Zinc vapourisation from sludge wastes under thermal processing conditions

Zinc enrichment in HIsarna flue dust

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Abstract

HIsarna is a new furnace technology in the steel industry, featuring a large reduction of CO_2-emissions of up to 80%, and offering larger tolerances for gangue materials. Additionally, it has potential for zinc enrichment in the flue dust, as it can quickly vapourise zinc in the feed material and reject it to the flue dust. Increasing the zinc fraction in the flue dust up to 50% would allow for zinc recovery in the zinc smelters.

The larger tolerances of the furnace make it possible to include material streams currently mostly land filled. In this thesis, the focus has been on three of these waste streams, goethite, Blast Furnace (BF) dust, and Basic Oxygen Furnace (BOF) dust. The research focussed on acquiring fundamental knowledge on the behaviour of these waste dusts at high temperatures and various retention times. This will aid their future use as a alternative feed stream material for enriching the HIsarna flue dust with zinc, without compromising the longevity of the furnace or the quality of the steel.

In a literature study, several alternative materials were investigated. Of particular interest are the sludge wastes from the steel industry for their large iron and zinc contents, the sludge waste from the zinc smelters for the same reason, and galvanised steel scrap, possibly in combination with EAF dust. There are a few challenges to overcome, such as the copper concentration in the zinc smelter residues, or the variation in composition and quality of steel scrap. However, these materials were identified as high potential for inclusion in HIsarna.

It was found that zinc can effectively be reduced and vapourised from the waste dusts regardless of its mineral form, in case there is carbon. The carbon acts as a reductant for the iron oxides, including zinc ferrite, and for zinc oxide. Goethite does not contain any carbon, however, mixing with BF sludge will allow the vapourisation of zinc. A model is proposed for estimation of the amount of carbon, and by extension BF dust,that is needed to achieve a full reduction of the iron oxides with native carbon sources. This will aid future mixing of these waste streams, allowing more control over the composition of the feed stream.

A competing mechanism to direct reduction of zinc oxide was identified. Zinc oxide can react with S_2 gas which forms during the thermal shock treatment, forming a zinc sulfide fine particle. At high temperatures, this intermediate species decomposes over time to release the zinc vapour, however, the exact mechanism could not be deduced from the experiments.

The mechanism and timescale was verified at various temperatures, and holds up until 1300 °C. The timescale shortens significantly when increasing the temperature. Therefore, from the work conducted, it was concluded that the zinc can be effectively removed at a relevant timescale for HIsarna and collected in the flue dust.

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

1-1 Motivation for the Study

In steelmaking, there are two dominating routes to produce molten steel. The Electric Arc Furnace (EAF) is the main processor of recycled steel, whereas the Blast Furnace (BF) - Basic Oxygen Furnace (BOF) route mainly deals with iron ore. A flowsheet is presented in Figure 1-1 [1]. In the latter route, the BF functions to create a stream of hot metal of consistent quality and composition. This stream is fed to the BOF, where the molten steel is produced.

Within the BF - BOF route, the first step takes place outside the furnace. Before the iron ore is fed to the top of the BF, it is sintered and/ or pelletised, to agglomerate the iron. The iron sinter and the coke/ coal containing feed streams are alternated to create a layered structure within the furnace. Lime and limestone are fed as fluxing agents. Several products are created, of which the hot metal liquid iron layer at the bottom of the furnace is the most important. On top of the hot metal lies the slag layer, which acts as a sponge to collect the gangue elements.

In addition to the solid feed, a gas feed is added to the furnace. This allows for gas bubbles of reducing CO to be formed, which rise upwards in the furnace and travel through the other layers. Small particles and elements are carried with it, allowing for excretion of gangue elements from the iron sinter. Most of the chemistry takes place at the interface between the slag layer, the CO bubbles, and the interface between the hot metal and the slag layer. By controlling the feed, this chemistry can be influenced, allowing for a large degree of control over the final hot metal product.

The disadvantage of this technique is the waste streams it creates. Many valuable elements are lost within the slag layer and the off-gas stream, including iron, and without cleaning or recovery implemented, these present both an economic threat and an environmental hazard. The current steelmaking technology has been in-use for decades, and the technology is mature. Regardless, the quantity of steel produced world wide is immense, and the impact of

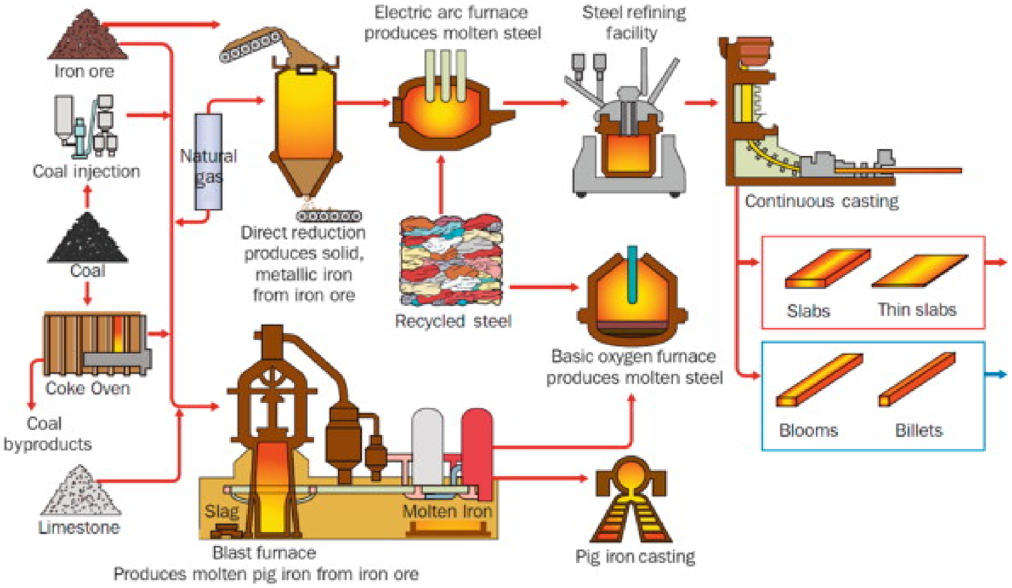


Figure 1-1: flowsheet illustration of iron and steel making. Reproduced from [1]

the waste streams and the lack of treatment, show the necessity for solutions. The current steelmaking technology is mature, and has been in-use for decades. Couple this to the sheer quantity of steel produced world wide, the impact of these waste streams, and the lack of treatment, and it paints the necessity for solutions. At the moment, most of these waste streams are being land filled, leading to loss of valuable resources and economic loss. Another popular option is to include it in the making of cement, or use it as road fill. Nevertheless, in light of the sustainability debate and the push for a circular economy, none of these options can be regarded as truly future-proof.

Firstly, these sources contain quite a few elements of value. Some of these elements are present in significant but fluctuating concentrations, including zinc, lead, cadmium, and iron. Other elements are present in lower concentrations, but present a large economic value or are scarce, such as the rare earth elements. Despite the ongoing research in reclaiming these elements, the economics of these processes are unfavourable, and even today these streams are discarded. Treatments are scarce, and storage needs to meet strict qualifications, in order to prevent heavy metal leakage to the environment.

To that end, many innovations are proposed to deal with these waste streams. In order to unlock the potential of these hidden resources for society and clean up the environmental hazards, much research effort has been spent. Solutions proposed often generate new waste streams, and are costly, hence why these are not widely implemented in industry despite being described in literature. In other industries, it is already common to use the waste stream of another, for example the inclusion of a copper-bearing waste stream from the zinc smelters. Whatever the solution looks like however, it is clear that some innovative new process is needed for the steel industry waste products.

One of those proposed innovations is HIsarna, a new furnace in the steel industry. First tests have indicated that its tolerance limits for gangue elements are significantly higher than for the traditional blast furnace. Although HIsarna is not necessarily developed with recovery of resources in mind, the ability to treat waste streams warrants further research. In this specific case, being able to handle higher zinc concentrations, it is plausible that the zinc can be concentrated in the flue dust. Potentially, these concentrations can reach levels of purity that allow further treatment in a zinc smelter. Additionally, iron can be recovered directly in HIsarna, and perhaps lime and silica can be utilised in the slag. This opens new ways of treating waste streams. More details on the furnace and its tolerances will be given in Chapters 2 and 3.

1-2 Research aims and objectives

In order to best achieve the separation of the zinc to the process dust, more fundamental knowledge of its behaviour under thermal treatment is needed. As part of the Reclamet project, a joint cooperation between Nyrstar, Tata Steel, and TU Delft, the enrichment of the HIsarna process dust with zinc is further investigated, while producing steel. The focus of this specific writing is to look into the direct (self-)reduction and vapourisation of zinc and the (self-)reduction of iron from three separate waste dusts from the steel and zinc industry. More fundamental knowledge on the materials behaviour under thermal treatment is needed, and therefore the research question is formulated as follows:

Will the zinc present in an industrial waste dust be reduced and vapourised under thermal treatment, and be removed effectively, efficiently, and selectively?

To further substantiate the claims resulting from the research into the main research question, the following subquestions will be investigated as well:

1. What is the effect on the thermal reduction behaviour of zinc being present in different zinc-bearing compounds?
2. What mechanism is followed during zinc reduction and vapourisation, and at what timescale?
3. Mixing several secondary materials, can the reduction and vapourisation behaviour be enhanced?
4. What behaviour is observed from the other elements present, with particular focus on iron?

These questions together should lead to a solid foundation for further research. It can help determine which zinc sources are more efficient to input, whether mixing adds to selectivity or efficiency, and what intermediates the zinc goes through. The end-goal is to use the dusts as a feed material in HIsarna for enrichment of the zinc, and for that this fundamental basis will aid further research.

Within the research, the focus will primarily be on the three waste dusts Goethite provided by Nyrstar, and BF dust and BOF dust provided by TaTa Steel. This will help create the further understanding needed to implement waste dust recycling into HIsarna.

1-3 Thesis outline

The thesis will start with detailing the background of the project, including a description of zinc within the steel industry and the HIsarna furnace. Additionally, a short literature study of the behaviour of EAF dust when recycled to the EAF will be conducted, as it resembles similarities to the goal of the HIsarna dust recycling. A larger literature study will futher investigate which resources are available, or hold promise, for recycling into HIsarna.

Before diving into the experiments, some consideration will be given to the sustainability challenges today's society faces. It is important for any researcher to ocassionally take a step back and evaluate what the impact of their work would be. As such, an essay will be included after the literature study, however, it will be written as a stand-alone chapter that, while relevant to the thesis work, can be read disconnected from the thesis.

The research aims will be further expanded upon, and more in-depth descriptions given for the subquestions. An experimental method will be developed for analysing the dusts, which will then be implemented. The dusts will be subjected to thermal shock and high temperatures for different retention times, both individually and mixed, and the results will be given and discussed in detail. This will lead to answers to the posed research questions, and can be used to drawn conclusions. Further recommendations will be provided, and the results will be placed within the larger Reclamet project.

Chapter 2

Project Background

HIsarna is developed mostly for environmental reasons, for example for carbon dioxide emission reduction compared to the Blast Furnace (BF). A side-effect of HIsarna is its potential for recovery of resources, including zinc. However, fundamental knowledge on the furnace is still being investigated. At the same time, understanding of the thermal behaviour of zinc-rich alternative resources is still lacking.

Within this chapter, the challenges surrounding zinc in steelmaking will be explored, as will the role of HIsarna in sustainable steelmaking. As an addendum to this chapter, it is described how currently Electric Arc Furnace (EAF) dust is recycled within the EAF, as it resembles similarities to the recycling of dust to the HIsarna. Together, this should provide the theoretical background needed for the research.

2-1 Status Overview: Zinc

Zinc metal holds significant importance. In 2014, it was listed as fourth on the list of metals most traded by weight, only surpassed by iron, aluminum, and copper [4]. While zinc metal is not often used directly, there are many industrial applications where it is applied in alloys and as coatings. Most notably, 51% is used to galvanise steel, 34% is used in zinc alloys, and 10% is used in electrical appliances [5].

As for all metals, the European Commission has performed a criticality assessment, and while zinc is not rated as critical, its economic importance is high [5]. The supply risk is low, as zinc is found and mined abundantly nearly everywhere. It is mined as a sulphide ore mostly, and its ores often contain a wide array of other elements that require to be removed. Especially zinc and lead are closely connected in mining, and other rarer metals found within the zinc ores include gallium and indium, key technology enablers. These elements are valuable, and need to be recovered.

Despite the large global reserves, estimated at 1.9 billion tonnes in 2017, it is vital to create a circular loop [5]. In light of the sustainable development goals, it is essential to recover and recycle zinc metal, substituting primary production with secondary recovery. Additionally, a spear point for the European Union is to secure its own supply pathways. Since it currently supplies only 7.5% of its demands, secondary source mining of zinc can help reach this directive [4].

Current recycling rates of zinc lie at around 31%, leaving a lot of room for improvement [5].the relatively high recycling rate is mostly thanks due to the high collection rate from industrial and machinery applications, and most of the recycled zinc is from brass alloys and the automotive industry [5, 6]. Improvement can be found in the treatment of the waste streams from the steel production and galvanisation processes. These wastes often have a significant zinc content, but are often land filled due to the difficulty of treatment [6]. Hence, more research is needed to find viable recovery pathways.

2-1-1 Presence in Steelmaking practice

Zinc enters the steelmaking cycle via the feed material, and is mostly present as ZnO, $ZnFe_2O_4$, and ZnS. Its present in small quantities within the iron ore, and it is present in galvanised steel scrap. Additionally, internal recycling via waste dusts reintroduces it into the process [7]. After entering the furnace, the zinc is quickly reduced to its metal form by carbon monoxide or hydrogen [7]. Due to its relatively low boiling point of 907 °C, and the high temperature of the furnace, the zinc quickly volatilises and igets carried to the cooler top part by the gas stream. There, the zinc gas reacts again with water vapour or carbon dioxide, creating a solid ZnO particle. This particle will then float down, where it is reduced and volatilised, effectively creating a continuous circle.

Regardless of being ever-present within the steel industry, the zinc poses a significant instability to the process, and poses a danger to the quality of the steel product [8]. High concentrations of zinc within the furnace cause refractory deterioration, as the small ZnO particles that form can adhere to the lining. The particles have a higher thermal expansion coefficient, causing severe damage. Heavy and dense crusts of ZnO on the lining can mismanage the heat balance in the furnace by causing local cooler zones. This drives up the coke requirements and the CO_2-emissions, and imbalances the thermodynamics of the system. Additionally, the large crusts can fall down into the slag/ hot metal, adding extra zinc dissolute to the hot metal product.

Zinc leaves the furnace in several ways, however, the largest part of the zinc is carried out by the off-gas stream. There it can be cleaned and collected. The off-gas system of a BF is scrubbed, creating two main fractions. The dry dust, the flue dust, is responsible for 15-25% of the zinc loss, while the wet dust, sludge, holds about 45-70% of the zinc that leaves the furnace. These two waste streams are therefore interesting to evaluate for recovery of the zinc.

2-2 HIsarna process

The HIsarna reactor vessel is a merger of 2 technologies, the Cyclone Converter Furnace (CCF), and the HIsmelt Smelt Reduction Vessel (SRV), to create a new iron smelter. HIsarna is an emerging technology still, with a demo plant in India. HIsarna opens up several possible resource feeds as well as promising significant CO_2-emission reductions, energy savings and recycling options [9]. The process details will be explained below, separated between the CCF and SRV.

HIsarna offers both environmental benefits and economical benefits by removing the need for ore agglomeration and coal coking. Due to its lower requirements on quality of feed material, it is likely that lower grade iron ore with higher phosphorus and titanium concentrations can be used, significantly cutting the cost of raw feed material, as well as using thermal coals instead of metallurgical grade coals. Additionally, due to no longer needing 2 pre-processing steps and the higher efficiency of the HIsarna reactor, 20% CO_2-emission reduction and primary energy savings can be achieved.

CCF

Traditionally the CCF consists of two parts, a hearth at the bottom and a cyclone at the top. In HIsarna, only the cyclone part will be implemented. Finer iron particles and oxygen will be injected in the CCF directly, causing a pre-reduction of the iron ore with the rising CO gas from the lower parts of the furnace. Coupled with the high heat of the cyclone, the iron particles are subsequently melted, and will trickle down to the iron bath [10, 11].

An advantage the CCF offers is an early separation of gangue metal elements. Iron will not volatilise in the CCF, however metallic zinc and lead will. The volatilised metals will be rejected to the flue dust in this stage, preventing their entrance in the iron bath where they can cause contamination. This easier and earlier separation entails a higher tolerance for these elements in the feed material compared to the traditional furnaces. Potentially, this technique can be used for enrichment of the flue dust with zinc, however, that is still under investigation.

The primary idea of the CCF is to couple the pre-reduction and melting stage for iron ore, removing the need for coke making and ore agglomeration in pre-processing [12]. This will lower the energy demand of the process, making it more efficient, and thereby reducing CO_2-emissions. Additionally, the iron droplets trickling down provide heat to the iron bath, coupling the heat requirements of the CCF and the iron bath. A lower degree of post-combustion in the iron bath of up to 25% is then sufficient, which can be achieved with the cheaper high-volatile coals. Gasses entering the cyclone have a lower combustion degree, allowing high post-combustion rates up to 90%. Due to the higher efficiencies and the relatively low investment costs of the CCF, the total production costs will be lower than is the case now [13].

SRV

In essence, the HISmelt SRV is a modern smelt reduction vessel. It consists of a refractory lined hearth containing the molten iron bath and a water-cooled top space [14, 15]. Iron ore fines, coal and hot air fluxes are injected directly into the melt, causing rapid heating and a reduction effect. HISmelt offers several unique features over other SRVs, and coupled to the CCF, they can be used fully.

By directly injecting the coal and oxygen deep into the melt, a strong buoyancy driven upward plume is formed, which causes rapid turnover of liquid [14]. These large splashing effects allows for metal and slag to cycle through the upper parts of the vessel as droplets. Using the combustion heat from the fuel gases, heat can be effectively carried by the droplets from the upper region to the lower region of the reactor [11]. As such, the temperature gradient within the reactor can be limited to roughly 10 degrees Celsius, without compromising the oxygen gradient in the reactor. Feeding coal directly into the melt allows for more active dissolved carbon, which would be achieved to a lesser extend when using top-fed coal [14].

Better mixing leads to higher rejection rates of contaminants, such as phosporus, sulphur and titanium [11, 14]. This allows for sources of iron ore that are not feasible with the conventional BF technologies, such as titano-magnetite. Additionally, combining the SRV with the CCF into the HIsarna potentially opens the reactor for alternative iron ore sources, such as slags and waste dusts from the conventional steel industry [11, 14]. Although it is as of yet uncertain to what extend these claims hold, this opens a whole new paradigm of iron resources which are currently being disposed off.

2-2-1 The promises of HIsarna

For a new steel smelter technology like HIsarna to succeed, it has to compete with mature, in-place technology optimised for cost-effectiveness and efficiency. External driving forces are needed to promote these innovations, and an important driver for the steel industry are the targets set for cutting down CO_2-emissions. Within the Ultra Low CO_2 Steelmaking (ULCOS) project, significant research funds have been spent on HIsarna. It promises large CO_2-emission reductions, and promises other sustainable advantages for the future steel making process.

A large drawback of the current BF is its intolerance for gangue elements, for example zinc and copper. Offering higher tolerances, HIsarna can effectively use new feed stream materials of lower quality without compromising the product. Since these lower grade feed materials are cheaper, upon maturity, the HIsarna could proof an effective way to secure a both a constant stream of material and a reduction in cost.

The higher material tolerances allow for the use of waste streams currently land filled. Unlocking these resources can proof vital in securing raw materials for the future, and can aid the European Union in securing its own supply pathways. Coupled to the other advantages above, upon maturity, it is likely that HIsarna can in time replace the current technologies.

2-2-2 Waste dust treatment in HIsarna

An interesting prospect opened up by HIsarna is the use of lower grade materials and the recycling of zinc-rich waste dust fractions. Especially the latter will introduce large quantities of gangue elements into the furnace, and require appropriate handling in order to guarantee a high quality hot metal stream.

The CCF holds a much higher temperature than the conventional BFs, and here the dust will be fed into the furnace. Due to the strongly reducing atmosphere in the top part, consisting mostly of carbon monoxide gas, the zinc oxides and sulphides will efficiently be reduced and expelled to the off-gas system for further cleaning. A similar route is likely for other volatile metals, including lead.

