reducing gas will enter the shaft furnace to reduce the iron ore pellets. Water will be separated from the stream, leaving the top of the shaft furnace. The remaining stream will be split. A fraction of this stream is used to deliver heat to the gas heater by burning it. The carbon dioxide produced by this burning process is not pure enough to use directly for CCUS. Hence, it is called a "non-selective" CO<sub>2</sub> emission. The other fraction of the stream will go to a compressor and subsequently to the carbon dioxide removal plant (amine-based absorption [81]). The separated carbon dioxide by this removal plant is pure enough to make it directly suitable for CCUS and thus called a "selective" CO<sub>2</sub> emission. The remaining stream, containing mostly hydrogen, is recycled. As explained in the section on the MIDREX technology, this technology also has the opportunity to cool the DRI in the cooling zone of the shaft furnace.



Figure 2.9: HYL III process scheme [30].

The hydrogen content in the reducing gas of the HYL III is typically 84 - 86% [92]. In the 1990s, Tenova HYL experimented with hydrogen contents of more than 90% in a pilot plant in Hysla Monterrey [17]. This led to the development of the zero reformer configuration of the plant, which will be discussed next.

Tenova HYL's newest and most competitive plant configuration is based on in-situ reforming instead of an external reformer. In 2006, Tenova and Danieli collaborated to design and construct a gas-based direct reduction plant under the name ENERGIRON. The ENERGIRON Zero Reformer (ZR) with the addition of pure hydrogen is shown in Figure 2.10. This process is explained first by using only natural gas as the feed. The natural gas will first be humidified to ensure the reforming (by formula 2.14) in the shaft furnace. Afterwards, the gas will be heated in the process gas heater by any desired fuel. Before the gas enters the shaft furnace, oxygen can be injected into the combustion chamber for the partial oxidation of natural gas. The gas entering the shaft furnace still contains a high amount of natural gas, which will reform in the presence of formed iron. The iron acts as a continuous and renewable catalyst in the reforming process. The hot top gas will be cooled down using a recuperator to condense the water. The heat is used in the carbon dioxide removal plant, and the water is used in the humidifier. The process gas heater will burn a fraction of the remaining stream. The remainder will go to the carbon dioxide removal plant. The stream leaving the carbon dioxide removal plant, rich in hydrogen and carbon monoxide, will be added to the natural gas feed. At this point, pure hydrogen can also be injected to reduce the plant's carbon emissions. Similarly, as in the HYL III plant, the plant contains selective and non-selective CO<sub>2</sub> emissions. Moreover, it also has the opportunity to use the cooling zone.

The hydrogen content in the reducing gas of the ENERGIRON ZR technology is similar to the HYL III, but it has the flexibility to add pure hydrogen to the process. Whenever the feed contains more than 80% of hydrogen (on an energy basis), the process scheme can be modified, as can be seen in Figure 2.11 [101]. In this process,  $CO_2$  emissions are strongly reduced, making the removal plant unnecessary. Besides that, the humidifier can be bypassed since less water is required to reform the natural gas. On December 17, 2020, Tenova announced the collaboration with Salzgitter Flachstahl GmbH to build a 100% hydrogen demonstration plant named "µDRAL" [79]. This plant is part of the



H<sub>2</sub>O TOP GAS HEAT REMOVAL RECUPERATOR PG COMPRESSOR COOLING REMOVAL REMOVAL HUMDIFIER HEATER HEATER HUMDIFIER DRP TAIL GAS FUEL

Figure 2.10: ENERGIRON process scheme with hydrogen addition [101].



SALCOS project and will be built in Germany. The ENERGIRON plant will have a nominal production of 100 kg per hour and will show flexibility in terms of reducing gas. Another ENERGIRON pilot plant with a capacity of 100 kg per hour is built as a part of the HYBRIT project. This plant is located in Sweden. In June 2021, it completed a test production of DRI using 100% hydrogen, which shows the feasibility of making green steel [92].

## 2.2.3. Comparison of MIDREX and ENERGIRON

This section compares the two most competitive reduction technologies: MIDREX and ENERGIRON. Typical operating conditions are shown in Table 2.1. However, some aspects require clarification. The hydrogen content entering the shaft furnace of an ENERGIRON plant is higher than in the case of a MIDREX plant, making this technology intrinsically more suitable for operating with pure hydrogen injection. The carbon content of both technologies is highly dependent on the operating conditions. Due to a higher natural gas composition of the reducing gas at the inlet of the shaft furnace, typically, more carbon is formed in the ENERGIRON process. Moreover, the high temperature in the shaft furnace favours the diffusion of carbon into the iron matrix and the precipitation of cementite (Fe<sub>3</sub>C). Carbide formation in the form of cementite is more beneficial than soot since it reduces the reactivity of the produced DRI to re-oxidize. Furthermore, it is embedded in the DRI, making it advantageous for the REF process. The MIDREX process has less intensive operating conditions (pressure and temperature), resulting in a larger shaft furnace size, which is safer. Besides that, the MIDREX process is an older and, therefore, more mature technology compared to the ENERGIRON process.

|                          | MIDREX                            | ENERGIRON                            |
|--------------------------|-----------------------------------|--------------------------------------|
| Temperature              | 850-950 °C                        | 930-1050 °C                          |
| Pressure                 | 1-2 atm                           | 6-8 atm                              |
| Hydrogen content         | 55-58%                            | 84-86%                               |
| Carburization            | Worse                             | Better                               |
| CO <sub>2</sub> emission | Only non-selective                | Selective and non-selective          |
| Reformer                 | External                          | In-situ                              |
| Catalyst                 | Sensitive to poisoning by sulphur | Continuous renewing                  |
| Flexibility              | Reformer and shaft furnace sepa-  | Reformer and shaft furnace combined, |
|                          | rated, increasing flexibility     | decreasing flexibility               |
| Shaft furnace size       | Larger                            | Smaller                              |
| Safety                   | Safer                             | Less safe                            |
| Maturity                 | More mature                       | Less mature                          |

Table 2.1: Comparison of the MIDREX and ENERGIRON technologies [30].

## 2.3. The pellet model

Besides experimental and analytical studies on the reduction behaviour of hematite pellets, researchers have also put a lot of effort into mathematical modelling. Generally, two models have been developed: the Unreacted Shrinking Core Model (USCM) and the Grain Based Model (GBM). Various types of each model are developed, distinguished by different assumptions. These assumptions are made based on the state of the reduction process, isothermality, reducing gas compositions, and the number of reduction steps. Moreover, combinations of the USCM with the GBM have also been developed.

#### 2.3.1. Unreacted Shrinking Core Model

The USCM has been developed for one to three reduction steps and was first proposed by Levenspiel [41]. This model assumes that the reactions occur strictly topochemical, which means that the reactions only occur at the sharp round interface of the unreacted shrinking core with the gaseous reducing gas. The USCM assumes that the seven transport phenomena steps, described in Paragraph 2.1, occur succes-However, steps 3 and 5 are mostly ignored. sivelv. This results in a resistances in series model, similar to the one classically used to describe electrical or thermal resistances in series. The model is only valid when the overall reaction is rate-limited by the inward pore diffusion of the gaseous reactants, as shown in the situation (b) of Figure 2.3 [97]. Therefore, the model will only be valid for very dense pellets.

The USCM with one reduction step is the simplest model, shown in Figure 2.3. This model assumes that the reduction of hematite results directly in iron. Whenever the reaction proceeds, the unreacted core shrinks and forms an inert product called ash. An example of the reaction rate equation of reaction i for this model is given below [1]. Since only one reduction step is taken into account in this model, reaction i can either be reaction (2.7) or (2.8).



Figure 2.12: Schematic image of the USCM using three reduction steps [34].

$$r_{i} = \frac{\nu_{i} M_{s} a_{s} (c_{i,eq} - c_{i,\infty})}{\frac{r_{o}^{2}}{r_{uc}^{2} k_{i}} + \frac{1}{k_{q}} + \frac{r_{o} (r_{o} - r_{uc})}{D_{eff} r_{uc}}}$$
(2.15)

Experiments have shown that the reduction of hematite towards iron occurs in three steps, even when the pellet is really dense [44]. An USCM model using three reduction steps has been developed to mimic this feature, as shown in Figure 2.12. The denser the pellet, the narrower the thickness of each layer. Similar to the USCM with one reduction step, the overall reaction is described as a sequence of steps assuming the reactions occur topochemically. First, the reducing gas must penetrate through the gas film and iron layer towards the first reaction front (wüstite to iron). A fraction of the reducing gas reacts, and the remainder flows further inwards through the wüstite layer towards the second reaction front (magnetite to wüstite). At this interface, the same mechanism occurs. The remaining reducing gas flows subsequently through the magnetite layer towards the unreacted hematite core to react. The gaseous products follow the same path but in the opposite direction and sequence. The model depends on multiple kinetic reaction constants, diffusion coefficients, and mass transfer coefficients. These parameters are determined experimentally.

#### 2.3.2. The grain based model

The USCM shows good agreement with experimental data in certain situations, for example in [36]. However, the model assumes that the reactions proceed topochemical, which is a critical flaw. In fact, the chemical reaction and gaseous diffusion proceed simultaneously in a porous pellet. Due to this limited assumption, the USCM becomes a kind of curve-fitting method that cannot be used in situations outside those used in the experiments to determine the kinetic parameters. On the other hand, when pore diffusion is the rate-limited step, the USCM is valid. This is most likely only the case when having a really dense pellet, which in general is not the case.

More complex grain-based models are developed to incorporate the simultaneous chemical reaction and gaseous diffusion in a pellet. These models assume that the porous pellets contain non-porous small spherical grains of hematite. These grains are so small (typically  $20 \,\mu$ m) that the diffusion time through the grains is neglected. The reactions occur at the gas-solid interface of the grains. Researchers incorporated the three reduction steps of hematite to iron into the grain model, as shown in Figure 2.13. Besides that, some researchers even considered the complex morphological development of the reduction process of the pellets in their model [30, 62]. The governing equations of the reduction of hematite to iron, using the GBM, depend on all further assumptions. However, these governing equations always result in a set of coupled partial differential equations. One example of these equations for one reduction step in dimensionless form is given below [54].

$$\frac{1}{y^2}\frac{\partial}{\partial y}(y^2\frac{\partial a}{\partial y}) = \frac{\sigma^2 r^{\star 2}a}{1+6\sigma_g^2(r^{\star}-r^{\star 2})}$$
(2.16)

$$\frac{\partial r^{*}}{\partial \theta_{p1}} = -\frac{a}{1 + 6\sigma_{g}^{2}(r^{*} - r^{*2})}$$
(2.17)

Where,

 $\sigma = r_o \sqrt{F_g k(1-\epsilon)/D_{eff} r_{g,ini}} = \text{Reaction modulus for the pellet [-]}$   $\sigma_g = \sqrt{kr_{g,ini}/2D_sF_g} = \text{Reaction modulus for the grains [-]}$   $\theta_{p1} = kc_{i,\infty}M_st/\rho_sr_{g,ini} = \text{Dimensionless time for the grain model [-]}$   $a = c_i/c_{i,\infty} = \text{Dimensionless gas concentration [-]}$  $r^* = r_{g,uc}/r_{g,ini} = \text{Dimensionless unreacted radius in the grain [-]}$ 



Figure 2.13: Schematic figure of the grains inside a pellet. Each grain is reduced in three steps [86].

Exact analytic solutions of these equations only exist for situations that are totally rate-limited by one specific transport phenomenon. Hence, a general analytical solution does not exist. Therefore, a complicated numerical method is required to solve these equations, which results in a long calculation time. Sohn [71] proposed approximate solutions to the governing equations to reduce the calculation time. This law is called "the law of additive reaction times" which states that the time required to reach a
specific conversion is approximately the sum of the time required to reach the same conversion of each individual transport phenomenon step in the absence of the other steps. For example, when looking at a pellet without external mass transfer resistance, the time required to reach a specific conversion is approximately the sum of the time required to reach the same conversion when the chemical reaction is the rate-limiting step and the time required to reach the same conversion when pore diffusion is the rate-limiting step, as graphically shown in Figure 2.14. This law makes it possible to represent a mixed rate-limited system in an approximate analytical solution, which generally is the case for the reduction of hematite pellets. The approximate solution represents the exact solution quite well, as can be found in [71].



Figure 2.14: Graphical representation of the law of additive reaction times in the case of a pellet without external mass transfer resistance [71].

# 2.4. The shaft furnace model

The behaviour of the shaft furnace is characterized by a combination of chemical reactions, heat transfer, and mass transfer, making it quite complex. Luckily, many different mathematical shaft furnace models have been developed by researchers, as shown in Tables 2.2 and 2.3. The MIDREX and EN-ERGIRON shaft furnaces themselves are identical, although the geometry can be different. The basic description included in all these models is that of an axisymmetric counter-current moving bed consisting of porous pellets, while the gas ascent and solid descent. However, the models differ in:

- The number of dimensions. These models differ from simple 1D models to comprehensive 2D Computational Fluid Dynamics (CFD) models. The 2D models considered variations along the height and radius of the shaft furnace.
- The solid- and gas composition. Natural gas mainly consists of methane (CH<sub>4</sub>), thus included in some models. The same counts for nitrogen (N<sub>2</sub>), which can be found in normal outside air.
- · The pellet model.
- The number of reduction steps. Models that include one reduction step only consider the reduction from hematite to iron. Models that include two reduction steps also consider the intermediate wüstite stage (mentioned as FeO in the tables). Models that include three reduction steps also include magnetite.
- The presence of the cooling and transition zones in the shaft furnace, next to the reduction zone.
- The supplementary reactions besides the six reduction equations (2.1 2.6). These reactions are the earlier mentioned Boudouard reaction (2.11), dry reforming (2.12), and steam methane reforming (2.14). Besides that, three other supplementary chemical reactions are taken into account in some models: water-gas shift (2.18), methane deposition (2.19), and coal gasification (2.20). All reaction equations are given below [30, 53]. Both water-gas shift and methane deposition are catalysed by the formed iron in the shaft furnace.
- · The types of heat transfer.
- The inclusion of pressure drop.
- The manner of validation of the model.

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g) \qquad \Delta H_{900^\circ C} = -33 \text{ kJ mol}^{-1} \qquad (2.18)$$

$$CH_4(g) \longrightarrow C(s) + 2H_2(g)$$
  $\Delta H_{900^\circ C} = 89 \text{ kJ mol}^{-1}$  (2.19)

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$
  $\Delta H_{25^{\circ}C} = 131.1 \text{ kJ mol}^{-1}$  (2.20)

In general, one can conclude that 2D models show more accurate results than 1D models. Moreover, all solids and gases (except  $N_2$ ) play a role in the reactions of the reactor. Besides that, the grain model and three reduction steps result in the best representation of the pellet behaviour. Furthermore, adding the cooling and transition zone, more supplementary reactions, more types of heat transfer, and the pressure drop depict the reactor more accurately.

Nouri et al. [54] & Rahimi and Nikisar [60, 61] both simulated the shaft furnace using the GBM and the USCM. Nouri et al. concluded that the GBM describes the solid conversion more accurately. Rahimi and Nikisar stated that the GBM and the USCM forecast comparable outcomes for the shaft furnace when pore diffusion is the rate-limiting step. This happens when the pellet size is large. Thus, in a moving bed composed of relatively large pellets, the USCM might be as accurate as the GBM. Contradictory, increasing the pellet porosity will result in faster diffusion. As a consequence, the USCM results in substantial inaccuracies. Besides that, Nouri et al. discovered that increasing the reducing gas flow rate results in an increase in solid conversion, which they attributed to a greater reducing gas concentration near the solid input. Moreover, they concluded that a lower gas oxidation degree results in better reduction. This result is in agreement with Figure 2.2.

Parisi and Laborde [56] developed the first model to satisfactorily simulate two MIDREX shaft furnaces. However, the kinetic and diffusion constants for each MIDREX shaft furnace were adjusted to get the right results. This implies the model is not able to simulate other operating conditions without changing the kinetic and diffusion constants.

Ranzani da Costa et al. [62] constructed a two-dimensional stationary model, named "REDUCTOR". to simulate the reduction zone of a counter-current reactor using only hydrogen. This model uses the finite volume approach for numerical solutions. Using Sohn's law of additive reaction times, a pellet submodel was incorporated into the shaft furnace model to replicate the three reduction steps with the GBM. In fact, this pellet submodel has been developed by Wagner [89] and incorporates the morphological structure changes during the reduction process, which are established during experiments. Hamadeh et al. [30, 31] further developed the "REDUCTOR" model by including all relevant gases and supplementary reactions. This model was developed for the ULCOS program. As can be seen in Tables 2.2 and 2.3, it is the most comprehensive model published so far. Moreover, they could accurately simulate two different MIDREX shaft furnaces without changing any diffusion or kinetic coefficient. To accurately simulate the ENERGIRON shaft furnace, they had to change just one kinetic parameter because the kinetic parameter was not valid at the higher operating pressure of the ENERGIRON shaft furnace. This implies that the model can accurately simulate different operating conditions. The temperature and composition map of a MIDREX and an ENERGIRON shaft furnace simulation are shown in Figures A.1 and A.2. Both shaft furnaces produce CDRI. Based on Figure A.1 they were able to divide the MIDREX shaft furnace into eight different zones, as shown in Figure 2.15

| Reference                    | Dimensions | Solids   | Gases   | Pellet model | Reduction steps | Cooling & transition |
|------------------------------|------------|--|---|--------------|-----------------|----------------------|
|                              |            |  |   |              |                 | zones                |
| Shams and Mozeni [68]        | 1D         | Fe <sub>2</sub> O <sub>3</sub> , FeO, Fe, C                                  | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> | USCM         | 2               | yes                  |
| Parisi and Laborde [56]      | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe  | $H_2$ , CO, $H_2$ O, CO <sub>2</sub>                                    | USCM         | 1               | no                   |
| Valipour and Saboohi [87]    | 2D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe    | $H_2$ , CO, $H_2$ O, CO <sub>2</sub>                                    | USCM         | 3               | no                   |
| Alamsari et al. [3, 4]       | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe    | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , $N_2$          | USCM         | 3               | yes                  |
| Alhumaizi et al. [5]         | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe, C | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , $N_2$          | USCM         | 3               | yes                  |
| Ranzani da Costa et al. [62] | 2D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe    | $H_2, H_2O$   | GBM          | 3               | no                   |
| Nogare et al. [53]           | 2D         | $Fe_2O_3$ , FeO, Fe, C   | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , $N_2$          | USCM         | 2               | no                   |
| Nouri et al. [54]            | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe  | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , $N_2$          | GBM & USCM   | 1               | no                   |
| Rahimi and Nikisar [60, 61]  | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe    | $H_2$ , CO, $H_2$ O, CO <sub>2</sub>                                    | GBM & USCM   | 3               | no                   |
| Zugliano et al. [101]        | 2D         | $Fe_2O_3$ , FeO, Fe, C   | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , $N_2$          | USCM         | 2               | yes                  |
| Hamadeh et al. [30, 31]      | 2D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe, C | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> | GBM          | 3               | yes                  |
| Béchara et al. [8, 9]        | 1D         | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeO, Fe, C | $H_2$ , CO, $H_2$ O, CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> | GBM          | 3               | yes                  |

Table 2.2: Summary of the most relevant mathematical models of the shaft furnace (1).

