Sustainable Aluminium and Iron Production

Reza Beheshti

Doctoral Thesis

Stockholm 2017

School of Chemical Science and Engineering
Royal Institute of Technology
SE-100 44 Stockholm
Sweden

Reza Beheshti  
*Sustainable Aluminium and Iron Production*

School of Chemical Science and Engineering  
KTH Royal Institute of Technology  
SE-10044 Stockholm  
Sweden

TRITA-CHE Report 2017:3  
ISSN 1654-1081  
The Author
Abstract

Aluminium and iron/steel are truly sustainable materials. As a result the global metallurgical industry strives to produce products, which contribute to the global effort by reducing resource use, recycling and reusing materials where possible, and to help create the economic and supply frameworks needed to do this.

Aluminium is a material that is infinitely recyclable and remarkably plentiful. Almost three quarters of all the aluminium that has ever been produced is still in use today, and approximately 90% is used in the transport- and construction sector. Recycling aluminium scrap requires 95% less energy than primary production with no loss of quality or volume. The Black Dross (BD) produced during secondary production of aluminium contains high amounts of water-soluble compounds, i.e. NaCl, KCl, and AlN. As a result it is considered as a toxic waste. In the present work, salt removal from BD by thermal treatment has been investigated in laboratory scale. The optimum conditions for treatment were established, i.e., temperature, gas flow rate, holding time, rotation rate, and sample size. The overall degree of chloride removal was established to increase as a function of time and temperature. Even Pretreated Black Dross (PBD) was evaluated as a possible raw material for the production of a calcium aluminate-based ladle-fluxing agent to be used in the steel industry. The effects of different process parameters on the properties of the produced flux were experimentally investigated, i.e. CaO/Al₂O₃ ratio, temperature, holding time, and cooling media. The utilization of PBD as the alumina source during the production of a calcium aluminate fluxing agent shows promising results.

Iron/steel is one of the few materials with a truly closed recycling loop, as it is not consumed. It is used again and again without any loss of quality or strength. Unlike most materials, iron/steel can be “upcycled” meaning that its quality and strength can be enhanced through recycling. The iron/steel industry is responsible for nearly 9% of anthropogenic energy and process CO₂ emissions. It is believed that the only way to a long-term reduction of the CO₂ emissions from the iron/steel industry is commercialization of alternative processes such as Direct Reduction (DR) of iron oxide. Detailed knowledge of the kinetics of the reduction reactions is, however, a prerequisite for the design and optimization of the DR process. To obtain a better understanding of the reduction kinetics, a model was developed step-by-step, from a single pellet to a fixed bed with many pellets. The equations were solved using the commercial software COMSOL Multiphysics®. The final model considers the reaction rate and mass transfer inside the pellet, as well as the mass transfers and heat transfer in the fixed bed. All the models were verified against experimental results, and where found to describe the results in a satisfying way.

Keywords: Sustainability, Optimization, Black Dross, Salt removal, Steel flux agent, Waste processing, Greenhouse gases, Direct reduction, COMSOL Multiphysics®
Sammanfattning

Aluminium och järn/stål kan återvinnas oräkneligt antal gånger vilket ger stora miljövinster och kostnadsbesparingar vilket är i linje med globala metallindustrins strävan att tillverka produkter som bidrar till de globala målen att minska resursanvändningen. Detta åstadkoms genom att skapa ekonomiska ramar och produktionsförutsättningar för att återvinna och återanvända material där det är möjligt.


Järn/stål är ett av få material som har en sluten återvinningscykel då det inte förbrukas. Det används om och om igen utan att kvaliteten eller styrkan försämras, även om vissa föroreningar till viss del anriknas efterhand. Då järn-/stålindustrin är ansvarig för nästan 9% av människans utsläpp av CO₂ kräver en långsiktig minskning av de globala CO₂-utsläppen att järn-/stålindustrin övergår till alternativa processer för järnframställningen. Alternativen är processer med minskade CO₂-generering, såsom direktreduktionsprocesser (DR) baserade på naturgas, eller nya vägar såsom vägaspaserad direkreduktion av järnoxid. Ingående kunskaper om kinetiken bakom de reduktionsreaktioner som sker under DR av järnoxid är emellertid en förutsättning för design och optimering av dessa processer. En modell som beskriver reduktionsskibern en stegvis utvecklats för att erhålla en bättre förståelse för rådande processmekanismer. Utvecklingen har skett stegvis, från att beskriva skeenden i en enda pellet till att beskriva vad som sker i en pelletsbådd. Ekvationerna som användes i modellen har löst med hjälp av den kommersiella programvaran COMSOL Multiphysics®. Den slutliga modellen tar hänsyn till både reaktionshastigheten och massöverföringen inne i pelten, såväl som massöverföringen och värmeöverföringen i den fasta pelletsbädden. Samtliga modeller har
verifierats med experimentellt uppmätta resultat, och det fastslogs att de beskrev mekanismerna på ett tillfredsställande sätt.
Supplements


Other related reports not included in this thesis:

The contributions by the author to different supplements of this thesis:

I. Literature survey, main parts of experimental work, parts of analyses and writing.

II. Literature survey, experimental work, major parts of analyses and writing.

III. Literature survey, parts of modelling work, major parts of experimental work, evaluation work and writing.

IV. Literature survey, major parts of experimental work, modelling work, evaluation work and writing.

V. Literature survey, experimental work, modelling work, evaluation work and writing.
Preface

Aluminium and iron/steel are extremely versatile materials that are the main constituent of a wide range of products from drinking cans to vehicles and buildings. Iron/steel represent about 91% of the mass of metal produced annually by the metallurgical industry, and aluminium, as the second, represents 3% of the remaining metal. Chromium with less than 1.7% of the annual world metal production is the third. It is therefore obvious that environmental issues such as gaseous emissions and solid wastes produced by the aluminium and iron/steel industries will have a profound effect on metallurgical sustainability.

The present doctoral thesis summarizes the knowledge I have gained in the field of sustainable process metallurgy during my period as a Ph.D. student. The Swedish partners in the project have been the Department of Material Science and Engineering and the Department of Fibre and Polymer Technology at KTH (Royal Institute of Technology) in Stockholm, and the Norwegian partners the Northern Research Institutes (Norut) in Narvik, and the Department of Material Science and Engineering at NTNU (Norwegian University of Science and Technology) in Trondheim.

This thesis will in particular discuss the following challenges of sustainable metal production:

- **Secondary Aluminium Dross Treatment and Utilization**
  “Black” Dross (BD), a by-product of the aluminium recycling process, needs to be treated before landfilling or alternatively applied as a raw material in other processes. Thermal treatment was investigated as a possible salt removal process to reduce the environmental impact of the dross and rendering it non-toxic and suitable for use in other processes.
  Calcium aluminate is used as a fluxing agent during ladle treatment in steelmaking. The Pre-treated Black Dross (PBD) was proposed as an alternative cheap source of alumina in calcium aluminate production. The process of calcium aluminate production was studied and modified based on this potential new raw material.

- **Optimization of Direct Reduction Iron Production**
  The Direct Reduction (DR) process is considered to be an ironmaking method with a growing utilization. The overall performance of a DR reactor is strongly affected by the interaction between the gaseous reducing agents and the solid pellets in terms of both heat and mass transfer. Hence, the investigation of the kinetics of the reduction processes is a prerequisite for understanding the different steps of the DR process, as well as for the future optimization of the process. Therefore, the kinetics of iron oxide reduction as a single pellet and as several pellets in a fixed bed has been studied both experimentally and analytically.
This main structure of the thesis is as follows:

Chapter 1 gives an introduction to the work covered in the present thesis.

Section A, chapters 2-4, is on BD treatment and PBD utilization. Chapters 2, gives an introduction to aluminium production and a general overview on aluminium dross and industrial dross treatment. The primary goal is to give the reader a brief overview of the pertinent literature. The reader is referred to literature citations for further details. The objective of the work performed is presented in Chapter 3, and a summary of the appended thesis-related papers can be found in Chapter 4.

Section B, chapters 5-9, explores the optimization of the DR process. Chapters 5-7, give an introduction to the iron- and steellmaking industry and a general overview on environmental challenges that these industries face. The aim is to give the reader an overview of the related literature. The reader is referred to the cited works for further details. The objective, background and state-of-the-art in regards to modelling of the reduction process occurring in the DR are presented in Chapter 8. A summary of the appended thesis-related papers can be found in Chapter 9.

Overall conclusions, Chapter 10, will cover concluding remarks and future prospects for continuation of the work. Acknowledgment and references are summarised in Chapter 11 and Chapter 12 respectively.

It is hoped that this thesis will give the reader a better understanding of the environmental challenges of aluminium and iron/steel production, and how this production can become more environmentally sustainable in the future.
**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_s$</td>
<td>Special reaction surface</td>
<td>$(1/m)$</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Concentration of i-th component of the reducing gas</td>
<td>$(\text{mol/m})$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat at constant pressure</td>
<td>$(\text{J/Kg K})$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity of gaseous species</td>
<td>$(\text{m}^2/\text{s})$</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Binary diffusivity</td>
<td>$(\text{m}^2/\text{s})$</td>
</tr>
<tr>
<td>$\rho_o$</td>
<td>Molar density of the reducible oxygen within the pellet</td>
<td>$(\text{g-atom O/m}^3)$</td>
</tr>
<tr>
<td>$Ea_{i,l}$</td>
<td>Activation energy of the reaction with i-th component at interface l</td>
<td>$(\text{K J/mol})$</td>
</tr>
<tr>
<td>$f_i$</td>
<td>Local fractional reduction of l-th iron oxide component</td>
<td>(-)</td>
</tr>
<tr>
<td>$f$</td>
<td>Total local fractional reduction</td>
<td>(-)</td>
</tr>
<tr>
<td>$(-\Delta H)_{i,T,l}$</td>
<td>Heat of reaction with i-th gas component at interface l at temperature T</td>
<td>$(\text{J/mol})$</td>
</tr>
<tr>
<td>$h$</td>
<td>Convective heat transfer coefficient</td>
<td>$(\text{W/m}^2 \text{K})$</td>
</tr>
<tr>
<td>$k_{r,i,l}$</td>
<td>Reaction rate constant for reaction of i-th species at interface l</td>
<td>$(\text{m/s})$</td>
</tr>
<tr>
<td>$k_{o,i,l}$</td>
<td>Frequency factor of reaction with i-th component at interface l</td>
<td>$(\text{m/s})$</td>
</tr>
<tr>
<td>$K_{e,i,l}$</td>
<td>Equilibrium constant of reaction with i-th component at interface l</td>
<td>(-)</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight</td>
<td>$(\text{g/mol})$</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Pellet radius</td>
<td>$(\text{m})$</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>$(\text{J/mol K})$</td>
</tr>
<tr>
<td>$r_g$, $r_l$</td>
<td>Radii of the grain and reaction interface within the grain respectively</td>
<td>$(\text{m})$</td>
</tr>
<tr>
<td>$T$</td>
<td>Time</td>
<td>$(\text{s})$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$(\text{K})$</td>
</tr>
</tbody>
</table>
$R_{i,j}$  
Rate of chemical reaction with i-th gaseous species at interface l, (mol/m² s)

$Y_i$  
Mole fraction of i-th component of the reducing gas (-)

$\alpha_i$  
Reducible oxygen in each step of reduction, (-)

$\rho$  
Mass density, (kg/m³)

$\varepsilon$  
Porosity of the pellet, (-)

$\lambda$  
Thermal conductivity, (W/m K)

**Subscripts**

$I$  
Related to gaseous component

$L$  
Related to reduction interfaces

$S$  
Related to solid (iron oxides)

$G$  
Related to reducing gases

$Eff$  
Effective parameters

$B$  
Related to bulk flow of gases

$t$  
Related to total value of parameter

$h,m,w$  
Related to hematite-magnetite, magnetite-wüstite and wüstite-iron interface, respectively

$0$  
Related to initial value of parameters

**Superscripts**

$K$  
Related to Knudsen diffusivity

$M$  
Related to molecular diffusivity
# Content

**Chapter 1: Introduction** ........................................................................................................................................... 1  
Aim ........................................................................................................................................................................... 2  

**Section A: Secondary Aluminium Dross Treatment and Utilization** ............. 5  

**Chapter 2: Aluminium Production** ........................................................................................................................................... 7  
Primary production ........................................................................................................................................................... 8  
Secondary production .......................................................................................................................................................... 10  
Sources and types of scrap consumed ................................................................................................................................. 11  
Melting furnaces ................................................................................................................................................................. 12  
Fluxing .................................................................................................................................................................................. 13  
Dross ...................................................................................................................................................................................... 15  
Dross treatment ................................................................................................................................................................. 16  
“White” dross treatment ...................................................................................................................................................... 17  
**Hot processing** ............................................................................................................................................................... 17  
**Cold processing** .............................................................................................................................................................. 17  
“Black” dross treatment ...................................................................................................................................................... 19  
Economics of technologies for the recycling of “black” dross ......................... 20  
Potential applications for “black” dross ............................................................. 21  
Benefits and barriers ........................................................................................................................................................... 22  

**Chapter 3: Objectives of the Present Study** ................................................................. 23  
Paper I. Black Dross Processing: Salt Removal from Black Dross by Thermal Treatment ........................................................................................................................................................................................................... 25  

**Chapter 4: Summary of Appended Papers** ................................................................. 25  
Salt evaporation in a stationary furnace ................................................................. 25  
Experiments conducted under atmospheric- and reduced pressure ............... 26  
Experiments conducted in a rotary furnace under atmosphere pressure .......... 26  

XI
Concluding results............................................................................................................. 27

Paper II. Black Dross Processing: Utilization of Black Dross in the Production of a Ladle Fluxing Agent .................................................................................................................. 28

PBD as a potential alumina source for calcium aluminate production ............ 28

Experimental work ................................................................. 28

Concluding results............................................................................................................. 30

Section B: Optimization of Direct Reduction Iron Production ...................... 31

Chapter 5: Iron- and Steelmaking .............................................................. 33

BF- BOF .................................................................................. 33

Blast Furnace (BF) ...................................................................... 33

Basic Oxygen Furnace (BOF) .......................................................... 35

Direct Reduction - Electric Arc Furnace (DR-EAF) process ..................... 37

Direct Reduction (DR) ................................................................... 37

MIDREX® process ........................................................................ 39

HYL/ENERGIRON process ......................................................... 41

Electric Arc Furnace (EAF) ................................................................... 42

Smelting Reduction (SR) ................................................................... 44

COREX process ........................................................................... 44

Chapter 6: Sustainable Iron- and Steelmaking ............................................. 47

Conservation of natural resources................................................................. 47

Reduction of GreenHouse Gas (GHG) emissions ........................................ 48

Present scenario .................................................................................. 49

DR the environmental friendly ironmaking process .................................. 50

Carbon Capture and Storage (CCS) ....................................................... 52

Chapter 7: Modelling of Iron Reduction ....................................................... 53

Gas-solid reaction modelling ......................................................................... 54

Concepts and assumptions .......................................................................... 55

Thermodynamic ...................................................................................... 56

Rate equation for chemical reaction .......................................................... 57

Effective diffusivity ..................................................................................... 59

Chapter 8: Objectives of the Present Study .................................................. 61

Paper III. Modelling and Simulation of Isothermal Reduction of a Single Hematite Pellet in Gas Mixtures of H₂ and CO ................................................................. 63
Chapter 9: Summary of Appended Papers ................................................. 63
  Modelling ........................................................................................................ 63
  Experimental work .......................................................................................... 64
  Concluding results .......................................................................................... 64
  Paper IV. Reduction of commercial hematite pellet in isothermal fixed bed—experiments and numerical modelling .......................................................... 66
    Modelling ........................................................................................................ 66
    Experimental work ........................................................................................ 66
    Concluding results ........................................................................................ 67
  Paper V. Reduction Kinetics of Commercial Hematite Pellet in a Fixed Bed at 1123-1273 K ................................................................. 68
    Modelling ........................................................................................................ 68
    Experimental work ........................................................................................ 68
    Concluding results ........................................................................................ 68

Chapter 10: Concluding remarks Future Prospects ........................................... 70
  Section A .......................................................................................................... 70
  Section B .......................................................................................................... 71

Chapter 11: Acknowledgment ........................................................................... 73

Chapter 12: References ..................................................................................... 74
Chapter 1: Introduction

Metals have played a major role in human social and industrial development. Traditionally, all our material needs are ultimately met from natural resources found within the ultimately limited eco-system of the Earth (e.g. the atmosphere, water, land in its natural state and their products, minerals and fossil fuels). In recent years, growing environmental concerns and increasing social responsibility have given sustainable metal production an increased interest. Sustainable metal production includes reduction of Green House Gas (GHG) emissions and reprocessing of metal scrap and wastes. This saves resources by reducing production from virgin metal, as well as minimizing the waste production and landfilling. This is done, for example, by providing lighter, safer, longer-lasting and more intelligent structures for transport and construction, as well as the design of products that are easy to dismantle and recycle at the end of their life. The European Union (EU) is implementing several strategies (e.g. Europe 2020 Strategy and COM (2011) 0112 - A Roadmap for moving to a competitive low carbon economy in 2050), to turn Europe into a world leader in smart, sustainable and inclusive growth [1, 2].