The idea behind this quick separation of the zinc from these waste streams is two-fold. First, it prohibits entering the SRV, with the detrimental effects that includes. This prohibition will elongate the life of the refractory lining and ensure high quality hot metal. Second, an efficient separation allows for enriching the flue dusts. When the zinc can be concentrated into a sludge of over 50 wt%, the waste dust can be recycled back to the zinc smelters [16]. Early trials with a pilot HIsarna furnace by Tata Steel show that the enhancement of the flue dust with zinc is possible, furthering the push for a circular metal economy. More research is required however.

2-3 EAF as a means of dust recycling

Being able to handle nearly all sorts of scrap in order to produce all types of steel, the EAF has become a popular steelmaking furnace [17]. A common load, especially in developed countries, can consist of 100% scrap metal, and as such most of the ferrous scrap worldwide is recycled and refined to special steels using the EAF. In addition to the recycling of steel scrap, the EAF can to some extend recover internal wastes as well as some social wastes, including tires and plastics.

The possibility to recover industrial waste materials is particularly interesting, as there are often only limited options of recovery. Recovery of the valuable metals is an important goal within the industry. A possible load of HIsarna could reintroduce a dust waste stream into the furnace, which is already being done in the EAF. Hence, some further data on how this dust behaves in the EAF is presented.

2-3-1 EAF Operation Principle

The EAF functions based on electrical power as well as chemical energy [17]. A basket with scrap is pre-heated and loaded into an Ultra High Power (UHP) furnace. The furnace itself is an U-shaped, refractory lined vessel, with oxygen burners mounted on its sides and carbon graphite electrodes mounted to the lid. Using the electrodes as the cathodes and the scrap as the anode, an electrical arc is formed that generates enough heat to melt the scrap down.

By introducing oxygen, carbonaceous material, and natural gas, heat is generated by redox reactions, improving on the heat profile of the furnace.

The refining step after melting involves several mechanisms to create a consistent, high quality hot metal stream low on impurities. Foaming the slag, it acts as a sponge for impurities, provides thermal insulation, reduces refractory wear, and improves arc stability [17]. The refining step consists of dephosphorisation, decarburisation, and temperature adjustment, as other refinements are better applied within the laddle furnace following the EAF. For steel grades having strict limits on metallic impurities, the scrap needs to be selected carefully, since the use of high-in-scrap charges introduce more impurities than using virgin materials.

2-3-2 EAF Dust Characterisation

Typically, during the smelting operation in the EAF, 1-2% of the charge is rejected to the gas outlet as dust, later collected in the baghouse [18]. This rejection is mainly due to the volatilisation of metals such as zinc, lead, and cadmium, with a high vapour pressure at steelmaking temperatures, due to the well-understood phenomenon of CO bubble bursting causing metal droplet ejection, iron vapourisation directly under the electric arc, and entrainment of solid particles [19].

The composition of the EAF dust varies with the type of steel produced, the nature of the scrap added, the alloying components, and the method of expulsion of gangue elements from the hot metal [2]. As a result, the composition can change not only from day-to-day and from heat-to-heat, but also during the progress of a particular steelmaking cycle. Typical composition ranges of EAF dust are given in Table 2-1. The dust particles are relatively small, often under 10 micrometre. They are poly-mineralic, exhibiting a variety of internal crystalline configurations [19].

2-3-3 Behaviour of EAF dust in the EAF

EAF dust is fed into the EAF in the form of briquettes as an addition to the steel scrap feed. Several different forms of briquettes are in use, however oftentimes both a reducing agent and an agglutinant agent are added to aid the thermal reduction [20]. With a higher zinc fraction in the feed, an enriched process dust is created. In the EAF, this does not lead to an increase of zinc in the hot metal. Since this would deteriorate the quality of the iron metal, this is vital within both EAF and in HIsarna.

The briquettes are carbothermically reduced, forming elemental iron and zinc species [20]. The iron remains in the iron bath, while the zinc evaporates out. Owing to the low volatilisation temperature of zinc and the high vapour pressure, this is a smooth and efficient process.

Silicon plays an important role in slag formation and iron reduction, acting as a reducing agent for iron oxides at rates faster than carbon can achieve [21]. The resulting SiO_2 is reduced by carbon, forming carbon monoxide, allowing silicon metal to reduce iron oxide again.

Table 2-1: Average compositions of the EAF dust, produced from Nyirenda, 1991 [2]

Element	Carbon Steel Dusts Range [wt%]	Stainless Steel Dusts Range [wt%]
Fe (Total)	24.9 - 46.9	22.2 - 35.9
Zn	11.12 - 26.9	1.77 - 6.22
Pb	1.09 - 3.81	0.23 - 0.78
Cd	0.03 - 0.15	0.006 - 1.79
Cr	0.06 - 0.58	2.01 - 10.1
Ni	0.01 - 0.12	0.15 - 3.34
Mo	0.02 - 0.08	0.37 - 1.46
Mn	2.46 - 4.60	2.36 - 4.59
Mg	0.77 - 2.93	1.70 - 4.74
Cu	0.06 - 2.32	0.09 - 1.26
Ca	1.85 - 10.0	1.76 - 6.93
Si	1.35 - 2.49	1.36 - 4.83
Cl	0.51 - 2.36	0.47 - 1.17
F	0.01 - 0.88	1.36 - 4.83
K	0.06 - 1.12	0.80 - 5.07
Na	0.29 - 2.31	0.47 - 4.60

This reaction lasts roughly until the silicon is mostly in the slag layer, and not in the liquid metal. It aids in the enrichment of the process dust as well [21].

Other elements present in the dust play a role as well, an example being sodium. Sodium promotes electron transfer, catalysing the Bedouard reaction, $2\,C + 2\,CO_2 \longrightarrow 4\,CO$, thereby allowing for better reduction and higher zinc recovery rates [18]. Not for all elements it is known how they help with the process of hot metal formation and purification, however, many of these elements are present within the EAF dust. Using the EAF dust as a source for these will reduce the need for virgin material [18].

In another study, the direct addition of EAF dust as powder into liquid carbon-saturated iron was investigated [22]. The zinc initially dissolves into the melt, and it takes a short time before the zinc starts evaporating. Additional carbon, in the form of solid carbon, does not speed up or change the dissolution of zinc, as carbon diffusion to the bubbles is not rate-limiting. Higher carbon in the gas stream reduced the amount of zinc that reported to the flue dust, most likely due to the more violent boiling and ejection of more iron fume. The reported zinc recovery rates are, however, similar to that of other reports.

Summarising, the possibility of EAF dust recycling into the EAF furnace is well established, even if not all kinetics are understood. Using the recovery of zinc metal as an extra driving force next to the iron recovery provides enough economic incentive to make it attractive [23]. The process itself is rather simple, leading to good recycling rates. This makes it attractive to investigate for HIsarna, and could lead to an effective recycling of the high zinc flue dusts.

Chapter 3

Alternative Feed Materials: a Literature Study

An important innovation target for the coming decades is to figure out a way to lower the environmental impact of society, and in conjunction with that, the production industry. Within smelting and refining, targets are set or will be set for recovery of materials, lower waste generation, and lower emissions. The creation of circular metal cycles will prove inevitable for reaching the sustainable development goals, and it will require adequate recovery of valuable compounds currently in waste streams that are being disposed off.

The HIsarna reactor holds the promise of allowing the treatment of several waste dusts such as the iron sludges, due to its higher natural tolerances than the conventional iron smelters [11]. As such, the feed mix can contain more gangue elements, unlocking the usage of a myriad of lower quality sources. Not only will this provide a high quality hot metal stream, it has been shown that the furnace can be used as a method for producing a flue dust enriched in zinc. This enriched flue dust can be send to the zinc smelters, for further processing.

What is needed, however, is an inventory of waste streams that can be incorporated into the feed mix for HIsarna. These alternative streams need to meet several criteria, and each can bring its own challenges. To investigate these streams, within the literature study the following research question and subquestions were defined:

Which alternative sources exist that can be mixed into the HIsarna feed mix in order to improve the zinc enrichment of HIsarna flue dust and create a high quality hot metal iron product?

1. What restrictions are imposed by the HIsarna furnace?
2. What determines the attractivity of an alternative feed material?

Together, these questions should provide an adequate answer to the research target of this chapter. The chapter will start with a description of the boundary conditions placed on the alternative streams, in terms of composition, physical appearance, and availability. This will lay the framework for the detailed analysis of the various identified streams. The chapter will end with a summary of the findings and how these can play a role in later HIsarna development cycles.

3-1 Boundary Conditions

An important criterium to determine the attractivity of an alternative feed material lies within the restrictions the HIsarna furnace will impose. Aside from the technical details of a stream, there are several more common sense factors that shed some light on alternative feed material attractiveness. First and foremost, HIsarna is a steel smelter, so the quality of the hot metal cannot be endangered by an alternative feed mix. Secondly, there must be a purpose for the added material, as for example a feed with low iron concentrate is economical neither environmental.

The availability of an alternative feed material is important, as in order to become part of the steel industry flowchart it must meet the high volume demands. The steel industry deals with large production volumes, and marginal cost considerations prefer a continuous flow of new feed material of consistent composition. As such, the generation of the material must be high, and be available at a cheap rate. Especially for many waste streams, decades of research has been spent to come up with less harmful solutions than land filling, and alternative routes indicate competitors and a reduced availability. So, in order for an alternative material to be considered, it must be widely available.

Economic considerations play an important role in assessing whether a new feed material is attractive or not, as the steel industry operates with large quantities and in a competitive environment. A small improvement in the marginal cost can mean millions of profits, while an increase in marginal cost can undermine the position of a steel mill on the global steel market. As such, alternative streams must be cheap, and offer reasonable advantages over conventional methods if they are to be considered.

Despite the importance, economic feasibility will not be a part of this study. In large part, this is due to the low maturity level of the market for industrial waste streams. It is unclear how prices will fluctuate with time, nor can it easily be predicted what incentives will be given by policy makers for incorporating waste streams. Added to the current development stage of HIsarna, which is still in pilot and testing phase, it is currently considered too early to give definite assessment on the economics.

3-1-1 Restrictions imposed by HIsarna

The technical restrictions revolve around the main target of a steel smelter, to deliver a high quality, consistent stream of hot metal iron that can be processed further into steel. Any material stream that endangers this process will not be added, nor will a material that will shorten the life span of the furnace significantly. It is therefore imperative to investigate which elements are detrimental to the process, the furnace, or the economics of the process. As indicated earlier, HIsarna shows higher tolerances for many deleterious elements, however, due to being in pilot phase, there is no exhaustive and precise list of elements or compounds that violate these conditions.

From the HIsarna process description within the Project Background, it can be argued that several of elements are far less detrimental than they would be in the Blast Furnace (BF) or Basic Oxygen Furnace (BOF). With the additional Cyclone Converter Furnace (CCF), higher concentrations of zinc, lead, and other more volatile metals at the furnace temperatures can be more effectively dealt with, and can therefore be tolerated in higher quantities [9]. The HIsmelt Smelt Reduction Vessel (SRV) is more efficient in rejecting gangue elements, such as phosphorus, sulphur, and titanium to the slag [24]. The exact percentages are not specified in literature, so only a general assessment can be made.

Nonetheless, there are several elements and compounds that should not be added in large quantities. An example would be copper, which is detrimental to the quality of the steel, or alkali metals, which lead to higher corrosion levels and lower the melt temperature. These will be treated as they are encountered within the alternative feed material.

An additional requirement lies in the thermodynamic, chemical, and heat balance of the furnace. A material that is not necessarily detrimental, but adds no value, can still imbalance the system. Before a material can be added, careful quantification is required. To illustrate, a material containing large quantities of silica and lime will change the slag composition if not accounted for, which could deterioriate the quality of the steel.

Generally speaking, efficiency dictates that even if an element does nothing of the above and gets rejected effectively to the waste streams, it is still unviable to add. It needs to be heated, maybe goes through pre-treatment, all of which cost energy and generate more waste, and by extension, costs money. Thus, a material with large quantities of unreactive compounds will not be viable to add to the furnace either.

3-1-2 Restrictions imposed by zinc smelters

Similarly to the considerations surrounding adding new and alternative feed materials to HIsarna, the zinc smelters need to consider their main aim of creating a high quality, consistent product stream. As such, many elements or compounds are detrimental, a non-exhaustive list is provided in Table 3-1. Additionally, within the most common process of Roasting-Leaching-Electrowinning (RLE) there is an electrolytic step at the end of the process, where build-up of metals is a real concern.

When studying the process in more detail, the main gangue elements can be categorised into roughly 4 sections. First off, most metals are purified out, and are of little concern, copper being a prime example. Notable exception is lead, as a concentration of over 4% will

Table 3-1: Deleterious elements affecting the zinc process and their removal procedures (if applicable). Adaptation from Porter, 1991 [3]

Element	Effect	Removal Stage
Na, K, Mg, Mn	salts increasing required cell voltage	-
Fe	reduction in current efficiency	leaching, neutralisation
Pb [25]	contaminate zinc product	roasting, neutralisation
Cu, Cd	contaminate the zinc product	separately purified
Co	prevent electrolysis	purification
As, Sb, Ge	prevent electrolysis	neutralisation
Ni	causes holes in cathodically deposited zinc	purification
halides, Cl, F	corroding the electrolytes [26]	-

cause agglomeration in the fluidised bed roasting. Additionally, halides and to a lesser extent alkali metals, are to be avoided as much as possible, as these hinder the electrolysis and are costly to remove. A last pollutant category are the organic materials that will hinder the fluidised bed roasting. However, these are not expected to be present in the flue dust after the HIsarna smelter where they will be incinerated.

3-1-3 Identified alternative feed materials

The main goal is to identify materials that on one hand can help with the enrichment of HIsarna flue dust with zinc, and on the other are non-detrimental to the steel industry. Looking at the anthropogenic zinc cycle, it becomes apparent that while there are many interesting streams, only very few are accessible [6, 27]. In many fields, zinc is used in conditions where it is lost to the environment, such as coatings or as fertiliser. In other fields, die castings being a prime example, the collection rates are very low, meaning that the availability for addition to the raw materials mix for HIsarna is too low [28]. However, a promising source emerging from analysing the zinc cycles, are rubber tires, and have previously been shown to be promising within the steel industry as a raw material [29].

Two large streams which are of interest, are the galvanised steel scrap, and industrial waste streams similarly to those the steel industry itself creates. The former is often recycled within the Electric Arc Furnace (EAF), and to a lesser extent the BOF, and obviously presents a large source of iron and zinc. The value of the latter is more diffuse, as the composition of industrial waste streams is often variable. More detailed assessment is given to the waste streams from the steel industry, the zinc industry, and to the copper and lead industry, both of which contain iron and zinc in larger quantities. A common theme within all industrial waste streams is the large variation, as the composition is dependent on various factors. It is beyond the scope of the literature study to describe all of these, however, as a result, the composition of the sources will be given in a range. The actual composition does not only differ from furnace to furnace, it can differ from day to day or even from hour to hour. This will only be mentioned later on when relevant to the assessment.

3-2 Steel industry waste streams

Direct recycling of the waste streams from the steel industry holds many advantages. The alternative feed is produced in-house, so no need to buy material, and no transportation costs and emissions. Any part of the waste stream that is recycled does not need to be disposed off, and the loss of valuable material can be reduced. Significant parts of the steel wastes are already recycled, although finding accurate and up-to-date recycling rates is hard. A good example of a stream that is largely being recycled internally is EAF dust.

As described in the 1, there are two main routes, each of which produce their own waste streams. The waste stream from the EAF has been described in the Project Background, and will only briefly be considered in this literature study. The BF-BOF route has its own set of wastes, with similar generation mechanisms. These wastes and their generation will be considered in more detail. Lastly there is the ladle furnace, however the only stream available in large enough quantity is the slag waste.

3-2-1 slag wastes

Slags play an important role in the rejection of gangue elements from the hot metal, acting as a sponge to absorb all these elements. The layer forms on top of the hot metal layer, and can be tapped from there. In the steel smelters, it is often created to control the composition of the hot metal product, and for that purpose limestone and silica is added. In Table 3-2, the general compositions of the various furnaces are shown.

Compared to high grade iron ore, the slag waste contains low amounts of iron. Additionally, the slag wastes contain large amounts of silica and lime, and low to no zinc. As such, the usefulness of these sources for zinc enrichment of HIsarna flue dust is insignificant.

Slag waste disposal is nonetheless harmful to the environment, due to heavy metal leaching and the basicity [30]. As such, alternative uses have been developed where the slag waste can be implemented somewhat safely. Its small particle sizes, the general morphology of the steel slag material, and its relatively low cost compared to alternatives make it a compelling choice for roadfilling, cements, and mortars [30, 31]. This does mean, however, that the valuable metals within the slag are not recovered.

Another alternative is the implementation of slag waste streams as a replacer of lime and silica within the furnaces, an example of which is the use of BOF slag into the BF [32]. This presents its own challenges, as build-up of phosporus, manganese, and aluminium is a real concern. Currently about 30% of the BOF slag within the EU is reycled this way [32].

3-2-2 off-gas wastes

Within the steel smelters, part of the material volatilises, including the zinc. These volatile elements leave through the off-gas system, where the gas is collected. The treatment there is

Table 3-2: the compositions of various steel slags. Ranges are an average of literature sources and can be much larger in reality.

Compound	BF [31, 32]	BOF [32, 33]	EAF [33]	ladle [33]
Fe_2O_3, FeO	1-10%	10-25%	10-40%	0.5-5%
SiO_2	15-40%	10-15%	15-18%	10-20%
CaO	38%	45-50%	25-40%	40-60%
Al_2O_3	7-9%	1-3%	6-9%	5-25%
MgO	12%	1-8%	3-6%	7-12%
MnO	0-15%	0.5-4%	3-6%	0-2%
P_2O_5	1-1.5%	1-4%	0-1.2%	0-0.4%
SO_3	0.5%	0.1-0.3%	0.1-0.6%	0.1-1%
TiO_2	-	0.5-1%	0.6-0.8%	0.3-0.9%

dependent on the furnace type, and will result in various fractions which will be highlighted. The waste streams considered and their composition are shown in Table 3-3.

In the BF, two fractions are created. The off-gas stream is separated in a zinc-poor and a zinc-rich faction. Water-cooling and scrubbing the off-gas yields a dry zinc-poor fraction as a very fine dust, and a zinc-rich fraction as a coarser, wet sludge. A common practice for the poor zinc fraction is to recycle it in the sinter plant, adding it to the feed mix for the BF [32, 34]. Both fractions would be viable to recycle into HIsarna.

The composition of the dust allows for recycling the iron fraction well, as there is a lack of gangue elements that would be damaging to the steel process or the furnace. The silica and lime contents are relatively high, and so is the carbon. When accounted for properly, none of these will cause a problem. The silica and lime will reinforce the slag formation, whereas the carbon will be a source of fuel. The morphology nor the mineralogy will provide issues for the HIsarna. The iron is mostly present in the form of crystal structures, magnetite, haematite, wustite. Small amounts can be found in other crystal structures such as calcine and silica [34]. For better feeding, the fine dusts will be made into microgranulates.

The main issue with this zinc poor fraction is in the distinct lack of zinc. So while this dust is definitely good to implement within HIsarna, it will not support the enhancement of the zinc concentration is the flue dust.

The wet sludge fraction presents a different set of challenges than the dry dust, generally containing more heavy metals. Not all of these are listed due to their low concentrations, however, their presence means that the storage needs to prevent leakage to the environment. Additionally, there is a distinct lack of recycling options in practice, resulting in large landfills [32]. Investigations for alternate solutions are being proposed, as well as recovery options, however none of these are en-masse implemented.

For the sludge, HIsarna might present a viable alternative. The iron and zinc content are generally high, and the contaminants are in low concentrations, often around a few 100 ppm.

Table 3-3: The average composition of various steel wastes from the off-gas system. Ranges are an average of literature sources and can be much larger in reality.