Table 2.3: Summary of the most relevant mathematical models of the shaft furnace (2).

| Reference                    | Supplementary reactions        | Heat contribution               | Pressure drop | Validation             |
|------------------------------|--------------------------------|---------------------------------|---------------|------------------------|
| Shams and Mozeni [68]        | (2.14), (2.18), (2.19)         | reaction, convection            | yes           | MIDREX                 |
| Parisi and Laborde [56]      | no                             | reaction, convection            | no            | 2 MIDREX               |
| Valipour and Saboohi [87]    | no                             | reaction, convection, diffusion | yes           | MIDREX                 |
| Alamsari et al. [3, 4]       | (2.14), (2.18)                 | reaction, convection            | no            | yes                    |
| Alhumaizi et al. [5]         | (2.11), (2.14), (2.18), (2.19) | reaction, convection            | no            | MIDREX                 |
| Ranzani da Costa et al. [62] | no                             | reaction, convection, diffusion | no            | no                     |
| Nogare et al. [53]           | (2.14), (2.18), (2.19), (2.20) | reaction, convection            | yes           | ENERGIRON              |
| Nouri et al. [54]            | no                             | reaction, convection            | no            | MIDREX                 |
| Rahimi and Nikisar [60, 61]  | no                             | reaction, convection, diffusion | no            | Experimental data      |
| Zugliano et al. [101]        | (2.14), (2.18), (2.19), (2.20) | reaction, convection, diffusion | yes           | ENERGIRON              |
| Hamadeh et al. [30, 31]      | (2.11), (2.14), (2.18), (2.19) | reaction, convection, diffusion | yes           | 2 MIDREX & 1 ENERGIRON |
| Béchara et al. [8, 9]        | (2.11), (2.14), (2.18), (2.19) | reaction, convection, diffusion | no            | 2 MIDREX               |



Figure 2.15: Different zones in the MIDREX shaft furnace, based on CFD calculations [31].

Multiple researchers have investigated the effect of the ratio  $H_2/CO$  and temperature of the reducing gas on the metallization and carburization of the MIDREX shaft furnace. The best description can be given using Figure 2.16. Whenever the temperature of the reducing gas increases, the metallization also increases. This result is also obtained by [3, 62, 86]. This can be explained by the fact that in most simulations, the concentration of hydrogen is higher than the concentration of carbon monoxide in the reducing gas. As explained in Paragraph 2.1, the kinetics and thermodynamics are favourable for reduction by hydrogen at higher temperatures. However, even when the concentration of carbon monoxide is higher than that of hydrogen, a higher temperature results in a slightly better metallization, meaning that the kinetics are decisive instead of the thermodynamics.



Figure 2.16: The effect of the ratio H<sub>2</sub>/CO and temperature of the reducing gas on the metallization (left-hand side) and the carburization (right-hand side) of the MIDREX shaft furnace [30].

From this same figure, one can conclude that a higher  $H_2/CO$  ratio results in worse metallization. This result is similar to the results of [54, 60, 61]. This result begs for discussion because this is not the case when a single pellet is reduced. In fact, it is a thermal effect that occurs throughout the shaft furnace, as shown in Figure 2.17. Increasing the hydrogen concentration results in a more endothermic reduction, lowering the temperature. Since hydrogen's reduction kinetics and thermodynamics are favourable at higher temperatures, the reduction slows down. In the case of carbon monoxide, thermodynamics are favourable at lower temperatures, making the reduction possible at lower temperatures. Figure 2.17 also shows that the shaft consists of a colder central zone in which the metallization decreases even more. This central zone is partly created by the fact that the shaft furnace of Figure 2.17 uses the cooling zone to produce CDRI. A fraction of the cold cooling gas does not leave the furnace radially before it enters the reduction zone. The temperature in this zone is even further decreased by the endothermic methane deposition of the cooling gas. Additionally, even in the case of producing HDRI, this central zone exists, as concluded by [101]. This is because the reducing gas entering the shaft furnace radially has difficulties reaching the centre of the shaft furnace.



Figure 2.17: Behaviour of the MIDREX shaft furnace, producing CDRI, for different  $H_2/CO$  ratios. Note that when the figures on the right-hand side show that the composition does not contain any FeO, it can still contain hematite and magnetite [30].

Concerning the carburization, it should be logical that a higher  $H_2/CO$  ratio results in less carburization, independent of the temperature. In fact, reduction by only hydrogen would result in no carburization at all. However, the carburization at a fixed H<sub>2</sub>/CO ratio for different temperatures requires clarification. First, it must be stressed that carburization is either by the Boudouard reaction (2.11) or the methane deposition reaction (2.19). Carbon formation by the Boudourd reaction increases at lower temperatures while it decreases in the case of methane deposition. In the case of  $H_2/CO > 1$ , it should be noted that since carbon is primarily formed by methane and secondarily by CO, increasing the temperature of the gas promotes methane decomposition, which increases the carbon content. This result is also emphasized by [3, 86]. In the case of  $H_2/CO < 1$ , the formation of carbon by the Boudouard reaction becomes as significant as the formation of carbon from methane and is added to it, particularly at low temperatures when this process is favourable. This also clarifies the higher carburization of the ENERGIRON process compared to the MIDREX process. The reducing gas of the ENERGIRON shaft furnace is at higher temperatures with a higher methane concentration. Moreover, at the position where methane enters the shaft furnace, low water and carbon dioxide concentrations are available, decreasing methane reforming. Hamadeh et al. [30] even found two times higher carburization for the ENERGIRON case than the MIDREX case.

Béchara et al. [8, 9] made an Aspen Plus model based on the shaft's physical division as shown in Figure 2.15. Aspen Plus is a simulation platform using the sequential modular approach [6]. The Aspen Plus reactor model was divided into four distinct zones, as shown in Figure 2.18. Zones 1 and 2 relate to the reduction zone. Zone 1 is the largest peripheral zone, including the reducing gas and the bulk of the pellets. This zone completes the metallization of the iron ore pellets. Zone 2 (the same as zone 6 of Figure 2.15) is smaller and more centrally located, receiving just a tiny proportion of pellets and



Figure 2.18: Division of the shaft furnace into four zones (right-hand side) by the results of a 2D CFD simulation (left-hand side) performed by Hamadeh et al. [30]. Zone 2 in this figure is the same as zone 6 in Figure 2.15 [9].

gas from the transition zone. This zone results in incomplete metallization of the iron ore pellets. The transition zone is the third zone. This zone receives a portion of the hot cooling gas and descending hot reduced pellets as inputs. When natural gas is utilized as the cooling gas, the most significant reaction in this zone is carbon deposition. The cooling zone is the fourth and final zone. Its inputs are cooling gas and hot carbonized metallized iron, while its outputs are CDRI and a part of the cooling gas. The cooling zone was modelled using a basic heat exchanger, while zones 1, 2, and the transition zone were modelled using a 1D version of the REDUCTOR code programmed in Fortran. Fortran is a general-purpose compiled imperative programming language. The finite-difference technique was used to solve the equations. The 1D model with different zones was able to satisfactorily simulate multiple different MIDREX shaft furnaces without changing any diffusion or kinetic parameters.

# 2.5. Total plant model

The MIDREX and ENERGIRON plants, described in Paragraph 2.2, have entirely been modelled by researchers. Most of the research aimed to simulate the complex interaction between the shaft furnace and all other components of the plant to identify options for optimization. Besides the shaft furnace, auxiliaries such as reformer, gas heater, compressor, and  $CO_2$  removal plant determine together the total  $CO_2$ , energy, and material balance of the plant. Moreover, researchers even extended their plant models by modelling the following steel-making production steps.

Muller et al. [51] modelled the ENERGIRON plant in Aspen Plus. Their shaft furnace was modelled by a sequence of built-in reactor blocks and heat exchanger blocks, which is an extreme simplification of reality. They could simulate the ENERGIRON plant with reasonable results, but only by modifying the parameters until the results were correct. Furthermore, they extended their plant model with electrolyser and EAF models to simulate the  $CO_2$  emission of the whole steel production process, which is an exciting feature. Sarkar et al. [66] similarly modelled the MIDREX plant, using the program FactSage, to compare the performance of the DRP + EAF production route to the blast furnace + basic oxygen production route. FactSage is a platform for the solution of complex thermochemical problems. Both mentioned types of research simplified the shaft furnace model by unreasonable assumptions, making the simulation of other operating conditions unreliable.

Rechberger et al. [63] simulated a MIDREX plant using the m.simtop model library for metallurgy processes, which is an equation-oriented process simulation platform. Primetals Technologies and Voestalpine have developed the model. They simulated a MIDREX plant with a 100% natural gas feed and compared this to the case of a MIDREX plant with a feed containing 95 vol% hydrogen and

5 vol% natural gas. This simulation's gas and solid flow compositions can be found in Figures B.1 and B.2. Substituting natural gas with hydrogen implies less reforming of natural gas and thus less required energy for the reformer. On the other hand, this results in a more endothermic reduction of the iron oxides in the shaft furnace. This heat has to be supplied by burning natural gas or hydrogen. They concluded that up to 91% of direct  $CO_2$  emissions from the core process could be avoided by using 95 vol% hydrogen instead of pure natural gas. Besides that, they emphasized the problem of the equipment and operating pressure when substituting natural gas with pure hydrogen in the feed of the process. With more hydrogen, more endothermic reduction of the iron ore pellets occurs. The reducing gas must carry enough heat inside the reactor to maintain the solid at a sufficiently high temperature for the reactions. Operating with a gas flow rate higher than stoichiometry is hence necessary. Utilization of 100% hydrogen instead of natural gas would considerably increase the gas volume in the shaft furnace, increasing gas velocity, pressure loss, and gas density. At the same time, gas distribution is impacted. A significant drawback of this model is that lots of the information required to use it is leaking.

Looking at the shaft furnace models from Tables 2.2 and 2.3, Alhumaizi et al. [5], Zugliano et al. [101] and Béchara et al. [8, 9] extended their shaft furnace models with a plant model. Alhumaizi et al. [5] qualitatively investigated the effect of different operating parameters on the performance of a MIDREX plant. Despite adjustments to the kinetic parameters, the comparison with the plant data is unsatisfactory.

Zugliano et al. [101] investigated the effect of the ratio  $H_2 / CH_4$  in the feed of the ENERGIRON plant on the carburization and temperature of the DRI while producing HDRI. Furthermore, they looked at the plant's selective and non-selective  $CO_2$  emissions. According to this article, increasing the  $H_2 / CH_4$  ratio of the feed of the plant has a different effect on the MIDREX and ENERGIRON plants. In a MIDREX plant, increasing the  $H_2 / CH_4$  ratio requires less energy in the external reformer and results in a higher  $H_2 / CO$  ratio entering the shaft furnace. Consequently, this results in more endothermic  $H_2$  reduction in the reactor, which decreases the temperature. Hence, less metallization occurs. At the ENERGIRON plant, increasing the  $H_2 / CH_4$  ratio results in less highly endothermic in-situ reforming. However, more endothermic  $H_2$  reduction takes place. According to this article, the total endothermicity of the reactor decreases, resulting in higher metallization and outlet temperature of the DRI. Due to the lower  $CH_4$  content of the reducing gas, less carburization occurs. Unfortunately, no information is given on how the model is made.

Béchara et al. [8, 9] implemented their 1D shaft furnace model, written in Fortran, in Aspen Plus to simulate and optimize multiple MIDREX plants with accurate results. The representation of the Aspen Plus model of the MIDREX plant is shown in Figure 2.19. It includes all relevant unit operators of the plant, except the compressor, using design parameters to specify and simplify the simulations. The compressor is not considered because the pressure drop is not included in the model. However, this model is the most comprehensive and accurate model ever built by researchers. The model is used to optimize the plant to reduce  $CO_2$  emissions. Moreover, lots of modelling information is given, increasing the interest in using the model. Thus, the plant model is explained hereafter.

From the shaft furnace's top gas exit, the first stage is the scrubber which separates a portion of the water (H<sub>2</sub>O) vapour. The Aspen Plus submodel chosen is a splitter, in which the portion of H<sub>2</sub>O separation is set by a fixed design parameter *split<sub>H20</sub>*. The residual off-gas is then separated into two streams by the design parameter *split<sub>gas</sub>*. One stream is sent to the reformer, while the other is directed to the burner. The natural gas feed is divided into two fractions by the design parameter *split<sub>gas</sub>*. One stream goes before the reformer, and one goes after. The reformer was modelled using the built-in 'Gibbs reactor' in Aspen Plus. This reactor disregards kinetics in favour of calculating the product composition with the lowest Gibbs energy, representing the composition at equilibrium. This is a frequent simplification in the literature, used to decrease the calculation time. The reformer temperature  $T_{ref}$  is the design parameter. The reformer gas stream is subsequently mixed with natural gas and air before being returned to the shaft furnace. This step has been introduced as a Gibbs reactor, which performs oxygen (O<sub>2</sub>) injection and combustion. The reactor temperature  $T_{r,O_2}$  is the design parameter in this case. Additionally, the combustion system must supply the heat of the reforming system. This system accepts residual off-gas, natural gas, and air as inputs.



Figure 2.19: Process flow diagram of the modelled MIDREX plant in Aspen Plus [9].

temperature, burned inside the burner, and cooled before being discharged. The burner was modelled as a stoichiometric reactor using the gas combustion process, with its temperature  $T_{bur}$  serving as the design parameter. The burner's primary function is to provide energy to the reforming system. Flue gas cooling is used to recover energy for pre-heating applications. The design parameter of the flue gas cooling is  $T_{flue}$ .

# 3

# **Basis of Design**

The basis of the design creates a strong foundation for the thesis by first establishing the scope of the project. Afterwards, the inputs and outputs at the battery-limits of the shaft furnace are specified. Further, different cases with different H<sub>2</sub> / CO ratios in the reducing gas are defined, which are required to answer the research question. At last, all modelling assumptions are summed up.

# 3.1. Scope of the project

TSN has planned to produce HDRI with an annual capacity of 2.5 Mt per year, using a DRP located at the Tata Steel terrain in IJmuiden. The shaft furnace will have a diameter of 7.25 m, and the reduction zone will have a height of 16 m, as shown in Figure 3.1. These dimensions are defined by TSN. The shaft furnace model can handle six gaseous components: hydrogen, water, carbon monoxide, carbon dioxide, methane, and nitrogen. Furthermore, the shaft furnace model is able to deal with six solid components: hematite, magnetite, wüstite, iron, carbon, and gangue. Gangue and nitrogen have been treated as inert components. The properties of the pure gas and solid components are given in Appendix C. All other components are neglected in the reactor.

To investigate the influence of the ratio of hydrogen to natural gas inserted in the direct reduced iron plant on the performance of the reactor, a mathematical model of the reactor is required. State-ofthe-art research on the simulation of the shaft furnace has been started by Ranzani da Costa et al. [62]. They developed a 2D model named "REDUCTOR" to simulate the shaft furnace. Hamadeh et al. [30, 31] further developed the model and simulated multiple shaft furnaces satisfactorily. To simulate the whole plant, the calculation time of the shaft furnace had to decrease. Thus, Béchara et al. [8, 9] translated the 2D model into a 1D model with multiple zones and implemented it on the Aspen Plus simulation platform. This reduced the calculation time while considering radial variations in the shaft furnace. Moreover, the grain based pellet model considers the morphological structure changes during the reduction process of the pellet to increase accuracy, while using Sohn's law of additive reaction times to decrease the calculation time. Furthermore, the model is the most comprehensive model as shown in Tables 2.2 and 2.3. Hence, the modelling work of the shaft furnace in this thesis is similar to the model made by Béchara et al. [8, 9]. However, due to the time restrictions of the thesis period, only two of the four zones of the shaft furnace are being modelled. On the other hand, in this thesis, the pressure drop of the reactor is included since it is an important parameter to determine the total energy consumption of the DRP (including the electricity consumption of the compressor). This could be useful in future potential research.