Applications for iron, and subsequently steel, were discovered thousands of years ago and they have a strong hold over human civilization. On the other hand, the industrial-scale production of aluminium metal is barely a century old. Nevertheless, in this short time, the aluminium industry has grown and is presently in tonnage the second largest metal producing industry in the world (the iron and steel industry being the largest). Many of the goods that are in everyday use depend on the physical properties of these metals, i.e. the longevity, malleability, strength and conductivity of aluminium, steel and their alloys. The metals can be found in items as varied as cars, computers, buildings and packaging [3-5].

In 2009, the total aluminium production was ~56 million tonnes (with over 18 million tonnes produced from recycled scrap). In 2015, primary aluminium production reached ~58 million tonnes. By 2020 the aluminium demand is projected to increase to around 97 million tonnes (with around 31 million tonnes recycled from scrap) [6]. World crude steel production stood at 1.6 billion tonnes in 2015. This represented a worldwide increase in production of 2.5% compared to 2012, and it is 38% more than in 2003 [7, 8].
Aim

As the title of this thesis suggests, this work has been dedicated to the investigation of two of the main challenges to sustainable production of aluminium and iron/steel. The European aluminium industry plans to reduce its direct emissions (\(-70\%\) in absolute terms), combined with reductions of emissions from power generators (\(-92\%\)), to a total of 79\% reduction by 2050. In view of the present energy constraints, and the small number of bauxite mines in the western world, Europe has a huge stake in maximizing the collection of all available scrap aluminium, and in developing the most resource-efficient recycling and melting processes. More than half of all the aluminium currently produced in the European Union (EU) originates from end of life structures/products, and the trend is increasing [10, 11]. The percentage of aluminium recycled continues to increase, and may be looked upon as a cornerstone for the reduction of greenhouse gases in aluminium processing. Recycled aluminium needs just 5\% of the energy and emits only 5\% of greenhouse gases, but the re-melting of scrap aluminium produces a slag phase that presents its own environmental problems. During the smelting of aluminium scrap, a mixture of fluxes consisting of the salts NaCl and KCl are added to the metal bath to prevent oxidation of the molten metal, and to facilitate the transfer of solid inclusions into the slag phase. As a result, an aluminium salt slag, i.e. “Black” Dross (BD), is formed that contains water-soluble compounds, which can release chlorides into water and emit toxic gases into the atmosphere. As a result of this, BD is considered to be a hazardous waste, and landfilling is prohibited in Europe [12]. In the USA, BD is still being landfilled, but only in isolated sites [13]. To partly solve this environmental issue, leaching is currently the most commonly applied process for salt removal from BD. The leaching process is relatively simple, but very expensive to operate due to the amount of energy needed to evaporate the large volume of process water used to recover the salt removed from the BD. To minimize the noxious gases generated during the process, the pH level of the process...
water must at all the times be kept below 8 and preferably above 5 [14]. The addition of acid to the water further increases the cost of the process. The residue from the leaching process is considered non-toxic, and can therefore be landfilled [14-17]. The key factors influencing the economics of dross treatment today are the landfill disposal costs in those countries where this is still permitted, the amount and value of the recyclable material, and the capital and operating costs of the recycling process.

It is important to point out that besides aluminium, BD also contains some other relatively valuable compounds that may be worth recovering, e.g. alumina (Al₂O₃) and spinel (MgO-Al₂O₃) [18]. Consequently, attempts have been made to efficiently remove the salt from the BD, and convert the obtained residue directly into valuable materials [19, 20].

The aim of the present study has been to investigate the development of an economically viable treatment process for BD that will secure the recovery of all dross constituents, as well as recycling of all salt fractions. This has been achieved by identifying the most important parameters contributing to an increased removal efficiency of salt from BD using pyrometallurgical rather than hydrometallurgical processing. The use of Pre-treated Black Dross (PBD) as a possible raw material for the production of metal refining fluxing agents, thereby converting it into a value-added product has also been investigated. The focus of this part of the work was to investigate the potential to replace the alumina content in calcium aluminate flux used in the steel industry by PBD. It is believed that the steel production process will benefit from the addition of a pre-melted slag former instead of the traditional slag formers such as lime, dolomite and alumina. The reason for this is the higher individual melting points of the pure constituents, e.g. CaO, Al₂O₃, etc., in comparison to a compound of pre-fused slag formers [21], and the rapid melting and dissolution that can be achieved using the highly homogenous pre-melted slag former. The production of a calcium aluminate flux from BD has proven to be beneficial based on a theoretical economic and environmental evaluation [22].

Experimental methods for investigating different aspects related to BD treatment and salt recycling have been developed, and optimum process conditions identified. The influence of the following parameters on the salt removal efficiency have been systematically investigated, i.e. the optimum heat treatment technique, as well as the influence of (i) the surrounding atmosphere/vacuum, (ii) the temperature, (iii) the holding time, (iv) the gas flow velocity, and (v) rotation speed. A possible means for the conversion of PBD to a refining flux agent has been developed, and the lab-scale optimum conditions established. During this development emphasis has been given to a systematic investigation of the influence of the (i) temperature, (ii) cooling media, (iii) cooling rate, (iv) holding time, and (v) ratio of CaO/Al₂O₃ in the calcium aluminate product.

Steel contains more than 90 % recyclable materials, and in terms of tonnage steel is the most recycled material in the world [8]. The demand in the market, however, is for more steel than the quantity of scrap that can be recycled. Steelmaking is estimated to have consumed 29 EJ (E = 10¹⁸) globally in 2010, or 6% of the total global energy consumption, while emitting 2.6 Gt CO₂ equivalent of greenhouse gases [1], or 6% of human emissions of CO₂ [23, 24]. At present, optimizing the conventional BF-BOF route, i.e. Blast Furnace - Basic Oxygen Furnace, is much more difficult than in earlier decades since most of the ‘‘low hanging fruit’’ has already been picked’. As a highly mature process each incremental gain is more complex to achieve,
and new trends are often seen in smaller steps. So a fundamentally different and more environmental sustainable process is needed to produce iron from virgin material.

The Direct Reduction (DR) process is believed to be the required alternative production method of iron [25-28]. This process has lower capital and operational costs than the Blast Furnace (BF); it is more energy efficient and has lower emissions of greenhouse gases. It is generally accepted that the DR-EAF (Electric Arc Furnace) route produces 0.8 - 1.2 tonnes of CO2 per tonne of liquid steel, compared to the BF-BOF route, which produces 2 - 2.25 tonnes of CO2 per tonne of liquid steel [29-31]. The worldwide production of Direct Reduced Iron (DRI) has increased remarkably in countries where low cost natural gas is available. From 1970 to 2015, worldwide production of DRI increased from 0.8 to 72.6 million tonnes [32]. However, the DR share of the ironmaking market is still only about 7% [30]. Compared to the BF process, the DR process is considered as new and has a high potential for further optimization.

For the design and optimization of the DR process, detailed knowledge of the kinetics of the reduction reactions is a prerequisite. Therefore, a methodical step-by-step approach has been taken in the present work to model the DR process from single pellet to a packed bed of several pellets. To verify the models, two sets of experiments were designed and carried out, i.e. single pellet reduction at 1173 K and fixed bed (~200 pellets) reduction at 1123–1273 K. The reducing gas composition ratio (H₂/CO) was varied from 0.8 to 2.
Section A: Secondary Aluminium Dross Treatment and Utilization
Chapter 2: Aluminium Production

Aluminium is the second most used metal in the world and it is the most abundant metal in the Earth's crust [33]. Some of the characteristics that make this metal so important are its (i) high corrosion resistance (due to the formation of a passivating oxide layer), (ii) low density, (iii) high electric conductivity, (iv) good thermal conductivity, (v) non-magnetic properties, and (vi) high mechanical strength to weight ratio [5, 34]. Aluminium and its alloys are used in a wide variety of applications, including transport, packaging, electrical, medicinal, construction and furniture. Since aluminium is strong and light, it is also fundamental to both the automotive and aircraft industries.

Primary production of aluminium requires a large amount of energy, and as a result most of the producers and smelters in the world are located near abundant energy sources (hydroelectric, natural gas, coal, or nuclear) [5]. More than a third of all of the aluminium currently produced globally originates, however, from old, traded and new scrap. Compared with the production of primary aluminium, recycling of aluminium products requires only ~ 5% of the energy, and emits only ~ 5% of the greenhouse gases [13]. With this in mind recycling is of the utmost importance when it comes to minimizing energy consumption and reduces GHG emissions both locally and globally, see Figure 2.

![Figure 2. Comparison of primary and secondary aluminium production [13.]](image)
Primary production

Aluminium has a strong affinity for oxygen, and due to this, it is almost never found in the elemental state in earth’s crust; instead it is found as oxides or silicates. In primary production, aluminium is extracted from its ore bauxite. Bauxite, however, contains only 30-54% alumina ($\text{Al}_2\text{O}_3$), the rest being a mixture of silica, various iron oxides, and titanium dioxide. The alumina present in the bauxite must be purified before it can be refined to aluminium metal. Aluminium production from bauxite is a costly process, which is carried out in several clearly defined process steps, first transforming the bauxite into alumina, i.e. the Bayer process, and further to aluminium, i.e. the Hall-Héroult process, sees Figure 3.

Figure 3. A schematic flow chart of the primary aluminium production [35].

In the Bayer process, alumina is extracted from bauxite using a series of steps including (i) grinding, (ii) absorption, (iii) leaching, (iv) filtering, (v) cooling, (vi) precipitation, and (vii) drying and calcining, see Figure 4.

Figure 4. A schematic drawing of the Bayer process used during primary production of aluminium [36].
First the bauxite is heated with caustic soda at a high pressure (30.4 \times 10^5 \text{ Pa}) and temperature (between 373 and 593 K [34]), producing sodium aluminates. While the bauxite is dissolved as soluble aluminate, the insoluble iron oxides, titanium oxides, and silicic acid are separated from the liquid melt using settling tanks, forming a waste by-product, the so-called ‘red mud’. The hydroxide solution is further cooled, resulting in the precipitation of the aluminium hydroxide precipitates. When it is later calcinated at 1273 K, the aluminium hydroxide decomposes to alumina (Al$_2$O$_3$) [37, 38].

In the Hall-Héroult process, alumina is dissolved in carbon-lined electrolysis ‘pots’, which contain a bath of molten cryolite, (Na$_3$AlF$_6$). Aluminium oxide has a normal melting point of \sim 2273 K, while cryolite has a much lower melting point (1285 K). As a result, by dissolving the produced alumina in cryolite, it can be electrolyzed at a lower temperature, e.g. when 13% aluminium oxide has been dissolved in the cryolite bath the melting point of the obtained mixture is 1273 K [34]. Aluminium fluoride (AlF$_3$) is also added to the mixture to enhance the reduction of the melting point of cryolite.

During the electrolysis of alumina dissolved in cryolite, liquid aluminium deposit onto the cathode, while the carbon anode is oxidized to carbon dioxide. The cells are self-heating electrically due to the resistance of the bath, and operate at a temperature of 1213-1253 K. The anode regulator system varies the current passing through the cell by raising or lowering the anodes, thereby changing the cell resistance. Solid cryolite is denser than solid aluminium at room temperature, but at 1273K, the produced liquid aluminium is denser than the molten cryolite. Consequently, the aluminium will sink to the bottom of the cell from where it can be periodically collected. As the dissolved alumina is consumed in the cryolite bath, more alumina is added by a hopper system to maintain the alumina content in the bath, see Figure 5. The electrolysis process produces exhaust gases, CO$_2$ as a result of the anode oxidation, and Hydrogen Fluoride (HF), which originates from the cryolite and the flux [5, 34].

![Figure 5](image.png)

Figure 5. A schematic drawing of the Hall-Héroult cell used for the primary production of aluminium [39].

The Hall-Héroult process is today the main industrial process for primary production of aluminium. The process has several disadvantages such as high specific energy consumption, as well as emission of GHG. The GHGs directly emitted in the primary aluminium production process include carbon dioxide (CO$_2$) and PerFluoroCarbons (PFCs), as well as fluoride.
Fluoride is a toxic gas that is strictly regulated to be below 0.5 kg per tonne of aluminium produced. The current level of GHG emissions per tonne of aluminium production is 1.6 tonnes of CO₂ and 0.6 tonnes of CO₂ equivalents of PFCs. The PFC emissions can be controlled by optimizing process operations, and by adopting automation technologies. Figure 6 illustrates the PFC reductions in North America since 1990 [40].

![Figure 6. Aluminium industry PFC emission reductions in North America [40].](image)

Nevertheless, the level of CO₂ emissions is fixed by anode consumption. As a result of this, researchers all over the world are focusing on the development of alternative processes. The main obstacles to the development of an alternative process / process step are the present lack of combined units, i.e. units offering integrated reduction and refining, as well as a controlled system approach. Improved quality, might be achieved by new methods for low temperature electrolysis producing solid aluminium, with decreased consumption of chemical and electrical energy [5, 34].

**Secondary production**

Recycling of aluminium scrap is known as secondary production of aluminium. Aluminium metal and its alloys are 100% recyclable without loss of properties, and can be melted and re-cast over and over again [5, 41]; hence, aluminium is a renewable resource that has endless opportunities for generations to come. Recycling of aluminium is therefore an important subject both economically and environmentally [37].

Recycling of aluminium needs, as previously mentioned, only 5% of the energy required for primary aluminium production [13]. According to a report published by the International Aluminium Institute in 2007 [42], recycling of 1 kg of aluminium beverage cans will save up to 8 kg of bauxite, 4 kg of chemical products and 14 kWh of electricity. In other words, by recycling just one aluminium beverage can, enough energy to keep a 100-watt light bulb burning for approximately 3.5 hours can be saved [43]. Hence, aluminium recycling is both
economically and environmentally beneficial. It should also be emphasised that the production of 1 tonne virgin aluminium results in around 2 tonnes of red mud, which cannot be disposed of easily [34]. Beside the generation of red mud, fluorides are also released into the environment [34, 37].

**Sources and types of scrap consumed**

Aluminium undergoes a variety of processes during the transformation from either ore or scrap into saleable metals and alloys. Some of these process steps result in loss of aluminium. Examples of such losses are (i) metal loss as droplets during the skimming of ladles and casting, (ii) edge trimmings and billet ends during rolling and extruding, (iii) turnings, millings and borings during various machining processes, (iv) off-cuts during stamping and punching processes, as well as (v) defective goods and/or quality problems at all production stages. This material is in the present work referred to as “new scrap”. Most “new scrap” is generated and recycled within the same facility. This scrap has a known composition and is in most cases clean, which means that it does not need significant treatment before re-melting (machine turnings must be dried and de-oiled before remelting) [4, 5, 34, 41].

“Old scrap” is defined here as end-of-life material. Recycled aluminium is limited by the supply side, i.e. the availability of used aluminium products. Today, over 69% of the mass of end-of-life products are already collected and recycled. Used Beverage Cans (UBCs) and materials from the building/transport sector is already part of integrated recycling operations. With the continued growth of the aluminium market, and the fact that many aluminium products have a long lifespan, the current market demand for scrap cannot be satisfied with recycled aluminium in spite of high recycling rates. Increasing the recycling rates for specific products may lead to diminishing returns due to lower recycling efficiency and higher logistics costs. The aluminium industry is increasingly focused on optimizing product design for maximum recycling in order to improve the scrap supply, in an attempt to eliminate this bottleneck in the aluminium-recycling sector.