Compound	**BF dust**		**BOF dust**	**EAF dust**
	dry dust [32, 34]	sludge [35, 36]	[37, 38]	[2, 21]
Fe	30-50%	30-40%	55-70%	15-45%
C	25-35%	15-30%	1%	1%
SiO_2	2-9%	2-5%	0.5-1%	1.5-2.5%
CaO	2-8%	1-5%	4-7%	2-10%
MgO	1%	0.5-2%	0.5-2.5%	0.5-3%
Al_2O_3	2.5-5%	0.5-2%	-	0-1%
Zn	<0.05%	1-8%	0.5-6%	10-25%
Pb	<0.04%	0.05-2%	0.03-0.2%	1-4 %
K	<1%	0.1-1%	<0.05%	0.5-2%
Na	0.5-1%	<0.5%	<0.01%	0.5-5%
Cu	-	<0.1%	0.1%	0.05-2%
Cl	-	-	-	<1%
F	-	-	-	0.5-1%

Composition wise, challenges are presented by the alkali metals, which hinder the normal operation of the BF. A second cumbersome contaminant is presented within the copper, for which the tolerance is around a 100 ppm. Lead will follow a similar behaviour as the zinc, and never reach the hot metal, so the high lead concentration can only be harmful when it is concentrated to a level that is too high for the zinc smelters.

The morphology and mineralogy require some attention. Being a wet sludge, it needs to be sintered and granulated. The main constituents are iron oxides, silica, calcine and quartz, as well as ferrite. The behaviour of ferrite within the HIsarna is currently still under investigation, but the others should not present a challenge.

Considering recycling into HIsarna, the BOF sludge is very similar to the BF sludge. Appreciable amounts of lime, zinc, and a large content of iron make it an attractive source. Generally, there are contaminants in the form of alkali metals, heavy metals, and some carbon. The morphology and mineralogy is similar. As stated before, the main issue is that the sludge is wet, and thus an extensive drying procedure is needed. This might diminish the economic viability of a sludge waste in HIsarna. It can be concluded that both sludge wastes are of interest for further investigation and implementation within the HIsarna furnace.

EAF dust presents another valuable source, and its composition is listed in Table 3-3. As has been described in the Project Background, the EAF dust is to roughly 50% recycled back into the EAF, however, after some cycling this dust reaches a zinc level that prohibits another cycle [21]. At this point, HIsarna would be a worthy alternative for recovery of the resources within this enhanced EAF dust.

Moreso than in other waste streams, the composition of the EAF dust is highly variable, as it is dependent on what kind of steel scrap is loaded. Some general comments can be made however, being rich in iron and zinc. These are most often in oxide form, and thus easily reduced within the HIsarna, with the exception of zinc ferrite. The worrying components are similar to the sludge waste, containing alkali metals, and significant lead. Additionally, it contains a larger amount of copper, and the presence of halides. Halides can cause build-up in the electrolyte in the zinc purification at zinc smelters, and when present in flue dusts, require to be cleaned out. This presents a large cost factor, diminishing the attractiveness of the HIsarna flue dust. Nonetheless, EAF dust into HIsarna warrants further consideration.

3-3 Steel and galvanised steel scrap

Steel scrap, and galvanised steel scrap especially so, can provide an interesting source of both iron and zinc recovery in HIsarna. The picture painted is quite complicated, as there are many different sources and types of steel that need to be considered, not to mention the impurities that can be dragged along. The exact concentration of zinc depends on the coating thickness, and is generally between 2-4% [39]. In the EAF, as described in the Project Background, the flue dust is enhanced with zinc due to the usage of galvanised steel scrap, and a similar enhancement can be expected in HIsarna.

The composition of the steel is vital in determining whether it can be used. Exact data is hard to come by, especially on the alloying elements [40]. This further complicates matters, however, especially for in-house scrap where the composition is known in detail this is not expected to cause trouble for HIsarna. When the alloying elements are precisely known, it can be predicted what will end up in the hot metal and what will be rejected to the slag or flue dust. Using this information, the type of steel produced in the furnace can be adjusted so that the alloying elements remaining in the hot metal can again be used as alloying elements. After all, an alloying element that ends up in the hot metal while undesired will only deteriorate the quality of the hot metal.

An additional challenge is presented when the composition is not known, such as for EOL scrap. The precision with which separation is performed is insufficient to separate into types of steel, creating a mixture of steel scrap with varying contents of alloying elements [40]. This presents two consequences. Firstly, the alloying elements can contaminate the hot metal quality, and secondly, the alloying elements that do get rejected to the slag are often lost entirely. Neither is desirable, and diminishes the value of HIsarna recovery. While setting up better separation routes would help in creating a more circular metal economy, this is for many types of steel difficult and by extension costly.

Looking at the impurities more closely, the EOL scrap can carry concentrations far above the tolerable limit for the conventional furnaces. Some, zinc, lead, and cadmium, are unlikely to present a challenge to HIsarna. Plastics or oils can be harmful, depending on their nature. Alloying elements such as nickel, chromium, and molybdenum will mostly stay within the hot metal, and are only useful when desired in the type of steel to be produced [41]. Copper can range up to a percent in these types of scrap as well, and would cause an issue with dilution loss. Dilution loss is a loss presented when a secondary stream of raw material needs to be diluted with higher purity virgin material [42].

In conclusion, steel scrap can provide a good addition to the HIsarna when the composition is known. Especially in-house scrap generated during production will present a good source. Scrap from outside the steel mill is likely to be contaminated and of unknown origin due to mixing, and as such will provide challenges for metal recovery. Adequate sorting would be required, but this is costly, if even technological feasible in all cases.

3-4 Zinc industry waste streams

Another obvious candidate for the zinc enrichment of HIsarna flue dust is the implementation of the iron-rich waste faction from the zinc smelters. Iron interferes with the electrowinning of zinc, and is leached out as a result. The remaining product stream has both considerable iron and zinc concentrations, and is thus worth an assessment.

The presence of iron causes roughly two problems, the earlier mentioned adverse effects on the electrorefining in a later stage of the zinc refining, and the formation of zinc ferrite during roasting. Zinc ferrite ($ZnFe_2O_4$), or franklinite, does not decompose easily in the used process, leading to loss of valuable zinc metal. As a side note, this explains why often the steel waste dusts rich in zinc are of less value to the zinc smelters, as the main form of zinc in these dusts is zinc ferrite.

The leaching of iron from the roasted zinc concentrate happens in multiple steps, in order to recover as much zinc as possible. An overview will be given as an adaptation from [43]. In most zinc removal processes, an inevitable step is the leaching of ZnO from the solution, converting it into $ZnSO_4$. A second so-called neutral leach solution is created, in which zinc ferrite is dissolved, and as such is prime for further processing to recover the zinc. To deal with the ferrite, the remaining zinc is brought into solution using an excess of H_2SO_4. Iron dissolves into the leachate as well, requiring another leaching step to further recover the zinc. The next step can be one of many routes, however the most common routes are the jarosite and the goethite route, both named after the main form of residue produced. These two waste streams will be investigated in more detail. A third route that is less common is the haematite route. Since this is less widely implemented, it is not considered further due to lower availability. The average concentrations of the jarosite and the goethite are detailed in Table 3-4.

3-4-1 Jarosite

In the jarosite process, detailed in Equation (3-1a), $Fe_3{}^+$ is brought into solution, in which the $NH_4{}^+$ ion is used to form the jarosite. The $NH_4{}^+$ ion can be changed into a variety of species, most notably K^+, H_3O^+, Ag^+, Na^+, $NH_4{}^+$, and $0.5\,PB_2{}^+$ [49]. Jarosite is stable in acidic conditions, and thus allows for high zinc recovery rates of up to 99%. An alternative

Table 3-4: The average composition of jarosite and goethite. Ranges are an average of literature sources and can be much larger in reality.

Compound	jarosite [44, 45, 46]	goethite [46, 47, 48]
Fe	25-50%	50-70%
Zn	8-13%	13-17%
Pb	2-4%	6-8%
Si	4-8%	2-4%
Ca	4-8%	0.1-1%
Al	0.5-7%	0.5-1%
Mg	0.5-2%	-
S	12%	<10%
Na, K	0.5-1%	<0.1%
Cu	<0.1%	0.5-0.6%

process is available in which the jarosite is precipitated in the same step as the ferrite is leached. This is detailed in Equation (3-1b).

$$3\,Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12\,H_2O + 6\,ZnO \longrightarrow 2\,NH_4[Fe_3(SO_4)_2(OH_6)] + 6\,ZnSO_4 \tag{3-1a}$$

$$3\,ZnFe_2O_4 + 6\,H_2SO_4 + (NH_4)_2SO_4 + 12\,H_2O \longrightarrow 2\,NH_4[Fe_3(SO_4)_2(OH_6)] + 3\,ZnSO_4 \tag{3-1b}$$

Owing to its high iron and zinc content, jarosite is an interesting waste for recycling within HIsarna. The main mineral structure is a jarosite matrix, and the waste consists mostly of clay and silt like particles. The high moisture content and acidity of the jarosite will require a washing step and drying step. [44]. As such, preparing the jarosite waste for addition into HIsarna requires pre-treatment, similar to any industrial waste sludge.

Jarosite is one of the most used routes within the zinc smelters, and is widely available for further treatment. Owning to its heavy metal content, it is highly toxic and leaching to the environment poses a real problem when land filled. The range of contaminants is much wider than described in the table, as it can be precipitated with a large variety of metals as the X^+ metal, for example nickel, cobalt, zinc, and cadmium. Additionally, it is a suitable medium for metal ions of germanium, indium and other valuable metals [49]. Combined, this leads to a waste stream that is disposed off, rather than used [43].

Considering the composition of jarosite for HIsarna, there is potential. There is significant zinc and iron, while many of the other elements present in large quantities are unlikely to cause much harm, including lead, silica, and lime. A concern would be the circulation of valuable (REE-) elements, and their respective build-up. However, the concentrations are low, and with adequate monitoring of their concentrations, real problems should not be expected. The sulphur content is somewhat high, as is the copper content. Copper remains problematic, and could mean dilution losses.

3-4-2 Goethite

In the goethite process, goethite is precipitated using iron in the ferrous form [43]. Ferrous iron is formed by reducing ferrite using the concentrate, after which goethite is precipitated using oxygen and calcine. The two reactions are shown in order in Equations (3-2a) and (3-2b). An important factor within the precipitation of goethite is the concentration of iron within the concentrate added to neutralise the reaction, as a higher concentration of iron will reduce the zinc recovery.

$$\mathrm{ZnO \cdot Fe_2O_3 + 4\,H_2SO_4 + ZnS \longrightarrow 2\,FeSO_4 + 2\,ZnSO_4 + S + 4\,H_2O} \tag{3-2a}$$

$$\mathrm{6\,FeSO_4 + 1.5\,O_2 + 3\,H_2O + 6\,ZnO \longrightarrow 6\,FeOOH + 6\,ZnSO_4} \tag{3-2b}$$

The goethite process is not as widely implemented as the jarosite route, mostly due to its higher cost compared to the simpler jarosite process. Goethite waste is a red mud sludge like material, with high humidity of 44-47%, similar to the jarosite waste [47]. Its main phases are goethite FeOOH, maghemite γ-Fe_2O_3, magnetite Fe_3O_4, and sulphates of iron and zinc. The goethite waste mainly consists of small particles, 80% smaller than 23 µm [47].

Goethite is less toxic than jarosite, and its treatment is therefore better explored in literature. Additionally, there has been more research into a use of the goethite rather than resource recovery. In that case, goethite waste is first treated using inertisation and solidification, or smelting and slag fuming, in order to retrieve an inert product [50]. This material is then used in the contruction industry or as a component of a raw material mix used for glass and ceramics [47, 48]. Actual recovery routes are scarce however, and thus valuable resources are lost. Further treatment in a recovery scheme such as HIsarna would therefore be preferred.

Regardless of being less toxic, goethite bears many similarities to jarosite in terms of composition. High levels of iron and zinc make the material attractive, while there is an abundance of sulphur. Silica and lime levels are lower, and a similar range of heavy metal elements can be found in low concentrations. Problematic is the copper content, which could pose serious harm to the quality of the hot metal.

Concluding, both jarosite and goethite present a promising alternative for use in HIsarna. Featuring good availability and high iron and zinc contents makes the material attractive. Pre-treatment is most likely needed in order to be able to feed the wet sludge wastes, potentially hampering the economic attractivity, and the presence of large quantities of sulphur and significant copper presents a technical challenge. Considering the larger picture, it warrants further research for using jarosite as well as goethite in the HIsarna furnace.

3-5 Alternative industrial waste streams

A few other waste streams are worth considering, as they generally contain significant iron and zinc content in their streams. Two alternatives worth discussing are the copper and lead smelters, both of which generate a slag waste that could hold potential value.

3-5-1 Copper refinery waste

Copper ores tend to contain 0.5-2% of copper, out of which the copper minerals are extracted by crushing and grinding the ore into smaller particles [51]. Using froth flotation, a 30 % Cu concentrate is created, which is then smelted. The matte smelting primarily oxidises Fe and S out of the Cu-Fe-S mineral, and produces a Cu-rich sulfide matte and an iron rich slag. The Cu-enriched matte is moved to a Pierce-Smith converter, which in two steps produces liquid copper. First, the remaining iron is oxidised and rejected to the slag, and when iron concentration falls to 1%, the coppermaking process starts. The liquid copper is further purified using electrochemical refining. Over recent years, an increase of hydrometallurgical processing of the copper sulfide ores has been reported.

Within the process, slag is produced that still contains 4 - 8% copper, and as such is first internally processed [52]. Only when the concentration of copper is reduced to 0.7-2%, is the slag discarded. Here the main issue with using the slag into HIsarna comes to light, as this amount of copper is too high and would be heavily diluted before use in the smelter. Despite holding considerable iron and zinc content, as well as silica and lime allowing the copper slag waste to function as a slag replacement, without additional leaching steps to remove all the copper it is unlikely this material will be considered [53].

Within the literature, ongoing research has proposed several routes that could leach the copper to a level where the remaining slag could be used in HIsarna. As an example, Yang and colleagues [54] proposed a leaching with sulfuric acid and sodium chlorate oxidant, Bese [55] proposed an acid dissolution including ultrasound, and Altundogan and colleagues [56] a ferric sulphate roasting method. As time progressed, within literature it can be observed that the recovery of copper goes up, while the recovery of iron goes down. While this is potentially good for the attractiveness within HIsarna, all of these routes also recover a large percentage of the zinc, thereby lowering the potential of copper slag as a method for zinc enrichment in HIsarna flue dust. As such, even with a, often costly, method in place to bring the copper down to acceptable levels for HIsarna, it is unlikely the copper slag will be used.

Another waste material produced is the copper flue dust. Owing to its high copper concentrations, these flue dusts are internally processed [52]. Despite these post-treatments, the copper concentration generally does not fall enough to make the flue dust attractive for HIsarna, for similar reasons as the slag.

However, assuming a technological solution for removing the copper selectively and economically, both the flue dust and the slag waste holds significant potential. The flue dust is somewhat low in iron, however holds considerable zinc [52]. As a result, these dusts seem more suitable for direct recycling to the zinc smelters rather than to HIsarna. Neither the slag waste nor the flue dust contain gangue elements in higher concentrations than the earlier discussed waste streams that were considered to warrant further investigation. However, without a proper method for selective copper removal, these waste streams are not attractive.

3-5-2 Lead refinery waste

Lead and zinc are ofter found in the same ores, and as such the lead waste streams might hold an attractive alternative source for zinc enrichment of the HIsarna flue dust. After mining, using floatation, a lead concentrate is produced, which is to be further processed using air roasting to turn PbS into PbO, then added to a BF to turn the concentrate into metallic lead [57, 58]. The lead is further refined using electrorefining or pyrorefining techniques, depending on the requested lead quality.

The waste stream of interest is the lead slag waste, produced in the BF. There is a variety of other wastes, most notably sulphur dioxide gas and the waste streams from the refining stage, however all of these are being treated on-site or moved to specialised recovery sites [57]. Being a slag material, it suffers from the same drawbacks as the other slag wastes described, both in its physical appearance as in its high concentration of silica and limestone, at 25-35% and 17-22% respectively. As with in any sulphide ore process, iron is added to reduce the sulphide [57], resulting in the formation of an iron-silica glass like matrix, and an iron concentration between 25-35% is common. The zinc content is relatively high, varying between 8 and 11%.

The iron content is somewhat low for an iron smelter, whereas the silica and lime are high. This can be overcome by using the slag waste as a lime replacement with added iron and zinc content, lowering the pure lime requirements of HIsarna. The lead concentration is somewhat more concerning, as this could easily result in lead build-up in the flue dust, causing rejection by the zinc smelters.

Considering the above, it becomes clear that there is some potential in this source, however it is complex. Incorporating a slag waste is more difficult than a dust waste, as it requires adequate monitoring of the slag composition. High lead content could hamper the attractiveness of the HIsarna flue dust for the zinc smelters, and the low iron content diminishes the economic interest. However, it warrants a more detailed analysis on whether it can be used as a slag replacement so the valuable zinc and iron can be recovered.

3-5-3 Rubber tires

In the analysis of alternative zinc sources to be used within the HIsarna, rubber tires might prove attractive. Rubber tires are often discarded, and the landfills present an excellent breeding ground for mosquitos, rodents and other pests, and if caught on fire emit toxic emissions [59, 60]. Due to the sheer production size of tires for cars and trucks, a solution to these issues is to be found, and in literature several uses within a variety of civil engineering applications have been proposed [60]. However, zinc leaching to the environment remains problematic .

The composition of rubber can vary, however it does so within set boundaries [59, 61, 62]. Generally, rubber tires contain 45% rubber and synthetic polymers, mostly isoprene, butadiene and styrene-butadiene. Filler material is added, mostly carbon black and heavy aromatic oils, including stearic acid. A variety of antioxidants, anti-ozonants and other organic compounds are used, as well as textiles. As such, a large part of a rubber tire consists of carbon-rich material. The remainder of the rubber tire is made of sulphur and zinc-oxide, with concentrations varying around 1 and 2-3% respectively. Lastly, tires contain about 12% steel belts in case of passenger car tires and 21% steel in case of truck tires [61].

The high carbon content makes it an interesting material to use as fuel, and indeed rubber tires have occasionally been used as such [29, 59]. Rubber granulates derived from the rubber tires have been used in a steel facility in Austria, in combination with waste plastics, as a replacement of coking coal, a practice that has been employed in more steelworks around the world [29, 63, 64]. Here, it was also shown that the organic material poses no threat to the quality of the hot metal, either being volatised producing reducing syngas or rejected to the slag.

As such, rubber tires might make an interesting source for the HIsarna process. The high carbon content allows it to be a coal replacement, the steel belts provide an potential source of steel, and, albeit the zinc concentration is somewhat low, it can serve as a source for enrichment of the flue dust with zinc. There are no other contaminants, although further investigation of the slag behaviour and the formation of syngas by the polymer material is required to provide a definite answer as to whether this is viable. Its attractiveness is diminished by the ease with which the steel strips can be recovered. Additionally, it is possible to leach the zinc, however this is not common practice due to the associated cost [60].

It is imperative to have good control over the heat gradient within the furnace, as well as over the reducing environment. Adding an unknown amount of carbon would prove to have an adverse effect on the hot metal quality as a result. As such, a pre-processing step to incinerate the carbon compounds, might be required. Further investigation is needed before rubber tires can offer a functionality as a carbon source replacement for coal.

It is, necessary to make a few notes on the usability. Coal within the HIsarna is added not to the cyclone converter, but rather directly to the melt. While this is optimal for the conversion of the rubber constituents to syngas, this might result in higher zinc contamination of the iron melt. This might prove problematic for zinc and sulphur contamination of the hot metal. As a last remark, it is not uncommon for tires to use an halogenated butadiene, which would lead to higher halide contamination of both the slag, the flue dust and potentially the iron melt. Higher halide concentrations are unfavourable in HIsarna, and lead to build-up within the flue dust, which could potentially lead to rejection by the zinc industry.

In conclusion, while an attractive alternative for coal adding a small amount of zinc oxide and potential steel, more information would be needed on the behaviour of the slag and slag rejection of metals and halides as well as detailed information on the formation of syngas out of polymer-containing waste materials.

Chapter 4

Metallurgy, Society, and Sustainability: A Vital but Strained Relationship

Introduction

Without any doubt, it can be stated that negating the impact of society on Earth's ecosystem is a much-focused on topic, in industry as well as in academia. Indeed, rightly so, as the effects of the uncontrolled economic growth, and the inevitably coupled environmental footprint, can be observed all around us. Social awareness is rising, and pressure on policy makers, and by extension the other stakeholders, is rising with it. Quick action is called for, seeing the alarming rate at which resources are being depleted, biodiversity is falling, and Earth's average temperature is rising.

Nonetheless, the complexity of the challenges being faced as a result is enormous, and careful consideration is required. To determine where the boundary must be placed to protect society from a depleted planet and still allow technological advancement is a complicated affair. As such, it is important to sometimes take a step back from one's core-activities, and reflect on the consequences. Impacts not only from the smaller, direct topic at hand, but also from a larger perspective, to look at the industry or even the field as a whole. That is the purpose of this chapter, to reflect on the research and, more broadly, on the metallurgy field as a whole, and relate that to the needs of society and its environment.