The modelling work by Béchara et al. is focused on the MIDREX DRP. Hence, this thesis has focused on this type of shaft furnace. Increasing the ratio  $H_2/CH_4$  in the feed of the MIDREX plant means hydrogen is injected into the reducing gas just before it enters the shaft furnace, and less methane is reformed in the reformer, as shown in Figure 2.8. This results in a different  $H_2/CO$  ratio of reducing gas entering the shaft furnace. The shaft furnace model has been written in MATLAB, using the pellet model as a submodel. Matlab is a programming and numerical computing platform used by millions

of engineers and scientists to analyse data, develop algorithms, and create models [46]. In further research, the shaft furnace model could be incorporated as a custom block in Aspen Plus to make it accessible for modelling the whole DRP. Matlab is chosen for its trouble-free integration with Aspen Plus.

To ensure the validity of the shaft furnace model, both the pellet model and the shaft furnace model are validated. The pellet model has been validated against the experimental data shown in [30]. The shaft furnace model has been validated against simulation results shown in [8] and against real plant data of an operational MIDREX plant, as is demonstrated in Chapter 4.

# 3.2. Battery limits

Figure 3.1 shows all the inputs and outputs of the reactor at the battery limits. As can be seen, some parameters are fixed to a specific value in all simulations. Other parameters are design parameters, which are changed along the different simulations. The residual parameters are the results of the simulations. More clarification on all parameters is given below.



Figure 3.1: Schematic representation of the inputs and outputs of the shaft furnace. Blue and green arrows represent the solid and gas streams, respectively.

#### Solid input

As explained in Chapter 1, the required production capacity of DRI is 2.5 Mt per year for TSN. Since the weight of the pellets decreases as they reduce, the mass flow of the produced DRI depends on the metallization. Assuming a metallization of 94%, the weight loss of the pellets is 27%, as calculated in Appendix D. Hence,  $439 \text{ t} \text{ h}^{-1}$  of the pellets must be fed to the shaft furnace. Even though the metallization differs in all simulations, the mass flow of solid input remains constant. This choice is made to avoid multiple iterations and an excessive calculation time. All other solid input constants also remain the same in all simulations. All values are specified by TSN.

#### **Reducing gas input**

The pressure, mole flow, temperature, and composition must be determined to fully specify the reducing gas input. The values of these process parameters are clarified hereafter.

- The mole flow, input pressure, and output pressure of the shaft furnace are connected, as will be explained in Chapter 4. When two of the three process parameters are fixed, the other is the result of the simulation. In this thesis, the output pressure is fixed in all simulations. The inlet pressure is a design parameter and varied in all cases between 135 000 Pa and 300 000 Pa, resulting in different input mole flows in the reactor.
- The inlet temperature of the reducing gas has been maximized in all simulations. This choice is made because the highest metallization and carburization are obtained when the temperature is maximized, as shown in Figure 2.16. However, the temperature is restricted to a maximum of 950 °C for a MIDREX shaft furnace [47].
- The composition of the reducing gas is a design parameter in all simulations, by specifying the mole fractions.

#### Solid output

The output specifications of the solid pellets are the results of the simulations.

#### Reducing gas output

As stated earlier, the outlet pressure of the reducing gas is a design parameter in each simulation. The value is chosen equal to the outlet pressure of the Gilmore MIDREX plant, which is used to validate the shaft furnace model in Chapter 4. The mole flow, temperature, and composition are the results of the simulations.

#### Cooling gas input and output

No cooling gas has been used in the simulations because HDRI will be produced.

# 3.3. Description of the cases

To answer the research question, a sensitivity study is performed in which multiple cases with different  $H_2/CO$  feed ratios of the reducing gas are investigated. Each case exists of multiple simulations, in which the inlet pressure of the reducing gas has been varied to change the mole flow in conjunction. In total, five cases with different  $H_2/CO$  ratios are worked out. All cases are shown in Table 3.1. However, the creation of this table begs for clarification. In reality, when the  $H_2/CO$  ratio of the reducing gas is increased in a MIDREX plant, the  $H_2/CH_4$  feed ratio of the entire plant is increased. Moreover, the exact composition of the reducing gas is the result of the steady-state operating conditions of the whole plant. Hence, without simulation of the whole plant, it is impossible to determine the reducing gas's true composition. Therefore, some assumptions are made based on real plant data from MIDREX [47]:

- The mole fractions of hydrogen and carbon monoxide are based on real plant data from [47].
- The mole fraction of water must scale in conjunction with hydrogen, hence it is assumed that the mole fraction of water is always eight times smaller than the mole fraction of hydrogen.
- The mole fractions of carbon dioxide and methane must scale in conjunction with carbon monoxide, hence it is assumed that the mole fractions of carbon dioxide and methane are always eight times smaller than the mole fraction of carbon monoxide.
- The mole fraction of nitrogen is in all cases fixed to 0.050, as taken from [47].

# 3.4. Modelling assumptions

The assumptions made during the modelling work are summed up below:

- The pellets are perfectly spherical and remain the same size during reduction. In reality, the pellets increase in size during reduction, as studied by [18]. However, taking into account the change in size would add extremely more complexity to the model and is thus neglected.
- All pellets have the same size.
- The pellets initially consist of only hematite and gangue.

- The pellets are equally distributed in the shaft furnace.
- The pellets have a uniform temperature. This assumption is valid since the average Biot number of the pellets in the shaft furnace is less than 0.1, which means that the temperature gradients inside the body are negligible [25].
- · The gas phase is considered an ideal mixture.
- The gas components are restricted to hydrogen, water, carbon monoxide, carbon dioxide, methane, and nitrogen. Nitrogen is treated as an inert component.
- The solid components are restricted to hematite, magnetite, wüstite, iron, carbon, and gangue. Gangue is treated as an inert component, and wüstite is assumed to be in the form Fe<sub>0.95</sub>O.
- The model does not take into account the difference between carbon in the form of soot (C) and cementite (Fe<sub>3</sub>C). Cementite is more beneficial than soot in the DRI, as explained in Paragraph 2.2.3.
- The 1D zones in the shaft furnace model are homogeneous over the radius of the shaft furnace.

The allowed chemical reactions in the shaft furnace are the six reduction reactions (2.1 - 2.6), Boudouard reaction (2.11), steam methane reforming (2.14), water gas shift (2.18), and methane deposition (2.19). All reactions are shown on one single page in Appendix E, to increase the readability of the thesis.

| Mole fractions                            | Case 1       | Case 2         | Case 3         | Case 4         | Case 5                  |
|---|--------------|----------------|----------------|----------------|-------------------------|
|   | $H_2/CO = 1$ | $H_2 / CO = 2$ | $H_2 / CO = 3$ | $H_2 / CO = 4$ | H <sub>2</sub> / CO = ∞ |
| <i>x</i> <sub><i>H</i><sub>2</sub></sub>  | 0.400        | 0.543          | 0.616          | 0.661          | 0.844                   |
| <i>x</i> <sub><i>H</i><sub>2</sub>0</sub> | 0.050        | 0.067          | 0.077          | 0.082          | 0.106                   |
| x <sub>co</sub>                           | 0.400        | 0.272          | 0.205          | 0.165          | 0                       |
| <i>x</i> <sub>CO2</sub>                   | 0.050        | 0.034          | 0.026          | 0.021          | 0                       |
| x <sub>CH4</sub>                          | 0.050        | 0.034          | 0.026          | 0.021          | 0                       |
| <i>x</i> <sub><i>N</i><sub>2</sub></sub>  | 0.050        | 0.050          | 0.050          | 0.050          | 0.050                   |

Table 3.1: Inlet mole fractions of the reducing gas in different cases.

# 4

# Modelling

This chapter provides all relevant modelling information used in this thesis. First, all sources and methods to determine the physical properties are given. Hereafter, the pellet model is explained and validated. In a like manner, the shaft furnace model is clarified, including the numerical methods and algorithms to solve the system.

# 4.1. Physical properties

The specific heat, enthalpy, entropy, and Gibbs free energy of all solid and gaseous components are taken from NIST using the Shomate equations, as shown below [42]. Constants A, B, C, D, E, F, and G are all taken from NIST and are component dependent. The value t is the temperature in Kelvin divided by 1000. The reference temperature is 293.15 K.

$$C_p^{\circ} = A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2}$$
(4.1)

$$H^{\circ} = At + \frac{Bt^2}{2} + \frac{Ct^3}{3} + \frac{Dt^4}{4} - \frac{E}{t} + F$$
(4.2)

$$S^{\circ} = Aln(t) + Bt + \frac{Ct^2}{2} + \frac{Dt^3}{3} - \frac{E}{2t^2} + G$$
(4.3)

The viscosities and thermal conductivities of all pure gaseous components are taken from NIST as a function of the temperature [42]. The thermal conductivities of all pure solid components, as a function of the temperature, are obtained from [10].

The binary diffusion coefficients of the gases are obtained using the Chapman-Enskog relation as a function of temperature and pressure [40]:

$$D_{ij} = \frac{3}{16} \sqrt{\frac{2\pi k_T T(m_i + m_j)}{m_i m_j}} \left(\frac{k_T T}{\pi \sigma_{ij}^2 \Omega_D p}\right)$$
(4.4)

in which  $m_i$  is the mass of molecule i and  $\sigma_{ij}$  is calculated according to:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{4.5}$$

The dimensionless collision integral of diffusion  $\Omega_D$  is calculated according to the following fit function:

$$\Omega_D = \frac{A}{\Theta^B} + \frac{C}{exp(D\Theta)} + \frac{E}{exp(F\Theta)} + \frac{G}{exp(H\Theta)}$$
(4.6)

Where,

A = 1.06036 B = 0.1561 C = 0.193 D = 0.47635 E = 1.03587 F = 1.52996 G = 1.76474 H = 3.89411

Θ is calculated according to:

$$\Theta = \frac{k_T T}{\sqrt{\epsilon_i \epsilon_i}} \tag{4.7}$$

The component-dependent values of  $\epsilon$  and  $\sigma$  are taken from [59].

#### 4.2. Pellet model

The pellet model used has been developed by Wagner [89] and is further developed by da Costa [62] and Hamadeh [30]. This model uses Sohn's law of additive reaction times to incorporate the grainy structure of the pellets while maintaining a reasonable calculation time [71]. This law states that the time required for the conversion of the pellet is approximately the sum of all characteristic times, as explained in Paragraph 4.2:

$$t_{conversion} \approx \tau_{ext} + \tau_{diff} + \tau_{chem} \tag{4.8}$$

Furthermore, the model incorporates the change in the intra particle morphological structure of the pellets observed during experiments, as shown in Figure 4.1. In the beginning, the hematite pellets consist of small dense hematite grains. To reduce these grains, either  $H_2$  or CO must diffuse between the grains within the pellet (intergranular diffusion). The hematite grains are subsequently reduced into dense magnetite grains. Either  $H_2$  or CO must diffuse between the grains and within the grains (intragranular diffusion) towards the unreacted interface to reduce magnetite into porous wüstite grains. These grains fall apart in even smaller pieces, called crystallites. The dense crystallites are then reduced towards iron, while the diameter decreases. To reduce the crystallites, either  $H_2$  or CO must diffuse between the crystallites (intracrystallite diffusion) and within the crystallites (intracrystallite diffusion).

#### 4.2.1. Description of the pellet model

The reaction rates of the six reduction reactions 2.1 to 2.6 can be calculated, as shown in Figure 4.2. The model considers the time required for external mass transfer  $\tau_{ext}$ , diffusion  $\tau_{diff}$  (which depends on the structure of the pellet), and the chemical reaction  $\tau_{chem}$ . The characteristic diffusion and chemical reaction times are multiplied by a factor that increases with increasing pellet conversion  $X_i$ . This ensures that the reaction rate decreases whenever the conversion of the pellet increases. All characteristic reaction times  $\tau_i$  are derived in [62, 89] and are not reproduced in this thesis. All input values for these characteristic reaction times are explained below.



Figure 4.1: Schematic representation of the morphologic structure change of the pellets during reduction [30].

#### General constants and variables

Various constants and variables are used in multiple equations. For the values of the molar masses, densities, and initial porosity and diameter of the pellets, the reader is referred to Chapter 3. The conversion of each reaction is calculated according to the following:

Numbers of moles i that are reduced

$$X_i = \frac{1}{\text{Numbers of moles i that need to be reduced for full reduction of component i}}$$
(4.9)

Where,

 $X_1 = X_4$  stands for the conversion of Fe<sub>2</sub>O<sub>3</sub> [-]  $X_2 = X_5$  stands for the conversion of Fe<sub>3</sub>O<sub>4</sub> [-]  $X_3 = X_6$  stands for the conversion of Fe<sub>0.95</sub>O [-]

The initial diameter of the crystallites depends on the temperature and the conversion [62]:

$$d_{crist\,ini} = 2.04575 * 10^{-3} exp(6.08 * 10^{-3}T)(0.57228X_3 + (1 - X_3))^{\frac{1}{3}} * 10^{-6}$$
(4.10)

The pellet model uses the initial apparent molar density in the characteristic time equations of the external mass transfer, intergranular diffusion, intercrystallite diffusion, and the reaction rate equation. In all other equations, the initial theoretical molar density is used. The initial apparent molar density is calculated according to the formula below. The initial theoretical molar density is calculated by the same formula, while putting the porosity equal to zero.

$$\tilde{\rho}_{i,ini} = \frac{\rho_i (1 - \epsilon_i)}{M_i} \tag{4.11}$$

The porosity of  $Fe_2O_3$  is equal to the initial porosity of the pellet, which is provided by TSN as explained in Chapter 3. The porosities of  $Fe_3O_4$ ,  $Fe_{0.95}O$ , and Fe are calculated based on the initial porosity of the pellet, the molar volumes, and the assumption that the volume of the pellet remains constant, as explained in [62].

 $\epsilon_{Fe_2O_3} = 0.265$   $\epsilon_{Fe_3O_4} = 0.279$   $\epsilon_{Fe_{0.95O}} = 0.398$  $\epsilon_{Fe} = 0.656$ 

|                               | Hematite to magnetite   | Magnetite to wüstite   | Wüstite to iron  |
|-------------------------------|---|--|--|
| External mass<br>transfer     | $\tau_{ext,i} = \frac{\tilde{\rho}_{Fe_2O_3,ini}d_p}{18k_gc_t(x_{k,\infty} - x_{k,eq(i)})}$                                 | $\tau_{ext,i} = \frac{8\tilde{\rho}_{Fe_3O_4,ini}d_p}{57k_gc_t(x_{k,\infty} - x_{k,eq(i)})}$   | $\tau_{ext,i} = \frac{\tilde{\rho}_{Fe_{0.95}O}d_p}{6k_g c_t (x_{k,\infty} - x_{k,eq(i)})}$                                      |
| Intergranular diffusion       | $\tau_{diff,interg(i)} = \frac{\tilde{\rho}_{Fe_2O_3,ini}(d_p)^2}{72(D_{k,eff})_{interg,i}c_t(x_{k,\infty} - x_{k,eq(i)})}$ | $\tau_{diff,interg(i)} = \frac{2\tilde{\rho}_{Fe_3O_4,ini}(d_p)^2}{57(D_{k,eff})_{interg,i}c_t(x_{k,\infty} - x_{k,eq(i)})}$                 | х  |
| Intragranular diffusion       | X   | $\tau_{diff,intrag(i)}$ $= \frac{2\tilde{\rho}_{Fe_3O_4,ini} (d_{grain,ini})^2}{57 (D_{k,eff})_{intrag,i} c_t (x_{k,\infty} - x_{k,eq(i)})}$ | х  |
| Intercrystallite<br>diffusion | х   | х  | $\tau_{diff,interc(i)}$ $= \frac{\tilde{\rho}_{Fe_{0.95}0} (d_p)^2}{24 (D_{k,eff})_{interc,i} c_t (x_{k,\infty} - x_{k,eq(i)})}$ |
| Intracrystallite<br>diffusion | х   | х  | $\tau_{diff,intrac,(i)} = \frac{\tilde{\rho}_{Fe_{0.950}} d_{crist,ini}^2}{24 D_{sol} (c_{ox,eq} - c_{ox,\infty})}$              |
| Chemical reaction             | $\tau_{chim,i} = \frac{\tilde{\rho}_{Fe_2O_3} d_{grain,ini}}{6k_i c_t (x_{k,\infty} - x_{k,eq(i)})}$                        | $\tau_{chim,i} = \frac{\tilde{\rho}_{Fe_3O_4} d_{grain,ini}}{2k_i c_t (x_{k,\infty} - x_{k,eq(i)})}$   | $\tau_{chim,i} = \frac{\tilde{\rho}_{Fe_{0.95}O} d_{crist,ini}}{2k_i c_t (x_{k,\infty} - x_{k,eq(i)})}$                          |

|          | Reaction rate $mol m^{-3} s^{-1}$   |
|----------|---|
| i=1 et 4 | $r_{l} = \frac{1}{3} \tilde{\rho}_{Fe_{2}O_{3}, ini} \left\{ \tau_{ext,i} + 2\tau_{diff, interg(i)} \left[ (1 - X_{i})^{-\frac{1}{3}} - 1 \right] + \frac{\tau_{chim,i}}{3} (1 - X_{i})^{-\frac{2}{3}} \right\}^{-1}$   |
| i=2 et 5 | $r_{i} = \frac{1}{3} \tilde{\rho}_{Fe_{2}O_{3},ini} \left\{ \tau_{ext,i} + 2 \left( \tau_{diff,interg(i)} + \tau_{diff,intrag(i)} \right) \left[ \left( 1 - X_{i} \right)^{-\frac{1}{3}} - 1 \right] + \frac{\tau_{chim,i}}{3} \left( 1 - X_{i} \right)^{-\frac{2}{3}} \right\}^{-1}$ |
| i=3 et 6 | $r_{i} = \frac{1}{3} \tilde{\rho}_{Fe_{2}O_{3},ini} \left\{ \tau_{ext,i} + 2 \left( \tau_{diff,interc(i)} + \tau_{diff,intrac,(i)} \right) \left[ (1 - X_{i})^{-\frac{1}{3}} - 1 \right] + \frac{\tau_{chim,i}}{3} (1 - X_{i})^{-\frac{2}{3}} \right\}^{-1}$                          |

Figure 4.2: Reaction rates of reaction equations 2.1 to 2.6.  $k = H_2$  for reactions 2.1 to 2.3. k = CO for reactions 2.4 to 2.6 [30].