It should be mentioned, that in most products aluminium is bolted, welded or by other means attached to other materials. Thus, before re-melting the collected aluminium scrap obtained from end-of-life products and aluminium by-products, the scrap should be sorted and processed in order to remove unwanted material. Such material may be other metals, organic materials and/or plastics. This separation can, however, be performed in different ways, such as by bulk sorting or hand-sorting. During bulk sorting, aluminium parts are separated based on physical characteristics such as density, shape, magnetic susceptibility, electrical conductivity, etc. This mature technology is low cost, and can separate metal from mixed shredded scrap in an efficient way. The hand-sorting concept is, as its name suggests, based on the scrap proceeding through a feed stream where the desirable items are removed by hand. In this case the separation is normally done based on colour, shape and texture [4]. Obviously, this is a labour-intensive process, and in some cases unhealthy for the people involved.

The cleanness of the aluminium scrap is also of importance. Contaminants like oil, lubricants and paints should be removed from the scrap before melting. Three principal technologies are applied by the industry today for de-coating, i.e. rotary kiln, belt and fluidized bed [38]. The
principle of all the above processes is the same, *i.e.* the scrap is heated to the temperature that burns off the organic materials without oxidizing the aluminium metal. A certain degree of metal loss is unavoidable with industrial processes, but due to aluminium’s high value, efforts are directed at minimizing the losses.

**Melting furnaces**

The two most common furnaces used for the aluminium recycling process are the oil or gas fired reverberatory furnace and the rotary furnace. The reverberatory furnace, see Figure 7, is ideally suited for melting all types of scrap that have a sufficient surface area to ensure good heat transfer. However, the scrap should not have too large an area, resulting in too much contact between the surface and oxygen/water vapour presents in the combustion products. Moreover, this kind of furnace is only suitable for melting scrap with high amounts of aluminium, *i.e.* more than 70% [35], and is today mostly used for melting material like extrusion shapes, ingots, engine blocks and gear casings. Reverberatory furnaces have proven to be inefficient for shredded material or swarf due to high impurity levels. In some cases the molten metal bath is covered with a chloride salt flux to protect it from further oxidation [35, 44].

The name reverberatory derives from the heat that reverberates (radiates) from the roof and walls of the furnace onto the molten bath. The main heat transfer is through radiation from the refractory brick walls to the aluminium, but convective heat transfer also provides additional heating from the burner to the aluminium. Burners are located at the end of the furnace opposite to the charge window. By mounting the outlet for the flue gases near the charge, the hot combustion gas stays in contact with the charge longer, which improves the energy transfer to the melt. When the melt reaches the desired temperature, the hot melt is tapped through a tapping hole in the bottom of the furnace or by tilting the furnace.

![Figure 7. Reverberatory furnace for recycling of bulky scrap](image-url)

The name reverberatory derives from the heat that reverberates (radiates) from the roof and walls of the furnace onto the molten bath. The main heat transfer is through radiation from the refractory brick walls to the aluminium, but convective heat transfer also provides additional...
heating from the burner to the aluminium. Burners are located at the end of the furnace opposite to the charge window. By mounting the outlet for the flue gases near the charge, the hot combustion gas stays in contact with the charge longer, which improves the energy transfer to the melt. When the melt reaches the desired temperature, the hot melt is tapped through a tapping hole in the bottom of the furnace or by tilting the furnace.

For melting shredded and swarf scrap with a large surface area, the rotary drum furnace is used, as shown in Figure 8. In this furnace, the rotation improves the separation of oxidation products and contaminants, based on their density. In order to promote the separation between metallic and non-metallic phases, a considerable amount of salt is added. Hence this kind of furnace is suitable for melts with a higher portion of oxide. The furnace is designed as a rotating drum where the burner is arranged at one end of the drum, while the flue gases leave through an opening at the other end. Firing occurs at the bottom of the furnace by using natural gas or occasionally fuel oil. The hot exhaust gas passes through the charge and increases its temperature. Due to the rotation, each individual piece of scrap will frequently be exposed to the combustion gases.

Figure 8. a) Illustration of the rotary drum furnace, and b) detailed sketch of the inside of the furnace [46].

During charging, the burner assembly is moved away, and the furnace charged through the opening situated at the side of the door. Due to the limited size of the opening, rapid charging and discharge is not possible. The rotary drum furnace consists of a long sloping tube designed in such a way that it may be tilted back for charging and firing, and tilted forward for slag and molten metal tapping.

Fluxing

All aluminium scrap has a thin oxide film on the surface. When the scrap is heated in the furnace the oxide layer will grow, especially at high temperatures in the presence of air, oxygen or water vapour. When the aluminium scrap has melted, aluminium oxide will float to the surface of the melt and form a second phase, i.e. the dross. As a result of the surface tension of the melt, a high amount of aluminium will be entrapped in the dross phase. In order to break the oxide
skin, and release the entrapped aluminium metal, a mixture of salts with low melting points are charged to the furnace before and during the charging of the aluminium scrap [47]. The salt flux used is based on an equimolar mixture of NaCl and KCl. This specific composition, corresponds to the minimum temperature of the isomorphism (eutectic mixture) existing between the phases present in the KCl-NaCl binary system, see Figure 9. Fluorides are also frequently added to the flux in order to improve the metal recovery by increasing the solubility of alumina in the chloride mixture and thereby decreasing the surface tension. The most common fluorides added are CaF₂, Na₃AlF₆ and NaF [47, 48]. The amount of the salt flux addition depends on the type of material charged. For recycling materials containing a high amount of light-gauge scrap or organic compounds, e.g. aluminium chips, a higher amount of the salt flux mixture is required. A value lower than 2 wt.% of the charge is the normal amount of salt flux added, and 1023 K is generally assumed to be the optimum temperature for fluxing [4, 47].

Figure 9. The NaCl-KCl binary phase diagram (Factsgage 6.4).

It is a well-known fact that controlling the furnace atmosphere can minimize the flux addition. Moreover, atmosphere control is also important to secure good quality products, as well as minimize the metal losses and reduces the environmental impact. Technologies have been developed for sealing the furnace door and maintain the pressure within the interior of the furnace by controlling the exiting flow of flue gas [4].

Aluminium oxide develops a chain microstructure that has a high specific surface area causing aluminium metal to be entrapped within the slag structure. Reducing the amount of aluminium
metal entrapped in the slag phase can be achieved by adjusting the flux chemistry. Addition of fluorides to the flux mixture decreases the interfacial tension of the dross and reduces the amount of aluminium metal that is found in the dross [47-49].

**Dross**

Aluminium has a high oxygen affinity that leads to the formation of a dense high resistant oxide film on the surface of the metal. The thickness of the oxide layer depends on the operating temperature, and the oxide layer gets thicker in the presence of heated air over time. As a result, it is very important to cover the surface of the liquid metal bath with a protective layer, *i.e.* a slag. Even with a flux covering the bath surface it will oxidize to some extent, which means that both aluminium metal and alumina will be incorporated into the slag phase, *i.e.* into the dross. In other words, dross is a mixture of aluminium metal and non-metallic components that is generated on the surface of the molten aluminium when in contact with oxygen during melting, holding, refining and transfer.

The chemical composition of the dross depends on the raw material, and the overall classification depends on the metal content in the dross and where in the process route it was produced. As a consequence, there is a clear distinction between “white” and “black” dross. Most of the dross, “white” or “black”, is a heterogeneous mixture of large lumps, fine oxides and small droplets of metal [41].

“White” dross forms during the primary production of aluminium, as well as in extrusion and lamination plants and in foundries. The main characteristic of this whitish/greyish dross is the absence of salt. The “white” dross contains approximately 70% metallic aluminium [50].

BD is a by-product of the secondary production (recycling) of aluminium, and is defined by its dark colour. This dross, which is tapped separately from the furnace, consists of 4-8% aluminium metal, 25-45% salt and 50-70% non-metallic compounds [4, 14, 16]. Most of the aluminium present in the dross is present as compounds, *such as*: MgO, Al₂O₃, Al₂O₃, and small amounts of AlN, Al₄C₃ and/or Al₂S₃ [12, 37]. Different aluminium compounds forms at different times/plants. This is a result of the variations that exists in the chemical composition, as well as origin of the used scrap. Carbides are also present in the dross originating from the oil contamination on the surface of the aluminium scrap [51]. Overall, approximately 0.5 tonnes of BD is produced per one tonne of secondary aluminium [19]. From an environmental point of view, BD is classified as a toxic and hazardous waste in Europe (Directive 96/61/CE, Law 16/2002, BOE 157/2002) [52]. Its toxicity is primarily due to its high reactivity in the presence of water or moisture, and is directly related to the generation of gases such as H₂, CH₄, NH₃ and H₂S, as well as heat. Ammonia is produced from the hydrolysis of nitrides that are generated during the melting process. The reaction between atmospheric nitrogen and the aluminium metal is presented as reaction (I) below. Hydrogen is generated from the hydrolysis of metallic aluminium (presented as reaction (II)), and methane is formed by the reaction of carbides with water (presented as reaction (III)). The formation of ammonia hydroxide, presented as reaction (IV), will over time, increase the pH of the surrounding environment. This will dissolve the protective alumina film present on the surface of unrecovered aluminium particles and expose the surface to further oxidation [14, 53].
2 AlN + 6 H₂O = 2 Al(OH)₃ + 2 NH₃ \hspace{1cm} (I)
2 Al + 2 H₂O + 4 OH = 2 Al(OH)₃ + H₂ \hspace{1cm} (II)
Al₄C₃ + 12 H₂O = 4 Al(OH)₃ + 3 CH₄ \hspace{1cm} (III)
NH₃ + H₂O = NH₄OH \hspace{1cm} (IV)

Another expression commonly used to define dross with very low amounts of metallic aluminium is “salt cake”. The amount of entrapped aluminium in the dross has, however, decreased through improvement of the fluxing practices. There is therefore at present no significant difference between what is referred to as a “salt cake” and what is referred to as a BD.

**Dross treatment**

The main aim of dross treatment is to recover the metallic aluminium and salt, in order to minimize the environmental risk and amount of waste material to be disposed of after the treatment. In Figure 10, an overview of both “white” and “black” dross treatment is presented, where the different process routes available are shown in detail. The dross treatment process step closes the loop of the secondary aluminium production process.

![Figure 10](image_url)

*Figure 10 A schematic flow sheet of possible cold and hot process routes for treatment of both “white” and “black” dross [4].

**“White” dross treatment**

As can be seen from Figure 10, a variety of process steps/routes exists for the treatment of “white” dross. The choice of the process steps/route to be used is determined by the amount of
entrapped aluminium that is present in the dross to be treated. Both hot and cold processing routes are available.

**Hot processing**

Due to the presence of high amounts of aluminium in the “white” dross, it is of great importance to reduce the opportunity for oxidation by protecting the melt from coming into contact with the surrounding environment. The most commonly used approach for the treatment of “white” dross is hot processing (see Figure 10). In this process step the dross is immediately after skimming, while the entrapped aluminium is still molten, charged to the rotary furnace. This is the simplest way to retain the energy present in the hot dross. It is, however, difficult to synchronize the two processes, the skimming of the dross from the melting furnace and the operating cycle of the dross-processing step. Another alternative is to use a process step that squeezes the molten aluminium out from the oxide skin using high pressure [54]. With a proper design of the process steps involved in hot processing, up to half of the metal present in the dross prior to treatment can be recovered [4]. Hot processing requires equipment that can process dross at 973-1073K and under inert atmosphere to avoid reoxidation. The high investment cost of such equipment is the main disadvantage of hot processing. Moreover, oxidation of aluminium is an exothermic reaction, which releases a high amount of energy that can with time damage the equipment and increase the maintenance costs.

**Cold processing**

The other option for the treatment of “white” dross is cold processing (Figure 10). During the cooling step needed for this approach it is important to minimize the oxidation and metal losses, capital and operating cost, and the environmental impact.

The oldest and still perhaps the most commonly used approach for cooling the dross is spreading it out on the floor and allowing it cool naturally [54, 55]. While this definitely represents an approach with the lowest direct operating costs possible, a large amount of metal is lost due to oxidation. It also generates large amounts of oxide fume, which is hazardous for plant personnel and causes in-plant hygiene issues. By the use of this method only ~20-30% of the metal present in the dross prior to treatment is recovered [54], making the overall economic efficiency questionable.
In the late 1970s, rotary dross coolers were introduced for cooling of dross [55], see Figure 11. In this process, water is sprayed on the outer surface of a rotating drum extracting the heat from the dross inside the drum. The use of rotary dross coolers improves the metal recovery by up to ~50% in comparison with floor cooling [4]. It should be pointed out, however, that the lack of an inert environment within the drums still results in oxidation and loss of aluminium metal. By providing an inert atmosphere in the drum, the metal recovery could be improved even further by up to an additional 15% [4]. Generally the dross products obtained are in a wide size range, i.e. from dust to chunks of several centimetres [55]. The separation of the metallic aluminium can be improved by crushing, a process step that also increases the overall operating cost.

Rotary coolers have the advantage of being able to handle thermiting dross\(^1\). The disadvantages of this technology include high capital and maintenance costs. Even though relatively efficient, rotary coolers are seldom sold today due to safety concerns, i.e. hot dross and molten aluminium being processed over a pool of water.

Cold dross can also be directly fed together with aluminium scraps to the rotary furnace. In the 1990s, Rio Tinto Alcan Inc. introduced a salt free process for “white” dross processing [56]. In this process, dross is heated in a rotary furnace by using a plasma torch. The furnace is water-cooled. By applying high voltage power to the torch an electric arc is generated between the electrodes that heat the gas (air or nitrogen) to plasma temperature (5000K). Due to the low volume of the processing gas, the oxidation of the aluminium metal present in the dross is minimized with a metal recovery of up to 95%. However, high (and increasing) costs of electrical power and high capital costs are limiting factors to a successful commercialization of this process [35].

---

\(^1\) Thermiting is rapid loss of metal through oxidation of the original wet mushy skim, which during heating has been changed to a powdery form with aluminium droplets and non-metallic material on the surface.
It should be mentioned, that several researchers have successfully used the plasma torch rotary furnace to convert dross residue into useful non-metallic products. One example is the work performed by Lindsay et al. [57], where “white” dross was charged into a plasma torch rotary furnace and heated to its molten state. The free aluminium present in the dross fused together and was poured from the furnace. The resulting dross residue accumulated and lined the wall of the furnace. Periodically, the residue was scraped off and converted into useful Non-Metallic Products (NMP).

“Black” dross treatment

Treatment of BD is important not only for the environment, but also for the reduction of landfilling costs for the secondary aluminium industry. It has been estimated that for every 1000 tonnes of aluminium scrap recycled, 760 tonnes secondary aluminium, 240 tonnes of BD and 3 tonnes of dust were produced [35]. As a result, almost 800 000 tonnes of BD was landfilled in the United States alone in 2005 [38]. The amounts since then have continued to grow with the increased percentage of aluminium scrap being recycled. Within the European union, however, landfilling of this waste has been banned since 2002 [52, 58], due to its potential to contaminate surface water as well as groundwater [16, 59].

With regards to the treatment of BD, hot processing is not economically viable due to the low amounts of aluminium metal present in the dross, 4-8% [4]. Other processes available are the dry- and wet processes.

The dry process includes crushing and sieving to separate the aluminium metal, as well as non-metallic materials from the salt. The wet process is, however, a four steps process, which involves the following unit processes (a) leaching, (b) solid-liquid separation, (c) gas treatment, and (d) evaporation/crystallization.

a) Leaching: The oxide and salt powder is subjected to leaching with water. The oxides are insoluble, while the salts dissolve in water. This makes it possible to separate the salts from the oxides.

b) Solid-liquid separation: After dissolution of the salts, the solid–liquid mixture is pumped into a thickener. The underflow of the thickener is filtered and washed with recycled water. The overflow of the thickener and the filtrate salt-rich solutions are passed on for evaporation and crystallization.

c) Gas treatment: In the leaching, thickening and filtering processes, noxious and potentially explosive gases are generated. In order to eliminate the explosion risk, these gases must be captured and treated. They must then be scrubbed to remove the noxious constituents. To minimize the generation of noxious gases, the pH of the digester should be kept below 8, and preferably above 5. The addition of acid increases both the operating cost of the process and the difficulty of recovering salt and water without contamination.

d) Evaporation and crystallization: The clear salty water from the thickener and filter is boiled in a multi-effect evaporator in which water is boiled away and NaCl and KCl crystals grow.
from the resulting saturated solution. Finally, a salt product with a yield of about 50% can be produced from the dross.