In order to get a fair assessment, one that does not directly go into deep technical or economical details, this chapter will have an essay-like structure. It will start with some generalities on sustainability and the circular economy, continue with the challenges of metallurgy in relation to the circular economy and the demands from society. Then the focus will be narrowed down even more, to reflect on HIsarna and its potential and relevance within the larger debate, only to zoom out again to sketch a future society with an incorporated, hopefully green, materials production field.

The Push for Sustainability

As a target for 2030, the United Nations has formulated the Sustainable Development Goals, as "a blueprint to achieve a better and more sustainable future for all". These sustainable development goals address a wide range of topics, for the entire world, and are closely related to the definition the UN gives to sustainable.

"Sustainability is meeting the needs of the present, without compromising the ability of future generations to meet their own needs"

These goals call for the creation of an idealistic world, nearly utopian, in which humankind can live in prosperity and at the same time in harmony with the Earth and its resources. There are still large hurdles to overcome, however it is a world worth striving for. However, with a simple look at the daily news, it is clear that the necessity to fight for these ideals has not yet taken root everywhere in society. Regardless, with the rising awareness, the pressure to realise a more sustainable world is increasing on policy makers and industry.

This push is supported even from a juridical side, for example in the recent court ruling in the Netherlands. In this ruling, any actions or measures that would increase the nitrogen release to nature can no longer be given the required permits if the positive effects are not predetermined, in order to protect the landscape from more harm than is already done [65]. As a result, building projects have to be temporarily abandoned, resulting in an even larger housing shortage. This example from recent news clearly illustrates the difficult position we have found ourselves in. Court rulings and policies that are implemented to protect the environment directly and negatively impact the quality of individuals.

As a consequence, people feel the negative effects from policies more than the slower, more hidden, negative effects of climate change and pollution. It outlines another issue society faces, that of unbridled technological advancement to increase prosperity, versus a slower, more controlled growth in which the long-term needs of society and the planet are better accounted for. Careful consideration is needed on how to present and explain the sustainable development goals to the public, and why concessions need to be made.

An important facet of reaching the sustainable development goals is the circular economy. According to Kirchherr and colleagues [66], the circular economy can be described as follows: "*A circular economy describes an economic system that is based on business models which replace the "end-of-life" concept with reducing, alternatively reusing, recycling and recovering material in production/ distribution and consumption processes, thus operating at a micro level (product, companies, consumers), meso level (eco-industrial parks), and macro level (city, region, nation, and beyond), with the aim to accomplish sustainable development, which implies creating environmental quality, economic prosperity, and social equity to the benefit of current and future generations"*.

This definition captures the essence of circular economy for materials and products, and could help with several of the sustainable development goals. It encompasses several stages of life for products, with the aim to largely reduce, if not fully remove, the generation of waste, and the loss of resources, needed to maintain the current level of welfare and prosperity in western society. In doing so, it would reduce the environmental footprint, and ensures the availability of limited resources for future generations.

An important focal point of the circular economy is on materials, which are intimately related to keeping society running. Every product used by modern society, or even by any society in the past or in the future, is made of materials at some point extracted, then transformed into the product, and will at some point be discarded and requiring treatment. At every one of these steps other materials are needed to achieve these steps, and energy needs to be spent. Hence, ”greening” the materials cycles, and making them as circular as possible, will be an important aspect of lowering the environmental impact of society.

However, this is easier said than done, and to illustrate the complexity it is worth it to consider one of the challenges with these materials in more detail. The starting point being in a circular economy that products need to be designed in such way that they can easily be treated. New technological products often make use of complex compounds, with some elements being present in low quantities. Nanofilms are an excellent example of such a complex material. Nanofilms present qualities that cannot easily be recreated in thicker layers, and therefore present an important advancement, offering new opportunities for development. As of now, there is no real way to recycle these nanofilms to recover the material, let alone the energy spent to create it. The issue being, balance must be found between technological advancement and the circular economy. In an ideal world, these would go hand-in-hand, however in practice this might not be so easy.

Recent work from Xu and colleagues [67] outlays that it is focussed upon and that the goodwill is there. In their research, a substrate-immobilised nanocatalyst containing silver was made. The created catalyst is good at degrading nitroaromatic pesticides, and it shines in its reusability. The nanocatalyst is easily recovered from a reaction mixture, and was found to be equally efficient even after seven uses. While this reusability is a leap in the right direction compared to many of the other proposed nanocatalysts that cannot easily be recovered, the article lacks in the actual recovery of the silver in the nanocatalyst at the end of life. Silver is an expensive metal that requires considerable effort, energy, and other materials to be purified and transformed into an active nanoparticle. Yet, the article does not mention how to actually recover the silver from the substrate, while that is a large issue when creating a circular economy. On the other hand, the degradation of the nitroaromatic pesticides is an important task, as it can cause environmental damage. This shows that a choice must be made in which material that cannot currently be recovered is lost, in order to protect the environment short term.

It is exactly this complexity, and the need to find balance between what at first glance seem opposites, that poses the largest challenges for society. Detailed expertise is needed to understand the different facets of a field and how they interact with each other. However, no one can be an expert on everything, and as a result, the overview is often lost and focus becomes more singular. Reuter and colleagues [68] illustrate this problem beautifully: *”The story being told about the circular economy is a hero’s take in which there are only smoothly acting collaborators”*, while in practice this is hardly ever the case.

Metallurgy and the Circular Economy

Metallurgy is at the heart of the circular economy, supplying the base metals as well as the technological elements required by an advanced society. However, losses within this industry are inevitable, and cannot be ignored. In nearly every step in the production of a material there are waste streams being created, and energy is being spent. When considering a circular economy, it is therefore vital to consider these as well, and not just the material at hand. Generally, waste treatment facilities are in place, but even the cleaning of waste creates new streams that cannot always be reduced. This reality might not fit within the circular economy, however, will have to be dealt with to lower the environmental impact of society.

Another challenge within metallurgy is presented by the interconnectedness of metals and minerals. A good example here is the coupling between zinc and lead. Lead is a radioactive material, and is highly toxic. There have been concerns about lead poisoning in drinking water from older lead water pipes, which caused concerns especially for the health of children [69]. As a result, lead has a bad ring to its name and there is resistance to public exposure. While this is sensible, lead is mined from the same ores zinc is mined from, and zinc is a widely utilised material that does not have those concerns. However, mining and recovering zinc inevitable creates a lead product as well. Phasing out lead completely, understandable from a society perspective, would create an environmental hazard, as the lead will be mined, and if not used must be discarded. This either means we use lead, we allow a large heavy metal waste stream, or we stop mining zinc. None of these sounds particularly attractive, but is currently reality.

Another challenge within metallurgy that is often overlooked when recycling is presented by dilution losses. While metals are often presented as infinitely recyclable, as their quality does not degenerate, this is not an entirely honest picture. Materials are often used in conjunction with other elements, forming a complex matrix. While it is true that the metals themselves do not degenerate, in order to retrieve them from such complex mixtures, considerable effort and energy needs to be spent. And even then, in for example steelmaking, virgin material is added to furnaces in order to ensure the quality of the product, essentially creating a dilution loss of the original product.

The lack of adequate recycling and recovery routes is a society wide issue that extends beyond the metal industry only. For many newer technological advancements, just like for many large product groups such as plastics, collection and retrieval rates present their own challenges. Without the proper infrastructure to handle waste streams, a circular economy will be very hard to obtain.

It can be argued that building the infrastructure is a job for the manufacturer, and society wide leasing of technology products such as solar panels is rising in popularity for that reason. While an interesting perspective, especially for new markets, in the larger, polluting metal industries, this is near impossible if not implemented globally. The economics in these large established markets dictate that even the smallest of marginal cost reductions can equate to millions of extra profits. An increase in costs could easily lead to an increase in price, and in turn being out-competed by cheaper firms. Without a level playing field, industries in countries with visionary environmental protection laws will be forced to move to countries without, essentially defeating the purpose of these laws. Additionally, this would lead to a loss of jobs in these countries, and large metal industry complexes often offer thousands of jobs. Yet, if the policy makers do not pressure industry, nothing will change and pollution will continue.

Yet, the future for metallurgy and the circular economy is not all dark. Awareness is being raised, and large international institutions and government organisations push for a new way of thinking and evaluating, and innovation is being created at a dazzling speed. In new curricula at universities scientists are no longer only expected to be an expert in their field, they are often also made aware and taught to consider their impacts. Regardless of the resistance to change native to humankind, this is bound to seep through in the essence of the field and lead to change.

HIsarna: Potential Gamechanger?

New innovations in the metallurgy field are created in rapid succession, related to the sustainability push in society. One such example is the new HIsarna furnace, closely tied to the presented research in this thesis. Being a steel smelter, its main function is to create a consistent and pure hot iron stream, which can then be refined into steel in the next process step. An advantage of the HIsarna is its better performance on environmental indicators.

The Ultra Low CO_2 Steelmaking (ULCOS) project aimed to create a steelmaking technology with a significantly reduced CO_2 impact, and the HIsarna furnace is a result of that. Due to the earlier mentioned higher tolerances for impurities, the HIsarna does not require extensive coking nor iron ore agglomeration processes, cutting down its CO_2 emissions by 20% compared to traditional blast furnaces [9]. A reduction of 70% and 60% of NOx and SOx respectively is also achieved [70].

Additionally, the furnace can be equipped with carbon capture technology, either for storage (CCS) or for usage (CCU). Combined, this can lead to a reduction of 80%, which would be a big step towards a carbon neutral iron smelting process [70]. The resulting stream of CO_2 is of high quality, and can potentially be used in other applications. There are several examples, and the Scientific Advice Mechanism (SAM) has just last year briefed the European Commission of the potential of promoting utilisation of these high quality streams to, for example, make biofuels [71]. In their advice, it is made clear that the utilisation of high purity CO_2 streams has a potential for climate mitigation.

HIsarna features larger tolerances for several heavy metal elements, including zinc and lead, allows lower grade iron-bearing sources to be viable for treatment. This unlocks a whole new stream of both lower grade iron ore, and waste streams currently land filled. In line with the circular economy, this will help recover valuable resources.

Especially the potential unlocking of current land filled waste streams holds considerable environmental impact. Sludge wastes are toxic wastes, featuring significant heavy metal presence, which can leak to the environment. Additionally, these wastes are often highly basic, requiring treatment before they can even be stored. Even aside from the environmental hazards and the considerable economic costs, land filling these dusts implies the loss of valuable resources, and the energy spent to mine and refine them.

While there is plenty ongoing research into using these materials, only occasionally does it imply an economic recovery of metals. This is where the HIsarna furnace can make an impact, as recycling these waste streams as new feed material into a steel smelter furnace implies at least the recovery of the iron and the slag forming materials lime and silica. Initial tests with the furnace have implied the potential for zinc enhancement of the flue dust, to even higher levels than for the EAF. If living up to the potential, this enhancement of zinc in the flue dust allows this stream to be potentially fed back to a zinc smelter. This could in theory create an attractive route of recycling zinc smelter sludge into HIsarna, and feeding the flue dust from HIsarna back to the zinc smelters.

Despite the obvious positives, its not only positives. For the high level of zinc concentration that is required, over 50% of the flue dust composition, recirculating the dust is a necessity. This has two obvious downsides, requiring the already rejected zinc to be heated and vapourised again and again, and it is wise to verify this is an environmentally sound practice. Secondly, adding a higher percentile of zinc to a steel smelter means adding relatively less iron, lowering the overall efficiency of HIsarna. So while it might sound like a good idea to create a circulation like this, it is not necessarily beneficial, and an in-depth LCA is advised.

There is another point to be made regarding the implementation of the technology. Due to the longevity of steel furnaces, the time to maturity is long for new innovations, and changing an entire line of furnaces is inevitable slow. Additionally, it is unclear whether it is a sound practice to replace a furnace before the end of its lifetime. Energy has been spent to create the furnace, and replacing it earlier would therefore include a waste of resources. A slow replacement however means that waste streams keep building up, and emission-levels will remain high, illustrating the complexity for the steel industry.

For HIsarna to indeed become a revolutionary gamechanger, it needs to overcome these hurdles, especially in the coming 10-15 years. Implementation times are long, and it has not even been fully proven that it lives up to its environmental promises. It is up to policy makers to create a level-playing field to help alleviate competition disadvantages, and for researchers to determine what would be the ideal implementation process. Trade-offs will have to be made, and due to the high stakes, this needs to be done carefully.

Metallurgy, Integrated-to-Society

It can safely be stated that near-every tech product we use is either steel, contains steel, or has seen something made out of steel somewhere in its manufacturing process. Hence, the impact on everyday life is enormous, and it is easy to understand why society hinges on this industry, even more so for the metallurgy field as a whole. Yet, the general views of society on this industry is one of pollution, of emissions, of large waste streams, not one that enables their comfortable homes, their cars, their smartphones. Generally, especially for mining, it is one of those things everyone will agree that it is important, but nobody wants in their backyard.

Society cannot go without its materials, and economic progress will severely be hampered if no adequate solutions are found to the challenges we face. ”Greening” this industry should be top priority on a global scale, and concessions are needed. Trade-offs are inevitable, and society will have to make some harsh decisions, balancing its impact and its technological advanced communities. It can even be debated whether this balance is an illusion, as the environmental pressure might be building so high already, that the only two alternatives are significantly cutting back on technology or risking the planet.

It cannot be expected in the current capitalist economy that the industry will face these challenges alone, not in a world where focus for bulk goods is mostly on cheap access. Knowledge should be made available to make sure that the policies implemented are the ones that push the development of the industry into the right direction. The recent focus on greenhouse gas emissions has forced large corporations to invest R&D resources into cutting their emissions, and proved to be an effective measure.

An important role in this debate should be taken on by the government. Policy makers steer the direction of the developments, and by setting targets and priorities they can aid the transition to a more circular metallurgy industry. By creating level playing fields globally, and by taking control over the outlines of the metal chain, innovations get the chance to rise to maturity and revolutionise the production processes without running the risk of getting out-competed. This can only be achieved in case of open communication and smooth collaboration, however difficult this might be on the political scene. A long-term vision of where to go and what to achieve at what point in time would create stability and give a good indication of what needs to be done still to reach the UN development goals. With the deadlines of these goals quickly approaching and the potential disaster of climate change and resource depletion looming in the distance, the time for all the social, environmental, and corporate actors to set aside their differences and deliver has arrived.

Ideas on how to adequately handle the creation of as-circular-as-is-desirable material cycles are present, and the research potential is of such size that with enough available funds even ambitious targets should be within reach. Urban mining, as an example, is already being implemented more, and is a good first step to increase societal acceptance levels. What is needed is a global push, deciding where the balance between economics, environment, and technological advancement should be, and realising that doing nothing is simply no longer an option. If only to realise the dream of an idyllic, nearly utopian Earth, with prosperity for everyone, in harmony with nature.

Chapter 5

Research Aims

In order to regain focus on the experimental work and the goals of the thesis, the research aims will be repeated here. Some further explanations of the research questions will be given, and how these will help shed clarity on the topic at hand. The motivation for the research can be found within the Introduction and will not be repeated here.

The aim of the thesis is to investigate whether it is feasible to feed industrial waste dusts to the HIsarna for the recovery of valuable resources. Fundamental understanding on the high temperature behaviour of the dusts will allow for more effective enrichment of the HIsarna flue dust zinc fraction. The main research question is therefore formulated to depict this:

Will the zinc present in an industrial waste dust be reduced and vapourised under thermal treatment, and be removed effectively, efficiently, and selectively?

To further substantiate the claims resulting from the research into the main research question, four subquestions are postulated:

1. What is the effect on the thermal reduction behaviour of zinc being present in different zinc-bearing compounds?

Within the waste dusts, there are several zinc mineral forms that can be present. The mineralogy of the zinc will play a role in the thermodynamics and the kinetics of the reduction and vapourisation reaction.

2. What mechanism is followed during zinc reduction and vapourisation, and at what timescale?

Within HIsarna, the allotted time for the reduction and vapourisation is in the order of seconds. It can be expected several reactions are required to go from mineral to zinc vapour, and as such an indication of the mechanism pathway and the timescale is warranted.

3. Mixing several secondary materials, can the reduction and vapourisation behaviour be enhanced?

Within the steelmaking process, several waste streams are produced that can be applied to the HIsarna reactor. An investigation in the interaction at high temperature between the dusts would highlight whether mixing these sources will lead to more efficient treatment.

4. What behaviour is observed from the other elements present, with particular focus on iron?

Another important factor in the thermodynamics of the reactions forming the mechanism of zinc removal from the industrial waste dusts can be presented by the other elements present within the mixture. These elements can interact with the zinc directly, forming intermediate compounds. Alternatively they can interact indirectly with the zinc reduction and vapourisation reactions, for example by extracting heat locally or reacting with the atmosphere. Iron is of particular interest due to the presence of undesirable zinc ferrite, a compound detrimental in the zinc smelting process.

Chapter 6

Methodology

In this chapter, the performed experimental work will be detailed. A part of the thesis was to develop a method for dealing with these industrial waste dusts in the horizontal furnace, and a description will be given on how the method evolved into the final setup. As an addendum to this chapter, the accuracy of the acquired results will be discussed, providing some insights on the systemic errors within the thesis work.

6-1 Introduction to the three dusts

The dusts to be used are goethite, Blast Furnace (BF) sludge, and Basic Oxygen Furnace (BOF) sludge. Their physical appearance after a drying period of 2 hours at 105 °C is shown in Figure 6-1. Their origins are described within the Literature Study, and only a short recap is provided here.

The goethite waste dust is a zinc smelter residue, formed when separating the iron and the zinc in a leaching process. The remaining sludge is high in iron and zinc, and has a relatively high moisture content. The BF sludge and the BOF sludge originate form the steel industry, and are the wet fraction of the flue dust from the BF and the BOF respectively. The goethite is kindly provided for this research by Nyrstar, the BF dust and the BOF dust are kindly provided by Tata Steel.

In the entire thesis, these three waste streams will be referred to as dusts. Within literature, the difference between a sludge waste and a dust waste is often disregarded, as its origin is the same flue dust.

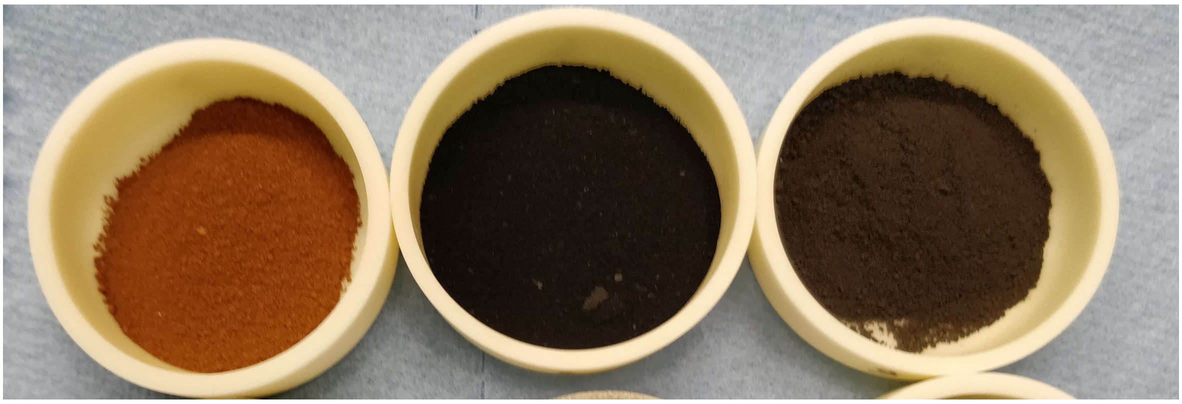


Figure 6-1: Three industrial waste dusts, goethite, BF dust, and BOF dust.

6-2 Performed Experiments

The as-received dusts were dried in a normal oven at 105 °C for 1 or 2 days, in order to remove the moisture contents. After this, the dusts were ground using a pestle and mortar, and stored in a glass vial for further use. The dusts were extensively characterised at this stage.

At the start of an experiment, the samples were added to an alumina crucible of predetermined weight. The crucibles are shown in Figure 6-2. Three types of crucibles were utilised with different volumes and shapes, which could affect the dynamics within the furnace. Thus, for each set of experiments a single type of crucible was used. The hot zone of the furnace was determined using thermocouples. The hot zone turned out to be long enough to hold the longest of the three crucibles, featuring an insignificant temperature decay of 12 °C over 10 cm from the center of the furnace.