The total gas concentration is calculated using the ideal gas law:

$$c_t = \frac{p}{RT} \tag{4.12}$$

In the formula for the intracrystallite characteristic time, oxygen concentration at the wüstite/iron interface  $c_{ox,eq}$  is assumed to be in equilibrium. On the exterior surface of the crystallite, where a layer of pure iron has formed, the oxygen concentration  $c_{ox,\infty}$  is assumed to be zero:  $c_{ox,\infty} = 0$ . Swisher and Turkdogan [75] experimentally determined the equilibrium concentration of oxygen in iron between 880°C and 1350°C. The following polynomial expression can well describe their experimental points:

$$c_{ox,eq} = 5.08 * 10^{-13}T^5 - 2.72 * 10^{-9}T^4 + 5.39 * 10^{-6}T^3 - 4.49 * 10^{-3}T^2 + 1.06T + 269$$
(4.13)

#### Thermodynamic properties $\Delta G$ , $K_{eq}$ and $x_{eq}$

The equilibrium constants of the reduction reactions by hydrogen (2.1 - 2.3) are calculated using the standard Gibbs free energy of the reaction and the mole fraction of water and hydrogen. The equilibrium constants of the reduction reactions by carbon monoxide (2.4 - 2.6) are calculated using the standard Gibbs free energy of the reaction and the mole fraction of carbon dioxide and carbon monoxide [62]:

$$\Delta G_i = \Delta G_i^\circ + RT ln\left(\frac{x_{H_2O}}{x_{H_2}}\right); \qquad \text{for reactions } 2.1 - 2.3 \qquad (4.14)$$

$$\Delta G_i = \Delta G_i^\circ + RT ln\left(\frac{x_{CO_2}}{x_{CO}}\right); \qquad \text{for reactions } 2.4 - 2.6 \qquad (4.15)$$

$$K_{eq_i} = e^{-\frac{\Delta G_i}{RT}} \tag{4.16}$$

The equilibrium mole fractions of hydrogen and carbon monoxide for each reaction i are calculated using the equilibrium constants. The derivation of the formulas are shown in [62]:

$$x_{k,eq_i} = \frac{1 - x_{Inert,\infty}}{1 + K_{eq_i}};$$
 for reactions 2.1, 2.3, 2.4, 2.6 (4.17)

$$x_{k,eq_i} = \frac{1 - x_{Inert,\infty}}{1 + (K_{eq_i})^{\frac{19}{16}}};$$
 for reactions 2.2 and 2.5 (4.18)

In the case of reduction by H<sub>2</sub>,  $x_{Inert,\infty} = x_{CO} + x_{CO_2} + x_{CH_4} + x_{N_2}$ In the case of reduction by CO,  $x_{Inert,\infty} = x_{H_2} + x_{H_2O} + x_{CH_4} + x_{N_2}$ 

### External mass transfer coefficient $k_g$

The external mass transfer coefficient is obtained using the Ranz and Marshall correlation, as shown below [2]. This coefficient must be determined for both  $H_2$  and CO and is valid for Re < 200 and Sc < 250. The validity of this formula has been checked after simulation.

$$Sh = \frac{k_g d_p}{D_{i,mixture}} = 2 + 0.6Re^{\frac{1}{2}} + Sc^{\frac{1}{3}}$$
(4.19)

in which,

$$Re = \frac{\rho_g d_p u_g}{\mu_g} \tag{4.20}$$

$$Sc = \frac{\mu_g}{\rho_g D_{i,mixture}} \tag{4.21}$$

The density of the gas mixture containing the six components can be calculated according to the ideal gas law:

$$\rho_g = \frac{P}{RT \sum_{i=1}^{6} (x_i M_i)}$$
(4.22)

The viscosity of the gas mixture containing the six components is calculated using Wilke's method [45]:

$$\mu_g = \sum_{i=1}^{6} \frac{\mu_i}{1 + \sum_{j=1, j \neq i}^{6} \phi_{ij}\left(\frac{x_j}{x_i}\right)}$$
(4.23)

in which,

$$\phi_{ij} = \frac{\left(1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right)^2}{2\sqrt{2}\left(1 + \frac{M_i}{M_j}\right)^{\frac{1}{2}}}$$
(4.24)

The diffusion coefficient of component i in the gas mixture can be calculated by [23]:

$$D_{i,mixture} = \frac{1 - x_i}{\sum_{j=1, j \neq i}^{6} \left(\frac{x_j}{D_{ij}}\right)}$$
(4.25)

## Effective diffusion coefficients $(D_{eff})_{interg}$ and $(D_{eff})_{intrag}$

The diffusion of a gaseous specie through a porous medium strongly depends on the void fraction, tortuosity, and pore size distribution, which all characterize the structure. Moreover, it depends on the binary diffusivities of the components of the gas. When the pore size is large compared to the mean free path of gas molecules, molecular diffusion is predominant. Conversely, Knudsen's diffusion mechanism prevails in a porous medium with fine pores. The following relationship gives the Knudsen diffusivity for a gaseous specie k:

$$D_{k,kn} = \frac{\bar{d}_{pores}}{3} \sqrt{\frac{8RT}{\pi M_k}}$$
(4.26)

The average intergranular and intragranular pore diameters are determined experimentally [62]:

 $\bar{d}_{pores,interg} = 6 \,\mu m$  $\bar{d}_{pores,intrag} = 1 \,\mu m$ 

The effective diffusion coefficient can subsequently be determined by the Bosanquet relationship, reflecting the two diffusion mechanisms through two resistors in parallel [96]:

$$D_{k,eff} = \frac{\epsilon}{\Gamma} \left( \frac{1}{D_{k,mixture}} + \frac{1}{D_{k,kn}} \right)^{-1}$$
(4.27)

Where,

$$\begin{split} &\Gamma_{interg}=\Gamma_{intrag}=1.7\\ &\epsilon_{interg}=\epsilon_{p,ini}=0.265\\ &\epsilon_{intrag}=0.18 \end{split}$$

These values of intergranular and intragranular tortuosity and porosity are obtained from [62].

# Effective diffusion coefficient $(D_{eff})_{interc}$ and solid state diffusion coefficient $D_{sol}$

The effective diffusion between the crystallites as a function of temperature is experimentally determined by Hamadeh [30]. He used the simplification that hydrogen diffuses as fast as carbon monoxide:

$$(D_{H_2,eff})_{interc} = (D_{CO,eff})_{interc} = 4.767751 * 10^{-7}T - 2.6851 * 10^{-4}$$
(4.28)

Once a dense iron layer has formed, oxygen ions must diffuse through the solid iron phase. Hence, for the characteristic reaction time of the intracrystallite diffusion, the solid-state diffusion of oxygen in iron is taken as a function of temperature. This function has been determined by Swisher and Turkdogan [75], by measuring the diffusivity of oxygen in dense iron, either in the  $Fe - \alpha(T \le 912^{\circ}C)$  or in the  $Fe - \gamma(T > 912^{\circ}C)$ :

$$D_{sol} = 3.72 * 10^{-6} exp\left(\frac{-97600}{RT}\right); \qquad T \le 912^{\circ}C \qquad (4.29)$$

$$D_{sol} = 5.75 * 10^{-4} exp\left(\frac{-168847}{RT}\right); \qquad T > 912^{\circ}C \qquad (4.30)$$

#### **Reation rate constant** k

To determine the characteristic reaction times of the chemical reactions, the reaction rate constants of all reactions 2.1 - 2.6 are required. Various kinetic parameters (frequency factors and activation energies) are proposed in the literature. The approach of Hamadeh [30] was to consider these parameters as unknown and to determine them by adjustment between the experimental and calculated kinetic curves. Then the Arrhenius law was used, as shown below. All values of frequency factors and activation energies are summarized in Table 4.1.

$$k_i = A_i exp\left(-\frac{E_{ai}}{RT}\right) \tag{4.31}$$

| Table 4.1: | Values | of the active | ation energies | s and pre-ex | conential fac | tors for the A | Arhenius rea | ction rate ec | uations. |
|------------|--------|---------------|----------------|--------------|---------------|----------------|--------------|---------------|----------|
|            |        |               |                |              |               |                |              |               |          |

| Reaction     | A [m/s]          | E <sub>a</sub> [J/mol] |
|--------------|------------------|------------------------|
| Reaction 2.1 | $7.79 * 10^{-4}$ | 27000                  |
| Reaction 2.2 | $1.11 * 10^{-2}$ | 55000                  |
| Reaction 2.3 | 16               | 136000                 |
| Reaction 2.4 | 13               | 113859                 |
| Reaction 2.5 | 0.053            | 73674                  |
| Reaction 2.6 | 0.0027           | 69488                  |

#### 4.2.2. Validation of the pellet model

The pellet model has been validated against numerical data from literature, as shown in Figures 4.3 and 4.4. The numerical data from the literature is validated against experimental data, which is obtained by reducing a pellet in a thermographic analysis system under isothermal conditions. The gas mixtures in these experimental analyses contain helium together with hydrogen and/or carbon monoxide. The helium is used as an inert component. The figures show the same reduction time as was determined in the literature for both cases. However, some small discrepancies are visible regarding the mass/mole fractions of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>0.95</sub>O. The mass/mole fraction of Fe<sub>3</sub>O<sub>4</sub> has a lower maximum value in this thesis's simulations than the values in the literature. The mass/mole fraction of Fe<sub>0.95</sub>O has a higher maximum value. This implies that the reduction reactions from magnetite towards wüstite (reactions 2.2 and 2.5) are a bit faster in the simulations of this thesis. These discrepancies can be attributed to the different sources of the physical properties used in the models.



Figure 4.3: Results (left figure) of the pellet model at reducing a pellet ( $d_p$  = 14 mm) by a mixture of H<sub>2</sub>/He 60/40 vol% at 900 °C. This figure is validated against literature (right figure) [62].



Figure 4.4: Results (left figure) of the pellet model at reducing a pellet ( $d_p$  = 14 mm) by a mixture of H<sub>2</sub>/CO/He 30/30/40 vol% at 900 °C. This figure is validated against literature (right figure) [30].

### 4.3. Shaft furnace model

The shaft furnace is modelled as a 1D model with multiple zones, as explained in Chapter 2. The representation of the different zones is shown in Figure 4.5. However, due to time restrictions, the model has been simplified to only zones 1 and 2. The solid input fraction that goes towards zones 1

and 2 is fixed by the "solid split" parameter. In reality, the solid leaving zones 1 and 2 go towards the transition zone and the cooling zone. In this thesis, the solid output leaving the shaft furnace has only gone through zones 1 and 2. Furthermore, in this thesis, the gas entering zone 2 is just a fraction of the reducing gas, determined by the "gas split" parameter. In reality, this gas is mixed inside the transition zone with a fraction of the cooling gas. The fraction of cooling gas that flows towards the transition zone is established at 13% by Hamedeh et al. [30], based on 2D CFD calculations. To account for the leakage of cold cooling gas entering zone 2, the input temperature of the reducing gas of zone 2 is decreased by the parameter "temperature drop", which reduces the temperature of the reducing gas input.



Figure 4.5: Representation of the different zones in the shaft furnace model. Blue and green arrows represent the solid and gas streams, respectively. Red zones are modelled in this thesis, the white zones are not taken into account.

Dividing the zones, including the solid and gas streams, requires three modelling parameters: the solid split, the gas split, and the temperature drop. The solid split is determined based on the papers of Béchara et al. [8, 9], in such a way that 8 mass% of the total solid input goes to the colder central zone 2. As a result of the earlier mentioned assumption that the pellets are equally distributed in the shaft furnace, the cross-section area of zone 2 is 8% of the total cross-section area of the shaft furnace. The other two parameters are not mentioned in the papers of Béchara et al. because the input of zone 2 in their paper was determined based on the leakage of cooling gas towards the transition zone. In this thesis, the gas split and temperature drop were both determined by varying them, until the best results of the validation of zone 2 (shown later on in Paragraph 4.3.5) were met:

- The gas split is calculated in such a way that the ratio of the number of gas moles per kilogram solid entering zone 2 is 70% of the ratio of the number of gas moles per kilogram solid entering zone 1.
- The temperature drop of the gas entering zone 2 with respect to the gas entering zone 1 is set to 25%.

Zones 1 and 2 are modelled as 1D zones, solving the local energy, mass, and momentum equations while using the pellet sub-model to obtain the kinetics of the six reduction reactions. All governing equations, as well as the solving method, are further clarified in this paragraph.

#### 4.3.1. Chemical reactions

The shaft furnace model enables six reduction reactions (2.1 - 2.6), two gas phase reactions (2.14 and 2.18) and two carburization reactions (2.11 and 2.19). All reaction equations are shown in Appendix E. The reaction rates of the six reduction reactions are determined as explained in Paragraph 4.2. The other reaction rates are discussed below. All reaction rate constants are summarized in Table 4.2. The porosity of the bed containing spherical pellets is calculated by the formula below [32]. This formula is valid for  $\frac{d_{shaft}}{d_p} > 10$ . The validity of this formula has been checked after simulation.

$$\epsilon_{bed} = 0.38 + 0.073 \left[ 1 + \frac{\left(\frac{d_{shaft}}{d_p} - 2\right)^2}{\left(\frac{d_{shaft}}{d_p}\right)^2} \right]$$
(4.32)

#### Reaction 2.14: Steam methane reforming

Steam methane reforming is catalysed by metallic iron. Hence, this reaction only takes place whenever enough iron is formed. It is assumed that this condition is met whenever the conversion of the pellets is greater than 50%. This same assumption has been made by Takahashi [78]. The reaction rate equation is taken from this source as well:

$$r_{2.14} = k_{2.14} (1 - \epsilon_{bed}) (1 - \epsilon_{interg}) \left( p_{CH_4} p_{H_2O} - \frac{p_{CO} p_{H_2}^3}{K_{eq,2.14}} \right)$$
(4.33)

#### Reaction 2.18: Water gas shift

The water gas shift reaction is catalysed by iron and all iron oxides, which are present in the shaft furnace. Hence, this reaction rate equation depends on the catalyst type and the amount of catalyst available. Similar to the research of Hamadeh et al. [30], two different reaction rate equations are defined, as shown below. The first reaction rate equation is for an iron or wüstite catalyst. The second reaction rate equation is for a magnetite or hematite catalyst.

$$r_{2.18,i} = k_{2.18,i} (1 - \epsilon_{bed}) (1 - \epsilon_{interg}) \left( p_{CO} p_{H_2O} - \frac{p_{CO_2} p_{H_2}}{K_{eq,2.18}} \right)$$
(4.34)

$$r_{2.18,i} = k_{2.18,i} \rho_c (1 - \epsilon_{bed}) (1 - \epsilon_{interg}) \left( p_{CO} p_{H_2O} - \frac{p_{CO_2} p_{H_2}}{K_{eq,2.18}} \right)$$
(4.35)

In the first reaction rate equation, it is assumed that the reaction is catalysed by iron if the conversion of the pellets is greater than 50%, else the reaction is catalysed by wüstite. The second reaction rate equation depends on the apparent density of catalyst (either magnetite or hematite) at the location of the reaction in the shaft furnace.

#### Reaction 2.11: Boudouard

For both the Boudouard reaction and methane deposition, the reaction rate depends on the activity of carbon in iron. This activity can be determined according to [13]:

$$log(a_{carbon}) = \frac{2300}{T} - 0.92 + \left(\frac{38760}{T}\right) + log\left(\frac{C}{1-C}\right)$$
(4.36)

in which C is the ratio of atoms carbon / atoms iron.