The main objective for the treatment of BD is to extract/recover potentially valuable materials such as aluminium metal and salt from the dross, to produce a less toxic residue to be sent for disposal, and to reduce the total waste volume.

**Economics of technologies for the recycling of “black” dross**

The wet processing of BD is currently not cost-effective without gate-fees. The key factors influencing the economics of the system are the landfill disposal cost (or legal permission to landfill), the amount and value of recyclable materials, and the capital and operating costs of the recycling process [60]. A considerable portion of the operating cost of the recycling process is the cost for the energy required to evaporate the water in order to recover the salts [61]. It has been concluded in literature that for the process of BD treatment to be economically viable, it is necessary to obtain a liquid effluent with a high content of salt in order to reduce the costs of the water evaporation and the later crystallization [58]. Furthermore, to be saleable the NMP must be relatively free from brines, i.e. less than 2% [37]. The lack of economic viability of the process without gate-fees is due to the difficulty of achieving both goals simultaneously. Wet treatment requires a significant capital investment, a considerable consumption of water and energy, while producing only low value added salts and NMP [58, 62]. External contractors do presently perform the processing of most of the BD produced in a number of large central facilities. An improved and economical process for the treatment of BD that can ideally be co-located at the source of the waste is therefore required.

The three key constituents, aluminium, NMP and salt, are the major potential contributors to the revenues derived from the sale of the recyclable components. Since most of the metallic aluminium is recoverable by crushing, magnetic separation and eddy current separation, salt and NMP recovery alone must justify the additional wet processing steps. In addition, NMP requires the use of energy for high temperature processing in order to convert it to a saleable product, which increases the operating cost of the process [51]. Salt can be produced at a lower cost from natural virgin raw materials. As a result, the revenues alone are insufficient to justify the cost of the process, and the economics become dependent on the saving on avoided landfill costs, or environmental legislation banning landfilling [61].

In the present situation, some researchers believe that the best alternative is to minimize BD production, as well as the amount of entrapped aluminium, maximize aluminium recovery from dross, and dispose of the remaining material, salts and non-metallic fractions, in an authorized landfill [17, 53, 58]. As a result, finding a suitable, economically viable alternative for BD treatment is still an open issue for research.
Potential applications for “black” dross

The increasing demand for valuable raw materials and their rising prices, combined with stricter environmental standards, *e.g.* banning of landfilling for some wastes, has resulted in the replacement of primary resources, *e.g.* smelter grade alumina, with secondary resources (recycled aluminium). These changes have triggered the development of recycling facilities for many former industrial wastes.

NMP contains high amounts of alumina and other oxides, *i.e.* MgO, SiO₂, CaO, *etc.* Thus, an opportunity exists to convert NMP into a valuable product instead of following the current practice of landfilling. Some efforts have been made to use the BD/NMP in preparation of raw materials or as filler material in ceramic products, but until now none have found broad commercial application. These attempts can be organized into two categories, *i.e.* (i) application of BD as is, or (ii) application as an upgraded NMP [16]:

- By leaching the BD with NaOH, aluminium is extracted as sodium aluminate and can then be precipitated in the form of aluminium hydroxide. The residue from leaching is calcinated to oxidize the remaining metals to oxide. This calcined oxide can then be mixed with aggregates and alumina cement to make high castable refractory materials [63-65].

- In another process, aluminium is precipitated out as aluminium hydroxide using a NaOH solution. This aluminium hydroxide powder can then be activated at 873K to obtain γ-Al₂O₃ [66, 67].

- H₂SO₄ has also been utilized for the manufacture of aluminium sulphate [68]. The produced aluminium sulphate had in this case various contaminants such as AlN, Al₄C₃, CuO, Fe₂O₃ and MnO. In order to tackle the contamination issue, an alumina leaching process was carried out in two steps. In the first step leaching was carried out with dilute H₂SO₄ to remove impurities, and in the second step alumina was extracted from the purified dross tailings using concentrated H₂SO₄ [69].

- In another study, the BD was leached with H₂SO₄ and the liquid obtained after treatment of the dross with acid was further processed to obtain aluminium hydroxide of an amorphous nature [20]. The experiments were performed by hydrolyzing the aluminium sulphate with aqueous ammonia and calcinating the formed aluminium hydroxide, which resulted in the formation of η-alumina at 1173K.

- Calcination of NMP in a direct fired rotary kiln above 1255K results in a refractory product, mainly spinel (MgAl₂O₄) and corundum (α-Al₂O₃). This has in some studies been used to convert NMP to (Mg, Si) Al₂O₄ spinel by induction synthesis [18, 56, 59].

- NMP can be mixed with inorganic additives and melted to form a silicate-based glass that can be blown to form fibers or granulated into abrasive particles [70].

- An alternative method, that involved adjusting the composition of NMP by adding alumina or silica and then heating the mixture to 1255-2200K to form a molten ceramic product, has also been proposed in the literature [70]. The molten ceramic was, in this case, formed into ceramic wool, as well as amorphous and crystalline structured products.
Another method was introduced where alumina hydrate, magnesium hydroxide and magnesium aluminate are recovered separately, thereby increasing their commercial values. This process treated the NMP in an acid digester to dissolve alumina and magnesia selectively, while the undissolved magnesium aluminate is separated by filtration. In order to recover the dissolved constituents, the pH solution is raised to about 9.5 – 12 to precipitate magnesium oxide. With a pH of about 10 – 11, the alumina is held in solution and the mixed oxides remain as solids. When the pH of the remaining liquid approaches neutrality, alumina trihydrate precipitates and the result is a substantially pure product [64].

Fine grains (less than 150 µm) of the NMP can also be used as raw material in cellular concrete. The aluminium content reacts with water during the production of the concrete and releases hydrogen. This reaction promotes pore formation and reduces concrete density without significantly affecting its strength [59].

BD has also been tested in calcium aluminate production. BD was, in this case, melted with a calcium base flux in a plasma arc furnace. Metallic aluminium was recycled and slag was tapped and allowed to solidify. The solidified slag was crushed for sale to the steel industry as a slag former agent [71].

In another process, NMP was mixed with lime to form pellets, and the pellets were subsequently sintered. Depending on the CaO:Al₂O₃ ratio, as well as the holding and sintering temperature, the product can be used as an addition to steel as a slag former agent, or as calcium aluminate in the cement industry [64].

**Benefits and barriers**

BD can be a suitable source for calcium alumina production. The main source for alumina production at present is bauxite, and it is expensive to produce and a finite resource, *i.e.* about a 100 years reserve base at current prices [22]. The presence of some compounds in the BD such as MgO, SiO₂ or CaO, can be favourable in some applications. Consequently, utilization of BD has benefits including:

- The aluminium industries gain value from their waste, and the aluminium-recycling loop is closed.
- Other industries get cheaper and suitable replacement for their raw material.
- Society benefits through less demand for landfilling and lower potential for environmental contamination.

However, there are significant barriers preventing the significant utilization of BD. None of the proposed processes was commercialized. The reasons for this are:

- NMP after leaching needs further processing such as by calcination [53, 65, 72].
- NMP has significant impurities.
- Variable composition based on the charged scrap [53].
Chapter 3: Objectives of the Present Study

The main objective of the present work has been to try to close the loop of aluminium recycling, and eliminate the need for landfilling of BD residue. To achieve these goals, two processes were investigated, i.e.:

1) Heat treatment of BD for salt removal as an alternative to leaching with water.

   The specific aims were:
   a) To identify the dominant controlling factors for salt evaporation in laboratory scale experiments (using 20gr BD samples).
   b) Evaluate two different techniques, i.e. evaporation under atmospheric and reduced pressure.
   c) Design pilot scale experiments in order to optimize the salt evaporation process. These experiments are based on the results obtained in small-scale experiments.

2) Improve the economy of the process by finding means to utilize PBD in the production of calcium aluminate fluxing agent for the steel industry.

   The specific aims were:
   a) Characterize the fluxing agents that can be produced from the PBD.
   b) Optimize the effect of the various parameters, i.e. holding time, temperature, and cooling media, on fluxing behaviour.

A schematic drawing of the overall flowchart of aluminium production and the focus of the present work is presented in Figure 12.
Figure 12. Schematic drawing of the overall flowchart of aluminium production and the focus in the present work.
Chapter 4:
Summary of Appended Papers

**Paper I. Black Dross Processing: Salt Removal from Black Dross by Thermal Treatment**

Salt evaporation in a stationary furnace

Salt removal from BD by thermal treatment for small samples (20 g) was studied in a stationary vertical resistance heated furnace in an argon atmosphere at both atmospheric and reduced pressure (20Pa).

Stena Aluminium AB, Älmhult, Sweden, delivered the compact and granular BD used in the present experiments. To secure a homogenized grain size distribution of the feed, the BD was crushed to less than 3 mm in size and thoroughly mixed before use, see Figure 13.

![Figure 13](image)

Figure 13. “Black” dross a) before grinding, and b) after grinding.

**Experiments conducted under atmospheric- and reduced pressure**

For the experiments conducted under atmospheric pressure, the samples (20 g) were thermally treated for different time intervals (6 and 10 hours) at 1273 - 1573K under inert atmosphere
(Ar) with a flow rate of 100 ml/min. During the experiments, the reaction tube was at all times kept at atmospheric pressure ($P_{in} = 10^5$ Pa).

In the case of the experiments conducted under reduced pressure, all experiments were conducted under conditions identical to those described in the previous section. The exception was the flow rate of Ar that was lowered to 40 ml/min. The reaction chamber was evacuated from the top, resulting in a pressure of approximately 20 Pa at the outlet of the furnace.

As Na and K are present in the raw material as oxides, i.e. Na$_2$O and K$_2$O, the experimental results obtained in the present work are reported as the yield of chlorine removal in percentage.

In both cases:

- Salt evaporation at temperatures lower than 1273K was slow, and after 10 hours the weight loss was less than 10%.
- Within the 1273 - 1573K temperature range, salt removal by evaporation improved because of increasing time and temperature.
- PBD that was prepared in these processes contains alumina and spinel as the main components.
- The best-obtained result was less than 2% wt residual chlorine and 97% salt removal, which were obtained after 6 hours thermal treatment at 1523K at atmospheric pressure, and at 1473K under reduced pressure.
- Salt removal showed a critical temperature above which removal was greatly improved:
  1. After 10 hours at 1423K using Ar, salt removal was ≈41%. At 1473K and the same holding time, this value rose to 86% under Ar atmosphere and 97% at reduced pressure.
  2. The critical temperature of 1473K was in agreement with theoretical calculations of the salt vapour pressures. The estimates were made using the thermodynamic calculation software Thermo-Calc® version 3.33 for atmospheric pressure.
  3. Based on thermodynamic calculations for 20 Pa, it was expected that the critical temperature would move to temperatures <1200K; however, this was not realized in practice (likely due to mass transport limitations in the solid phase). Therefore, reducing the pressure did not improve the results as much as expected.

**Experiments conducted in a rotary furnace under atmosphere pressure**

As previous results were promising, it was decided to conduct a new series of bench scale thermal treatment experiments. Larger samples (100-600g) would be used in the new experiments. Evaporation would then take place in the interface between the sample and the gas phase. As a result, salt diffusion could impede salt removal in the samples. Consequently, in this set of experiments a rotary furnace, see Figure 14, was employed for thermal treatment to enhance the mixing and improve the rate of mass transport.
The samples were held at constant temperature, \textit{i.e.} 1273 - 1573 \, K, during 10, 12, 14 hours, before being cooled down in the furnace to room temperature. Different gas flow rates, sample amounts and furnace rotation speeds were used, and the optimum conditions for chlorine removal identified. The rotation speed of the furnace was varied between 25-35 \, rpm. The effect of the gas flow rate was checked at 100, 150 and 200 \, ml/min.

**Concluding results**

- Salt evaporation from BD was extremely slow at temperatures under 1423 \, K.
- The treatment temperature and holding time were important in improving the removal.
- By reducing the pressure, the removal of chloride was improved.
- Application of the rotary furnace for thermal treatment of BD in pilot scale experiment is necessary.
- Formation of MgO·Al$_2$O$_3$ and oxidation of AlN will take place during the thermal treatment.
PBD as a potential alumina source for calcium aluminate production

Since PBD contains large amounts of alumina, it can be used as an alumina source for calcium aluminate production. In the present work, PBD was tested to investigate its potential to replace the alumina content in the calcium aluminate flux agent used in the steel industry. The PBD was consisting of approximately 56wt% alumina (Al₂O₃) and less than 1wt% salt. According to the CaO-Al₂O₃ binary phase diagram, see Figure 15, an addition of 32.8 - 36.4wt% CaO to the PBD would secure a fluxing agent with a melting temperature less than 1673K.

![Figure 15. The CaO-Al₂O₃ binary phase diagram [73]](image)

Experimental work

For the experiments conducted in the present work, PBD was crushed and thoroughly mixed with calcium oxide and 10% deionized water, before being pressed into tablets with a diameter of 12 mm using a pressure of 40 MPa. The tablets were sintered in an atmosphere of air in an induction furnace at different temperature, i.e. 1473, 1523 and 1573 K, and kept at the temperature in question for different period of time, i.e. 5, 15 and 30 minutes. Different media, i.e. water, water-cooled steel plate, air, or furnace atmosphere, were later used to cool the
thermally treated samples. The effects of the above parameters on the microstructure of the fluxing agent, as well as on the enthalpy of fusion, have been studied by SEM-EDS, XRD and DTA analyses.

One of the most important properties of a fluxing agent is its ability to rapid melt and dissolve in the carryover slag. Based on this, a set of experiments was designed to measure the dissolution rates of the produced flux tablets in a synthetically produced slag phase representing the carryover slag. A combination of a X-Ray (XR) unit and a graphite resistance furnace from Technology Inc., Santa Rosa, CA, USA [74] were used for the direct observation of the dissolution process, see Figure 16. Due to the size of the alumina shooter, which was used to drop the tablet on to the molten slag phase, the produced flux tablets had a thickness of 5 mm and a total weight of 300 mg. The porosity of the samples was measured before each experiment based on Archimedes’ principle. To keep a 3/1 ratio between the carryover slag and the flux [75], 1.2 g of the synthetically produced slag mixture where added during each experiment.

Figure 16. A schematic illustration of the X-Ray unit which was used for dissolution tests [74].

Concluding results

- The XRD results, for the samples sintered at 15 min and regardless of cooling media, proved that the phase 12CaO·7Al2O3, which was the phase with the lowest melting point, was the main phase in the samples. In the rest of the samples the XRD patterns proved that the CaO - Al2O3 and/or 3 CaO- Al2O3 had significant presence.
In the SEM-EDS micrographs of the samples that cooled by different media two different phases have been identified, i.e. the needle- and matrix phase. The needle phase had its greatest prevalence in the water-quenched samples.

The TGA results confirmed that the water-quenched samples had the least thermodynamically stable structure, and subsequently had the lowest enthalpy of melting.

The XR results of the dissolution test in the synthetic carried over slag did not show any significant differences between the samples that were cooled by the different methods.
Section B: Optimization of Direct Reduction Iron Production
Chapter 5:
Iron- and Steelmaking

According to the International Iron and Steel Institute (IISI) the total world production of steel in 2014 was 1636 Mt. produced from three different types of raw materials, i.e. hot metal, steel scrap, and sponge iron, through two different processes, i.e. Basic Oxygen Furnaces (BOF) and Electric Arc Furnaces (EAF) [7]. In BOF steelmaking ~75% of the feed material charged comes from the hot metal (iron) produced through the Blast Furnace (BF) process, and the remaining ~25% is steel scrap. The EAF process feed varies among plants from 100% steel scrap to 80% Direct Reduced Iron (DRI) [3, 30, 76, 77].

**BF- BOF**

**Blast Furnace (BF)**

The BF process has been, and will probably remain, the dominant ironmaking route in terms of the tonnage of iron produced for a foreseeable future. A BF has normally a daily production measured in the thousands of tonnes of hot metal, i.e. pig iron, which is converted into steel in an integrated steel plant [78].