The horizontal furnace was pre-heated at the start of the day. The temperature of the furnace was controlled by a Eurotherm 903 from Carbolite. The furnace was ensured to be air tight, creating a controlled atmosphere of Nitrogen or Argon depending on the experiment. A flow rate of 2L/min of inert gas was set, either N_2 or Argon depending on the experiment. The ends were water cooled, creating a quenching zone for sample in- and output. An illustration and a schematic of the furnace can be seen in Figure 6-3. In the schematic, the blue lines indicate the gas flow direction. The gas outlet goes to the ventilation and to the gas analyser.

Two set-ups were used for the furnace. At 850 and 1000 °C, the ends of the furnace were equipped with rubber stoppers. The sample was inserted at the gas outlet side by opening and closing the rubber stopper. After treatment, the gas outlet side was opened, and the sample was pushed to the quench zone at the gas inlet from which it was removed after 3 minutes of quenching. The furnace was flushed with inert gas for 3-5 minutes. This allowed for a high sample throughput. With the gas analyser a relatively narrow air band could be measured, indicating that the air stayed near the gas outlet.

Figure 6-2: Overview of the alumina crucibles used. The crucibles will be referred to as a boat crucible, a hooked crucible, and a round crucible. Sizes are 8x3x2, 9x3x2, and 3.5x1-1.25.

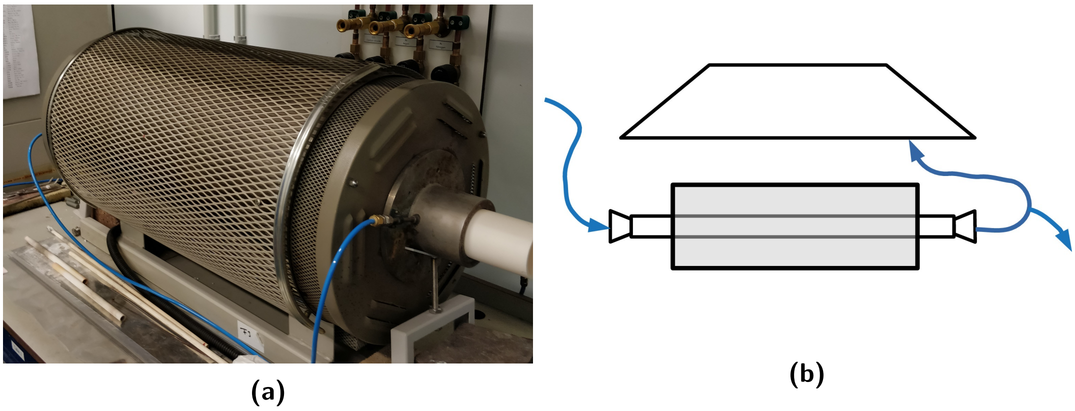


Figure 6-3: An image and a schematic of the horizontal furnace. The sketch represents the situation before installation of the metal flanges, as the depicted setup is used for the bulk of the experiments.

To operate at 1300 °C, the furnace was equipped with metal flanges at both ends. The metal flanges could be opened to insert or remove the samples from the quench zone, performed only on the gas outlet. The flanges have a small opening, used to push the hooked crucibles to the hot zone, then pull them out again, without having to open the furnace. Both upon insertion and upon removal, the samples were left in quench for 3 minutes. The sample throughput is significantly lower in this set-up.

Particle size analysis For the individual starting dusts, the particle size was determined using a Microtrack S3500. Two measurements were performed in water, one with ultrasound dispersion, and one without.

Weightloss determination The weight loss of the samples due to the thermal treatment was measured. The starting weight was determined by weighing the glass vial before and after emptying in the crucible. The end weight was determined by weighing the empty crucible before filling and after treatment. Subtracting one from the other gives the weightloss.

Gas analyser The gas analyser, a Hiden Analytical HPR-20 R&D, was used to monitor the off gas composition and the reaction progress. Being a mass spectrometer, adequate distinction between N_2 and CO is difficult. In those experiments Argon was used.

Thermal Gravimetric Analysis (TGA) The thermal profile of the individual dusts were measured using a Netzsch STA409 TGA, as an indicator of material behaviour at high temperature.

Morphology and phase determination Sample phases and morphology were monitored using the Bruker D8 Advance diffractometer for X-ray Diffraction (XRD), and a Jeol JSM 6500F Scanning Electron Microscopy - Electron Dispersive X-ray Spectroscopy (SEM-EDS).

Chemical composition analysis Chemical composition was monitored using X-ray Fluorescence (XRF), a Pananalytical Axios Max WD-XRF spectrometer. Carbon contents were measured using a LECO CS 744.

Mössbauer analysis Transmission ^{57}Fe Mössbauer spectra were collected, for quantification of the iron-bearing phases.

6-2-1 Measured samples

A list is provided of all the samples, the temperature at which they were measured, and the retention times of the experiments. Mixed dust sets of Goethite, BF dust, and BOF dust were created, the nomenclature of which can be found in Table 6-1.

Three different temperatures were used in the experiments. The lowest temperature 850 °C is just below the vapourisation point of zinc at 907 °C. The upper temperature limit is set at 1300 °C, as the melting temperature of pure FeO is 1377 °C. Due to the dissolution of carbon, some initial melting could be detected. The in-between temperature is set at 1000 °C.

The retention times of a full set includes 1, 5, 10, 20, and 30 minutes, as well as a 1 hour sample for the gas analyser. In case additional measurements were performed these are indicated in the list. A full analysis entails XRF, XRD, LECO, and Scanning Electron Microscopy (SEM)-EDS characterisation. Weight loss was determined for every sample. Note that the list is not exhaustive for the analysis techniques, and in selected cases a sample was analysed in more depth.

1. Individual dusts of goethite, BF dust, and BOF dust. Performed at 850 °C and 1000 °C, for the full set of retention times. Additionally, 15, 30, and 45 second samples were treated. Full analysis was performed on the 10 and 30 minute samples at 1000 °C.
2. The mixed samples were treated at 1000 °C, with the full set of retention times. Full analysis was performed for the 10 and 30 minute samples. Additional Mössbauer analysis is performed on the 5 and 30 minute samples of the 60% mixes and the triple mixes.
3. At 1300 °C a 1, 5, 10, and 30 minute goethite sample were treated, and a 1 and 5 minute 33% mix. The 33% mix samples and the 5 minute goethite sample were investigated with XRF and SEM.

Table 6-1: The mixed samples and the terminology used to describe them, and their constituents.

Sample mix	Goethite	BF dust	BOF dust
Goethite 40%	40%	60%	-
Goethite 60%	60%	40%	-
Goethite 80%	80%	20%	-
BOF dust 40%	-	60%	40%
BOF dust 60%	-	40%	60%
BOF dust 80%	-	20%	80%
33% mix	33%	33%	33%
40% mix	40%	20%	40%

6-3 Accuracy Determination

It is imperative in any experimental work to indicate the accuracy and the reliability of the experiments. This discussion is mostly focused on the systemic error within the experiments, which can roughly be divided into 2 parts. One is the error in the measurements, the other error is mostly due to sample inhomogeneity.

As has been discussed extensively in the Literature Study, the waste dusts are not of consistent composition. To ensure a composition as homogeneous as possible, several batches were taken from several locations within the received bulk waste. These batches were dried and ground, mixing them thoroughly. Due to time constraints and the large amount of samples, every sample was run only once.

To get an idea of the systemic error due to inhomogeneity, one sample was selected and ran four times. After this, the weight loss was determined, and compared for each run. The result is a median weight loss of 35.52%, with a standard deviation of 0.73%. The systemic error of the analytical balance is reported at d = 0.0001g, and thus the sample-to-sample error is generally much greater than the error of the analytical balance. Similar comparisons were made for the other techniques.

The systemic error is dominated by the sample inhomogeneity. Despite being minimal, efforts were made to reduce this term wherever possible, in a systematic way. As such, the above number can be used as an indication for the error, and all trends and numbers reported later in the thesis are deemed accurate. Wherever needed, an additional discussion is provided detailing the accuracy of a certain trend.

Chapter 7

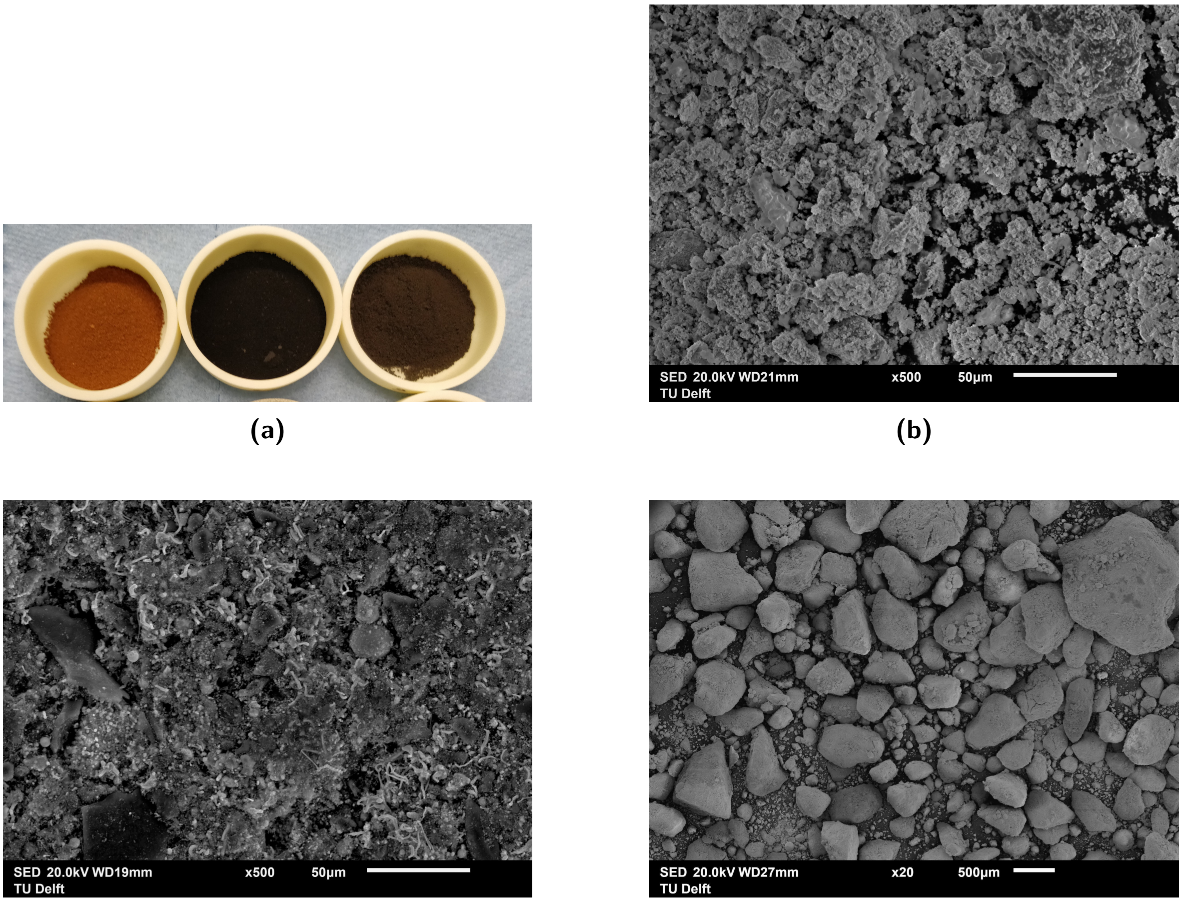
Results & Discussion

In this chapter, the results will be shown and discussed, leading to an answer to the research questions. First, an initial characterisation of the three dusts received from the industrial partners is given. After that, step-by-step the observations will be discussed, explained, proven, and then the reactions thermodynamically verified. The chapter will end with the described mechanism as a summary, after which the research questions will be answered.

7-1 Initial Characterisation

The finely ground dusts of goethite, Blast Furnace (BF) dust, and Basic Oxygen Furnace (BOF) dust vary in appearance, as can be seen in Figure 7-1. The goethite has a distinct red colour, likely originating from the dominant red haematite fraction. The other dusts are darker in colour, especially the rich-in-carbon BF dust. On the SEM images in the same figure it shows the differences in the nature of the particles as well as the size of the particles. The differences in particle size were confirmed in the particle size analysis, and can be found in the top part of Table 7-1. The BF dust consists mostly of particles under 15 µm and is thereby the smallest, the BOF dust is relatively sticky, leading to agglomeration of the particles on top of the already larger particles.

The X-ray Diffraction (XRD) spectra of the dust indicated a wide array of different mineral phases in the dusts, summarised in Table 7-1. Of particular interest are the differences in phases of zinc, present in zinc ferrite, zinc sulfide, and zinc oxide. Iron is present in all its oxidation states, and in metal complexes including zinc ferrite. Using X-ray Fluorescence (XRF), the composition of the samples were measured, and the results are shown in Table 7-2. The carbon contents were determined using the LECO, and the XRF results corrected for this LECO carbon value. There is a large variation between the dusts, which will give a markedly different dynamic to the high temperature behaviour between them. Goethite is rich in zinc



(a) (b)

(c) (d)

Figure 7-1: Top left is a picture of the three dusts before treatment, Goethite, BF dust, and BOF dust. From top right to bottom right, the Scanning Electron Microscopy (SEM) images of the untreated dusts goethite, BF dust, and BOF dust.

and sulfur, BF dust is rich in zinc and carbon, whereas BOF dust is more enriched with iron and lime.

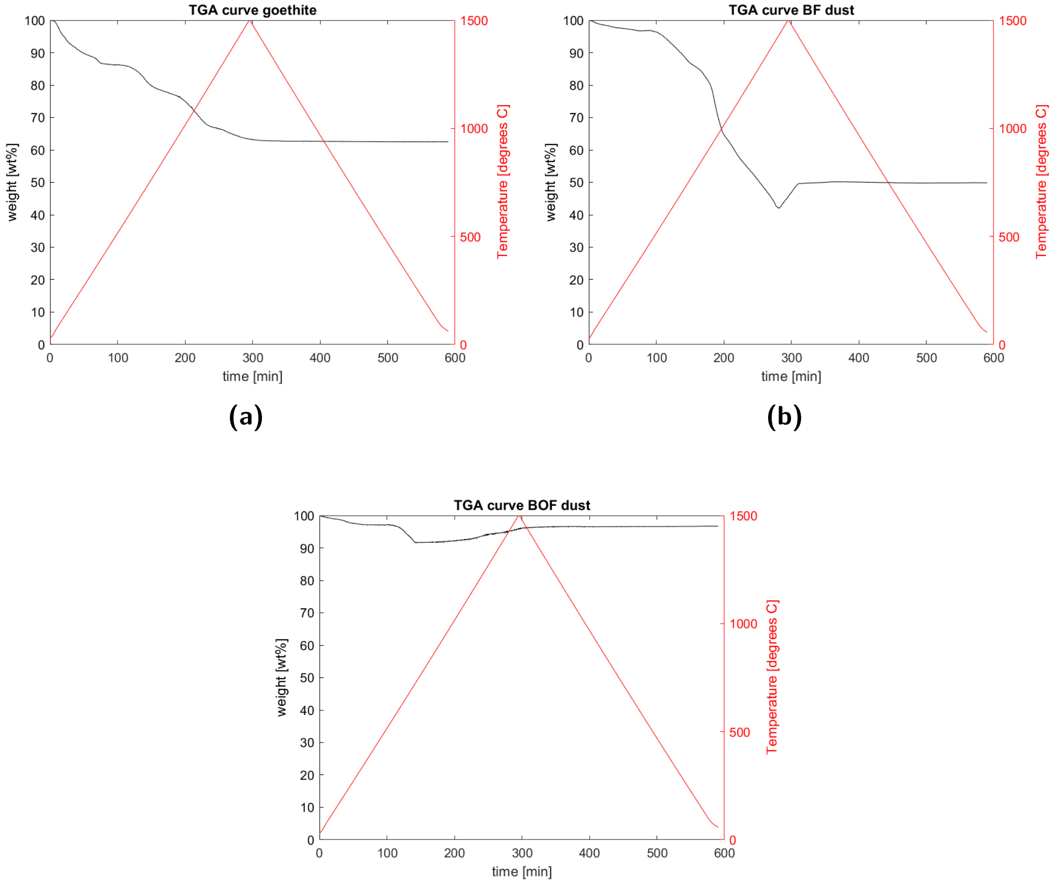
Table 7-1: The average particle sizes after drying, grounding, and ultrasonic for 1 minute, and a description of the main phases as a summary of the XRD spectra.

Goethite	**BF dust**	**BOF dust**
20% <10 µm 20 µm-50 µm	3 µm-15 µm	40% <20 µm 40% 20 µm-100 µm 20% 100 µm-300 µm
zinc ferrite $ZnO \cdot Fe_2O_3$	haematite Fe_2O_3	iron Fe
magnetite Fe_3O_4	fayalite Fe_2SiO_4	wustite FeO
lead sulfate PbS	zinc oxide ZnO	zinc oxide ZnO
$CaSO_4 \cdot 2\,H_2O$	quartz SiO_2	magnetite Fe_3O_4
$NaFe_3{}^{3+}(OH)_6(SO_4)_2$	calcite $CaCO_3$	calcite $CaCO_3$
	wurtzite ZnS	fayalite Fe_2SiO_4
		cohenite Fe_3C

Table 7-2: XRF values for the initial dusts, corrected for carbon using the LECO. Only elements with a concentration of over 0.5 wt% are shown. Most compounds are present in metal complexes, oxides, or sulphised, and as such are reported in elemental form. The sum before normalisation is given at the bottom.

Compound	**Goethite**	**BF dust**	**BOF dust**
Fe	55.40%	35.36%	85.36%
Zn	11.96%	6.22%	0.70%
Ca	8.69%	2.32%	8.14%
S	8.39%	1.63%	-
Pb	5.02%	1.64%	-
Si	4.03%	3.25%	0.80%
Cd	4.92%	-	-
Al	1.45%	1.96%	-
Cu	0.79%	-	-
Mn	0.78%	-	1.02%
Na	0.59%	0.62%	-
K	-	1.29%	-
Rb	-	0.87%	-
Mg	-	0.70%	1.09%
C	0.07%	39.90%	2.28%
before norm.	102.9 %	94.4 %	91.7 %

What becomes apparent is that the dusts are varied in all aspects. BOF dust is mainly larger particles on an iron-based matrix. Goethite features no consistent matrix, but rather several different particles. The majority is based on iron oxides however. The BF dust consists for



(a)

(b)

(c)

Figure 7-2: The TGA curves from the three dusts, goethite, BF dust, and BOF dust. The experiment was ran by increasing the temperature with 5 °C/min to 1500 °C, then cooling it down at the same rate.

the most part of very small, well dispersed particles. Remarkable is the high carbon content of the dust. This will lead to notably different thermal behaviour, as can be seen in the TGA curves in Figure 7-2. A TG curve was recorded for EAF dust by Omran and colleagues, and shows similar behaviour to the Goethite and BF dust curves [72]. Initial weightloss at low temperatures in all of the dusts is excess moisture. Around 400 °C, a dehydration of the calcium hydrate salts take place, and at around 600 °C a further decomposition of the calcium carbonate salts is observed. In the Goethite and the BF dust, calcium salts are abundantly present. Additional losses can be ascribed to the volatilisation of other elements, including cadmium, lead, and most notably zinc around 900 °C. BOF dust, being mainly an iron matrix, does not show significant weightloss. The effects will be detailed later on, however, the TGA curves give a good starting indication of the differences and similarities in behaviour of the dusts.

7-1-1 Expected iron and zinc reduction reactions

Before exploring the results from the individual waste dusts, it is important to evaluate the different species and what reactions can reasonably be predicted at a 1000 °C. Using the HSC Chemistry v6.12 software, the thermodynamics of the iron and zinc oxide reduction reactions were evaluated, to see their likelihood. This will ease the explanation of the later results.

What can be seen is that carbon is a key component in the reduction behaviour of the iron and zinc oxides. None of these decompose by themselves at the temperatures within the experiments, and need carbon to react. What becomes clear is that despite the vapourisation temperature of zinc, 907 °C, the threshold temperature is 950 °C, meaning that at a temperature below that CO cannot reduce zinc effectively. This will be further discussed when it comes up during the discussion of the results.