The Boudouard reaction rate equation is given by [5]:

$$r_{2.11} = (k_{2.11} p_{H_2}^{0.5} + k'_{2.11}) \left( p_{CO}^2 - \frac{p_{CO_2} a_{carbon}}{K_{eq,2.11}} \right)$$
(4.37)

#### **Reaction 2.19: Methane deposition**

The methane deposition reaction rate equation is given by [5]:

$$r_{2.19} = \frac{k_{2.19}}{p_{H_2}^{0.5}} (1 - \epsilon_{bed}) (1 - \epsilon_{interg}) \left( p_{CH_4} - \frac{p_{H_2}^2 a_{carbon}}{K_{eq,2.19}} \right)$$
(4.38)

Table 4.2: Reaction rate constants of reactions: 2.14, 2.18, 2.11, and 2.19.

| Reaction | Reaction rate constant   | Reference |
|----------|--|-----------|
| 2.14     | $k_{2.14} = 392 exp\left(\frac{6770}{RT}\right) (mol m^{-3} s^{-1})$ for p≤6 bar                               | [78]      |
| 2.14     | $k_{2.14} = 26.13 exp\left(\frac{6770}{RT}\right) (mol m^{-3} s^{-1})$ for p>6 bar                             | [30]      |
|          | $k_{2.18,Fe} = 93.3exp\left(-\frac{7320}{RT}\right) (mol m^{-3} s^{-1})$                                       | [78]      |
| 2 18     | $k_{2.18,Fe_{0.95}0} = 1.83 * 10^{-5} exp\left(-\frac{7.84}{RT}\right) (\text{mol}\text{m}^{-3}\text{s}^{-1})$ | [78]      |
| 2.10     | $k_{2.18,Fe_3O_4} = 2.683372 * 10^5 exp\left(-\frac{112000}{RT}\right) (mol kg^{-1} s^{-1})$                   | [70]      |
|          | $k_{2.18,Fe_2O_3} = 4.56 * 10^3 exp\left(-\frac{88000}{RT}\right) (\text{mol kg}^{-1} \text{ s}^{-1})$         | [70]      |
| 2 11     | $k_{2.11} = 1.8exp\left(-\frac{27200}{RT}\right) (mol  m^{-3}  s^{-1})$  | [5, 27]   |
| 2.11     | $k'_{2.11} = 2.2exp\left(-\frac{8800}{RT}\right) (mol  m^{-3}  s^{-1})$  | [5, 27]   |
| 2.19     | $k_{2.19} = 16250 exp\left(\frac{55000}{RT}\right) (mol  m^{-3}  s^{-1})$                                      | [5, 27]   |

#### 4.3.2. Gas phase equations

#### Mole fraction equation

The molar balances of the gaseous components:  $H_2$ ,  $H_2O$ , CO,  $CO_2$ , and  $CH_4$  are given below. Advection, diffusion, and a source term (chemical reaction) are taken into account. The discretization of this equation is given in Appendix F.

$$\frac{d(c_t x_i u_g)}{dz} = \frac{d}{dz} \left( c_t D_{axial,i} \frac{dx_i}{dz} \right) + S_i$$
(4.39)

The mole fraction of the inert component nitrogen is calculated by:

$$x_{N_2} = 1 - x_{H_2} - x_{H_20} - x_{C0} - x_{C0_2} - x_{CH_4}$$
(4.40)

The total gas concentration is again calculated using the ideal gas law (equation 4.12). The source terms are given in Table 4.3. The diffusion coefficients of the gaseous molecules in the axial direction of the shaft furnace have been correlated by Wen and Fan [15] for packed bed reactors with spherical particles. The bed of pellets in the shaft furnace is actually moving, but the very high axial velocity of the gas relative to that of the solid allows it to consider it as a fixed bed. The correlation as a function of the Reynolds en Schmidt number is given by:

$$D_{axial,i} = u_g d_p \left[ \frac{0.3}{Re * Sc_i} + \frac{0.5}{1 + \frac{3.8}{Re * Sc_i}} \right]$$
(4.41)

This correlation is valid for 0.008 < Re < 400 and  $0.28 < Sc_i < 2.2$ . The validity of this formula has been checked after simulation.

Table 4.3: Source terms of equation 4.39.

| Component        | $S_i  [mol  m^{-3}  s^{-1}]$                                   |
|------------------|--|
| H <sub>2</sub>   | $S_{H_2} = -r_1 - \frac{16}{19}r_2 - r_3 + 3r_7 + r_8 + 2r_9$  |
| H <sub>2</sub> O | $S_{H_20} = r_1 + \frac{16}{19}r_2 + r_3 - r_7 - r_8$          |
| со               | $S_{CO} = -r_4 - \frac{16}{19}r_5 - r_6 + r_7 - r_8 - 2r_{10}$ |
| CO <sub>2</sub>  | $S_{CO_2} = r_4 + \frac{16}{19}r_5 + r_6 + r_8 + r_{10}$       |
| CH <sub>4</sub>  | $S_{CH_4} = -r_7 - r_9$  |

#### **Energy equation**

The temperature of the gas depends on various heat transfer phenomena, as can be seen in equation 4.42. Advection, conduction, convection, and a source term are considered. The heat of all ten reactions is added to the solid phase. For the heterogeneous reactions, because they take place inside the pellet. For the homogeneous reactions, because they are catalysed by the solid surface. The discretization of this equation is given in Appendix G.

$$\rho_g C_{p,g} u_g \frac{dT_g}{dz} = \frac{d}{dz} \left( \lambda_g \frac{dT_g}{dz} \right) + a_s h(T_s - T_g) + \sum_{i=1}^5 S_i \int_{T_g}^{T_s} C_{p,i} dT$$
(4.42)

The conductivity of the multicomponent gas mixture is determined by Wilke's method, which was shown earlier (equation 4.23). The specific heat capacity of the multicomponent gas mixture is determined using the Kopp-Neumann law [38]:

$$C_{p,g} = \sum_{i=1}^{6} C_{p,i} W_i \tag{4.43}$$

The specific area of the solid pellets is calculated using:

$$a_s = \frac{6(1 - \epsilon_{bed})}{d_p} \tag{4.44}$$

The correlation of Wakao has been used to determine the heat transfer coefficient [90]:

$$Nu = \frac{hd_p}{\lambda_q} = 2 + 1.1Pr^{\frac{1}{3}}Re^{0.6}$$
(4.45)

This correlation is valid for 3 < Re < 3000. The validity of this formula has been checked after simulation.

#### Continuity and momentum equation

Considering the gas velocity is much higher than the solid velocity, it is assumed that the pressure drop in the shaft furnace can be calculated by the Ergun equation [21]. The equation correlates the pressure drop in a packed bed containing spherical pellets and is valid for laminar and turbulent flows.

$$K = \frac{150(1 - \epsilon_{bed}^2)}{\epsilon_{bed}^3 d_p^2} \mu_g + \frac{1.75(1 - \epsilon_{bed})}{\epsilon_{bed}^3 d_p} \rho_g u_g$$
(4.46)

Combining the Ergun equation with the gas continuity equation, results in:

$$\frac{d}{dz}\left(\frac{c_t}{K}\frac{dp}{dz}\right) = S_{mol,total} = 2r_{2.14} + r_{2.19} - r_{2.11}$$
(4.47)

in which the right-hand side of the equation includes all non-equimolar chemical reactions.

Whenever the pressure field is solved, the velocity of the gas can be determined according to:

$$u_g = -\frac{1}{K} \frac{dp}{dz} \tag{4.48}$$

Both equations 4.47 and 4.48 are discretized and shown in Appendix H.

#### 4.3.3. Solid phase equations

#### Weight fraction equation

The weight fractions equations of the solid components:  $Fe_2O_3$ ,  $Fe_3O_4$ ,  $Fe_{0.95}O$ , Fe, and C are given below. Since the velocity of the solid is constant, it is taken out of the differential. The discretization of this equation is given in Appendix I.

$$-u_s \frac{d(\rho_s W_i)}{dz} = S_i \tag{4.49}$$

The source terms are given in Table 4.4. The mass of the inert gangue is considered to remain constant in the pellets during the reduction. The weight fraction of gangue is calculated by:

$$W_{gangue} = \frac{m_{gangue}}{m_{total}} \tag{4.50}$$

The solid density is calculated by:

$$\rho_s = (1 - \epsilon_{bed}) \sum_{i}^{6} W_i \rho_i (1 - \epsilon_i)$$
(4.51)

Table 4.4: Source terms of equation 4.49.

| Component                      | $S_i  [{ m kg}  { m m}^{-3}  { m s}^{-1}]$   |
|--------------------------------|--|
| Fe <sub>2</sub> O <sub>3</sub> | $S_{Fe_2O_3} = -3M_{Fe_2O_3}(r_1 + r_4)$   |
| Fe <sub>3</sub> O <sub>4</sub> | $S_{Fe_3O_4} = M_{Fe_3O_4}(2r_1 - r_2 + 2r_4 - r_5)$   |
| Fe <sub>0.95</sub> O           | $S_{Fe_{0.950}} = M_{Fe_{0.950}} \left(\frac{60}{19}r_2 - r_3 + \frac{60}{19}r_5 - r_6\right)$ |
| Fe                             | $S_{Fe} = 0.95 M_{Fe} (r_3 + r_6)$   |
| С                              | $S_C = M_C(r_9 + r_{10})$  |

#### **Energy equation**

The temperature of the solid depends on various heat transfer phenomena, as can be seen in equation 4.52. Advection, conduction, convection, and a source term are considered. The discretization of this equation is given in Appendix J.

$$-\rho_s C_{p,s} u_s \frac{dT_s}{dz} = \frac{d}{dz} \left( \lambda_{eff} \frac{dT_s}{dz} \right) + a_s h(T_g - T_s) + \sum_{i=1}^{10} -(r_i \Delta_r H_i)$$
(4.52)

The specific heat capacity of the solid mixture is determined by the Kopp-Neumann law, as shown in equation 4.43. In order to take into account the different types of energy transport in the porous medium, the notion of effective conduction is used, as shown below [26]. The effective conductivity is calculated as the sum of two terms. The first is a static contribution, accounting for the effects of radiation, gaseous conduction in the voids of the pellets, and inter-particle conduction. The second term is a dynamic contribution, translating the influence of gas convection on effective conduction.

$$\lambda_{eff} = \lambda_{static} + \lambda_{dynamic} \tag{4.53}$$

The static term is calculated using the correlation of Zehner and Schlünder [98], which is valid for all bed porosities. The formula is not shown in this thesis due to its cumbersomeness. However, this correlation uses the conductivity of the solid mixture, which is calculated taking into account the porosity of the pellet itself, according to [83]:

$$\lambda_p = \frac{1}{4} \left[ \lambda_g (3\epsilon_p - 1) + \lambda_p (2 - 3\epsilon_p) \left[ \left( \lambda_g (3\epsilon_p - 1) + \lambda_p (2 - 3\epsilon_p) \right)^2 + 8\lambda_p \lambda_g \right]^{\frac{1}{2}} \right]$$
(4.54)

This correlation is valid for  $0.15 < \epsilon_p < 0.65$ . The validity of this formula has been checked after simulation.

The dynamic term is calculated by [30]:

$$\lambda_{dynamic} = \frac{c_t u_g C_{p,g} d_p}{Pe}$$
(4.55)

in which the Peclet number is calculated by:

$$Pe = \frac{u_g d_p}{\bar{D}_{axial}} \tag{4.56}$$

The average axial diffusion coefficient of the flow  $\bar{D}_{axial}$  is calculated by the weighted average of the axial diffusion coefficients of all gaseous components (which are calculated by formula 4.41):

$$\bar{D}_{axial} = \frac{\sum_{i=1}^{6} x_i D_{axial,i}}{\sum_{i=1}^{6} x_i}$$
(4.57)

#### 4.3.4. Numerical mathematics

The mentioned ordinary differential equations: 4.39, 4.42, 4.47, 4.48, 4.49, and 4.52 are discretized using the finite difference method. The used grid is shown in Figure 4.6. Increasing the number of grid points results in higher accuracy, but a longer calculation time. Hence, the number of grid points is varied in multiple simulations and eventually set to Imax = 1000, which gives accurate simulation results and a decent calculation time. The discretization of all differential equations are given in Appendices F to J. The advection term is most sensitive for numerical instability. Hence, when the system of differential equations is solved, the algorithm starts using first-order upwind discretization for the advection

terms. First-order upwind is stable and has good convergence properties. However, it can cause numerical diffusion [19]. After half the total number of iterations, the algorithm switches to second-order upwind to increase accuracy.

After discretization, all differential equations are written as a system of linear equations and solved simultaneously, using the explicit Gauss-Seidel method, which is an iterative process [11]. A relaxation factor is used to ensure stability. This relaxation factor ensures that the solution of the new iteration does not differ too much from the previous iteration, using the following method to solve for a variable X:

$$X_{new} = X_{new} * relaxation factor + (1 - relaxation factor) * X_{old}$$
(4.58)

The relaxation factor is set at a value between 0 and 1. Note that when a relaxation factor of 1 is chosen, the method is the same as the classical Gauss-Seidel method. The higher the relaxation factor, the faster the convergence, but the lower the stability of the system. Hence, the iteration process starts with a low relaxation factor to ensure stability. Later on, the relaxation factor is increased to enhance convergence speed.



Figure 4.6: The used numerical grid over the height of the shaft furnace.

The algorithm used to solve all equations is shown in Figure 4.7. Initially, all gas and solid streams are initialized equal to the shaft furnace's input gas and solid streams, respectively. The calculation starts from the bottom of the shaft furnace (i = 1) and proceeds toward the top (i = Imax). The boundary conditions used to solve the differential equations are given later in this paragraph. First, the combined continuity and momentum equation is solved, returning the pressure and velocity gradients over the height of the shaft furnace. The calculation is converged whenever the relative error between the new and old calculated value of the pressure is lower than  $10^{-8}$ , or whenever the number of iterations exceeds 5000. This strict tolerance has been chosen to ensure mass conservation of the system. The relative error between the new and old iterated value of a vector containing variable X is calculated as:

$$\epsilon = \frac{||X_{new} - X_{old}||}{||X_{new}||} \tag{4.59}$$

Second, the reaction rates of the ten chemical reactions are calculated. The reaction rates of the six reduction reactions are calculated as a function of the pellet's local solid and gas composition, temperature, pressure, and conversion. This calculation is performed using the pellet sub-model, as described in Paragraph 4.2. The reaction rates of the two homogenous and two heterogeneous reactions are calculated as described in Paragraph 4.3.1. Third, the solid mass and gaseous mole balances are solved, returning the solid weight fractions and the gaseous mole fractions. Fourth, the gas and solid energy equations are solved, returning the gas and solid temperature. The relative errors of all weight fractions, mole fractions, and both the gas and solid temperatures are calculated using formula 4.59. Afterwards, the errors are summed up using that the total error is equal to the square root of the sum of the squares of the individual errors. This calculation is converged whenever the total error is lower than  $10^{-4}$  or whenever the number of iterations exceeds 5000. At last, the results are exported and combined with the other zone of the shaft furnace.



Figure 4.7: The structure of the algorithm to solve zones 1 and 2 of the shaft furnace model.

#### **Boundary condtions**

The boundary conditions below are used to solve the ordinary differential equations. As discussed in Chapter 3, the inlet pressure, outlet pressure, and mole flow are coupled because the pressure and gas velocity are coupled by equations 4.47 and 4.48. In this thesis, the inlet pressure and outlet pressure are set as boundary conditions, whereas the mole flow is a result of solving both equations.

At the bottom of the shaft furnace:

$$T_{g}(0) = T_{g,inlet}$$

$$\frac{dT_{s}}{dz}\Big|_{z=0} = 0$$

$$x_{i}(0) = x_{i,inlet}$$

$$\frac{dW_{i}}{dz}\Big|_{z=0} = 0$$

$$p_{g}(0) = p_{g,inlet}$$
At the top of the shaft furnace:
$$\frac{dT_{g}}{dz}\Big|_{z=H_{shaft}} = 0$$

$$T_{s}(H_{shaft}) = T_{s,inlet}$$

 $\frac{1}{dz}|_{z=H_{shaft}} = 0$  $W_i(H_{shaft}) = W_{i,inlet}$ 

 $p_g(H_{shaft}) = p_{g,outlet}$ 

#### 4.3.5. Validation of the shaft furnace model

To validate the shaft furnace model, the operating MIDREX plant named "Gilmore", located in Oregon in the USA is simulated. This plant produces  $26.4 \text{ t} \text{ h}^{-1}$  of DRI. All characteristics of this plant are shown in Figure 4.8 [56, 68]. The simulation results are compared against the simulation results of Béchara et al. [8] and against the real plant data [56, 68]. Before comparing the present model, it should be emphasized that it only contains the two reduction zones of the shaft furnace. In reality and the model made by Béchara et al., the shaft furnace does have a transition zone and a cooling zone. As discussed in Paragraph 2.4, in the model made by Béchara et al., the input gas flow of zone 2 is a mixture of the reducing gas and a fraction of the cooling gas that does not leave the furnace radially before it enters the transition zone. Hence, comparing zone 2 of the present model to zone 2 of the model of Béchara et al. is not fair. Moreover, most DRI carburization occurs inside the transition zone, whereas in the cooling zone, no further reactions occur. Hence, the carburization of the DRI leaving the shaft furnace in the present model is unrealistic. On the other hand, the solid and gas inputs of zone 1 are equal in both the present model and the model made by Béchara et al., since these are not affected by the transition and cooling zones, making it plausible to compare.

Figures 4.9 and 4.10 show the simulation results of the solid mass flows and the gaseous mole flows, respectively, of zone 1 of the Gilmore plant simulation for both the model made by Béchara et al. [8] and the present model. Height zero corresponds to the reducing gas inlet. Looking at the solid mass flows, hematite disappears rapidly for both models (within 1 meter). In the present model, the reduction is caused only by hydrogen. Magnetite is reduced by hydrogen and carbon monoxide within approximately 5 meters for both models. Complete metallization of the pellets is obtained after 6 and 7.5 meters for the model of Béchara et al. and the present model, respectively. The most significant contrast between the solid mass flows of both models in zone 1 can be observed at wüstite. In the present model, wüstite reaches a maximum of  $7 \text{ kg s}^{-1}$ , and in the model of Béchara et al., it only reaches



Figure 4.8: Gilmore plant characteristics, used to validate the shaft furnace model. Values are obtained from [56, 68].

a maximum of  $3 \text{ kg s}^{-1}$ . As discussed earlier, while validating the pellet model (Paragraph 4.2), the reduction reactions from magnetite toward wüstite are a bit faster in the simulations of this thesis compared to those of Béchara et al., which clarifies the discrepancies in the mass flows of wüstite. The carbon content in the model of Béchara et al. increases gradually by the Boudouard reaction until the bottom of the shaft furnace, where it drops due to the inverse of this reaction. In the present model, the deficient concentration of methane entering the shaft furnace causes no carbon formation by the methane deposition reaction. Therefore, all carbon is also formed by the Boudouard reaction alone.



Figure 4.9: Simulation results of the model made by Béchara et al. [8] (left) and the results of the present model (right) of the solid mass flows in zone 1 of the Gilmore plant.