Generally, it is of interest to install larger BFs in order to exploit the advantages of economies of scale. A modern large BF has a hearth diameter of 14 - 15 m, and a height of 30 - 35 m with an internal volume of about 4500 m³. These furnaces produce 8 - 12 thousand tonnes of hot metal per day [25, 77]. One of the largest BFs in the world is located at the Oita Works of Nippon Steel, Japan, and has a volume of 5775 m³ [3, 79].

In a typical BF operation, iron oxide and coke are charged from the top of the furnace, and high velocity oxygen enriched air at a temperature of 1273-1373 K and a pressure of 2 bar is blown into the shaft from the bottom. A cavity called the raceway is formed in the lower part of the furnace. It is in the raceway that the coke combusts to generate reducing gases, and it is also where the smelting energy required for the production of molten iron is produced. As the solid travels downwards in the shaft, and the reducing gas upwards, the gas reduces and melts the iron ore forming liquid iron and slag in the temperature range of 1473-1673K. This happens in
a location of the BF called the cohesive zone. The produced liquid percolates through the coke bed, *i.e.* through the so-called dripping zone, to the hearth of the furnace. A schematic representation of a BF and its charged raw materials, products, and by-products is presented in Figure 17.

![Schematic representation of a BF for ironmaking](image)

**Figure 17.** Schematic representation of a BF for ironmaking [80].

In the BF coke and coal are used as the main reductant and sinter, and pellets and lump ores as the iron bearing components. Coke is the product of carbonization (or distillation) of mainly bituminous coal. Various alternative reducing agents, such as hydrocarbons, oil, natural gas and in some cases plastics, are also used [3, 81-83]. The purpose of the alternative reducing agents is to decrease the coke rate, which is defined as the amount of coke needed to produce a ton of hot metal. Today, the coke to iron ratio in a BF is about 0.6, so the overall coke demand is around 460 - 470 Mt/year for furnaces which do not used alternative fuel injections such as Pulverized Coal Injection (PCI) [25]. The reduction of the coke rate is desirable as a result of the hazardous emissions associated with the coke-making process, *i.e.* sulphur dioxide and carcinogenic organic compounds. Much effort is today devoted to increasing the efficiency of the BF, as well as reducing the emissions. In part, this is due to the short supply and costs of high-grade metallurgical coke, but it is also due to the increasing necessity for environmental controls in regards to coke production [25, 84, 85].
The size range of the solid raw materials is strictly controlled to optimize the gas flow and iron oxide reduction rate inside the BF. The top off-gas has a considerable fuel value as it is dedusted and used for preheating of air and running turbines to drive air blowers. The BF off-gas contains CO (20-28%), H₂ (1-5%), inert compounds such as N₂ (50-55%) and CO₂ (17-25%), some sulphur and cyanide compounds, and large amounts of dust from impurities found in the coal and iron ore. The production of BF gas is approximately 1200 to 2000 Nm³/t hot metal. A flux is also added to the BF charge to absorb some of the impurities present in the iron sources and coke ash. The flux added is essentially limestone (or calcium carbonate) and dolomite (calcium and magnesium carbonates).

A liquid slag is formed on top of the denser hot metal. The hot metal is separated from the slag at a temperature of no less than 1723K, before it is discharged from the bottom of the BF. The hot metal is than directly transported to the BOF where refining of the hot metal to steel takes place by removing elements such as sulphur, silicon, carbon, manganese and phosphorous. The pig iron produced in the BF is basically a carbon saturated silicon and manganese iron alloy with residual amounts of sulphur and phosphorus, i.e. 4 - 4.5 % C, 0.4 - 1.5 % Si, 0.15 - 1.5 % Mn, 0.045 - 2.5 % P and < 0.15 % S [25, 79].

**Basic Oxygen Furnace (BOF)**

The main idea of the BOF process is to convert carbon-rich liquid hot metal from the BF to low-carbon steel. The furnace lining and slag of the BOF are ‘basic’ with a high CaO content, and oxygen is used for carbon oxidation. The normal BOF charge is 70-75 % hot metal, i.e. pig iron, and 25-30% scraps for cooling of the melt.

A BOF convertor is a pear like vessel with a top blowing water-cooled oxygen lance at the centre, as shown in Figure 18. The position of the lance with respect to the bath and flow rate of oxygen is automatically controlled. The impingement of the oxygen jets at supersonic speed on the molten iron bath, results in metal droplets being ejected from the bath by the impact of the high jet momentum, thereby increasing the metal surface area and the rate of oxidation of impurities [86, 87].

The tap-to-tap time of each BOF heat, which is normally 30-40 minutes, is sequentially made up of the following steps, see Figure 17 for details [79]:

- Charging of scrap and hot metal into the convertor using a charging crane with the vessel inclined towards the charging side (5-8 minutes).
- Making the vessel upright, lowering the lance and then oxygen blowing at the desired rate (15-20 minutes).
- Stopping the blow, raising the lance, and then inclining the vessel again towards the charging side to take a metal sample and if necessary, also a slag sample, to check the bath composition and temperature (6-10 minutes).
• Tapping the vessel by rotating it to the opposite side so that the steel flows through the tap hole in the nose portion of the vessel into the ladle kept below the converter floor (4-8 minutes).

Figure 18. Schematic presentation of a BOF (a) with conventional lance, and (b) with lance provided with post combustion nozzles [87].

Figure 19. The basic oxygen furnace process steps for steelmaking [79].
Direct Reduction - Electric Arc Furnace (DR-EAF) process

Direct Reduction (DR)

Although it is expected that the BF-BOF will remain the primary routes for steel production long into the future, the tightening of environmental requirements and the depletion of natural resources, especially coking coals and high-grade iron ores, pose challenges for metallurgists. A number of alternative processes are presently at various stages of development or demonstration. Among the numerous alternative processes, Direct Reduction (DR) and Smelting Reduction (SR) processes have reached industrial implementation. Processes which produce iron by reduction of ore below the melting point of iron are generally classified as DR processes, and the product is referred to as Direct Reduced Iron (DRI) [88].

DRI as a raw material is used in EAF steel plants where it is melted with or without steel scrap. The DRI content of tramp elements is much lower than that of steel scrap. As a result, DRI products have become preferred charge materials for efficient high-quality steel production in the EAF [89-91]. In 2014, about 63% of the steel produced worldwide was made by the BF-BOF, and about 33% by the DR-EAF processes [7].

Compared to the BF, DR processes have advantages that make them suitable alternative technologies for the 21st century [25, 91], i.e.:

- Elimination of dependence on coking coal.
- Smaller module size.
- Lower total capital investment.
- Superior environmental performance.
- Easier process control and improved process flexibility in most cases.

DR was first successfully commercialized when the Höganäs process, developed in 1909, lead to the patent for the Wieberg process in 1918 [3]. The first DR plant was established in the late 1950’s in Mexico, by HYL [3, 78]. However, the commercial production of DRI did not achieve significant growth until the 1970’s [92]. From 1970 to 2013, worldwide production of DRI increased by a factor of more than 92, from about 800 thousand tonnes, to approximately 75 million tonnes [93]. The driving force behind this rapid increase in production was (as mentioned above) the smaller scale, low capital and operating cost, independence from high-quality coke and iron oxide feed stocks, as well as the demand for a high purity supplement to ferrous scrap in the EAF steelmaking process [31]. The initial advantages of DR plants over BF facilities have grown over the years, for several reasons, including the increased size of DR modules, lower energy and emissions (particularly CO₂), along with the flexibility to use a number of different reductants [31, 94]. However, because of the rapid increase in demand for steel in the market there has been almost no change in the percentage contribution of DRI to the total output of primary iron in the last two decades, remaining stable at 5 - 6% [28, 84], as shown in Figure 19.
Since the DR process does not involve any melting or separation of chemical impurities, the geometric shape and the gangue content of the oxide feed are preserved in the final product. The DRI exhibits a honeycomb structure under a microscope, and is therefore often referred to as sponge iron [3]. The true density of iron is 7.8 g/cm³, while the typical DRI pellet has a volume of about 0.9 cm³, a weight of 3 g, and hence an apparent density of only 3.5 g/cm³ [3, 91]. The carbon content varies, however, over a wide range, i.e. 0.1 - 0.15 % for coal based and up to 2.5 % for gas based DRI [28, 91].

Figure 20. Iron and steel production statistic between 1900 and 2008 [28].

The DR process produces three different product forms depending on the application, and they are cold DRI (CDRI), Hot Briquette Iron (HBI) and hot DRI (HDRI). CDRI is generally stored for later use in a nearby EAF. HDRI is discharged hot from the shaft furnace and transported directly to an EAF for melting. HDRI provides additional sensible heat to the EAF, and thus reduces the electric energy consumption and tap-to-tap times. When DRI is mechanically compressed after reduction and before cooling, it is called HBI [88]. HBI has a lower porosity than DRI, which facilitates safe shipping and storage, and reduces the danger of spontaneous combustion of wetted DRI.

DR processes roughly fall into two categories, i.e. natural gas based and coal based, depending on the reductant used. Natural gas-based DRI production is the more widely used and it is characterized with higher metallization and carbon content. Natural gas based processes include MIDREX®, HYL/ENERGIRON and FINMET, while the coal based included SL/RN, FASTMET®, FASTMELT®, COREX and ITmk3.
In 2013, 17.77 Mt of DRI was produced in India, making it the world’s largest DRI producer, while 32.32 Mt was produced in the Middle East and North Africa, 13.83 Mt in Latin America and just 0.5 Mt in western Europe (Germany) [32]. The MIDREX® technology was responsible for the production of 44.8 million tonnes of sponge iron. This amount was 59.7% of the total amount of sponge iron produced in the world. The HYL/ENERGIRON technology was used to obtain 11.7 million tonnes, or 15.8% of world sponge-iron output. The fluidized bed based process, FINMET, made more than five hundred thousand tonnes. The remaining 17.1 million tonnes was produced using rotary kiln technologies [32, 94]. The MIDREX® and HYL/ENERGIRON technologies have undergone significant improvements in recent years, especially in regard to the use of coke-oven gas, synthetic gas from coal, and COREX export gas as well as hot coupling of the DR process to the EAF [32, 95-97]. Simultaneously the productivity has been continuously increased, and the energy consumption decreased.

**MIDREX® process**

The MIDREX® process is the world’s most successful technology in terms of the tonnage of DRI produced. Today, there are over 50 modules operating in 20 countries, with capacities in the range of 0.4 – 2.7 Mt/year (Iran, Venezuela, Argentina, Canada, Qatar, Germany, Trinidad and Tobago, etc.) [78]. The process flow-chart of the MIDREX® process is presented in Figure 21.

![Figure 21. Schematic illustration of the MIDREX® process for production of DRI [32].](image-url)
As can be seen from Figure 21 the MIDREX® plant is composed of two main facilities, i.e. the shaft furnace where iron ore is reduced, and the reformer which generates the reforming gas to be injected into the shaft furnace. The reducing agents are reformed natural gas, or non-coking coal, which also act as the primary source of energy. The MIDREX® process includes three stages, i.e. reforming, reduction and heat recovery [30, 94, 97].

- **Reforming and Gasification:** The off-gas from the shaft furnace, after scrubbing and CO₂ removal, is replenished with fresh syngas for the reduction process. The off-gas is fed to a reformer consisting of a refractory-lined chamber containing alloy tubes. The gas is heated and reformed as it passes through the tubes. To enhance the reformation process, a catalyst (normally Ni) is placed in the tubes. The proper gas ratio in the MIDREX® process is H₂/CO = 0.5 - 4.0, and (H₂+CO)/(CO₂ + H₂O) ≥ 10 [28, 91, 98].

- **Reduction:** Iron ore (pellet/lump), is introduced by a proportioning hopper at the top of the shaft furnace. To increase the yield, up to 10% fine iron ore can be used [79]. For this process the iron ore is reduced in the shaft at a pressure of 1.5 bars [30, 78]. As the iron ore descends through the furnace by gravity, it is heated and the oxygen is removed from the iron ores by counter flowing gases that have a high H₂ and CO content. The reduction gases react with the iron oxide in the ore and convert it to metallic iron, producing water vapour and carbon dioxide. The DRI is cooled and carburized by counter flowing cooling gases in the lower portion of the shaft furnace. The DRI can also be discharged hot and fed to a briquetting machine for production of HBI, or fed hot to an EAF.

- **Heat recovery:** The MIDREX® direct reduction process recycles the used gas, which secures that the process has both low energy consumption and low environmental impact, making it an environmentally friendly process. The reformer is greatly enhanced by the heat recovery system. Sensible heat is recovered from the reformer flue gas to preheat the feed gas mixture, the burner combustion air and the natural gas feed. The use of recycled gas, and the ability to fed hot reformed gas to the shaft furnace without quenching and reheating, provides a very thermally efficient process. In Table 1 the typical characteristics of the MIDREX® DRI is presented.

### Table 1. Typical characteristics of MIDREX® DRI [97].

<table>
<thead>
<tr>
<th></th>
<th>CDRI</th>
<th>HBI</th>
<th>HDRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Total [%]</td>
<td>90 - 94</td>
<td>90 - 94</td>
<td>90 - 94</td>
</tr>
<tr>
<td>Fe Metallic [%]</td>
<td>83 - 90</td>
<td>83 - 90</td>
<td>83 - 90</td>
</tr>
<tr>
<td>Metallization [%]</td>
<td>90 - 96</td>
<td>90 - 96</td>
<td>90 - 96</td>
</tr>
<tr>
<td>Carbon [%]</td>
<td>1.0 - 2.5</td>
<td>0.5 - 1.5</td>
<td>1.0 - 2.5</td>
</tr>
<tr>
<td>Bulk Density [kg/m³]</td>
<td>1600 - 1900</td>
<td>2400 - 2800</td>
<td>1600 - 1900</td>
</tr>
<tr>
<td>Apparent Density [g/cm³]</td>
<td>3.4 - 3.6</td>
<td>5.0 - 5.5</td>
<td>3.4 - 3.6</td>
</tr>
<tr>
<td>Typical Size [mm]</td>
<td>4 - 20</td>
<td>30×50×110</td>
<td>4 - 20</td>
</tr>
<tr>
<td>Product Temperature [°C]</td>
<td>40</td>
<td>80</td>
<td>600 - 700</td>
</tr>
</tbody>
</table>
HYL/ENERGIRON process

The HYL technology, originally developed in Mexico, is now owned by the Italian technology company Tenova, and has been re-branded as ENERGIRON. In 1957, HYL I was developed using four batch process reactors in series. Today, the HYL I and II are only used in a few older facilities [30, 94].

In 1979, the HYL III process was developed in which iron ore is reduced in a moving bed shaft furnace at a pressure of 5 - 8 bar. Natural gas is cracked in the catalytic gas reformer, so that the reducing gas contains roughly 80% H₂ [28, 97]. The ore charge to the HYL III process averages about 80 % pellets and 20 % lump ore. In basic terms, the operation of the HYL III technology is quite similar to the MIDREX® process. A major difference is in the operation of the reformer. In the MIDREX® process, the reformer operates on a mixture of cleaned top gas and natural gas, with no steam necessary. The reformer product gas is then modified further in temperature and/or composition, as necessary. However, the HYL III process, only feeds fresh natural gas to their reformers, using externally generated steam to perform the reforming. The reformed natural gas must then be cooled to remove excess water. It is then combined with the top gas, from which much of the CO₂ has been removed, and the combined stream is heated and the chemistry adjusted if needed [30, 92]. The process flow-chart of the HYL/ENERGIRON process is presented in Figure 22.

In contrast to the classical HYL III technology, its later modification, i.e. the ZR technology, does not use a reformer. Inside the reactor, freshly reduced iron serves as a catalyst for reforming of the hydrocarbons. This process scheme includes the following features: partial combustion of the reducing gas, in situ reforming in the lower part of the reactor’s reduction zone, and adjustable composition of the reducing gas. This technology lowers the necessary initial investment and maintenance costs. The DRI that is produced is also of better quality and has a high carbon content (up to 5%) in the form of Fe₃C [78].