In the equations below, first the reaction is given, then the temperature at which the Gibbs free energy switches sign, the Gibbs free energy at 1000 °C in kJ, and lastly whether the enthalpy is positive or negative. This provides a solid thermodynamic ground for further explanations later on in the chapter.

Reaction		T_{onset}	$\Delta G^{1000\,°C}$	ΔH	
$Fe_3O_4 + C$	$\longrightarrow 3\,FeO + CO_{(g)}$	700 °C	−59 kJ	>0	(7-1a)
$Fe_3O_4 + CO_{(g)}$	$\longrightarrow 3\,FeO + CO_{2(g)}$	600 °C	−7 kJ	>0	(7-1b)
$Fe_2O_3 + C$	$\longrightarrow 2\,FeO + CO_{(g)}$	550 °C	−95 kJ	>0	(7-1c)
$Fe_2O_3 + CO_{(g)}$	$\longrightarrow 2\,FeO + CO_{2(g)}$	<0	−42 kJ	>0	(7-1d)
$FeO + C$	$\longrightarrow Fe_{(s)} + CO_{(g)}$	750 °C	−43 kJ	>0	(7-1e)
$FeO + CO_{(g)}$	$\longrightarrow Fe_{(s)} + CO_{2(g)}$	600 °C	9 kJ	>0	(7-1f)
$3\,ZnFe_2O_4 + C$	$\longrightarrow 3\,ZnO + 2\,Fe_3O_4 + CO_{(g)}$	600 °C	−82 kJ	>0	(7-1g)
$3\,ZnFe_2O_4 + CO_{(g)}$	$\longrightarrow 3\,ZnO + 2\,Fe_3O_4 + CO_{2(g)}$	<0	−30 kJ	>0	(7-1h)
$ZnFe_2O_4 + C$	$\longrightarrow ZnO + 2\,FeO + CO_{(g)}$	700 °C	−67 kJ	>0	(7-1i)
$ZnFe_2O_4 + CO_{(g)}$	$\longrightarrow ZnO + 2\,FeO + CO_{2(g)}$	250 °C	−14 kJ	>0	(7-1j)
$ZnO + C$	$\longrightarrow Zn + CO_{(g)}$	950 °C	−15 kJ	>0	(7-1k)
$ZnO + CO_{(g)}$	$\longrightarrow Zn + CO_{2(g)}$	1350 °C	9 kJ	>0	(7-1l)

7-2 Individual Dusts

The first experiments were ran at a temperature of 850 °C and 1000 °C, at various time lengths, for all three of the dusts. Using the gas analyser, it was verified that the chosen time lengths

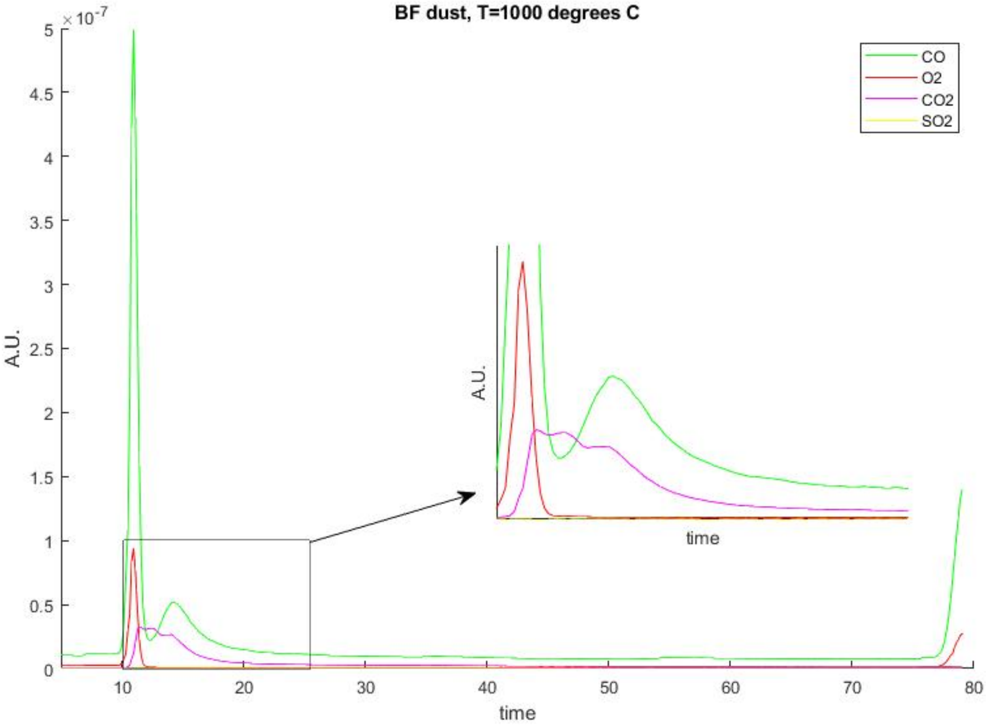


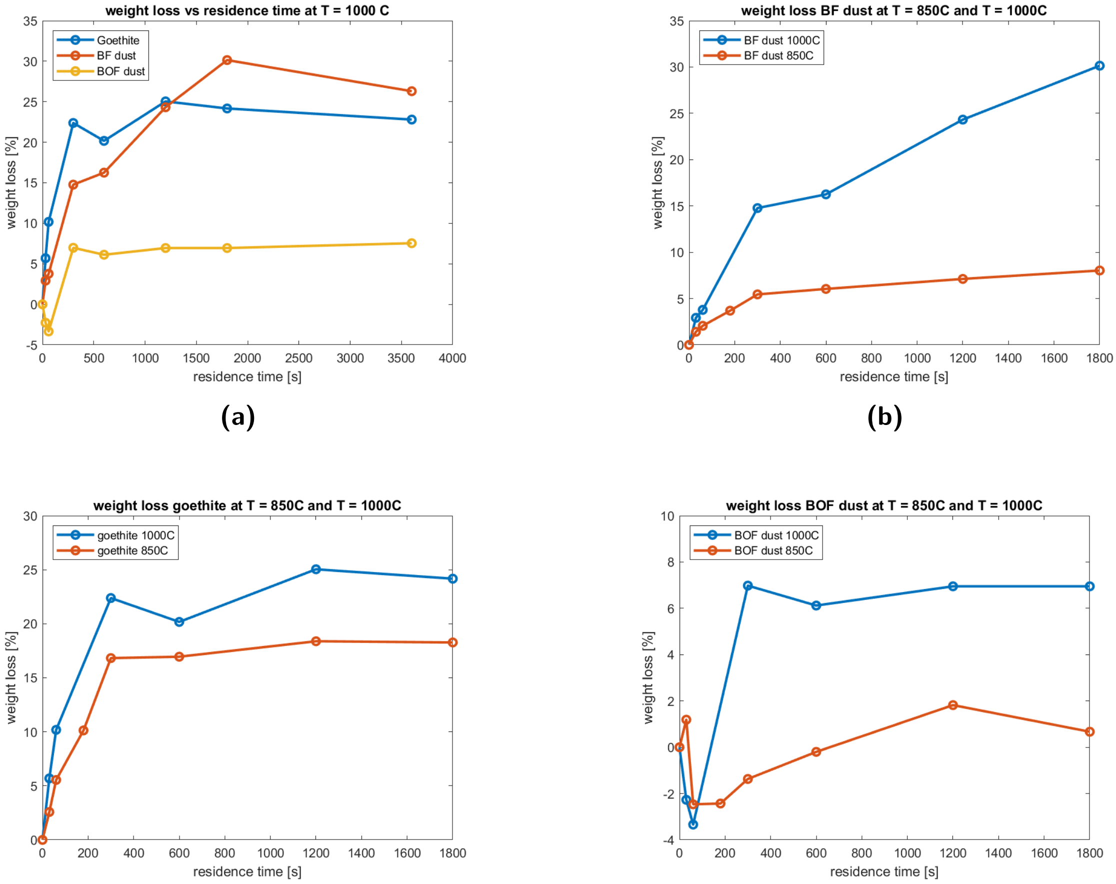
Figure 7-3: Gas analyser results of BF dust, treatment at 1000 °C, under Argon atmosphere. In the set-up with the rubber stoppers, air can enter the gas outlet at sample input, which can be seen in the high O_2 and CO peak.

are appropriate, the graph for BF dust can be seen in Figure 7-3. Upon opening the furnace to input the sample, the gas outlet is exposed to air, and this signal is clearly present on the spectrum in the form of a O_2 and CO peak at around minute 10. Directly after moving the sample to the hot zone, a strong CO_2 peak is observed, shortly followed by a stronger CO signal. After roughly 25 minutes, the intensity of the signal becomes very low, meaning that the reactions are nearing completion.

Note that N_2 and CO have similar weight, and can therefore not be distinguished by the mass analyser. It was chosen to only monitor CO. However, some N_2 signal, such as that of air at the start, is thus noted as CO.

The gas analyser results from the other samples are roughly similar, with the reactions being finished before the 30 minute mark. The goethite sample shows a stronger SO_2 peak, but a lower CO and CO_2 due to the lack of carbon and the abundance of sulfur in the sample. The results of the off-gas analysis were later confirmed in the closed system with the metal flanges.

Comparing the weight losses, large differences can be observed between the samples due to the varying compositions, shown in Figure 7-4a. These weightlosses are in line with the results from the TGA, with Goethite and BF dust showing large weight losses. The weightloss of



(a) **(b)**

(c) **(d)**

Figure 7-4: Weightloss results for the dusts at various temperatures and retention times. Top left compares all dusts at 1000 °C, the other three compare the 850 °C and 1000 °C curves per dust.

goethite is larger in the first few minutes due to excess moisture, and levels off sooner than that of BF dust. As expected, the BOF does not show much weightloss at all, instead showing a weight gain at the start of the experiment. This weight gain is ascribed to a reaction with air after the furnace treatment. It is accompanied by a change in colour, turning redder for the first two to three minutes after leaving the furnace. Red indicates that this is likely a formation of haematite.

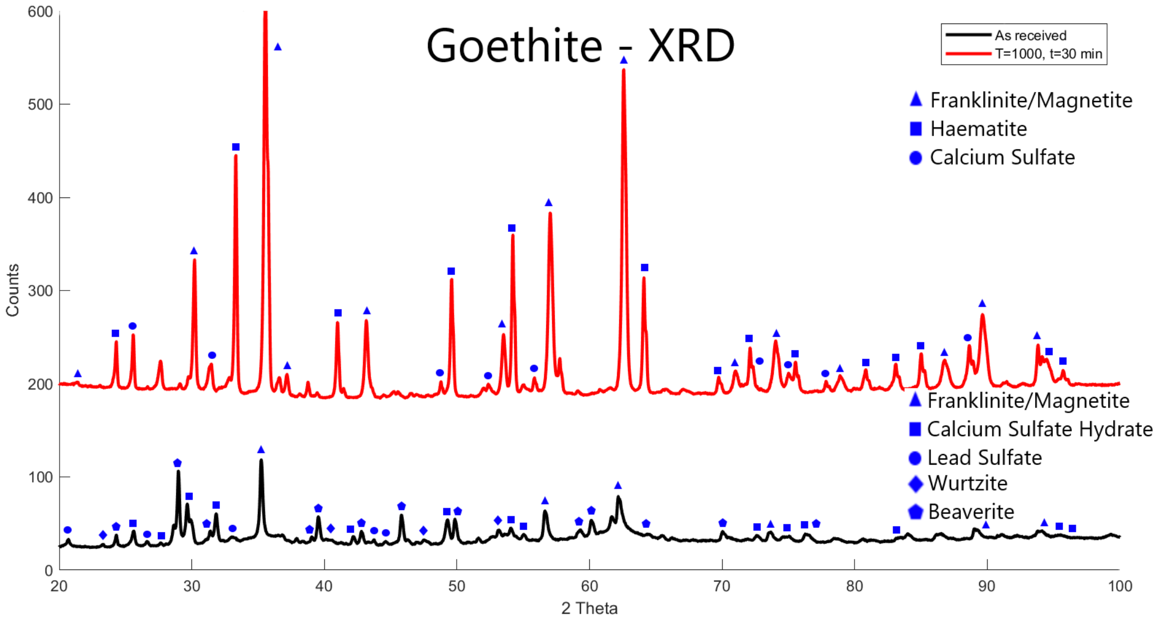
The weight loss is temperature dependent, and more weight is retained at lower temperatures. The trends are however similar, leveling off after 10 to 20 minutes, as can be observed in Figures 7-4b - 7-4d. The difference is most notable for the BF dust. This effect can be explained by the larger presence of carbon in BF dust and the temperature being below the vapourisation temperature of zinc. Carbon effects will be explored in more detail later.

Upon furnace treatment, physical changes became apparent, and were dependent on time and temperature in the furnace. Especially for the samples at longer retention times of over 30 minutes at 1000 °C, sintering could be observed. Comparing the untreated dusts in Figure

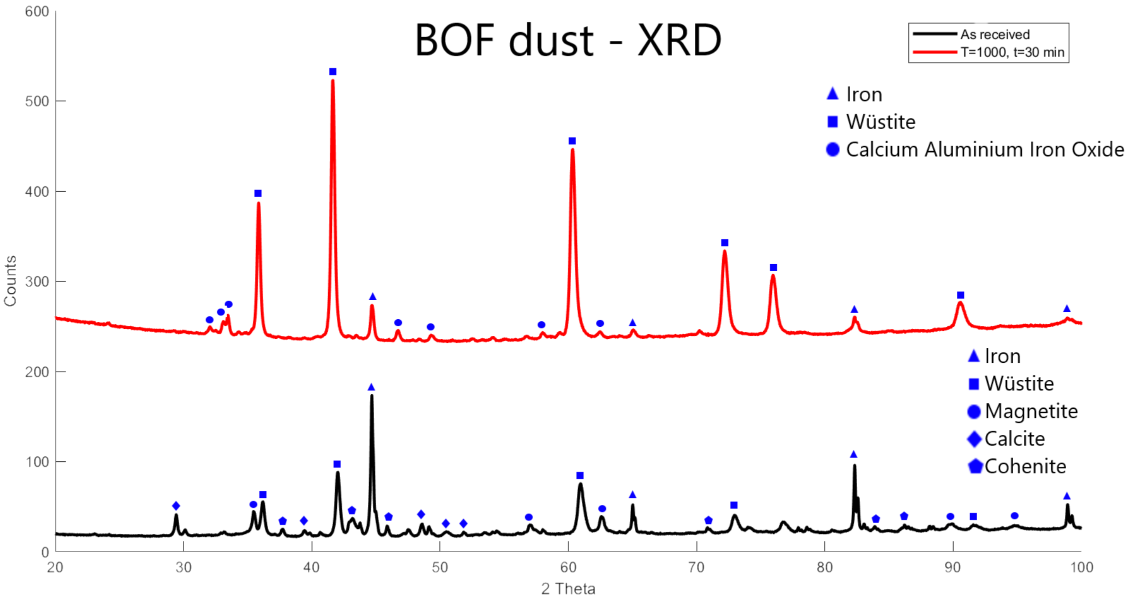
Figure 7-5: Goethite, BOF dust, and BF dust. During treatment, the dust undergo sintering.

7-1a and the treated dusts in Figure 7-5, these effects are apparent. The dust particles formed strong agglomerates, and all dusts take on a dark colour. The sintering effects are related to the high content of CaO and Fe.

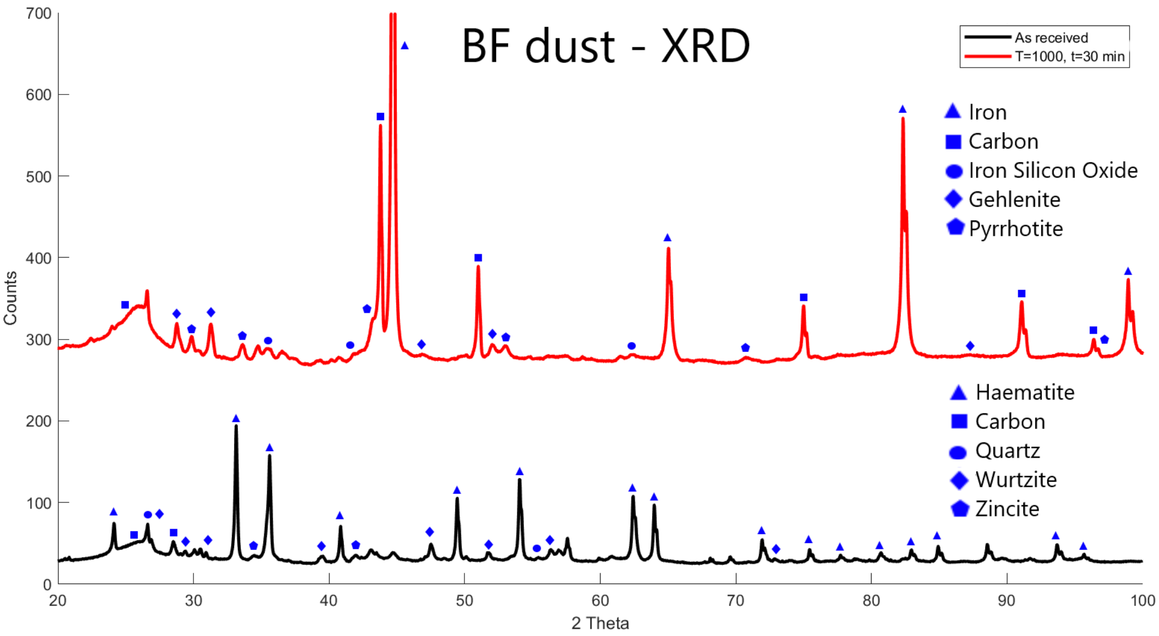
As has been shown in the TGA curves in the characterisation section, there are several different reactions that can take place during the thermal treatment. These phase changes are especially clear in the XRD spectra, shown in Figure 7-6. In goethite, the phase changes are a dehydration of calcium sulphate hydrate and desulphurisation reaction of the metal complexes, whereas the zinc-bearing franklinite remains untouched. A similar dehydration and desulphurisation could be observed in the BF dust, whereas the BOF dust contains too little of either to make that apparent. Additionally, in the carbon containing BF dust, the iron oxides are reduced entirely to elemental iron. This is in line with the expected reaction equations, most notable Equations 7-1c and 7-1e. Similar reducing behaviour can be seen in BOF dust, where the magnetite is reduced to wüstite and elemental iron according to Equations 7-1a and er1e. The reduction of wüstite is not complete, and LECO confirmed that the carbon has ran out after thermal treatment. Other observations from the XRD spectra include the formation of more complex matrices with several metal elements.


Goethite - XRD
As received
T=1000, t=30 min
Franklinite/Magnetite
Haematite
Calcium Sulfate
Franklinite/Magnetite
Calcium Sulfate Hydrate
Lead Sulfate
Wurtzite
Beaverite
Counts
0
100
200
300
400
500
600
20
30
40
50
60
70
80
90
100
2 Theta

(a)


BOF dust - XRD
As received
T=1000, t=30 min
Iron
Wüstite
Calcium Aluminium Iron Oxide
Iron
Wüstite
Magnetite
Calcite
Cohenite
Counts
0
100
200
300
400
500
600
20
30
40
50
60
70
80
90
100
2 Theta

(b)



(c)

Figure 7-6: Recorded XRD spectra. The bottom black line shows the spectrum before treatment, the red top line the spectrum after treatment. The symbols correspond to a single phase.

The dehydration and desulphurisation reactions cause significant weight loss in Goethite and BF dust. The reactions are shown in Equation set 7-2. The dehydration of $CaSO_4 \cdot 2\,H_2O$ takes place at low temperatures, and should be completed during the pre-processing. For $CaSO_4 \cdot 0.5\,H_2O$, the pre-processing drying temperature of 105 °C is not high enough to initiate the dehydration. Since the amount of calcium sulfate hydrate salts is more apparent in goethite, this explains the quick onset of the weightloss. The desulphurisation of $CaSO_4$ takes place around the lower temperature experiment, and is therefore another likely cause of the temperature sensitivity of the weight loss shown in Figures 7-4b - 7-4d.