Focussing on the gaseous mole flows in zone 1 of both models, the evolution of the components  $H_2$ , CO,  $H_2O$ , and  $CO_2$  look similar. However, two large differences are immediately visible. First, the total gas mole flow input at the bottom of the shaft furnace is approximately three times larger in the present model than in the model of Béchara et al. As a matter of fact, the input mole flow is mainly the result of the pressure drop calculation, and the real total gas mole flow input of the plant is unknown. Second, in the model by Béchara et al., the mole flow of methane reduces due to the methane reforming reaction. In the present model, the mole flow of methane remains constant because of the already very low concentration.



Figure 4.10: Simulation results of the model made by Béchara et al. [8] (left) and the results of the present model (right) of the gas mole flows in zone 1 of the Gilmore plant.

Although the inputs of zone 2 of the present model differ from that of the model made by Béchara et al., the simulation results are shown in Figure 4.11. Again, hematite disappears rapidly in both models. Due to the lower temperature in this colder central zone, in both models magnetite reaches complete reduction just before it leaves the bottom of the shaft furnace. However, in the present model the mass flow of magnetite gradually decreases until the outlet of the shaft furnace, whereas in the model made by Béchara et al., it remains almost constant until it drops rapidly before the outlet. Looking at wüstite, it does not reach complete conversion. In the present model, only 36% metallization is reached in zone 2. In the model of Béchara et al., the metallization is only 24%. In both models, negligible carbon is formed, hence not shown in the figures.



Figure 4.11: Simulation results of the model made by Béchara et al. [8] (left) and the results of the present model (right) of the solid mass flows in zone 2 of the Gilmore plant.

As a final point on the comparison of the present model with the model of Béchara et al., both models show similarities and differences. Unfortunately, no real plant data on the evolution of the gases and solids inside the shaft furnace is available. Hence, it is impossible to state which model gives the same results as reality. However, the output values of the real operating Gilmore plant are known as shown in Table 4.5.

The present model can simulate the Gilmore plant with an average relative error of 14.4%. This error is calculated by the sum of the relative errors of all parameters, divided by the total number of parameters, given in Table 4.5. Béchara et al. simulated the plant with an average relative error of 7.4%. The most significant relative error of the present model can be assigned to the carbon weight fraction in the solid (66.5%). This can be declared because most carburization occurs inside the shaft furnace's transition zone. Since the present model does not have a transition zone, the weight fraction of the carbon in the solid is inaccurate. Neglecting the carbon weight fraction simulation result, because they can be attributed to a missing transition zone, the average relative error of the shaft furnace model is **9.2%**. Moreover, in the transition and cooling zones of the shaft furnace, no further reduction of the pellets occur. Therefore, the model's accuracy for all components except carbon is considered sufficient to simulate the cases defined in the BOD.

Table 4.5: Simulation results of the shaft furnace model compared to real industrial data of the Gilmore plant [56, 68] and the simulation results of the model of Béchara et al. [8].

|        | Parameter                               | Plant data | Present model | Model of Béchara et al. |
|--------|---|------------|---------------|-------------------------|
| op gas | H <sub>2</sub> (vol%)                   | 37.00      | 31.33         | 42.20                   |
|        | H <sub>2</sub> O (vol%)                 | 21.20      | 26.12         | 17.60                   |
| Ĕ      | CO (vol%)                               | 18.90      | 16.99         | 19.00                   |
|        | CO <sub>2</sub> (vol%)                  | 14.30      | 17.51         | 14.60                   |
|        | CH <sub>4</sub> + N <sub>2</sub> (vol%) | 8.60       | 8.05          | 6.60                    |
| olid   | DRI production (t/h)                    | 26.40      | 26.10         | unknown                 |
| tom s  | Fe <sub>2</sub> O <sub>3</sub> (mass%)  | 0          | 0             | 0                       |
| Bott   | Fe <sub>3</sub> O <sub>4</sub> (mass%)  | 0          | 0             | 0                       |
|        | Gangue (mass%)                          | 6.30       | 6.96          | unknown                 |
|        | Carbon (mass%)                          | 2.00       | 0.67          | 1.80                    |
|        | Metallization (%)                       | 93.00      | 94.08         | 93.00                   |
|        | Average relative error (%)              | -          | 14.4          | 7.4                     |

# 5

# Sensitivity study and Discussion

This chapter provides a sensitivity study in which five cases with different  $H_2/CO$  ratios of the inlet reducing gas are studied. The composition of the inlet reducing gas of each case is specified in Table 3.1. For each case, multiple simulations are performed in which the inlet pressure of the reducing gas has been varied (to change the mole flow in conjunction), to obtain a sensitivity analysis. This chapter is subdivided into two paragraphs. The first paragraph only gives the factual results of the sensitivity study. The second paragraph interprets and clarifies the results.

# 5.1. Sensitivity study

Figure 5.1 shows that increasing the gas input pressure from 135 kPa to 300 kPa, increases the input gas mole flow for all H<sub>2</sub> / CO ratios. Moreover, at larger H<sub>2</sub> / CO ratios, the input gas mole flow is higher for the same input pressure.



Figure 5.1: Results of all simulations, showing the gas input mole flow vs the gas input pressure.

Figures 5.2(a) and 5.2(b) show that increasing the input pressure, which increases the input mole flow, increases the metallization for all  $H_2/CO$  ratios. Furthermore, the maximum achievable metallization decreases with an increasing ratio of  $H_2/CO$ . In case 1 ( $H_2/CO = 1$ ) and case 5 ( $H_2/CO = \infty$ ), the maximum metallization is 98.37% and 95.97%, respectively. Moreover, the increase in metallization is for all  $H_2/CO$  ratios the largest, until it reaches approximately 90%. The slope of both figures decreases rapidly for higher metallizations. Looking at Figure 5.2(a), it is clear that a higher  $H_2/CO$  ratio results in a lower metallization for the same input mole flow.



(a) Metallization vs the gas input mole flow.



(b) Metallization vs the gas input pressure.

Figure 5.2: Simulation results of all five cases, showing the metallization vs the gas input mole flow (a) and vs the gas input pressure (b).

Simulation of all five cases with all different input pressures gives abundant results and figures of the behaviour of the shaft furnace. Hence, only a few figures are given. The results of zone 1 for case 1 and case 5, both with a gas input mole flow of 4.8 kmol, are shown in Figures 5.3 and 5.4, respectively. Looking at figures (a), one can observe that full metallization in zone 1 is reached within 13 m and 15 m for case 1 and case 5, respectively. Moreover, no carbon is formed in case 5. For figures (b) and (c), it is visible that in case 1 all ten chemical reactions take place, which are shown in Appendix E. In case 5, only the three reduction reactions by hydrogen are viable. Inspecting figures (d), it is clear that the heat transfer is excellent in both cases. In case 1, the gas temperature immediately decreases whenever it enters the shaft furnace. Afterwards, it decreases gradually and remains quite high until it drops below 900 K after 11 m. In case 5, the gas temperature is already below this point after 7 m. Moreover, two temperature plateaus are visible in case 5. The first one is visible just after the gas has entered the shaft furnace. The second is visible between 4 and 6 m.


Figure 5.3: Simulation results of case 1 with a total gas input mole flow of 4.8 kmol. These four figures show the results of zone 1. z = 0 m and z = 16 m correspond to the inlet of the reducing gas and the pellets, respectively.



(c) Reaction rates

Figure 5.4: Simulation results of case 5 with a total gas input mole flow of 4.8 kmol. These four figures show the results of zone 1. z = 0 m and z = 16 m correspond to the inlet of the reducing gas and the pellets, respectively.

The results of the same simulation for zone 2 of case 1 and case 5 are given in Figures 5.5 and 5.6, respectively. Figure 5.5(a) shows that all magnetite is reduced before the pellets leave the shaft furnace. However, the pellets still contain wüstite, and full metallization is not reached. Figure 5.6(a) shows a large amount of magnetite, and no metallic iron is formed whenever the pellets leave the shaft furnace. Hence, no metallization is reached in this zone. Looking at Figure 5.5(d), one can observe that the temperature of the gas increases after it enters the shaft furnace and that it drops below 600 K after 15 m. For case 5, the gas temperature immediately drops after entering the furnace and reaches this point after 1 m. Hence, only reaction 2.1 takes place after this point.



Figure 5.5: Simulation results of case 1 with a total gas input mole flow of 4.8 kmol. These four figures show the results of zone 2. z = 0 m and z = 16 m correspond to the inlet of the reducing gas and the pellets, respectively.



Figure 5.6: Simulation results of case 5 with a total gas input mole flow of 4.8 kmol. These four figures show the results of zone 2. z = 0 m and z = 16 m correspond to the inlet of the reducing gas and the pellets, respectively.

### 5.2. Discussion

This paragraph will interpret and clarify the results given in the previous paragraph. First, it will be explained why the mole flow of the input gas increases with increasing  $H_2/CO$  ratio. Looking at the Ergun equation (4.46), the pressure drop in the shaft furnace increases with increasing gas viscosity and density. Since the viscosity and density of hydrogen are lower than carbon monoxide, the pressure drop decreases with an increasing  $H_2/CO$  ratio. This results in a higher input gas mole flow. Reaching a high metallization (say > 90%) for cases with a higher  $H_2/CO$  ratio, requires a high input pressure and in conjunction a high input mole flow. The power required for the process gas compressors in the MIDREX plant is related to the volume flow multiplied by the pressure difference over the compressor. Consequently, the process gas compressors will use more electricity in cases with higher hydrogen contents.

Figure 5.2(a) shows that a higher gas input mole flow results in better metallization. This can be explained by the fact that a larger mole flow results in more heat input into the reactor, so the temperature remains higher. Moreover, a larger input mole flow results in more hydrogen and carbon monoxide molecules, which in return causes a lower GOD of the gas along the reactor. The same figure shows that a lower  $H_2/CO$  ratio results in better metallization while maintaining the same input mole flow. This is mainly the effect of the exothermal reactions which take place by utilizing CO. In other words, more CO results in a higher temperature inside the reactor, which in return causes better metallization. This result matches the results obtained by other researchers, as discussed in Paragraph 2.4. Moreover, it is also obvious when comparing Figures 5.5 and 5.6. In Figure 5.6, the temperature drops rapidly after the gas has entered the shaft furnace, owing to the endothermic reduction reactions 2.2 and 2.3. Since the thermodynamics and kinetics of the reduction reactions by hydrogen are favourable at high temperatures, the low temperature decreases the extent of these reactions. On the other hand, the thermodynamics of the reduction by carbon monoxide is favourable at low temperatures. Hence, when the reducing gas containing carbon monoxide enters the cold zone 2, the exothermic reduction reaction 2.6 takes place and causes a small increase in the temperature of the reactor, as shown in Figure 5.5.

The temperature profiles of zone 1, shown in Figures 5.3 and 5.4, requires some clarification as well. As mentioned, the gas temperature in case 1 decreases just after it enters the shaft furnace, which is

the effect of the endothermic inverse of the Boudouard reaction (2.11), which takes place at this point due to the high temperature. In case 5 the two temperature plateaus are caused by the fact that only a few reduction reactions of reaction 2.3 takes place per second. Since this reaction is just slightly endothermic, the temperature remains almost constant. Similar to zone 2, the temperature in zone 1 of case 1 remains higher due to the heat input by CO.

Figures 5.2(a) and 5.2(b) show that the increase in metallization for all  $H_2/CO$  ratios is the largest, until it reaches approximately 90%. The slope of both figures decreases rapidly for a higher metallization. This is the effect of the two distinct zones in the shaft furnace model. Metallization in zone 1 is easily obtained. To further increase the shaft furnace's total metallization, once complete metallization is obtained in zone 1, the metallization in zone 2 must be increased. Because of the lower gas flow and input temperature in this zone, metallization is harder to obtain. Figure 5.2(b) shows that for an input pressure below 180 kPa the largest metallization is reached for an increasing  $H_2/CO$  ratio. Of course, the input mole flow is higher for an increasing  $H_2/CO$  ratio, which causes better metallization, but this effect only does not explain the higher metallization. This effect is also the result of the better reduction by hydrogen at elevated temperatures, which are present in zone 1.

# 6

## Conclusion and recommendations

This chapter concludes all findings of the thesis and answers the research question. Furthermore, it gives a critical look at the present thesis and provides recommendations for further research.

### 6.1. Conclusion

Due to the high  $CO_2$  emissions and the pressure of politics and society, TSN is forced to change its production process drastically. In fact, TSN emits 12.6 Mt  $CO_2$  per year while producing 7.2 Mt steel per year. Therefore, TSN decided to switch to the innovative production route using a DRP in combination with a REF to replace the blast furnace. By doing so, the basic oxygen furnace can maintain its current production process, and limited concessions must be made on the product's behalf. In addition, the production capacity, the economic value of the slag, and the position in the iron ore market are more beneficial than producing steel with the classic DRP-EAF production route.

Implementing the DRP and REF technologies operating on natural gas results in direct  $CO_2$  emission avoidance. To further reduce emissions, the natural gas feed of the DRP can be substituted with green hydrogen. When steel is produced using 100% green hydrogen as the reducing gas, it is called green steel. Producing green steel comes along with an awkward problem regarding the carbon content in the DRI. In fact, DRI produced by 100% hydrogen results in a carbon content of 0% instead of 2-4% when produced by natural gas. The carbon in the DRI is required for the primary process of the basic oxygen furnace, further reduction of the iron oxides in the REF, and decreasing the melting point of iron. It might be possible to add carbon in this REF, but this has not been proven in industry. Moreover, the carbon added in the DRP is embedded in the iron structure, resulting in a better reduction of the iron oxides in the REF and reduces the reactivity of the produced DRI to re-oxidize.

Besides the carburization of the DRI, metallization is a critical parameter in the production process using a DRP. To answer the research question "What is the influence of the ratio of hydrogen to natural gas inserted in the direct reduced iron plant on the performance of the reactor?", knowledge of the reduction process and reduction technologies is required, which is obtained from the literature. In addition, a mathematical model of the shaft furnace is made.

Iron ore pellets in the shaft furnace of the DRP are reduced in three subsequent reducing steps, going from  $Fe_2O_3$  towards  $Fe_3O_4$ ,  $Fe_{(1-x)}O$  and Fe. Reduction is either by hydrogen or carbon monoxide, which are endothermic and exothermic, respectively. The reduction step from wüstite to iron is the slowest. This reduction step is thermodynamically favourable at high and low temperatures for reduction by hydrogen and carbon monoxide, respectively. Looking at the kinetics of these gas-solid reactions, the kinetics are always favourable at higher temperatures. Hence, the reduction by hydrogen is always the most favourable at higher temperatures. In the case of carbon monoxide, it is a battle between thermodynamics and kinetics. An unambiguous statement about the rate-limiting transport phenomenon step of the reduction process is impossible, making this process mixed rate-limited. When comparing

the reduction times of iron oxides by hydrogen and carbon monoxide, numerous studies determined that the reduction time of hydrogen is far less at all temperatures. This implies that the diffusion rate is more important than the thermodynamic driving force.

The two most competitive direct reduction technologies using a shaft furnace available on the market are the technologies of MIDREX and ENERGIRON. A MIDREX plant uses an external reformer, whereas the ENERGIRON plant uses in-situ reforming. The ENERGIRON process is more intensive and has, in general, better technical specifications. Moreover, it has selective  $CO_2$  emissions which may be used for CCUS. On the other hand, the MIDREX process is safer, more flexible, and more mature. In this thesis, the MIDREX process is modelled.

This thesis's multiscale modelling work is similar to the state-of-the-art modelling work made by Béchara et al. However, due to the time restrictions of the thesis period, only two of the four zones of the shaft furnace are modelled. On the other hand, in this thesis, the pressure drop of the reactor is included since it is an important parameter to determine the total energy consumption of the DRP (including the electrical consumption of the reducing gas compressors).

The pellet scale model is grain-based and incorporates the change in the morphological structure of the pellets during the reduction process. Moreover, it uses "Sohn's law of additive reaction times" to reduce the calculation time while considering the characteristic times of the external mass transfer, diffusion, and chemical reactions. The pellet model is validated against numerical data, which is validated against experimental data. The comparison shows good agreement. However, some minor discrepancies are visible for the mass/mole fractions of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>0.95</sub>O. These discrepancies are caused by faster magnetite to wüstite reduction reactions in the simulations of this thesis. These discrepancies can be attributed to the different sources of the physical properties used in the models.

The shaft furnace model includes the two reduction zones, but is missing the transition and cooling zones. Zone 1 is the largest peripheral zone, receiving 92% of the pellet input. Zone 2 is smaller, colder, and more centrally located and receives residual pellets. The gas split between both zones is calculated so that the ratio of the number of gas moles per kilogram of solid that both enter zone 2, is 70% of the ratio of the number of gas moles per kilogram of solid entering zone 1. Moreover, the gas input temperature of zone 2 is 25% lower than zone 1. The shaft furnace model can handle six gaseous components: hydrogen, water, carbon monoxide, carbon dioxide, methane, and nitrogen. Furthermore, the shaft furnace model can handle six solid components: hematite, magnetite, wüstite, iron, carbon, and gangue. Gangue and nitrogen have been treated as inert components.

Zones 1 and 2 are modelled as 1D zones solving the local energy, mass, and momentum equations while using the pellet sub-model to obtain the kinetics of the six reduction reactions. In addition to these reactions, the homogeneous steam methane reforming and water gas shift reactions, and the heterogeneous Boudouard and methane deposition reactions are enabled in the shaft furnace model. The mass and energy conservation equations are defined for the solid and gas phase. The continuity and momentum equation for the gas phase is defined in its combined form. All ordinary differential equations are discretized and solved simultaneously using the explicit Gauss-Seidel method, which is an iterative process. The thesis provides a clear overview of the algorithm used to solve the equations using MATLAB as the programming language.