![Figure 22. Schematic illustration of the HYL/ENERGIRON process for production of DRI [99].](image-url)
DANIELI and HYL in collaboration developed the ENERGIRON technology on the basis of the ZR method. This new technology employs modules with capacities of 0.2 - 2.0 million tonnes per year. The technology allows the direct use of H₂, CO, or any gas that contains hydrocarbons. The gas that leaves the reactor is cleaned of H₂O and CO₂ and used again in the reactor after heating to 1123 K. Some of the natural gas that is oxidized as a result of the injection of oxygen, which heats the inside of the reactor to the temperature (1273 K), is needed to reform the hydrocarbons and form carbides. The temperature of the reducing gas is lowered to 1093 K by endothermic reduction reactions, and at this temperature the pellets do not stick together or form clusters.

One of the advantages of the ENERGIRON process is the wide flexibility for DRI carburization. The level of carbon can be adjusted by controlling the reducing gas composition and/or the oxygen injection. Formation of Fe₃C makes DRI very stable and more suitable for storage and shipping. Also the presence of less than 4% C in the DRI is favourable due to the reduction in energy consumption in the EAF process [78, 94, 97, 100].

**Electric Arc Furnace (EAF)**

Over the past 40 years the proportion of steel production by the EAF route has been experiencing a steady growth. The history of the EAF was started in a small way, essentially for scrap melting and production of alloy steel.

According to the IISI the steel production in 2014 was globally 1636 Mt. [7], of which 50% is accounted for by China. The amount of steel produced through the EAF route has surpassed more than 400 million tonnes, i.e. 30% of the world’s steel supply, and is expected to be approximately 650 million tonnes by 2020 [25, 101], as scrap recycling increases and energy efficiency in the EAF is improved. While earlier EAFs (about 100 years ago) were mostly between 10 tonnes to 50 tonnes, today 200-250 tonnes EAFs are the most common and even 400-500 tonnes EAFs are available.

The advantages of the EAFs for alloy steelmaking include:

- Relatively small size (low capital cost).
- Cleaner environment.
- Flexibility to produce a variety of grades.
- Precise control.

A schematic of the Alternating Current (AC) EAF process is presented in Figure 23. As can be seen from the figure, it is typically three electrodes in the EAF. The electrodes are almost always made of graphite, overlying the bowl or cup shaped hearth of the EAF, which acts as the container or store for the molten metal and slag. Electric current is passed through these electrodes and arcs are stuck between the electrodes and the charge, which must be conductive. Heating takes place by radiation and convection from arcs, and to a lesser degree by resistive heating created by the passage of electric current. The arc temperature is above 4273 K.
The inner lining of the EAF is basic, and is normally burnt magnesite. Charging is done from the top. During the charging, the electrodes are lifted up to allow the roof to be swung horizontally to one side, thus providing open access from furnace top. The EAF can be tilted to one side for metal tapping, and to the opposite side for slag tapping through a slag door. The electrodes get worn out and consumed during arcing, so to keep the electrode length sufficient, frequently another electrode is joined from the top. The electrodes are raised and lowered by motors, or hydraulic arms, to control the amount of power delivered in the furnace. For a fixed voltage, lengthening the arc increases the resistance, and thus reduces the current and the power input [25, 79, 103, 104].

The main advantage of the EAFs is their ability to accept scrap, DRI and even molten metal in various proportions. It is, however, important that the demand for external heat can be provided at all time by controlling the amount of electrical power supplied. Furnace efficiency can be improved by the combined injection of carbon and oxygen.

The EAF process route was initially developed for scrap recycling, however, the production of high quality specialty steel grades from scrap is sometimes only achievable with dilution of unwanted tramp elements, \textit{i.e.} Pb, Cu, Cr, Ni, Mo, Sn and non-metallic components, with highly pure materials such as DRI or hot metal. The DRI is highly suitable for economic production of high quality steel due to its low content of N, as well as very low content of P and H. The N content of tapped steel decreases from 40 to 100 ppm for a 100% scrap charged EAF to 15-25 ppm for DRI charges [105, 106].

The DRI has a bulk density that is greater than that of most types of steel scrap and greater than that of the EAF slag, which facilitates DRI melting at the slag/metal interface. The remaining FeO in the DRI reacts with the carbon in the liquid metal bath to improve the foaming of the slag that shields the refractory from the arc radiation. However, DRI feeding rate is an important parameter of the EAF process that has to be controlled. The optimum feeding rate depends on the DRI chemical composition, the bath temperature, and the mixing energy provided by the
oxygen carbon injectors and/or bottom stirring plugs. DRI feeding rates of most EAF furnaces are in the range between 27 and 35 kg/min/MW [106].

**Smelting Reduction (SR)**

The processes that produce pig iron directly from ore are referred to as the SR processes [107, 108]. The advantages of the SR processes in comparison to the BF process can be summarized as follows [78, 94, 107, 108]:

- Utilization of a widely available variety of non-coking coals as reducing–carburizing agents and energy instead of coke.
- Utilization of a wider range of iron oxide feed stocks, which are harder to beneficiate in the BF, *i.e.* waste oxides and high-phosphorus, sulphur- or titanium oxide-containing ores.
- Direct utilization of iron ore fines or a concentrate rather than pellets, sinters, and lump ore.
- Elimination of environmental emissions caused by the coke ovens, sinter plants, and induration kilns.
- Reduction of capital and operational costs by minimal ancillary plant and material-handling requirements.
- Overall lowered energy consumption per ton of pig iron production.

The SR processes can be subdivided into four categories according to their operational scheme [94, 107], *i.e.*:

1. Preliminary reduction of the iron oxide feed stocks in the solid state to direct-reduced iron and, subsequently, final reduction and smelting into the liquid state, *i.e.* the COREX, FINEX, FASTMET®, FASTMELT®.
2. Complete reduction and smelting of the iron oxides in a molten slag bath, *i.e.*, the ROMELT and AUSIRON processes.
3. Complete reduction and smelting of the iron oxides in a molten metal bath, *i.e.* the DIOS and HIsmelt processes.
4. Complete reduction and smelting of the iron oxides in a single reactor such as a rotary hearth furnace, *i.e.* the ITmk3 process.

**COREX process**

Among numerous SR processes, the COREX process using lump iron ore has found the greatest commercial implementation [78, 107]. In the COREX process reduction and melting are carried out in two separate process reactors, *i.e.* the reduction shaft and the melter-gasifier. A schematic of the COREX DRI process is presented in Figure 24.

The reduction gas consists of 95% CO + H₂ and is produced in the melter-gasifier as the result of non-coking coal gasification with oxygen. Flowing from the melter-gasifier, the gas is cooled
by the recycled process gas to the required reduction gas temperature between 1173 and 1223 K. After that it is fed to the reduction shaft where a mixture of lump ore, pellets and/or sinter are reduced to approximately 93% metallized DRI by a counter flow of process gas. By means of especially designed screw conveyors the DRI drops into the melter-gasifier, where apart from final reduction and melting, all metallurgical metal and slag reactions take place. The tapping procedure, tapping temperature, and further processing of the hot metal are the same as those for the BF hot metal.

Flux materials such as limestone, dolomite, and silica are added to the system, to adjust the basicity of the slag, and to ease the removal of impurities to the slag. They are charged either along with coal, or along with the iron oxide feed stocks. The amount of flux material to be added to the system is dictated by the coal ash analysis, and the amount of silica, alumina, and sulphur that is present in iron oxide feed stocks. It should be noted that high amounts of flux additions result in large slag volumes, which reduce the productivity of the process [94, 107, 108].

![Diagram of the COREX DRI process](image)

Figure 24. A schematic flowchart of the COREX DRI process [94].

The main incentives behind the development of direct SR processes were to eliminate the dependence on high-quality iron oxide and coke feed stocks, to reduce the preparation costs, and eliminate environmental problems. However, just like the conventional BF process, the COREX process utilizes lump ore, pellets, or sinters as iron oxide feed stocks. Thus, the COREX process still entails the dependency, substantial costs, and environmental problems associated with pellet or sinter preparation. It should be noted that iron oxide feed stocks that contain high amounts of S and P cannot be utilized in the COREX process. Operation in the reducing mode of the melter-gasifier, results in deportment of almost 90% of the S and P to the
final hot metal. Thus, just like the hot metal produced in the BF, COREX hot metal needs to be desulfurized after its production [107].
Chapter 6: Sustainable Iron- and Steelmaking

Increased production rates of iron and steel have proven to be a necessary part of modern economic growth. It should, however, be noted that this imposes challenges to sustainable development due to the emissions associated with iron- and steelmaking, as well as the increasing use of limited resources such as high quality lump ore and coking coals. The goals of sustainable iron- and steelmaking are defined as: (i) conservation of natural resources, (ii) reduction of greenhouse gas and volatile emissions, and (iii) reduction of hazardous waste and the elimination of landfilling [27, 109].

Conservation of natural resources

Recycling of steel scrap has had a continuous growth in the last forty years, and it is likely to be a more significant route for steel production into the future. As shown in Figure 25, while iron ore reserves are limited to the natural distribution and quality of available iron oxides, the availability of scrap is limited only to the end of life availability of various steel products and their replacement rates. It is apparent that the fraction of available scrap in any given year is less than 1% of the total reserves of iron ore. Hence, due to the rate of global steel demand growth and the scarcity of scrap, it is projected that more than 50% of the steel production in 2050 will still have to come from virgin materials [109].

Between the late 1990’s and 2012, steel production by scrap remelting increased approximately 60%, from 350 million tonnes to more than 550 million tonnes. In the same period, crude steel production increased by 90% [109, 110]. Recycling will not be sufficient to meet the future demand for steel products given the current rate of growth. Even a 100% recycling rate cannot supply a growing demand, therefore, it is concluded that policies for sustainable development cannot solely rely on recycling [24, 109, 111-113].
Reduction of GreenHouse Gas (GHG) emissions

In the last three decades, the global climate change caused by GHGs has become a ‘hot’ issue in the world. The global climate targets required for mitigating climate change are represented by a binding target, which corresponds to the stabilization of the global mean temperature increase between 2.4 and 3.2°C during the coming century [111]. As a result, the Kyoto Protocol, the United Nations Framework Convention on Climate Change, was entered into force on 16 February 2005. The Kyoto Protocol has set legally binding targets for industrialized countries to reduce GHG emissions during 2008 - 2012 by an average of 5% from the 1990 levels [114]. Later in 2010, the Cancun Agreement failed to set a clear reduction target from 2012. However, this agreement encouraged developed countries to reduce their emissions by 25 – 40 % below their 1990 levels by the year 2020[115].

Among the six GHGs, i.e. water vapour (H₂O), carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), ozone (O₃), and chlorofluorocarbon (CFCs), CO₂ is the most significant, accounting for half of the greenhouse effect [114, 115]. The concentration of CO₂ in the atmosphere has risen to a value of over 400 ppm today [116], from the preindustrial value of 280 ppm [117]. The CO₂ makes up for approximately 93% of all steel industry GHG emissions [118]. It should be noted, that the CO₂ emissions vary by production routes. On average, 1.8 tonnes of CO₂ is emitted for every ton of steel produced. Steel industry CO₂ emissions were 2.6 billion tonnes in 2010, and the global CO₂ emissions from all sources were 38.7 Gt. [23]. So the iron and steel industry account for approximately 6% of total global CO₂ emissions [23, 24, 118]. It is projected that steel production will reach 2 billion tonnes in 2020, and this is likely to be accompanied by an increase in the amount of CO₂ released to the atmosphere [43, 113]. Therefore, the possibility of developing energy efficient technologies, as well as energy recovery and CO₂ emission reduction alternatives, in the iron and steel industry has long attracted interest both within academia and at the plant operations level all around the world.
[29, 109, 112, 119-122]. The climate change externality has recently been included in the cost structure of products produced within some countries encouraging interest in more efficient technologies [111, 123].

**Present scenario**

The emissions from the steel industry are influenced by the production routes, product mix, energy efficiency, fuel mix and its carbon intensity, as well as the carbon intensity of the electricity consumed [29, 124]. Steelmaking globally is estimated to be responsible for 29 EJ ($10^{18}$ J) or 6% of total global energy consumption [123]. Since 1960, a 60% reduction in the energy required to produce a ton of crude steel has, however, been achieved. In the same period in United States (US), energy consumption in the steel industry was reduced from about 35.8 to 18.0 GJ/ton, but this still represents about 2 - 3% of the total energy used in the US [27]. This has been accomplished primarily due to the implementation of continuous casting, other yield improvements, a shift to scrap-based EAF production, and a decrease in the BF fuel rate. Indeed, by the drivers of mass production, quality control and cost reduction, technical progress has led to large energy savings, and to the systematic use of lean and clean processes [31, 119, 123, 125, 126].

![Breakdown of CO$_2$ emissions from the iron and steel production processes at a conventional integrated steel mill](image)

Figure 26. Breakdown of the CO$_2$ emissions from the iron and steel production processes at a conventional integrated steel mill [43].

Nevertheless, the global steel industry currently accounts for 25% of industrial energy related carbon emissions [31, 112, 127]. The trend has been levelling off, because the reservoir of achievable stepwise improvements has been almost exhausted [110]. More than half of all of the energy costs and atmospheric emissions generated in the production of steel are attributable to coke and sinter production, as well as BF smelting [25, 109, 128, 129]. The BF itself accounts
for almost 69% of total integrated steel plant CO\textsubscript{2} emission and 75% of the energy consumption [27, 43], as shown in Figure 26. Steel production is currently very coal intensive, since coke (devolatilized coal) is used in the BF, and often the electricity for the facility is generated from coal. Even many EAFs relies on electricity produced by coal combustion [130].

It is known that modern BFs, which use quality coke and iron ore bearing materials, have modern equipment for monitoring and controlling charge distribution in the top, and countercurrent heat and mass transfer in the furnace and auxiliary equipment (e.g. stoves). This equipment has already been made nearly as efficient as theoretically possible, and there is little room for improvement [128, 131, 132]. As a result, finding an alternative process may be a more practical alternative to achieve future gains [27, 43, 110, 132]. As a result, reducing CO\textsubscript{2} emissions through improved efficiency alone will not result in sufficient levels of reductions to achieve the requirements of the Kyoto and/or Cancun accords. Other novel or breakthrough technologies will be required.

DR the environmental friendly ironmaking process

Compared to EAF and DRI technologies, the BF/BOF route has higher energy consumption and emissions. The greatest difference between the technologies is in the level of emissions of priority pollutants such as SO\textsubscript{2}, NO\textsubscript{x}, CO, Hg and Cd, which are several orders of magnitude higher following the BF/BOF route [109, 130].

Currently, DRI production is the most environmental friendly technology option for production of iron from virgin materials, particularly in a scenario where Carbon Capture and Storage (CCS) is proven to not be commercially or technically feasible. There is also great potential to make the DR-EAF route become even more attractive. The carbon emissions from the DR plants can be further reduced by discharging hot DRI from the shaft furnace, transporting it to the melt shop, and charging it to the EAF at 600-700°C. This method lowers the electricity required per ton of steel produced, which also reduces the CO\textsubscript{2} emissions from coal-fired power plants. It should be noted, that the electricity consumption can be reduced with about 20kWh/t liquid steel for each 100°C increase in DRI charging temperature. Thus, the savings when charging at over 600°C are 120 kWh/t or more. In that case, the CO\textsubscript{2} emissions for the 80% DRI case drop from 1051 kg/t to 972 kg/t [29, 97, 106, 120, 130].

The composition of DRI can be modified to reduce the EAF energy consumption. A high degree of reduction or metallization in the DR process is desirable. A low degree of metallization means that more iron oxide has to be reduced in the EAF. The reduction by carbon is endothermic, resulting in higher electrical energy consumption and lower productivity in the EAF. On the other hand, a high metallization degree results in less CO generation and lower bath agitation in the EAF, which in turn reduces the heat transfer efficiency and accordingly increases the furnaces energy requirements. It is believed the optimal metallization of DRI lies between 94% and 96% [106].

Another approach is DRI carburization by methane injection in the reactor. About two-thirds of the carbon contained in DRI is present as iron carbide, Fe\textsubscript{3}C, and the balance is deposited as free carbon. The reactions involved in carburizing the DRI, for iron carbide production are:
\[ 3 \text{Fe} + \text{CH}_4 = \text{Fe}_3\text{C} + 2 \text{H}_2 \]  
\[ 3 \text{Fe} + \text{CO} + \text{H}_2 = \text{Fe} \text{ (free C)} + \text{H}_2\text{O} \]

The impact of DRI carbon on EAF operation is presented in Figure 27. As can be seen from the figure, the carbon injection is about 12 kg/t of Liquid Steel (LS) for DRI with 2.2% of carbon and only 0.5 kg/t of LS for DRI with 4.0% of carbon. For these operating conditions, the change from 2.2% to 4.0% carbon in cold DRI represents a decrease of 11 kg/t and 58 kWh/t of LS, respectively. This power saving is the result of the replacement of carbon by cementite [97, 106].