Reaction		T_{onset}	$\Delta G^{1000\,°C}$	ΔH	
$CaSO_4 \cdot 2\,H_2O$	$\longrightarrow CaSO_4 + 2\,H_2O$	<0	$-94\,kJ$	>0	(7-2a)
$CaSO_4 \cdot 2\,H_2O$	$\longrightarrow CaSO_4 \cdot 0.5\,H_2O + 1.5\,H_2O$	<0	$-30\,kJ$	>0	(7-2b)
$CaSO_4 \cdot 0.5\,H_2O$	$\longrightarrow CaSO_4 + 0.5\,H_2O$	150 °C	$-64\,kJ$	>0	(7-2c)
$CaSO_4 + C$	$\longrightarrow CaO + SO_{2(g)} + CO_{(g)}$	850 °C	$-65\,kJ$	>0	(7-2d)

Carbon plays a key role in the reduction reactions of other metal minerals as well. Zinc, lead, and some cadmium remain in the goethite, but not in BF dust and less in BOF dust. This can be found in Table 7-3, where the XRF and LECO values are shown of selected metals. The remainder can be found in the Appendix. Additional reductions of other metals can be found in the Equations Set 7-3, and explain the losses of other metals such as cadmium and lead. These reactions are detailed in the Equation set 7-3.

Table 7-3: Initial and after treatment at 1000 °C XRF values of selected elements, for the three dusts. The absolute weight is given assuming a 1g starting sample and accounting for the weight loss. The sum before normalisation is given for each of the samples.

Goethite

Compound	Initial value		after 30 min		
	wt%	weight *[g]*	wt%	weight *[g]*	Change
Zinc	12.0	0.12	14.5	0.11	−8.3 %
Sulphur	8.4	0.084	3.9	0.030	−64.3 %
Lead	5.0	0.050	6.2	0.047	−5.7 %
Cadmium	4.9	0.049	1.7	0.013	−73.1 %
Carbon	0.07	0.0007	0.04	0.0003	−55.5 %
before norm.	91.9		84.3		

BOF dust

Compound	Initial value		after 30 min		
	wt%	weight *[g]*	wt%	weight *[g]*	Change
Zinc	0.70	0.0070	0.18	0.0016	−76.4 %
Sulphur	0.07	0.0007	0.05	0.0005	−24.4 %
Carbon	2.3	0.023	0.10	0.0009	−95.9 %
before norm.	66.6		61.4		

BF dust

Compound	Initial value		after 30 min		
	wt%	weight *[g]*	wt%	weight *[g]*	Change
Zinc	6.2	0.062	0.26	0.0018	−97.0 %
Sulphur	1.63	0.016	1.18	0.0082	−49.4 %
Lead	1.64	0.016	n.d.	-	−100 %
Cadmium	3.55	0.035	0.02	0.0001	−99.6 %
Carbon	39.9	0.40	41.5	0.29	−27.4 %
before norm.	76.8		67.5		

Reaction	T_{onset}	$\Delta G^{1000\,°\mathrm{C}}$	ΔH	
$\mathrm{PbS + CaO + C \longrightarrow Pb + CaS + CO_{(g)}}$	550 °C	−85 kJ	>0	(7-3a)
$\mathrm{PbS + CaO + CO_{(g)} \longrightarrow Pb + CaS + CO_{2(g)}}$	<0	−33 kJ	<0	(7-3b)
$\mathrm{PbS + Fe \longrightarrow FeS + Pb}$	<0	−31 kJ	>0	(7-3c)
$\mathrm{CdO + C \longrightarrow Cd_{(g)} + CO_{(g)}}$	550 °C	−94 kJ	>0	(7-3d)
$\mathrm{CdO + CO_{(g)} \longrightarrow Cd_{(g)} + CO_{2(g)}}$	<0	−44 kJ	<0	(7-3e)
$\mathrm{CdO + Fe \longrightarrow Cd_{(g)} + FeO}$	<0	−51 kJ	<0	(7-3f)
$\mathrm{CdO + 3\,FeO \longrightarrow Cd_{(g)} + Fe_3O_4}$	<0	−9 kJ	<0	(7-3g)

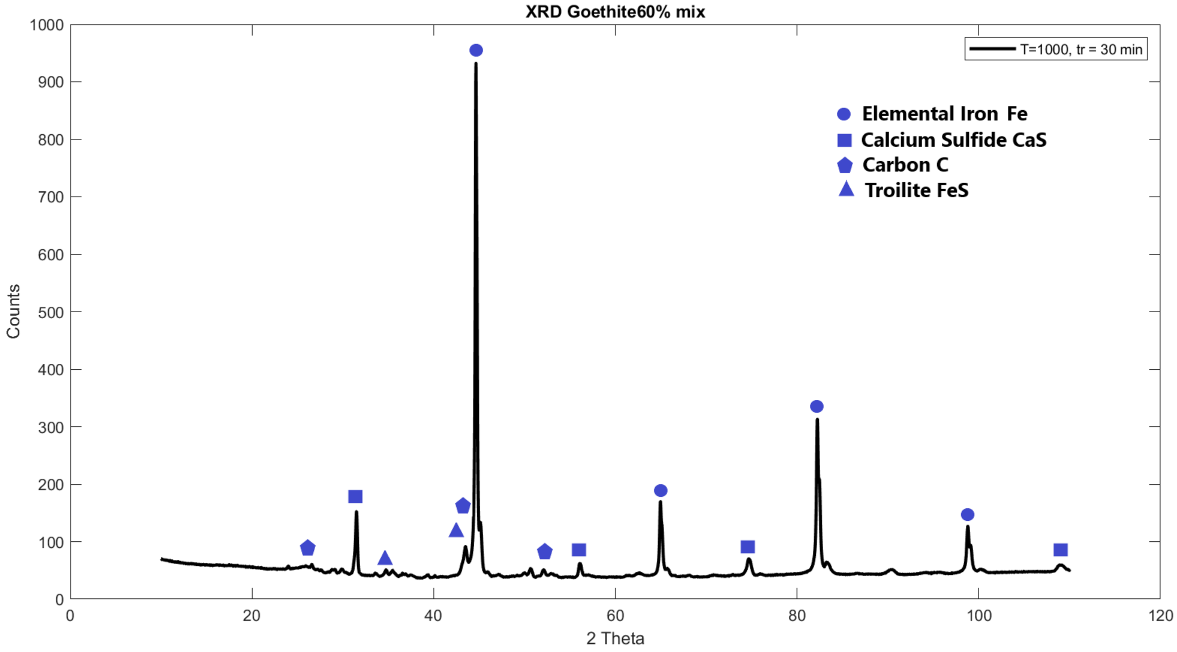
The kinetics play an important role in these reactions as well. An example being reaction 7-3g, in which wüstite is a possible reductant for cadmium oxide. Being a solid-solid reaction, this reaction will be slower, and the full reduction of cadmium oxide will take time. Cadmium has a vapourisation temperature of 767 °C, and will therefore not be present in elemental form after treatment. XRD has shown that cadmium is mostly in oxide form. The reduction of CdO is possible with more forms of iron oxides, however, these are all solid-solid. In absence of carbon in goethite, the reaction is therefore incomplete. The reaction equations detailing the reduction of lead, Equations 7-3a - 7-3c, all use a form of carbon or elemental iron. Neither is present in goethite, hence why lead gets removed effectively from BF and BOF dust but not from goethite.

The temperature dependence of the reactions in Equation set 7-1 can to some degree be explained by the lower reaction rates as well. Additionally, the vapourisation temperature of zinc is higher, at 907 °C. Hence, the large difference for BF dust, where the ZnO can no longer be reduced by carbon, and would not vapourise regardless.

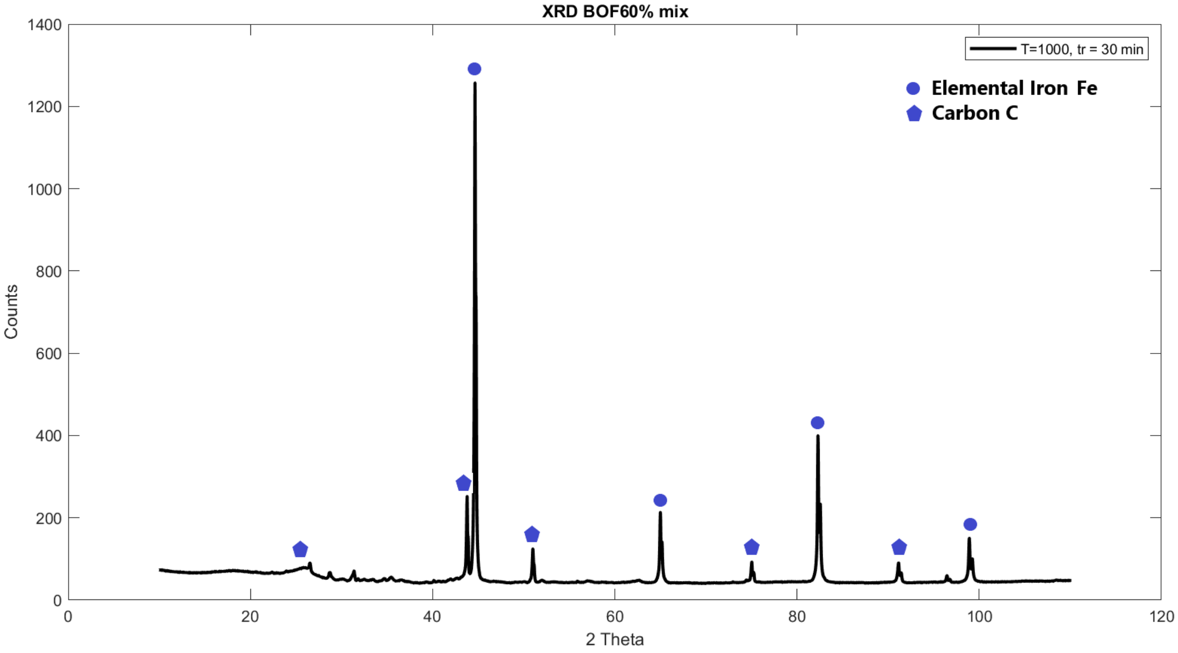
7-3 Mixing Secondary Sources

A key conclusion from the experiments performed on the individual dusts is that carbon is a key component. Its presence in the BF dust lead to full reduction of the iron ore and liberation of the volatile metals. A next step is to mix the dust, and see if the carbon from the BF dust can create similar reducing effects in the other dusts. From the XRD spectra of Goethite 60% and BOF dust 60%, shown in Figure 7-7, it can be concluded that this is indeed the case. Elemental iron dominates the spectra, indicating that the remaining iron oxides from BOF dust are effectively reduced. Zinc is released from the zinc ferrite in goethite, and the iron oxides reduced. Other species that could be detected in the goethite 60% are calcium sulfide and a form of iron sulfide. Other species and elements were impossible identify due to their low concentration or even absence.

From the XRF and LECO values, the same effectiveness can be seen. Selected species



(a)



(b)

Figure 7-7: XRD recorded for Goethite 60% (top) and BOF dust 60% (bottom). The iron reduction is complete in both cases, and the elemental iron peak dominates the spectrum.

Table 7-4: Initial and after treatment at 1000 °C XRF values of selected elements for the double mix dusts. The absolute weight is given assuming a 1g starting sample and accounting for the weight loss.

Goethite 60%

	Initial value		after 10 min			after 30 minutes		
	wt%	weight *[g]*	wt%	weight *[g]*	Δ %	wt%	weight *[g]*	Δ %
Zinc	9.9	0.10	9.1	0.054	45%	1.8	0.009	91%
Carbon	18.2	0.18	13.1	0.077	58%	12.3	0.065	65%
Sulphur	5.2	0.052	2.8	0.017	68%	4.3	0.023	56%
Pb	3.8	0.038	2.0	0.012	69%	0.0	0.0000	100%
Cd	4.8	0.048	0.0	0.0000	100%	0.0	0.0000	100%

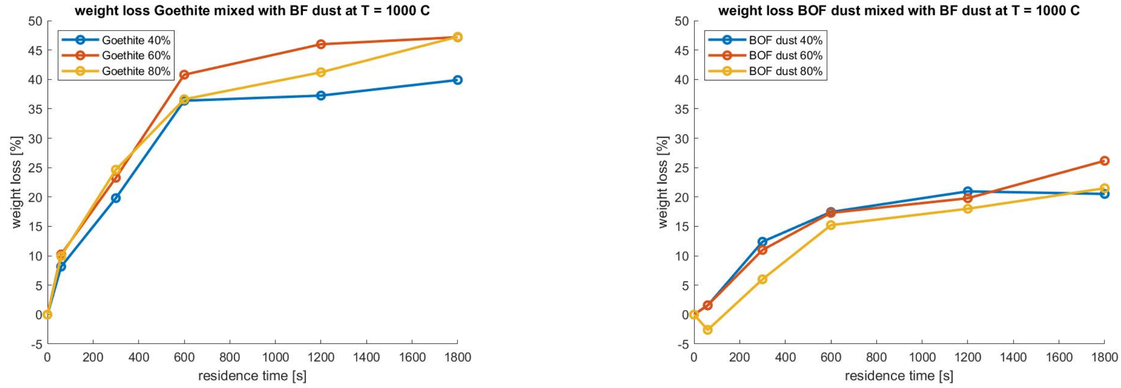
BOF dust 60%

	Initial value		after 10 min			after 30 minutes		
	wt%	weight *[g]*	wt%	weight *[g]*	Δ %	wt%	weight *[g]*	Δ %
Zinc	3.6	0.04	1.3	0.010	71%	0.17	0.0013	97%
Carbon	18.0	0.18	14.7	0.12	32%	13.7	0.10	44%
Sulphur	0.83	0.0083	0.48	0.0040	52%	0.43	0.0032	62%
Pb	0.82	0.0082	0.10	0.0008	90%	0.00	0.0000	100%

are tabulated in Table 7-4, the remaining values can be found in the Appendix. Zinc, lead, and cadmium are removed to a similar degree as in pure BF dust, although in the goethite mix slightly more zinc remains than in the case of the BOF dust mix. It goes to show that the franklinite is effectively broken down by the carbon, as was predicted by the reaction thermodynamics in Equation Set 7-3. It also becomes apparent that the goethite mix consumed significantly more carbon than the BOF mix, despite starting with a similar amount.

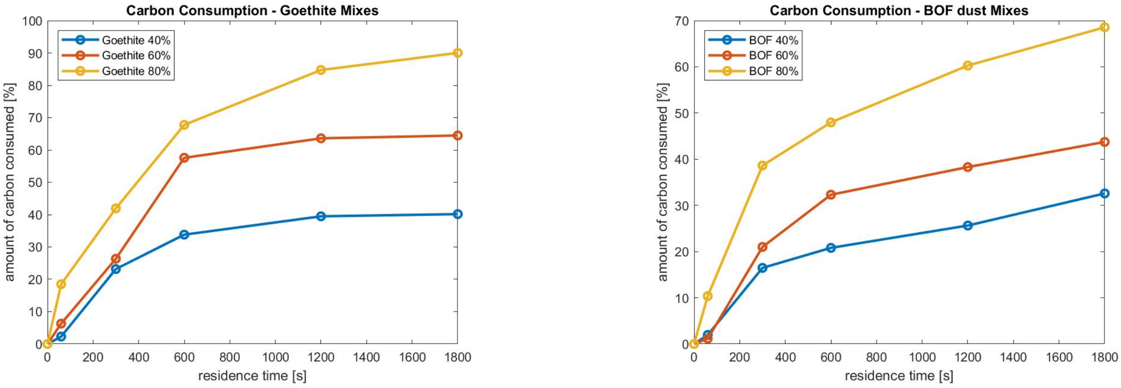
Now, it is imperative to estimate and/ or predict the amount of BF dust that needs to be added in order to reach an optimum reduction behaviour. In order to do so, the carbon consumption, as a measure of the amount of carbon available compared to the amount used, of the samples was measured for the different double mix samples. The weight loss and the carbon consumption graphs are shown in Figure 7-8. What becomes apparent directly from the graphs is that the weight losses are significantly higher than a cumulative value of the weight losses from the individually treated dusts, and that the weight losses between the samples are comparable.

When analysing the trends in the weight losses, a few notes can be made. The extra weightloss for Goethite 40%, Goethite 60% and Goethite 80% when compared to the cumulative weightloss of the individual goethite and BF dust is 12%, 21%, and 22% respectively. A resonable assumption would be that the main interaction between the dusts is due to the carbon, and that by extension there is no extra weightloss due to mixing for the BF dust. The extra weightloss can then be ascribed solely to the goethite species being reduced and vapourised. Extending that logic, the higher the goethite percentile, the higher the extra weight loss should become, a reasoning that holds true until the carbon within the BF dust



(a) Weightloss results after treatment at $1000\,^{\circ}\mathrm{C}$, over different resident times for the goethite mixes

(b) Weightloss results after treatment at $1000\,^{\circ}\mathrm{C}$, over different resident times for the BOF dust mixes



(c) Carbon consumption as a % of the measured total carbon content for the goethite mixes

(d) Carbon consumption as a % of the measured total carbon content for the BOF dust mixes

Figure 7-8: Weightloss results at the top and carbon consumption figures at the bottom for the double mix dusts, in which the goethite and the BOF dust respectively are mixed with BF dust in various concentrations, in which the BF dust acts as a carbon source is more or less fully consumed.

Looking at the carbon usage for the goethite 80% in Figure 7-8c, it can be seen that about 90% of the carbon is used. Upon SEM-EDS investigation, it shows that the remainder of the carbon is dissolved in the elemental iron matrix, or in small carbon particles. Additionally, the gas analyser results show that the reaction is more or less complete after 30 minutes. Extending the trend of the weightloss, expected weightloss for Goethite 80% would be around 30%. Due to the carbon running out, it cannot reach that value. This is confirmed by the XRD and XRF values which can be found in the Appendix, which show that Goethite 40% and Goethite 60% are entirely stripped of volatile metals, whereas Goethite 80% still has a small concentration of these left.

In case of the BOF dust, the trends can be explained following a similar reasoning. The only added weight loss is due to the extra CO and CO_2 escaping from the sample due to the extra iron reduction. Additionally, it can be stated that due to the relatively low values of the carbon consumption, the reactions are finished with plenty of carbon to spare in the sample. The carbon consumption trends are along expected lines, with the BOF dust 80% mix using more than BOF dust 60%, and both more than the BOF dust 40%. The weight losses for these samples are largely comparable, and the extra weight loss is in the range of 2-10%. Since these weightlosses are so similar, it is hard to find and predict a trend. What can be seen from the XRF values is that all volatile metals have been reduced and removed from the sample, both for BF dust and BOF dust. Any zinc that was present is therefore adequately removed, and mixing the dusts has proven an effective measure to improve the reduction rates of the waste dusts.

7-3-1 Carbon stoichiometry prediction

The next step is to make an estimation of of how much carbon is needed, and by extension how much BF dust should be added in order to reach a full reduction. In order to do so, another unit is defined, the carbon progress rate. The carbon progress rate is a measure for how much carbon is consumed over how much carbon is estimated to be needed in the reaction. In order to calculate this rate, the amount of carbon needed needs to be estimated.

The estimation of how much carbon is needed sounds trivial in theory, but in practice is near impossible to be precise. The amount of different carbon consuming reactions is considerable, not to mention that solid carbon as well as CO is able to react. Therefore, some assumptions need to be made in order to get a fair estimation. Thus, within the following estimation, only the full reduction of the iron oxides will be considered. Additionally, the CO contribution to this reduction will be ignored, instead assuming that all reduction is performed by the solid carbon. The first assumption is based on the fact that the samples are mostly iron oxides, making it the dominant species to reduce. Still, this will result in an underestimation. That underestimation is cancelled by the second assumption, as with this assumption more carbon is needed to reach full reduction. Assuming homogeneity in the sample, a prediction can be made by including these assumptions. The accuracy will be verified in later experiments.

In order to create a good estimate, using reactions 7-1a to 7-1f, the mol carbon per mol iron is estimated for the different iron oxides. The following $\frac{C}{Fe}$ are then created: Fe_3O_4 needs 1.33 $\frac{C}{Fe}$, haematite 1.5 $\frac{C}{Fe}$, wüstite 1 $\frac{C}{Fe}$, and franklinite needs 1 $\frac{C}{Fe}$. Additionally, the molar weights of iron and carbon are needed, iron $5.845\,\mathrm{g\,mol^{-1}}$, and carbon $12.011\,\mathrm{g\,mol^{-1}}$.