The shaft furnace model is compared to a real operating MIDREX plant, named "Gilmore". The simulation results are validated against the simulation results of Béchara et al. and the real plant data. The simulation results of this thesis are very similar to the results of Béchara et al. however some discrepancies are visible. Zone 1 shows complete metallization for both models. The most significant contrast between the solid mass flows in zone 1 can be observed at wüstite. These differences can be attributed to the faster reduction reactions from magnetite to wüstite in the present model, compared to the model of Béchara et al. Focussing on the gaseous mole flows in zone 1 of both models, the evolution of the components H<sub>2</sub>, CO, H<sub>2</sub>O, and CO<sub>2</sub> look similar. However, two significant differences are immediately visible. First, the total gas mole flow input at the bottom of the shaft furnace is approximately three times larger in the present model than in the model of Béchara et al. As a matter of fact, the input mole

flow is mainly the result of the pressure drop calculation, and the real total gas mole flow input of the plant is unknown. Second, in the model by Béchara et al. the mole flow of methane reduces due to the methane reforming reaction. In the present model, the mole flow of methane remains constant due to the already deficient concentration. Due to the missing transition and cooling zone in the present model, which influences the gas input of zone 2 in reality, comparing zone 2 of the present model to zone 2 of the model of Béchara et al. is not fair. Nevertheless, the zones are compared to gain insight into the performance of the present model. In both models, magnetite is fully reduced before the pellets leave the bottom of the shaft furnace. In the present model, the metallization of zone 2 is higher than in the model of Béchara et al.

Unfortunately, no real plant data on the evolution of the gases and solids inside the shaft furnace is available. Hence, it is impossible to state which model gives the same results as reality. However, the output values of the real operating Gilmore plant are known and compared against the result of the present model, resulting in an average relative error of 14.4%. The most significant relative error can be assigned to the carbon weight fraction in the solid. This can be declared because most carburization occurs inside the shaft furnace's transition zone. Since the present model does not have a transition zone, the weight fraction, because it can be attributed to a missing transition zone, the average relative error of the shaft furnace model is 9.2%. Moreover, in the transition and cooling zone of the shaft furnace, no further reduction of the pellets occurs. Therefore, the model's accuracy for all components except carbon is considered sufficient.

Increasing the ratio  $H_2/CH_4$  in the feed of the MIDREX plant means hydrogen is injected into the reducing gas just before it enters the shaft furnace, and less methane will be reformed in the reformer. This results in a different  $H_2/CO$  ratio of reducing gas entering the shaft furnace. To answer the research question, the validated shaft furnace model is used to simulate five different cases with different  $H_2/CO$  ratios. The shaft furnace used for these simulations has a diameter of 7.25 m, a reduction zone height of 16 m, and produces 2.5 Mt DRI per year. In all simulations, the reducing gas temperature is maximized to 950 °C to reach the highest metallization. The reducing gas input pressure, together with the input mole flow, are varied in the simulations.

The results of the simulations of the five cases show that the mole flow of the gas input increases with an increasing ratio of  $H_2$  / CO, while the gas input pressure remains the same. This can be explained by the fact that the pressure drop in the shaft furnace increases with increasing gas viscosity and density. A larger gas input mole flow results in better metallization, because a larger mole flow results in more heat input into the reactor. Hence, the temperature remains higher. Moreover, a larger input mole flow results in more flow results in more hydrogen and carbon monoxide molecules, which cause a lower GOD of the gas along the reactor.

Increasing the  $H_2/CO$  ratio of the reducing gas reduces the metallization of the DRI, independent of the input gas mole flow. This result is similar to the literature and is caused by a thermal effect that occurs throughout the shaft furnace. Increasing the hydrogen concentration results in a more endothermic reduction, lowering the temperature. Since hydrogen's reduction kinetics and thermodynamics are favourable at higher temperatures, the reduction slows down. In the case of carbon monoxide, thermodynamics are favourable at lower temperatures, making the reduction possible at lower temperatures and increases the temperature in the shaft furnace. Especially in zone 2, where the temperature is lower, this effect is dominant, and metallization is harder to obtain. Besides that, increasing the metallization from a level already above approximately 90% requires a significantly more increase in the mole flow of the input gas than below this point, for all  $H_2/CO$  ratios. This is the effect of the two distinct zones of the shaft furnace. To further increase the total metallization of the shaft furnace, whenever complete metallization in zone 1 is obtained, the metallization in zone 2 must be increased. Because of the lower gas flow and input temperature in this zone, metallization is harder to obtain.

To reduce the CO<sub>2</sub> production of TSN, natural gas must be substituted with hydrogen in the feed of the DRP. The more hydrogen is added, the higher the input pressure together with the input mole flow of the reducing gas must be to reach the same metallization, which increases the electrical consumption

of the process gas compressors of the MIDREX plant. Thus, even without considering the extremely high amount of electricity required to produce green hydrogen, using more hydrogen results in a higher electrical demand for the process gas compressors. Substituting natural gas with hydrogen also influences the other utilities of the plant. Therefore, the present model could be incorporated as a custom block in Aspen Plus to make it a fundamental first step in modelling the whole DRP. Further, increasing the hydrogen content in the feed of the DRP still causes the awkward problem regarding the carbon content in the DRI. However, since two of the four zones in the present shaft furnace model are missing, the carbon content in the DRI leaving the shaft furnace could not be investigated. To conclude, substituting natural gas with hydrogen does have its disadvantages, but it is highly necessary to become  $CO_2$  neutral in the future.

### 6.2. Recommendations

This thesis provides a strong literature review that covers all the fundamental information required to understand and build a mathematical model of the DRP. The model is based on the state-of-the-art research provided in the literature. However, it is not completed yet and contains some flaws.

The average relative error of the present model (neglecting the carbon weight fraction) is 9.2%. Hence, the results of the simulations could differ from reality by this percentage. Besides that, the present model separates the reduction zone into two distinct zones, where the input mole flow and the temperature of the reducing gas differ. In reality, as you approach the centre of the shaft furnace, the temperature and mole flow of the reducing gas will gradually decrease. Hence, this is a rough modelling assumption.

This thesis explains the problems regarding the leaking carbon content in the DRI when green steel is produced. Moreover, it explains the need for carbon in the DRI for subsequent production processes. The present shaft furnace model does not include the transition zone where most of the DRI's carburization occurs. Hence, this zone is necessary to determine the carburization of the DRI. In further research, adding the transition and cooling zones to the shaft furnace model is recommended to investigate the influence of the ratio  $H_2/CO$  on the carburization of the DRI and to improve accuracy of the model. Furthermore, the present model makes no distinction between soot and cementite. Cementite is more embedded in the iron structure, resulting in a better reduction of iron oxides in the REF. Hence, information about the amount of cementite and soot in the DRI is essential. Further research into reaction kinetics involving the differences between cementite and soot should be added to improve the model.

Solving all ordinary differential equations involves numerical mathematical methods, which are explained in this thesis. However, some improvements could be made to this aspect. The discretization of the differential equations could be done by higher-order methods to increase the accuracy of the solutions. This thesis uses the Gauss-Seidel method to solve the system of linear equations. No detailed research is conducted to investigate whether this method is the most suitable for the proposed problem. Hence, some opportunities are available for further research on these aspects to increase numerical accuracy and reduce the calculation time.

Whenever the present shaft furnace model is improved, the most exciting implementation is to make a complete plant scale model using Aspen Plus. To couple the shaft furnace model to the other utilities of the DRP, the MATLAB code of the shaft furnace model can be implemented in Aspen Plus as a custom block. All other utilities of the MIDREX plant are built-in blocks in Aspen Plus and can easily be added to the shaft furnace model. This provides the capability to investigate the influence of substituting natural gas with hydrogen in a direct reduced iron plant on the performance of the whole plant. For instance, the total  $CO_2$ , energy, and material balance of the plant could be mapped for different  $H_2 / CH_4$  ratios of the feed of the plant. This might be a very welcome feature for TSN and thus highly recommended.

# **Appendices**



# Shaft furnace simulation results from literature



Figure A.1: MIDREX shaft simulation results. The solid fractions are depicted by the mass fraction whereas the gas fractions are depicted by the mole fraction. The simulated MIDREX shaft produces CDRI. [30].



Figure A.2: ENERGIRON shaft simulation results. The solid fractions are depicted by the mass fraction whereas the gas fractions are depicted by the mole fraction. The simulated ENERGIRON shaft produces CDRI. [30].



# **MIDREX** plant simulations from literature



Figure B.1: Gas and solid flow composition of a MIDREX plant simulation, operating with 100% natural gas [63].



Figure B.2: Gas and solid flow composition of a MIDREX plant simulation, operating with 95 vol% hydrogen and 5 vol% natural gas [63].

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# Pure component properties

Table C.1: Properties of relevant pure gaseous components in the system [42].

| Characteristics  | Hydrogen       | Water            | Carbon<br>monoxide | Carbon<br>dioxide | Methane         | Nitrogen       |
|--|----------------|------------------|--------------------|-------------------|-----------------|----------------|
| Formula  | H <sub>2</sub> | H <sub>2</sub> O | CO                 | CO <sub>2</sub>   | CH <sub>4</sub> | N <sub>2</sub> |
| Molecular weight $[g mol^{-1}]$  | 2.02           | 18.0             | 28.0               | 44.0              | 16.0            | 28.0           |
| Atmospheric boiling point [°C]   | -252.8         | 99.97            | -191.5             | -56.56            | -161.5          | -195.8         |
| Atmospheric melting point [°C]   | -259.1         | 0.000            | -205.0             | X                 | -182.5          | -210.0         |
| $\begin{array}{c} \mbox{Atmospheric density at} \\ \mbox{20 °C } [\mbox{kg}\mbox{m}^{-3}] \end{array}$ | 0.08375        | 998.2            | 1.164              | 1.839             | 0.6682          | 1.165          |

Table C.2: Properties of relevant pure solid components in the system [30, 42].

| Characteristics  | Hematite                       | Magnetite                      | Wüstite              | Iron   | Carbon |
|--|--------------------------------|--------------------------------|----------------------|--------|--------|
| Formula  | Fe <sub>2</sub> O <sub>3</sub> | Fe <sub>3</sub> O <sub>4</sub> | Fe <sub>0.95</sub> O | Fe     | С      |
| Molecular weight $[gmol^{-1}]$                             | 159.69                         | 231.53                         | 69.05                | 55.845 | 12.011 |
| Atmospheric melting point [°C]                             | 1565                           | 1583                           | 1377                 | 1538   | 3642   |
| Atmospheric density at $20 \degree C [kg m^{-3}]$          | 5275                           | 5200                           | 5867                 | 7874   | 2260   |
| Molar volume at 20 °C [cm <sup>3</sup> mol <sup>-1</sup> ] | 30.27                          | 44.53                          | 11.77                | 7.09   | 5.31   |

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# Pellet input

The input pellets do have the following composition (specified by TSN):

65.6 mass% Fe in the form of Fe $_2O_3$ 28.2 mass% O $_2$  in the form of Fe $_2O_3$ 6.2 mass% gangue

Hence, for each kg of pellet input, the masses are:

 $\begin{array}{l} 0.656 \ \mathrm{kg} \ \mathrm{Fe} \\ 0.282 \ \mathrm{kg} \ \mathrm{O}_2 \\ 0.062 \ \mathrm{kg} \ \mathrm{gangue} \end{array}$ 

When the metallization of 94% is reached, 94 mass% of all iron is in the form of metallic iron (Fe). All other iron is in the form of wüstite. For each kg of pellet input, the produced DRI will contain:

0.94 \* 0.656 = 0.6166 kg metallic iron (Fe)

Thus, 0.656 - 0.6166 = 0.0394 kg of Fe will be in the form of Fe<sub>0.95</sub>O, which are 0.706 moles Fe. Hence, the DRI output will contain:

 $\frac{0.706}{0.95}*0.06905=0.0513\,\mathrm{kg}\,Fe_{0.95}O$ 

The amount of DRI produced per kg pellet is:

 $0.6166 + 0.062 + 0.0513 = 0.730 \,\mathrm{kg} \,\mathrm{DRI}$ 

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# **Chemical reactions**

This appendix shows all allowed chemical reactions in the shaft furnace model.

$$3 \operatorname{Fe}_2 \operatorname{O}_3(s) + \operatorname{H}_2(g) \longrightarrow 2 \operatorname{Fe}_3 \operatorname{O}_4(s) + \operatorname{H}_2 \operatorname{O}(g)$$
(2.1)

$$Fe_3O_4(s) + \frac{16}{19}H_2(g) \longrightarrow \frac{60}{19}Fe_{0.95}O(s) + \frac{16}{19}H_2O(g)$$
 (2.2)

$$\operatorname{Fe}_{0.95}\mathrm{O}(\mathrm{s}) + \mathrm{H}_{2}(\mathrm{g}) \longrightarrow 0.95 \operatorname{Fe}(\mathrm{s}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{g})$$

$$(2.3)$$

$$3 \operatorname{Fe}_2 \operatorname{O}_3(s) + \operatorname{CO}(g) \longrightarrow 2 \operatorname{Fe}_3 \operatorname{O}_4(s) + \operatorname{CO}_2(g)$$
(2.4)

$$Fe_3O_4(s) + \frac{16}{19}CO(g) \longrightarrow \frac{60}{19}Fe_{0.95}O(s) + \frac{16}{19}CO_2(g)$$
 (2.5)

$$Fe_{0.95}O(s) + CO(g) \longrightarrow 0.95 Fe(s) + CO_2(g)$$
(2.6)

$$2 \operatorname{CO}(g) \longleftrightarrow \operatorname{C}(s) + \operatorname{CO}_2(g)$$
 (2.11)

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$
(2.14)

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$$
 (2.18)

$$CH_4(g) \longrightarrow C(s) + 2H_2(g)$$
 (2.19)

# Discretization of the gaseous mole fraction equation

The gaseous molar balances for component i are formulated as:

$$\frac{d(c_t x_i u_g)}{dz} = \frac{d}{dz} \left( c_t D_{z,i} \frac{dx_i}{dz} \right) + S_i$$
(4.39)

#### Advection term

Using first-order upwind discretization, we end up with:

$$\frac{d(c_t x_i u_g)}{dz} = \frac{1}{\Delta z} \left[ c_t(i) x_i(i) u_g(i) - c_t(i-1) x_i(i-1) u_g(i-1) \right]$$

Rearrange all terms in the form:  $A(i)x_i(i-1) + B(i)x_i(i) + C(i)x_i(i+1) + D(i)x_i(i-2) = RHS(i)$  gives:

$$A(i) = -\frac{1}{\Delta z} \left[ c_t (i-1) u_g (i-1) \right]$$
$$B(i) = \frac{1}{\Delta z} \left[ c_t (i) u_g (i) \right]$$
$$C(i) = 0$$
$$D(i) = 0$$

Using second-order upwind discretization, we end up with:

$$\frac{d(c_t x_i u_g)}{dz} = \frac{1}{2\Delta z} \left[ 3c_t(i) x_i(i) u_g(i) - 4c_t(i-1) x_i(i-1) u_g(i-1) + c_t(i-2) x_i(i-2) u_g(i-2) \right]$$

$$A(i) = -\frac{1}{2\Delta z} \left[ 4c_t(i-1) u_g(i-1) \right]$$

$$B(i) = \frac{1}{2\Delta z} \left[ 3c_t(i) u_g(i) \right]$$

$$C(i) = 0$$

$$D(i) = \frac{1}{2\Delta z} \left[ c_t(i-2) u_g(i-2) \right]$$

### **Diffusion term**

$$\frac{d}{dz}\left(c_t D_{z,i} \frac{dx_i}{dz}\right) = \frac{1}{\Delta z}\left[(c_t)_R (D_{z,i})_R \left. \frac{dx_i}{dz} \right|_R - (c_t)_L (D_{z,i})_L \left. \frac{dx_i}{dz} \right|_L\right] = \frac{1}{\Delta z}\left[(c_t)_R (D_{z,i})_R \frac{x(i+1)-x(i)}{\Delta z} - (c_t)_L (D_{z,i})_L \frac{x(i)-x(i-1)}{\Delta z}\right]$$

The concentration and diffusion at L and R will be linear interpolated between the two surrounding nodes. This results in:

$$\frac{1}{\Delta z} \left[ \left( \frac{1}{2} \left( c_t(i+1) + c_t(i) \right) \right) \left( \frac{1}{2} \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right) \left( \frac{1}{\Delta z} \left( x_i(i+1) - x_i(i) \right) \right) \\ - \left( \frac{1}{2} \left( c_t(i-1) + c_t(i) \right) \right) \left( \frac{1}{2} \left( D_{z,i}(i-1) + D_{z,i}(i) \right) \right) \left( \frac{1}{\Delta z} \left( x_i(i) - x_i(i-1) \right) \right) \right]$$

Rearrange all terms in the form:  $A(i)x_i(i-1) + B(i)x_i(i) + C(i)x_i(i+1) + D(i)x_i(i-2) = RHS(i)$  gives:

$$\begin{split} A(i) &= \frac{1}{4(\Delta z)^2} \left[ \left( c_t(i-1) + c_t(i) \right) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) \right] \\ B(i) &= -\frac{1}{4(\Delta z)^2} \left[ \left( c_t(i-1) + c_t(i) \right) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) + \left( c_t(i+1) + c_t(i) \right) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ C(i) &= \frac{1}{4(\Delta z)^2} \left[ \left( c_t(i+1) + c_t(i) \right) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ D(i) &= 0 \end{split}$$