![Figure 27. Effect of DRI temperature and carbon content on the electricity consumption [97].](image)

It is apparent, compared to the EAF and DRI technologies, the BF/BOF route has two to four times higher consumption of energy, water and land, while emitting more GHG, priority pollutants and metals to the environment [109, 130].

Three options in regards to further optimization of steel production are presently available and considered by many researchers around the world [110, 133], i.e. (1) CCS embedded in current steel production technologies, (2) decarbonized steel production using hydrogen or electrolysis in the reduction process [83, 84], and (3) use of biomass as reduction agent [134, 135]. These processes have high potential to reduce emissions, but their implementation will require significant investments, which are not foreseen in the short-term.

**Carbon Capture and Storage (CCS)**

Energy efficiency improvements of current processes will not be sufficient to meet the current climate targets, but will require additional technology such as CCS. Sequestering or capturing the \( \text{CO}_2 \) is a reasonable short-term solution for many industries, so the steel industry can
probably rely on developments driven from others, e.g. in regards to CSS for coal fired power generation. However, the steel industry should also examine processes that could work with sequestering technologies. For example, sequestering CO₂ for steelmaking may be accomplished by injecting CO₂ into deep wells, which requires a relatively pure CO₂ stream. If the removed CO₂ is used for enhanced oil recovery, sequestered underground, or sold, stack CO₂ emissions per ton of DRI are reduced by 250 kg/t DRI which is ~50%. At a CO₂ cost of 45 € /t this represents 11.2 € /t DRI.

Use of enhanced oil recovery is an excellent approach. Many producers worldwide are now injecting CO₂ or steam in old oil fields, which can increase production two to three-folds. This should be a good possibility for direct reduction plants, since they are located in gas-rich areas, which often have oil in addition to natural gas [130].

New innovative techniques with lower climate impact will be vital for mitigating climate change. As a result, there are a number of activities in regards to CCS under way in the iron and steel industry worldwide. The ULCOS (Ultra Low CO₂ Steel-making) project, financed through the European Commission 2008-2017, was early identified as the most advanced. Three of the technologies investigated by ULCOS incorporate CCS to modify existing BF, DR and SR plants. ULCOS aims at reducing CO₂ emissions from steel production technologies by 50% compared to current best practice [136]. Japan has also a national program running from 2007-2018, i.e. the COURSE50 (CO₂ Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 50) project where new amine solvents are being developed for CO₂ capture in the BF. It is expected that the COURSE50 technologies will be commercialized by 2050 [43, 111, 137, 138].

It is estimated that at the present time, implementing CO₂ capture using commercial MonoEthanolAmine (MEA) solvent at a conventional iron and steel mill (BF/BOF) costs from 56€ to 176€/t of CO₂ avoided. At a direct reduction iron process, such as the MIDREX® process, the cost of CO₂ capture from the process off-gas is estimated at about 63€/t of CO₂ avoided. A cost of approximately 77€ to 99€ /t of CO₂ avoided is estimated for the EAF used in the steel production route for the MIDREX®- and mini-mill processes [43].
Chapter 7: Modelling of Iron Reduction

In the gas-based DR process, iron ore (hematite, Fe₂O₃) reacts with syngas, a mixture of H₂, CO, CO₂ and water vapour in a counter-current moving bed reactor. The overall performance of the reactor is affected by the interaction between the gaseous mixture and solid pellets in terms of heat and mass transfer. As a result, an investigation of the behaviour of a single pellet during the reduction process is a prerequisite for the understanding and modelling of DR systems.

Iron pellets are usually formed by compacting and sintering fine grain particles with or without the addition of a binder. The grains have normally an irregular shape, and vary both in size and porosity (20-30%). The pellets, however, are approximately spherical in shape with a radius of 5 - 8mm [30, 139], see Figure 28.

Figure 28. Optical picture of an iron ore pellet.

The reaction kinetics in the DR process can be determined by the rate at which iron oxide is converted into metallic iron by the removal of oxygen. A literature survey based on the reaction kinetics of the iron ore reduction made it clear that the reduction of hematite pellets with a multicomponent gas mixture is a very complicated matter. The main reason for this is that there are chains of reactions that happen simultaneously, i.e. hematite - magnetite - wüstite - iron.
Some of the rate-determining steps are associated with the nature of the reaction system and the contact between the reacting phases, and others are associated with the nature of the ore. The ore’s reduction process is determined by the particle size and size distribution, shape, porosity and pore size distribution, as well as the crystal structure and gangue content and distribution [140].

There are two main aspects in regards to reaction chemistry that need to be considered, i.e.:

- The thermodynamic of the system, which deals with the driving force for the reactions, and how it influences the rate of conversion throughout the reaction.
- The geometry and the available area for the reactions, as well as the mean distance that the gases need to travel by diffusion in order to reach the reaction interphase.

Isothermal conditions and Pseudo-steady state approximations are two simplifications adopted in many of the modelling studies reported in literature in regards to the reduction of iron ore pellets [141]. In spite of the fact that the reactions are both endothermic and exothermic, the iron ore pellets are about a centimetre in diameter. In other words, the isothermal assumption should not be far from the truth. By the Pseudo-steady state approximation, the accumulation term in the gaseous phase is neglected and the governing equations are relatively simplified. This approximation has been shown to be valid for isothermal gas–solid reactions [98, 142, 143].

**Gas-solid reaction modelling**

In kinetics, chemical reactions can be divided into three categories [144], i.e.:

The heterogeneous model: The porosity of the unreacted solid is negligible so that the solid is practically impervious to the gaseous reactants, or the intrinsic solid reactivity is so high that most of the reaction occurs in a zone near the external surface of the pellet. The unreacted shrinking core technique has been used frequently to analyse this type of reactions. This model is generally implemented in the modelling of non-porous solid reactants as a sharp interface model [139, 145, 146].

The homogeneous model: The solid contains enough pores for the gaseous agents to pass freely, which makes the gaseous reactants available all-over the pellet at nearly bulk concentration. The chemical reactions take place all-over the pellet in which solid reactants have been distributed homogeneously. This type of reaction model has been described in the literature for the highly porous solid phase [139].

The intermediate model: In the intermediate region where the resistance by chemical reaction and pore diffusion is of comparable magnitude, both processes must be considered simultaneously. Although the assumption of uniform grain size and regular shape are not accurate. The reaction rates between each grain and the gas reactants that diffuse into the solid may be described by one of the above-mentioned cases. The overall reaction rate depends on many parameters such as distribution of the grains of reactant in the solid, structure of solid,
intrinsic reaction velocities, and transport properties of gaseous species within the porous media. This type of model is called grain model [144, 146, 147].

Some of the studies reported in literature in regards to modelling the DR process have applied the grain model. Based on the results obtained, it is clear that the grain model introduces a higher degree of complexity and drastically increases the computation time at the cost of only small accuracy improvements [148, 149].

**Concepts and assumptions**

In the present work a kinetic model have been developed that describes how the gas diffusion proceeds in a porous iron oxide pellet in which a reduction reaction take place. The thermal behaviour of the porous media throughout the reduction step is also considered. The molar concentration of the species is used to treat both the gas-solid reaction systems simultaneously.

It is a well-known fact that gaseous reactants and products flow through connected pores along concentration gradients, as well as by gaseous diffusion, from the bulk flow at the external surface to the reaction site in the interior of the pellet. The reduction of the grains is reversible and precedes topochemically, see Figure 29 for a schematic configuration of this system.

Figure 29. A schematic configuration of a solid porous pellet in a gas stream [150].

**The gas-solid reaction may be divided into the following steps:**

1. Gaseous mass transfer of species from the bulk flow of the gas mixture to the external surface of the solid pellet.

2. Diffusion transport of the gaseous species through the solid matrix, which could consist of a solid reactant and solid products.

3. Heterogeneous chemical reactions at the phase interfaces.

4. Diffusion of the gaseous products through the pores of the pellet.
5. Gaseous mass transfer of the reaction products from the external surface of the pellet to the bulk flow of the gas mixture.

Each of these steps has its own kinetics that can limit the overall rate of the conversion of the pellets. It is believed that steps (2) and/or (3) are the rate controlling steps [151], so the diffusion and chemical reaction are the reduction kinetics controlling parameters.

In regards to the heat transfer the following phenomena must be taken in to account:

- Convection (and possibly radiation) heat transfer between the gas stream and the surface of the solid.
- Heat generation or consumption by progressing of reactions.

To be able to model the process, the following assumptions must be taken into consideration:

- Constant porosity of the pellet is maintained during the course of the reaction.
- The bulk flow concentration and temperature is assumed to remain constant.
- No variation occurs in the gaseous flow velocity outside the pellet.
- The pellet is spherical and during the reduction its diameter is not changed, and no cracks are formed.
- The chemical reaction is irreversible and of first order.
- The reduction of each pellet includes three steps, i.e. converting hematite to magnetite, magnetite to wüstite and wüstite to iron.

**Thermodynamic**

The simultaneous gas-solid reactions may generally be divided into three classes, namely independent, parallel and consecutive reactions [152].

\[
\begin{align*}
3 \text{Fe}_2\text{O}_3 + \text{H}_2 &= 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} & \Delta H^\circ_{298} &= -1.0 \text{kJ/mol}_{\text{Fe}} & (\text{VII}) \\
3 \text{Fe}_2\text{O}_3 + \text{CO} &= 2 \text{Fe}_3\text{O}_4 + \text{CO}_2 & \Delta H^\circ_{298} &= -7.8 \text{kJ/mol}_{\text{Fe}} & (\text{VIII}) \\
\text{Fe}_3\text{O}_4 + \text{H}_2 &= 3 \text{FeO} + \text{H}_2\text{O} & \Delta H^\circ_{298} &= 24.9 \text{kJ/mol}_{\text{Fe}} & (\text{IX}) \\
\text{Fe}_3\text{O}_4 + \text{CO} &= 3 \text{FeO} + \text{CO}_2 & \Delta H^\circ_{298} &= 11.2 \text{kJ/mol}_{\text{Fe}} & (\text{X}) \\
\text{FeO} + \text{H}_2 &= \text{Fe} + \text{H}_2\text{O} & \Delta H^\circ_{298} &= 25.4 \text{kJ/mol}_{\text{Fe}} & (\text{XI}) \\
\text{FeO} + \text{CO} &= \text{Fe} + \text{CO}_2 & \Delta H^\circ_{298} &= -15.7 \text{kJ/mol}_{\text{Fe}} & (\text{XII}) \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 & \Delta H^\circ_{298} &= -41.1 \text{kJ/mol} & (\text{XIII})
\end{align*}
\]

Reactions (XIII) is the water gas shift reaction that may take place simultaneously as the other reactions.
The overall reaction between the iron oxides and the reducing gases can be presented as:

\[
\text{FeO}_x + \text{H}_2(\text{CO}) = \text{FeO}_{x+1} + \text{H}_2\text{O} (\text{CO}_2)
\]

(XIV)

The driving force for reduction of iron oxide may be visualized as differences in partial pressure of the reducing gases (H₂, CO) and the produced gases (H₂O, CO₂), i.e.:

\[
\Delta G = \Delta G^o - RT \ln \frac{a_i a_{\text{FeO}_x}}{a_{i}^* a_{\text{FeO}_{x-1}}}
\]

\[i = \text{H}_2, \text{CO}\] (Eq. 1)

where \(\Delta G\) is the Gibbs free energy for reaction (XIV), and \(\Delta G^o\) the Gibbs free energy for reaction at equilibrium condition, \(a_i\) the activity of spices, \(R\) the universal gas constant. By considering the solid phases (iron, iron oxides) as a pure component and at the equilibrium condition this leads to:

\[
\Delta G^o = RT \ln \frac{P_i}{P_i^*}
\]

(Eq. 2)

where \(p_i\) is the partial pressure of product gas and \(p_i^*\) is the partial of the reducing gas.

**Rate equation for chemical reaction**

Most heterogeneous reactions occurring in metallurgical systems are considered as first order, however, this assumption is not always true [98, 146].

\[
R = a_s k_{r,i} C_i
\]

\[i = \text{H}_2, \text{CO}\] (Eq. 3)

\[
R = 4\pi r_j^2 k_{r,i} (1 + \frac{1}{k e_i})(C_i - \frac{c_i^*}{k e_i})
\]

(Eq. 4)

where \(a_s\) is the special reaction surface, \(k_{r,i}\) the chemical rate constant, \(C_i\) the concentration of i-th component, \(K_{e_i,i}\) the equilibrium constant of the reaction with i-th component at interface \(l\).

It was assumed that \(k_{r,i}\) is following the Arrhenius expression:

\[
k_{r,i} = k_{0,i} e^{-\frac{E_a}{RT}}
\]

(Eq. 5)

where \(R\) is the universal gas constant, \(E_a\), the activation energy and \(k_0\) frequency factor.

To eliminate the radius of the reaction interface within the grain (\(r_g\)), the following is considered:

\[
f = \frac{V_g - V_{c,g}}{V_g} = 1 - \left(\frac{r_j}{r_g}\right)^3
\]

(Eq. 6)
\[ R_{t,i} = 4\pi r_g^2 k_{r,i} (1 + \frac{1}{k_{e_l}}) (1 - f_i)^\frac{2}{3} (C_i - \frac{c_i^*}{k_{e_l}}) \]  
(Eq. 7)

\[-\rho_{FeO_x} \frac{\partial r_c}{\partial t} = k (C_i - \frac{c_i^*}{k_{e_l}}) \]  
(Eq. 8)

\[ \frac{\partial f_i}{\partial t} = \sum_{i=CO,H_2} \frac{3(1 - \varepsilon)}{r_g} R_i \]  
(Eq. 9)

where $\rho_o$ is density of the gases, and $f$ is the total local fractional reduction calculated based on the following relationship, which indicates the reducible oxygen content at each stage of the reduction:

\[ f = \alpha_h f_h + \alpha_m f_m + \alpha_w f_w \]  
(Eq. 10)

Where $\alpha$ is reducible oxygen at each step of reduction.

The overall fractional reduction of the pellet may be estimated as an integration of $f$ over the entire pellet as follows:

\[ F = \frac{3}{R_p^3} \int_0^{R_p} r^2 f dr \]  
(Eq. 11)

where $F$ is overall fractional conversion of solid reactant and $R_p$ pellet diameter.

Therefore, the continuity of gaseous species yields mass equation for gaseous reactant and product species as follows:

\[ \frac{\partial (\varepsilon C_i)}{\partial t} = \nabla (D_{eff,i} \nabla C_i) + \sum_l \nu \frac{3(1 - \varepsilon)}{r_g} R_i \]  
(Eq. 12)

where $\nu$ is the stoichiometric coefficient for species $i$ appearing in $l$-th reaction interface. For reactant species the stoichiometric coefficient has a positive value, $\nu > 0$, and for the products it has a negative value, $\nu < 0$.

**Effective diffusivity**

The diffusion of gaseous species through a porous solid depends on its structure, *i.e.* the void fraction, tortuosity factor, and pore size distribution. When the pore diameter is large compared to the mean free path of the gas molecules, the molecular diffusion is predominant and molecular binary diffusivity is estimated by the use of the Wilke-Lee equation [146] as function of temperature and gas properties:

\[ \frac{1}{D^m_i} = \frac{1}{1 - Y_i} \sum_{i \neq j} \frac{Y_j}{D_{ij}} \]  
(Eq. 13)

\[ D_{eff,i} = \frac{\epsilon}{\tau} D^m_i \]  
(Eq. 14)
Equally, in solids with fine pores the Knudsen diffusion mechanism prevails, but in pores with intermediate size a mixed type of diffusion may occur. In this situation, the effective intra particle diffusion of each gaseous species obtained by the following correlation:

\[
D_{\text{eff},i}^k = \frac{4K_0}{3} \left( \frac{8RT}{\pi M_j} \right)^{1/2}
\]

(Eq. 15)

where \(K_0\) is the effective Knudsen flow parameter with dimensions of length, and \(M_j\) molecular weight.