### Total

Putting all the terms together gives the functions below for first-order upwind discretization of the advection term:

$$\begin{split} A(i) &= -\frac{1}{\Delta z} \left[ c_t(i-1)u_g(i-1) \right] - \frac{1}{4(\Delta z)^2} \left[ (c_t(i-1) + c_t(i)) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) \right] \\ B(i) &= \frac{1}{\Delta z} \left[ c_t(i)u_g(i) \right] + \frac{1}{4(\Delta z)^2} \left[ (c_t(i-1) + c_t(i)) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) + (c_t(i+1) + c_t(i)) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ C(i) &= -\frac{1}{4(\Delta z)^2} \left[ (c_t(i+1) + c_t(i)) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ D(i) &= 0 \\ RHS &= S_i(i) \end{split}$$

Putting all the terms together gives the functions below for second-order upwind discretization of the advection term:

$$\begin{aligned} A(i) &= -\frac{1}{2\Delta z} \left[ 4c_t(i-1)u_g(i-1) \right] - \frac{1}{4(\Delta z)^2} \left[ (c_t(i-1) + c_t(i)) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) \right] \\ B(i) &= \frac{1}{2\Delta z} \left[ 3c_t(i)u_g(i) \right] + \frac{1}{4(\Delta z)^2} \left[ (c_t(i-1) + c_t(i)) \left( D_{z,i}(i-1) + D_{z,i}(i) \right) + (c_t(i+1) + c_t(i)) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ C(i) &= -\frac{1}{4(\Delta z)^2} \left[ (c_t(i+1) + c_t(i)) \left( D_{z,i}(i+1) + D_{z,i}(i) \right) \right] \\ D(i) &= \frac{1}{2\Delta z} \left( c_t(i-2)u_g(i-2) \right) \\ RHS &= S_i(i) \end{aligned}$$

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# Discretization of the gas energy equation

The gas energy equation is given by:

$$\rho_g C_{p,g} u_g \frac{dT_g}{dz} = \frac{d}{dz} \left( \lambda_g \frac{dT_g}{dz} \right) + a_s h(T_s - T_g) + \sum_{i=1}^5 S_i \int_{T_g}^{T_s} C_{p,i} dT$$
(4.42)

#### Advection term

Using first-order upwind discretization, we end up with:

 $\rho_g \mathcal{C}_{p,g} u_g \frac{dT_g}{dz} = \frac{\rho_g(i) \mathcal{C}_{p,g}(i) u_g(i)}{\Delta z} \left[ T_g(i) - T_g(i-1) \right]$ 

Rearrange all terms in the form  $A(i)T_g(i-1) + B(i)T_g(i) + C(i)T_g(i+1) + D(i)T_g(i-2) = RHS(i)$  gives:

$$A(i) = -\frac{\rho_g(i)C_{p,g}(i)u_g(i)}{\Delta z}$$
$$B(i) = \frac{\rho_g(i)C_{p,g}(i)u_g(i)}{\Delta z}$$
$$C(i) = 0$$
$$D(i) = 0$$

$$RHS(i) = 0$$

Using second-order upwind discretization, we end up with:

$$\rho_g C_{p,g} u_g \frac{dT_g}{dz} = \frac{\rho_g(i) C_{p,g}(i) u_g(i)}{2\Delta z} \left[ 3T_g(i) - 4T_g(i-1) + T_g(i-2) \right]$$

Rearrange all terms in the form  $A(i)T_g(i-1) + B(i)T_g(i) + C(i)T_g(i+1) + D(i)T_g(i-2) = RHS(i)$  gives:

$$A(i) = -\frac{4\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z}$$
$$B(i) = \frac{3\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z}$$
$$C(i) = 0$$
$$D(i) = \frac{\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z}$$
$$RHS(i) = 0$$

#### **Diffusion term**

$$\frac{d}{dz}\left(\lambda_g \frac{dT_g}{dz}\right) = \frac{1}{\Delta z}\left[(\lambda_g)_R \frac{dT_g}{dz}\Big|_R - (\lambda_g)_L \frac{dT_g}{dz}\Big|_L\right] = \frac{1}{\Delta z}\left[(\lambda_g)_R \frac{T_g(i+1) - T_g(i)}{\Delta z} - (\lambda_g)_L \frac{T_g(i) - T_g(i-1)}{\Delta z}\right]$$

Rearrange all terms in the form  $A(i)T_g(i-1) + B(i)T_g(i) + C(i)T_g(i+1) + D(i)T_g(i-2) = RHS(i)$  gives:

$$A(i) = -\frac{(\lambda_g)_L}{(\Delta z)^2}$$
$$B(i) = \frac{(\lambda_g)_L + (\lambda_g)_R}{(\Delta z)^2}$$
$$C(i) = -\frac{(\lambda_g)_R}{(\Delta z)^2}$$
$$D(i) = 0$$

$$RHS(i) = 0$$

The conductivity will be linear interpolated between the two surrounding nodes. This results in:

$$\begin{split} &(\lambda_g)_L = \frac{1}{2} \left( \lambda_g(i) + \lambda_g(i-1) \right) \\ &(\lambda_g)_R = \frac{1}{2} \left( \lambda_g(i) + \lambda_g(i+1) \right) \end{split}$$

#### **Convection term**

$$a_s h(T_s - T_g) = a_s h(i)(T_s(i) - T_g(i))$$

Rearrange all terms in the form  $A(i)T_g(i-1) + B(i)T_g(i) + C(i)T_g(i+1) + D(i)T_g(i-2) = RHS(i)$  gives:

$$A(i)=0$$

 $B(i) = a_s h(i)$ 

$$C(i)=0$$

$$D(i)=0$$

 $RHS(i) = a_s h(i) T_s(i)$ 

### Source term

 $\sum_{i=1}^{5} S_i \int_{T_g}^{T_s} C_{p,i} dT = \sum_{i=1}^{5} S_i(i) \int_{T_g(i)}^{T_s(i)} C_{p,i}(i) dT$ 

Rearrange all terms in the form  $A(i)T_g(i-1) + B(i)T_g(i) + C(i)T_g(i+1) + D(i)T_g(i-2) = RHS(i)$  gives:

$$\begin{aligned} A(i) &= 0 \\ B(i) &= 0 \\ C(i) &= 0 \\ D(i) &= 0 \\ RHS(i) &= \sum_{i=1}^{5} S_i(i) \int_{T_g(i)}^{T_s(i)} C_{p,i}(i) dT \end{aligned}$$

### Total

Putting all terms together gives the function below for first-order upwind discretization of the advection term:

$$A(i) = -\frac{\rho_g(i)C_{p,g}(i)u_g(i)}{\Delta z} - \frac{(\lambda_g)_L}{(\Delta z)^2}$$
  

$$B(i) = \frac{\rho_g(i)C_{p,g}(i)u_g(i)}{\Delta z} + \frac{(\lambda_g)_L + (\lambda_g)_R}{(\Delta z)^2} + a_s h(i)$$
  

$$C(i) = -\frac{(\lambda_g)_R}{(\Delta z)^2}$$
  

$$D(i) = 0$$

 $RHS(i) = a_s h(i) T_s(i) + \sum_{i=1}^5 S_i(i) \int_{T_g(i)}^{T_s(i)} C_{p,i}(i) dT$ 

Putting all terms together gives the function below for second-order upwind discretization of the advection term:

$$\begin{aligned} A(i) &= -\frac{4\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z} - \frac{(\lambda_g)_L}{(\Delta z)^2} \\ B(i) &= \frac{3\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z} + \frac{(\lambda_g)_L + (\lambda_g)_R}{(\Delta z)^2} + a_s h(i) \\ C(i) &= -\frac{(\lambda_g)_R}{(\Delta z)^2} \\ D(i) &= \frac{\rho_g(i)C_{p,g}(i)u_g(i)}{2\Delta z} \\ RHS(i) &= a_s h(i)T_s(i) + \sum_{i=1}^5 S_i(i) \int_{T_g(i)}^{T_s(i)} C_{p,i}(i) dT \end{aligned}$$

# Discretization of the momentum equation

The gas momentum equation combined with the continuity equation is given by:

$$\frac{d}{dz}\left(\frac{c_t}{K}\frac{dp}{dz}\right) = S_{mol,total} = 2r_7 + r_9 - r_{10}$$
(4.47)

Discretization of the left-hand side gives:

 $\frac{1}{\Delta z} \left[ \frac{(c_t)_R}{(K)_R} \left. \frac{dp}{dz} \right|_R - \frac{(c_t)_L}{(K)_L} \left. \frac{dp}{dz} \right|_L \right] = \frac{1}{\Delta z} \left[ \frac{(c_t)_R}{(K)_R} \frac{p(i+1) - p(i)}{\Delta z} - \frac{(c_t)_L}{(K)_L} \frac{p(i) - p(i-1)}{\Delta z} \right]$ 

Rearrange all terms in the form: A(i)p(i-1) + B(i)p(i) + C(i)p(i+1) = RHS(i) gives:

$$A(i) = \frac{1}{(\Delta z)^2} \frac{(c_t)_L}{(K)_L}$$

$$B(i) = -\frac{1}{(\Delta z)^2} \left[ \frac{(c_t)_R}{(K)_R} + \frac{(c_t)_L}{(K)_L} \right]$$

$$C(i) = \frac{1}{(\Delta z)^2} \frac{(c_t)_R}{(K)_R}$$

$$RHS(i) = 2r_7(i) + r_9(i) - r_{10}(i)$$

In which the concentration and permeability coefficient at L and R will be linear interpolated between the two surrounding nodes:

$$(c_t)_L = \frac{1}{2} (c_t(i-1) + c_t(i))$$
  

$$(c_t)_R = \frac{1}{2} (c_t(i+1) + c_t(i))$$
  

$$(K)_L = \frac{1}{2} (K(i-1) + K(i))$$
  

$$(K)_R = \frac{1}{2} (K(i+1) + K(i))$$

Given the pressure field, the velocity of the gas can be determined according to:

$$u_g = -\frac{1}{K}\frac{dp}{dz} \tag{4.48}$$

Discretization of this equation gives:

 $u_g(i)=-\tfrac{1}{2K(i)\Delta z}\left(p(i+1)-p(i-1)\right)$ 

# Discretization of the solid weight fraction equation

The solid mass balance of component i is given by:

$$-u_p \frac{d(\rho_p W_i)}{dz} = S_i \tag{4.49}$$

Using first-order upwind discretization, we end up with:

$$\frac{d(\rho_p W_i)}{dz} = \frac{1}{\Delta z} \left[ \rho_p(i+1) W_i(i+1) - \rho_p(i) W_i(i) \right]$$

Rearrange all terms in the form:  $A(i)W_i(i-1)+B(i)W_i(i)+C(i)W_i(i+1)+D(i)W_i(i+2) = RHS(i)$  gives:

A(i) = 0

$$B(i) = -\frac{\rho_p(i)}{\Delta z}$$
$$C(i) = \frac{\rho_p(i+1)}{\Delta z}$$

D(i)=0

$$RHS(i) = -\frac{S_i(i)}{u_p}$$

Using second-order upwind discretization, we end up with:

$$\frac{d(\rho_p W_i)}{dz} = \frac{1}{2\Delta z} \left[ -\rho_p (i+2) W_i (i+2) + 4\rho_p (i+1) W_i (i+1) - 3\rho_p (i) W_i (i) \right]$$

Rearrange all terms in the form:  $A(i)W_i(i-1)+B(i)W_i(i)+C(i)W_i(i+1)+D(i)W_i(i+2) = RHS(i)$  gives:

$$A(i) = 0$$
  

$$B(i) = -\frac{3\rho_p(i)}{2\Delta z}$$
  

$$C(i) = \frac{4\rho_p(i+1)}{2\Delta z}$$
  

$$D(i) = -\frac{\rho_p(i+2)}{2\Delta z}$$
  

$$RHS(i) = -\frac{S_i(i)}{u_p}$$

# Discretization of the solid energy equation

The solid energy equation is given by:

$$-\rho_s C_{p,s} u_s \frac{dT_s}{dz} = \frac{d}{dz} \left( \lambda_{eff} \frac{dT_s}{dz} \right) + a_s h(T_g - T_s) + \sum_{i=1}^{10} -(r_i \Delta_r H_i)$$
(4.52)

#### Advection term

Using first-order upwind discretization, we end up with:

$$-\rho_s C_{p,s} u_s \frac{dT_s}{dz} = -\frac{\rho_s(i)C_{p,s}(i)u_s}{\Delta z} \left(T_s(i+1) - T_s(i)\right)$$

Rearrange all terms in the form  $A(i)T_s(i-1) + B(i)T_s(i) + C(i)T_s(i+1) + D(i)T_s(i+2) = RHS(i)$  gives:

$$A(i) = 0$$
  

$$B(i) = \frac{\rho_s(i)C_{p,s}(i)u_s}{\Delta z}$$
  

$$C(i) = -\frac{\rho_s(i)C_{p,s}(i)u_s}{\Delta z}$$
  

$$D(i) = 0$$

RHS(i) = 0

A(i) = 0

Using second-order upwind discretization, we end up with:

$$-\rho_{s}C_{p,s}u_{s}\frac{dT_{s}}{dz} = -\frac{\rho_{s}(i)c_{p,s}(i)u_{s}}{2\Delta z}\left(4T_{s}(i+1) - 3T_{s}(i) - T_{s}(i+2)\right)$$

Rearrange all terms in the form  $A(i)T_s(i-1) + B(i)T_s(i) + C(i)T_s(i+1) + D(i)T_s(i+2) = RHS(i)$  gives:

$$B(i) = \frac{3\rho_s(i)C_{p,s}(i)u_s}{2\Delta z}$$
$$C(i) = -\frac{4\rho_s(i)C_{p,s}(i)u_s}{2\Delta z}$$

 $D(i) = \frac{\rho_s(i)C_{p,s}(i)u_s}{2\Delta z}$ RHS(i) = 0

### **Diffusion term**

$$\frac{d}{dz}\left(\lambda_{eff}\frac{dT_s}{dz}\right) = \frac{1}{\Delta z}\left[\left(\lambda_{eff}\right)_R\frac{dT_s}{dz}\Big|_R - \left(\lambda_{eff}\right)_L\frac{dT_s}{dz}\Big|_L\right] = \frac{1}{\Delta z}\left[\left(\lambda_{eff}\right)_R\frac{T_s(i+1)-T_s(i)}{\Delta z} - \left(\lambda_{eff}\right)_L\frac{T_s(i)-T_s(i-1)}{\Delta z}\right]$$

Rearrange all terms in the form  $A(i)T_s(i-1) + B(i)T_s(i) + C(i)T_s(i+1) + D(i)T_s(i+2) = RHS(i)$  gives:

$$A(i) = -\frac{(\lambda_{eff})_L}{(\Delta z)^2}$$
$$B(i) = \frac{(\lambda_{eff})_L + (\lambda_{eff})_R}{(\Delta z)^2}$$
$$C(i) = -\frac{(\lambda_{eff})_R}{(\Delta z)^2}$$
$$D(i) = 0$$
$$RHS(i) = 0$$

The conductivity will be linear interpolated between the two surrounding nodes. This results in:

$$\begin{aligned} &(\lambda_{eff})_L = \frac{1}{2} \left( \lambda_{eff}(i) + \lambda_{eff}(i-1) \right) \\ &(\lambda_{eff})_R = \frac{1}{2} \left( \lambda_{eff}(i) + \lambda_{eff}(i+1) \right) \end{aligned}$$

### **Convection term**

$$a_s h(T_g - T_s) = a_s h(i)(T_g(i) - T_s(i))$$

Rearrange all terms in the form  $A(i)T_s(i-1) + B(i)T_s(i) + C(i)T_s(i+1) + D(i)T_s(i+2) = RHS(i)$  gives:

- A(i) = 0
- $B(i) = a_s h(i)$
- C(i)=0
- D(i) = 0

 $RHS(i) = a_s h(i)T_g(i)$ 

### Heat of reaction term

$$\sum_{i=1}^{10} -(r_i \Delta_r H_i) = \sum_{i=1}^{10} -(r_i(i) \Delta_r H_i(i))$$

Rearrange all terms in the form  $A(i)T_s(i-1) + B(i)T_s(i) + C(i)T_s(i+1) + D(i)T_s(i+2) = RHS(i)$  gives:

$$A(i)=0$$

B(i)=0

$$C(i) = 0$$
  

$$D(i) = 0$$
  

$$RHS(i) = \sum_{i=1}^{10} -(r_i(i)\Delta_r H_i(i))$$

### Total

Putting all terms together gives the function below for first-order upwind discretization of the advection term:

$$A(i) = -\frac{(\lambda_{eff})_L}{(\Delta z)^2}$$

$$B(i) = \frac{\rho_s(i)C_{p,s}(i)u_s}{\Delta z} + \frac{(\lambda_{eff})_L + (\lambda_{eff})_R}{(\Delta z)^2} + a_sh(i)$$

$$C(i) = -\frac{\rho_s(i)C_{p,s}(i)u_s}{\Delta z} - \frac{(\lambda_{eff})_R}{(\Delta z)^2}$$

$$D(i) = 0$$

 $RHS(i) = a_s h(i) T_g(i) + \sum_{i=1}^{10} -(r_i(i) \Delta_r H_i(i))$ 

Putting all terms together gives the function below for second-order upwind discretization of the advection term:

$$A(i) = -\frac{(\lambda_{eff})_L}{(\Delta z)^2}$$

$$B(i) = \frac{3\rho_s(i)C_{p,s}(i)u_s}{2\Delta z} + \frac{(\lambda_{eff})_L + (\lambda_{eff})_R}{(\Delta z)^2} + a_sh(i)$$

$$C(i) = -\frac{4\rho_s(i)C_{p,s}(i)u_s}{2\Delta z} - \frac{(\lambda_{eff})_R}{(\Delta z)^2}$$

$$D(i) = \frac{\rho_s(i)C_{p,s}(i)u_s}{2\Delta z}$$

$$RHS(i) = a_sh(i)T_g(i) + \sum_{i=1}^{10} - (r_i(i)\Delta_r H_i(i))$$

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