The so-called “dusty gas” model by Mason et al. [146] can be used to find \(K_0\):

\[
K_0^{-1} = \left( \frac{128}{9} \right) \left( \frac{\tau n_d}{\varepsilon} \right) r_g^2 \left( 1 + \frac{\pi}{8} \right)
\]

(Eq. 16)

where \(n_d\) is the number of spheres per unit volume of solid, and \(r_g\) the radius of the grains.

In pores with intermediate size a mixed type of diffusion may occur. In this situation the effective diffusion of each gaseous species is obtained by (Eq.17).

\[
\frac{1}{D_{\text{eff},i}} = \frac{1}{D_{\text{eff},i}^k} + \frac{1}{D_{\text{eff},i}^m}
\]

(Eq. 17)

where \(D_{\text{eff},i}^k\) is the effective Knudsen diffusion and \(D_{\text{eff},i}^m\) the effective molecular diffusion of the \(i\) species.
Chapter 8: Objectives of the Present Study

The worldwide iron production using the DR process, either through natural gas or coal-based technologies, has increased significantly during the last 30-40 years. Nevertheless, the DR process has still just 7% of the ironmaking market share, so there is potential for the DR technology to become even more appealing.

It is a well-known fact, that the DR reactors are extremely complicated systems as multiple reactions proceeding subsequently and/or in parallel, diversity exists in the mechanisms of the gas–solid reactions, and heat- and mass transfer occurs simultaneously. To obtain a better understanding of the reduction kinetic, a model has been developed that step-by-step describes the process from a single pellet (as small component a DR reactor) to a fixed bed with several pellets (~200 pellets) with and without consideration of the temperature gradient in the bed. The developed model is expected to be useful for the process analysis of the direct reduction shaft furnace.

The specific objectives were, see Figure 30:

- Experimental studies on single pellets with varying gas composition to investigate reaction kinetics under controlled conditions.
- Application of multiphysics simulation software (COMSOL) in order to generalize single pellets measurements to the multiple pellet bed situations.
- Bench scale experimental studies to provide data to compare with simulations.
- Investigate the critical and optimum operational conditions.
Figure 30. A schematic drawing of the overall flow and the focus of the work conducted in the present study.

**Paper III**
- Single pellet reduction.
- Reaction kinetics and mass transfer in a single pellet.

**Paper IV**
- Fixed bed reduction.
- Reaction kinetics and mass transfer in a single pellet.
- Mass transfer in the bed.

**Paper V**
- Fixed bed reduction.
- Reaction kinetics and mass transfer in a single pellet.
- Mass transfer and heat transfer in the bed.
Chapter 9: Summary of Appended Papers

_Paper III. Modelling and Simulation of Isothermal Reduction of a Single Hematite Pellet in Gas Mixtures of H₂ and CO_

An important factor for the ironmaking industry in regards to the DR process is the dynamic control of the process. The dynamic control and optimization of the process are key points to ensure smooth process operation and the production of high quality products. This will, however, not be possible without the development of a reliable, accurate, simple (if possible) and fast response model. The smallest unit in a DR shaft furnace is the single iron oxide pellet. Hence, the investigation of the behaviour of a single pellet during the reduction process is a prerequisite for understanding the different steps of the process, as well as for modelling of the DR shaft furnace. The present work consists of two parts, _i.e._ the development of a simple model, and the benchmarking/verification of the model with experimental results.

**Modelling**

A time dependent, one dimensional model have been developed to simulate the isothermal reduction of a hematite pellet by a gas mixture consisting of different compositions of CO and H₂ at 1173 K (the conventional DR process temperature). The developed model is based on the Shrinking Core Model (SCM) for gas-solid reactions.

In the model it is assumed that the pellets are axisymmetric in shape, and that the reduction progress in all directions are identical. The diffusion in the porous hematite pellet, as well as in the product layers is taken into consideration in the model. The kinetics of the reduction is discussed in detail in Chapter 7.

Finite Element Modelling (FEM) was used to solve the equations, employing the commercial COMSOL Multiphysics® software (Version 4.3b). For the modelling, some assumptions were made, _i.e._ (i) the pellet is isothermal spherical with uniform porosity, (ii) the reactions are
irreversible and of first order, (iii) the pellet diameter does not change during the reduction process, and (iv) no cracks are formed.

**Experimental work**

All experiments in the present study were performed in a lab-scale Thermo Gravimetric Analyser (TGA), see Figure 31 for a schematic drawing of the experimental set-up. The sample was commercial available KPRS pellets from LKAB, Sweden.

![Figure 31](image)

Figure 31. A schematic drawing of the crucible set-up in the TGA.

**Concluding results**

The experimental results have been used for validation of the model estimation. As can be seen in Figure 32, the reduction taking place with a gas ratio = 0.8 can initially be reproduced with good accuracy by the model, as well as the final overall reduction. Deviations do, however, exist in the middle region of the plot. The same trend was observed even for other gas compositions. It is believed, that this is the result of the irregular shape of the pellets, and the formation of cracks during the reduction process, see Figure 33.
Figure 32. Experimental results (exp.) and model predictions (mod.) for the reduction fraction versus time at $T = 1173$ K and $\frac{H_2}{CO} = 0.8$.

Figure 33. Iron oxide pellet a) before and b) after the reduction process.
In order to determine the impact of the scale-up on the overall rate of iron oxide reduction, the model described in Paper III was extended for modelling of an isothermal fixed bed.

**Modelling**

The model of the single pellet was used as a sub-model and coupled with a model of the fixed bed. It was assumed that the high gas flow rate adopted, as well as the alumina balls placed at the bottom of the retort ensured an even flow of gas radially across the bed. Hence, the velocity profile in the bed was assumed to be uniform, and thereby the radial concentration gradients (if any) could be neglected. The fixed model is based on following assumptions:

- Steady state operation.
- The gas stream in the reactor is plug flow.
- Both temperature and bed porosity are constant over the whole bed and during the duration of the process.
- The pressure inside the reactor is constant atmospheric pressure.

The bed model simulates the reduction rate by considering the composition gradient in the bulk gas. The equations were, even in this case, solved by FEM using the commercial COMSOL Multiphysics® software version 4.4. The developed model was used to study the effects of the gas composition on the reduction of the pellets.

**Experimental work**

The modelling result was validated against TGA experimental data. The same type of experiments that were performed on a single pellet was also carried out on a 0.5 kg fixed bed (~200 pellets). The TGA experiments were carried out at CK-lab, LKAB, Malmberget, Sweden, see Figure 34 for a schematic drawing of the experimental set-up.

During the experiments the pellets were located in a double wall retort, and the gas was preheated (1173 K), before it was put in contact with the pellet. A layer of alumina balls was placed under the iron oxide pellet to ensure the “bests” possible gas flow in the retort.

The experimental condition is summarized in Table 2.
Figure 34. A schematic drawing of the experimental set-up used for the fixed-bed experiments.

**Concluding results**

- The modelling-and experimental results for the four gas mixtures investigated, *i.e.* H$_2$/CO ratio of 0.8, 1.2, 1.6 and 2, were all in reasonably good agreement with an average error of 2.5%.

- The deviation between the modelling- and experimental results is believed to be due to the temperature gradient in the bed.

Table 2. The conditions used during the fixed bed experiments.

<table>
<thead>
<tr>
<th>Holding time (min)</th>
<th>Sample weight (g)</th>
<th>Gas flow (NI/min)</th>
<th>Pellets size (mm)</th>
<th>Oxygen content of the pellets (%)</th>
<th>Porosity of the pellet (%)</th>
<th>Bed depth (mm)</th>
<th>Gas composition (H$_2$/CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>500</td>
<td>50</td>
<td>10 - 12.5</td>
<td>29.1</td>
<td>27</td>
<td>60</td>
<td>0.8, 1.2, 1.6, 2</td>
</tr>
</tbody>
</table>
Although, the model described in Paper IV reproduces the experimental results fairly accurately, there was a desire to improve the model accuracy even further. It was, at the same time, desirable to keep the level of complexity low and the convergence time short.

As described in Paper IV, it was assumed that the temperature in the bed is constant during the process, i.e. over time. However, the different reduction reactions of iron oxide are either endothermic or mildly exothermic. In other words, the pellets can deviate in temperature either positively or negatively from the overall average bed temperature. The present study seeks to determine the overlapping range of the previous model and a model that even considers heat transfer, to identify the simplest and most accurate approach.

**Modelling**

The previous model consists of two sub-modules, i.e. a single pellet model, which considers the reaction kinetics and the mass transfer inside the pellet in the form of diffusion, and a fixed bed model, which considers mass transfer in the porous bed through convection and diffusion. In the present model another sub-model was added to consider even the heat transfer in the fixed bed. Since the gas flow velocity was high it was assumed that the gas temperature axially was constant and that the temperature gradient formed radially. The model results were compared to the experimental data obtained from a lab-scale reactor in the temperature range 1123-1273 K, as well as to the output from a simple model assuming isothermal conditions.

**Experimental work**

The experimental setup was the same as the set-up used to generate the results reported in Paper IV, but the experimental temperatures were different, i.e. 1123-1273.

**Concluding results**

- Experimentally it was seen that the pellets initially reduce quickly, i.e. 70% reduction achieved during the first 10 minutes. Since the reactions taking place are highly endothermic it caused the temperature to drop significantly (maximum 60 K).

- Although both models, i.e. the model developed in paper IV and the present model, predicted the variations observed in the experimental results, it was established that the more rigorous in regards to the heat transfer the model was the better representation of the behaviour actually taking place in the reducing bed was obtained. The present model lowered the average error analysis for the reduction at 1173 K from ±2.5% to ±1.1%.
Some discrepancies exist between the experimental- and modelling results (using the present model) in the case of reduction by pure H₂ or CO. This is believed to be due to limitations in the experimental set-up rather than fundamental issues in the model.
Chapter 10: Concluding remarks and Future Prospects

Section A

In the current work, the salt removal from BD by thermal treatment has been studied experimentally under different conditions in a stationary resistance furnace as well as a laboratory scale rotary furnace. The experiments were designed based on partial pressure calculations using the Thermo-Calc® software 4.4. The salt removal efficiency was evaluated and the optimum conditions established, i.e., temperature, gas flow rate, holding time, rotation rate, and sample size. In the case of thermal treatment of 200g samples in a rotary furnace, the optimum condition was recognized to be 14 h at 1523 K, representing a removal of 87% of the salt.

PBD was also investigated as a possible raw material for the production of a calcium aluminate flux to be used during steelmaking with promising results.

Future prospects in regards to the work performed are:

- It was established that for samples > 200g the contact between the carrier gas and the BD is the main parameter controlling the rate of salt removal. However, for samples > 200g the size of the presently used reaction chamber was not sufficient to obtain optimum condition for salt removal. As a result, it is of interest to investigate the effect that the size of the reaction chamber has on the overall salt removal.

- It was established that for fine particles a high gas flow rate will increase the particles which carried out of the reactor. As a result, it is of interest to investigate the effect of high flow rate on coarser particles.

- It is important to note, that all experiments were carried out on the same batch of BD. As a result, it is of interest to take samples from different compositions of BD, i.e. BD that have been produced from recycling different scrap materials, and conduct similar experiments as in the present work.

- PBD have in literature been reported to have good potential for application in the production of cement [19], as an abrasive material [70, 153], as a refractory material [18, 51, 63, 65], in
glass [154], and as a flux material [21, 71, 155]. Hence, utilization of PBD in these processes should continue to be studied. It should in this regard be noted that the thermal treatment process proposed could be modified for each process based on their requirements.

- It is of interest to perform desulfurization experiments to investigate the influence that the calcium aluminate flux produced by utilization of PBD has on the slag viscosity and refractory lifetime. The viscosity of molten slag is important since it has an impact on the kinetics of the refining reactions. It should in this regard be noted that the calcium aluminate flux in question contains considerable amounts of magnesium oxide, which is believed to partially saturate the slag and reduce the refractory corrosion.

- It is of interest to vary the ratio of PBD/CaO in regards to optimising the composition in view of using it as an addition during cement production. Preliminary experiments were carried out as part of the present project with promising results.

- It is of interest to perform industrial scale trials in a rotary tiltable furnace (common in the recycling industry).

- The overall economics of the proposed approach needs to be studied and compared to that of water leaching. It should in this regard be noted that the economics of the process could be improved if hot BD is treated directly after skimming.

Section B

The principal objective of the present work was to develop a simple, yet improved model, consistent with experimental measurements, for the reduction of iron oxide pellets in the DR process. The model was intended for future use in the modelling of a moving-bed reactor for the production of DRI. To achieve the final goal, the following three steps were implemented:

1. A time dependent computerized model that fairly accurately simulates the isothermal reduction of a single hematite pellet, with the use of a gas mixture of CO and H₂, has been developed. Small-scale laboratory experiments were also performed under well-controlled conditions. The experiments were designed to get an understanding for the weight loss of the pellets as a function of time, and the results obtained were incorporated into the model. The results obtained shows, for some parts of the reduction process, clear deviations from the experimental results, which is believed to be due to the existing variations in the shape and size of the pellets, the porosity distribution in the pellets, and the pelletizing history.

2. Fixed bed reduction experiments were conducted at 1173 K over a range of H₂/CO ratios from 0.8 to 2.0, and subsequently modelled numerically. The model consists of two 1D, isothermal and time dependent models. The gas-solid reactions were kinetically modelled using the model developed under Step 1 and a model on mass transfer in a fixed bed. The temperature of the bed was assumed to be constant during the reduction process. The simulation results proved to agree with the experimental results with an average discrepancy of ±2.5%.

3. The reduction reaction of iron oxide is either endothermic or mildly exothermic, and proceeds rapidly. Constant temperature conditions can therefore not be assured in the whole
bed. The dynamic variation of temperature, which influences the degree of conversion, made it therefore necessary to add another 1D model for a radial temperature gradient in the bed. The gas-solid reactions were modelled using the models developed under Step 1 and Step 2, and a model describing the radial temperature gradient in the bed. The obtained non-isothermal model permits a more accurate representation of the experimental data than the isothermal estimates, with a typical discrepancy of only ±1.3%. The discrepancy is thought to be due to limitations in the experimental set-up rather than fundamental issues in the model.

Future prospects in regards to the work performed are:

- It is of interest to perform the experiments with better temperature control and compare those results with the final model.
- It is of interest to further develop the non-isothermal model to account for the bulk flow of pellets. This modification is expected to improve the model in such a way that it becomes a useful tool for the process analysis and optimization of industrial moving bed DR furnaces.
Chapter 11: Acknowledgment

First and foremost, I would like to express my deepest gratitude and appreciation to Prof. Ragnhild E. Aune, Dept. of Material Science and Engineering (DMSE), Norwegian University of Science and Technology (NTNU), Trondheim, Norway, for her constant encouragement and professional guidance throughout the project, and for supporting me in other aspects of life. She is more than a good supervisor to me.

It is a pleasure to thank my other supervisor’s Associate Prof. Emma Strömberg, Dept. of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden, and Dr. John Moosberg-Bustnes, Norut, Narvik, Norway, for his highly qualified help, discussions and guidance during this work. I would also like to thank Dr. Shahid Akhtar, Hydro Aluminium, Karmøy, Norway, Dr. Mark W. Kennedy, DMSE-NTNU, and Dr. Ross Wakelin, Norut for all their valuable help and many enthusiastic discussions.

I wish to thank the DMSE-NTNU for the use of the rotary furnace and Disvadri (TGA setup), as well as Harold Holm and Dr. Eli Ringdalen for helping with construction of the experimental apparatuses.

The supply of Black Dross from Stena Aluminium AB, Älmhult, Sweden, and KPRS pellets from LKAB, Kiruna, Sweden, is gratefully acknowledged. I like to thank the CK-lab, LKAB, Malmberget, Sweden, for the use of their TGA furnace.

I am also grateful to Norut Narvik, BP Norge, Nordland fylkeskommune (Provincial Government), and the Norwegian Research Council through project number 195153, as well as LKAB and Jernkontoret in Sweden for their financial support.

Thanks to my friends and colleagues at DMSE at KTH and at NTNU, as well as Norut for many shared happy moments.

I am deeply grateful to my parents and my wife, Mona, for their never-ending love and support.

Stockholm, 2016-11-15

Reza Beheshti
Chapter 12:
References