In order to assess the carbon progress rate for BF dust, the 30 minute sample at 1000 °C is assessed. XRD has shown that this sample is fully reduced, and XRF has shown that the zinc has been fully vapourised from this sample. The four starting numbers are the initial and after treatment weight of the sample, 2.07g and 1.45g, the presence of iron, 35.4wt%, and the presence of carbon, 39.9wt%. Another important value is which minerals of iron oxide are present in BF dust. Mössbauer data has indicated that 66% is haematite, and the remainder elemental iron. The first step is now to assess how much mole iron is to be reduced, and how much carbon is required for that.

$$\frac{Fe_{wt\%} * W_{initial}}{M_{Fe}} = Fe_{mol} \tag{7-4}$$

$$\frac{C_{wt\%} * W_{initial}}{M_C} = C_{mol} \tag{7-5}$$

$$Fe_{mol} * 66\% * \frac{C}{Fe} = C_{mol}^{required} \tag{7-6}$$

The first and second equation show how much mol iron and carbon respectively are present in the sample, by multiplying the weight percentage with the initial weight and dividing by the molar mass. The third equation converts the mol iron into the required mol carbon for full reduction, by multiplying the mol iron present by the % of iron oxides to be converted, then converting that to mol carbon using the appropriate conversion factor. In case of BF dust, the % is 66% from Mössbauer, and the conversion factor is that of haematite, $1.5\frac{C}{Fe}$. It turns out that for BF dust, dividing the $C_{mol}^{required}$ by the total mol carbon, is 18.89% of the carbon present in BF dust.

To get to the carbon progress rate, and thereby assess whether these assumptions lead to a reasonable estimation, the amount of carbon used is needed. This can be calculated similarly to the mol carbon in the initial weight, substituting in the final weight of the sample after treatment and the carbon presence measured by LECO after treatment, 41.5%. This results in 27.33% of the total carbon being used in the thermal treatment. The carbon progress rate is then calculated as:

$$CPR_{BFdust} = \frac{C_{used}}{C_{needed}} \tag{7-7}$$

Substituting in the numbers, the CPR for BF dust is 144.7%. This means that in the current estimations, more carbon is needed than estimated, and as such that there are far more species requiring carbon for their reduction that just their iron. Regardless, the estimation is good enough to continue with, especially since BF dust has the lowest actual iron content of the three dusts and the estimation should therefore be more precise for the other dusts. A merit of this calculation is that it allows an estimation of carbon leftover for reducing the other dusts upon mixing. That would thus be 73% of the total amount of carbon is available for the other dusts.

For BOF dust, using the available Mössbauer data, a similar estimation can be made. Out of the iron oxides, 15% is magnetite, 29% is wüstite, and the rest is elemental iron. BOF dust has too little carbon, and following the calculation made for BF dust, it should be able to supply roughly half the carbon needed. Indeed, the CPR for BOF dust is 52.3%. The remaining needs to be supplied by BF dust, and this can be used to estimate how much BF dust needs to be added to supply the remaining carbon. This prediction is fairly simple, as it has been calculated how much carbon is still needed for full reduction in BOF dust, and it has been estimated how much carbon BF dust can supply per gram BF dust added. Aligning these shows that 6.7% of a sample of BOF dust needs to be BF dust to have enough carbon for predicted stoichiometry.

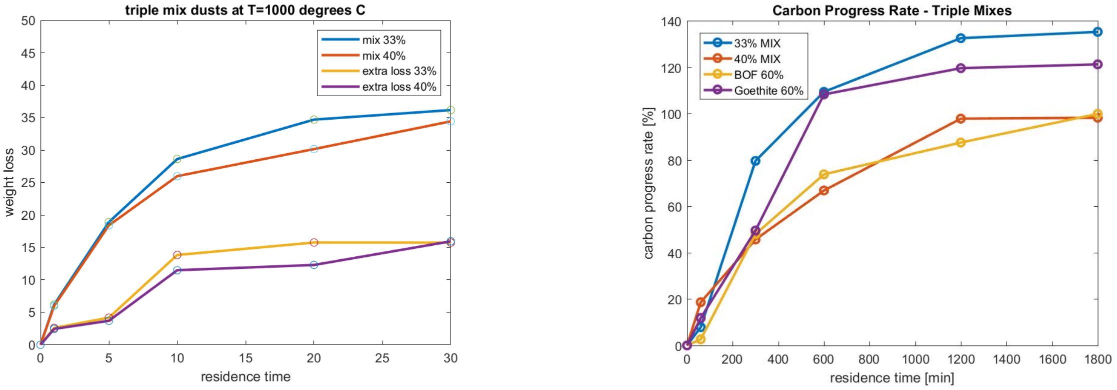
Goethite contains virtually no carbon, so all the carbon needs to be provided. A similar path will be followed for the goethite to get an idea of the stoichiometry ratio of Goethite and BF dust for full reduction of the iron oxides. The Mössbauer data indicates that 42% is zinc ferrite, and 58% is magnetite. Calculating a CPR for goethite is pointless, as it holds no significant carbon. The amount of BF dust needed for stoichiometry is 30.7% of BF dust in a goethite sample should result in full reduction.

Extrapolating this last estimation to the mixed samples, it becomes apparent that indeed the Goethite 80% sample had too little carbon to fully reduce, and thus the weight loss trends are correct. The carbon progress rate for Goethite 40% and 60% indeed exceed 100%, being 110% and 121% respectively, while the Goethite 80% levelled at 85%. Thus, the estimation is somewhat close to the expected value. For BOF dust the predicted results is even closer, having a carbon progress rates of 92, 100, and 94% respectively, from 40% to 80% mixes.

7-3-2 Triple mixes

Now using these estimations the triple mixes are created to test these theorems. For an almost stoichiometric ratio, the 40% mix is chosen, in which 20% BF dust is thus added to equal amounts of goethite and BOF dust. Taking into account that some carbon dissolves in the elemental iron matrix or is otherwise not consumed, this is considered stoichiometry. The 33% mix has an excess of carbon at 258 mmol, and needing about 160 mmol for stoichiometry. Note that for these estimations, not the estimated amount of carbon consumption from BF dust is used but the actual consumption figure from the 30 minute sample at 1000 °C. Also note that this estimation is probably an underestimation, and more carbon is needed than predicted by roughly 25% as shown by the Goethite 80% mix.

The weight losses for the triple mixes as well as the carbon progress rates for the triple mixes and for comparison the 60% double mixes are shown in Figure 7-9. What can be seen is that the 40% mix reaches a carbon progress rate of 98%, whereas the 33% mix reaches 135%. As expected, it seems that the estimated carbon progress rate is too low, and that there are indeed other species requiring carbon for their reduction.



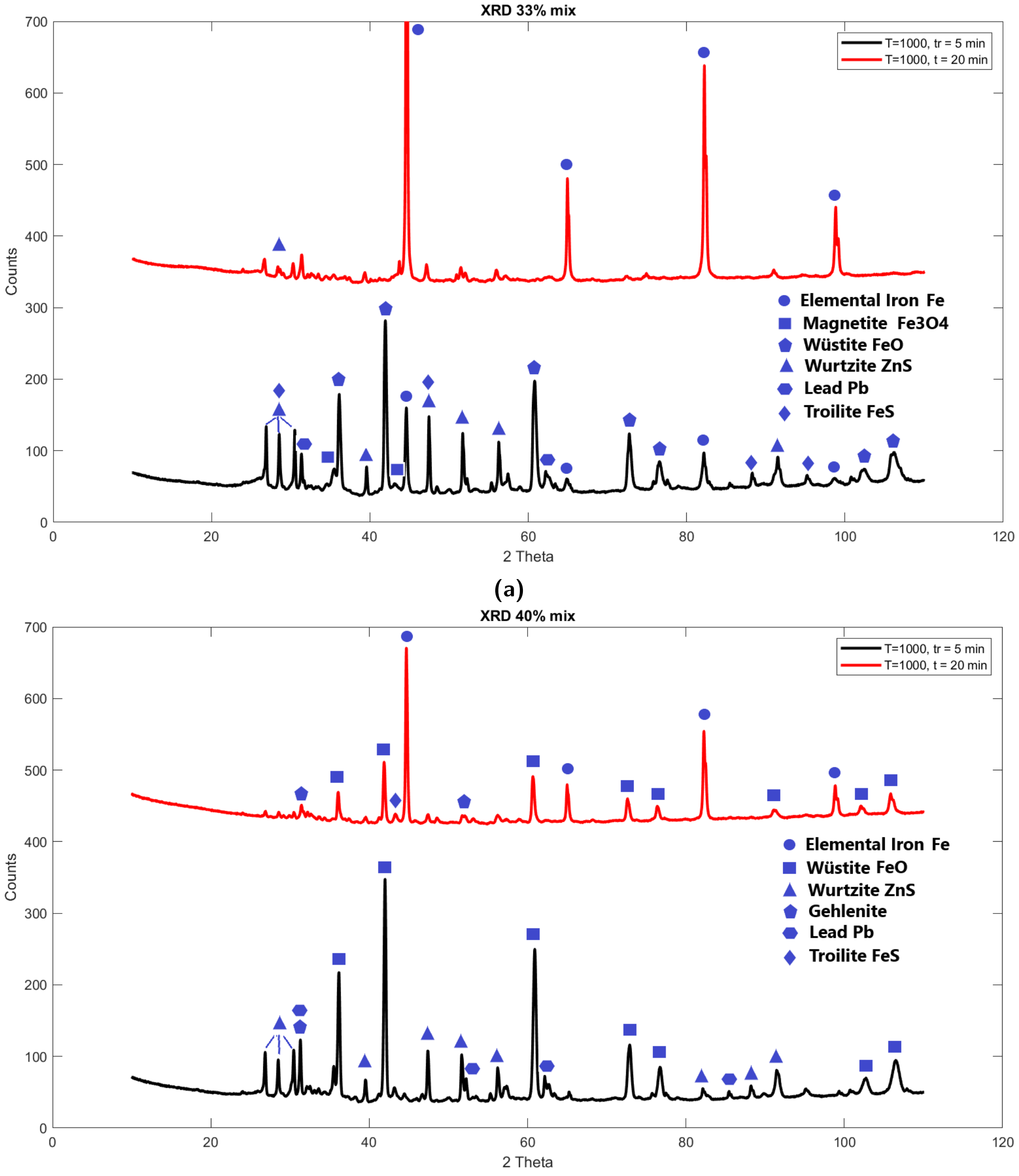
(a) **(b)**

Figure 7-9: Weightloss results on the left for the triple mixes after treatment at 1000 °C, and the carbon progress rate on the right for the 60% double mixes and the triple mixes

To further assess the reaction progress of the triple mixes and whether there is enough carbon content in either, the XRD and XRF spectra are recorded. In Figure 7-10, 4 XRD spectra are shown, with the 33% mix at the top and the 40% mix at the bottom, both after 5 minutes and after 20 minutes of treatment at 1000 °C. The XRF data are shown in Table 7-5 for selected metals, values given being the initial values, after 10 minutes, and after 30 minutes of treatment at 1000 °C. In the XRF values it can be seen that some zinc is still left after 30 minutes, 7% and 15% respectively, however that the lead and cadmium are effectively removed from the sample. The small amounts of zinc left correspond to the values found for the double mixes of goethite, where after 30 minutes of treatment generally 10% of zinc is still found in the sample. The XRD spectra show that the zinc goes through a zinc wurtzite intermediate, clearly seen in the 5 minute curves, and that in excess carbon these disappear in the 30 minute spectra. It clearly demonstrates that the 33% mix has sufficient carbon to reduce everything, while the 40% mix has a short supply, despite being the stoichiometric assumption. This is in line with the expectations based on the double mixes.

Before concluding that the 40% mix indeed contains too little carbon to fully reduce all the iron, the timescale of the reaction is verified using the gas analyser, the results for the 40% mix shown in Figure 7-11. It stands to reason to conclude that the reaction is concluded after roughly 30 minutes, and the bulk of the reduction takes place before that. Some reduction progress can be expected in the 40% mix compared to the XRD, but not enough to fully reduce all the remaining wüstite.

Thus, it can be concluded that the carbon progress rate is an interesting measure to quickly predict the reaction progress, however, that the sample must be analysed beforehand to investigate whether there are other compounds drawing on the carbon to be reduced. For the investigated dusts, it stands to reason that a carbon progress rate of roughly 125% will indicate that the reaction is complete. This can then be used to estimate stoichiometry. Note however, that not all the carbon generally gets used up, so that a slight excess of 5-10%



(a)

(b)

Figure 7-10: XRD recorded for the triple mixes. Two spectra are shown for each mix, 5 minutes in black and 20 minutes in red. It shows the carbon deficiency of the 40% mix.

Table 7-5: Initial and after treatment at 1000 °C XRF values of selected elements for the triple mix dusts. The absolute weight is given assuming a 1g starting sample and accounting for the weight loss.

Triple Mix 33%

	Initial value		after 10 min			after 30 minutes		
	wt%	weight *[g]*	wt%	weight *[g]*	Δ *%*	wt%	weight *[g]*	Δ *%*
Zinc	6.8	0.068	5.2	0.037	45%	0.75	0.0048	93%
Carbon	16.8	0.17	10.0	0.071	57%	7.6	0.049	71%
Sulphur	3.8	0.038	2.9	0.021	44%	3.3	0.021	44%
Pb	2.3	0.023	1.2	0.0089	61%	0.14	0.0009	96%
Cd	1.7	0.017	0.0	0.0000	100%	0.0	0.0000	100%

Triple Mix 40%

	Initial value		after 10 min			after 30 minutes		
	wt%	weight *[g]*	wt%	weight *[g]*	Δ *%*	wt%	weight *[g]*	Δ *%*
Zinc	7.3	0.073	5.4	0.040	45%	1.7	0.011	85%
Carbon	10.0	0.10	5.9	0.044	56%	2.6	0.017	83%
Sulphur	4.1	0.041	2.3	0.017	58%	2.8	0.019	54%
Pb	2.6	0.026	0.9	0.0063	76%	0.1	0.0008	97%
Cd	1.8	0.018	0.0	0.0000	100%	0.0	0.0000	100%

carbon is preferable.

7-3-3 Wurtzite

Another observation was recorded that is worth of discussion. The XRF data shows that there is some zinc left after the thermal treatment of 30 minutes at 1000 °C. In order to investigate where the remaining zinc is, an identification using SEM-EDS is performed. For the triple and double mixes, it turned out that some of the zinc is left in the wurtzite particles identified with XRD. Additionally, low concentrations of zinc are still scattered throughout the iron matrix. These concentrations are on the detection limit of the SEM-EDS, however show consistently. This excess zinc is dissolved in the iron matrix, as zinc is to some degree soluble in elemental iron.

An additional question can be raised looking at the results is the formation of wurtzite. These particles can be identified on the SEM, and a typical SEM image for the mixed dusts is shown in Figure 7-12. The mix shown is the Goethite 80% after 5 minutes of treatment. There are 5 distinct phases that can be identified, four of which are identified by colour coding. The particles indicated by the yellow squares are particles high in carbon. These particles shrink over the thermal treatment time, and due to being larger than the average particle, are easy to identify in every mix. The red particle is a $CaSO_4$ particle, which has earlier been shown to form upon dehydration. These rod like particles are present in any mix

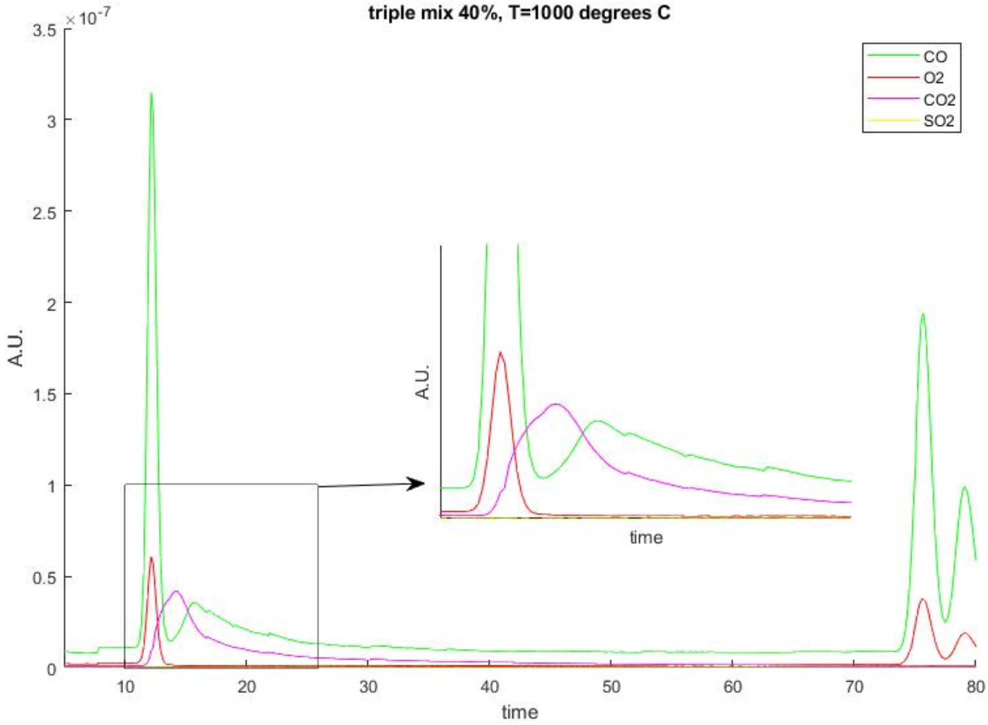
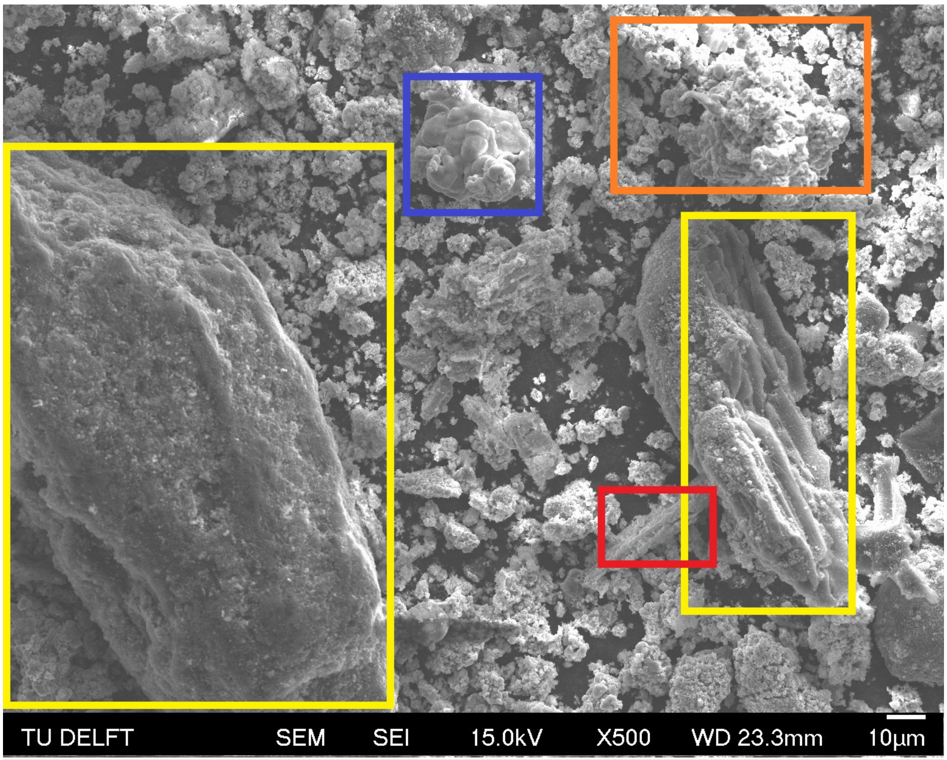


Figure 7-11: Gas analyser results of the 40% mix, treatment at $1000\,^{\circ}\mathrm{C}$, under Argon atmosphere. Using the set-up with the rubber stoppers. The air peak is the onset of the reaction, and it can be seen that for full completion, about 30 minutes of treatment are needed. This is very similar for the other mixes.



Particle	C	O	Fe	S	Zn	Ca
Yellow	50-65%	15-25%	12-18%			
Blue			6%	30%	45%	
Red	10%	33%	8%	20%		27%
Orange		20%	50%	10%	15%	

Figure 7-12: SEM image of Goethite 80%, after 5 minutes of treatment. This image is representative for the other mixed dusts containing goethite, and gives a good overview of the 5 main phases identified in the mixtures. The fifth phase are the small iron particles dispersed everywhere, with roughly similar composition to the Orange particles.

that contains goethite, which is therefore the most likely supplier. The particle indicated by orange is a typical particle with an iron matrix and a wide range of other elements dissolved in it. These particles are everywhere, and have the same composition as the fifth phase, the fine particles scattered everywhere. Upon performing EDS on the smaller particles, the carbon tape interferes with the signal, creating large amounts of carbon in these particles.

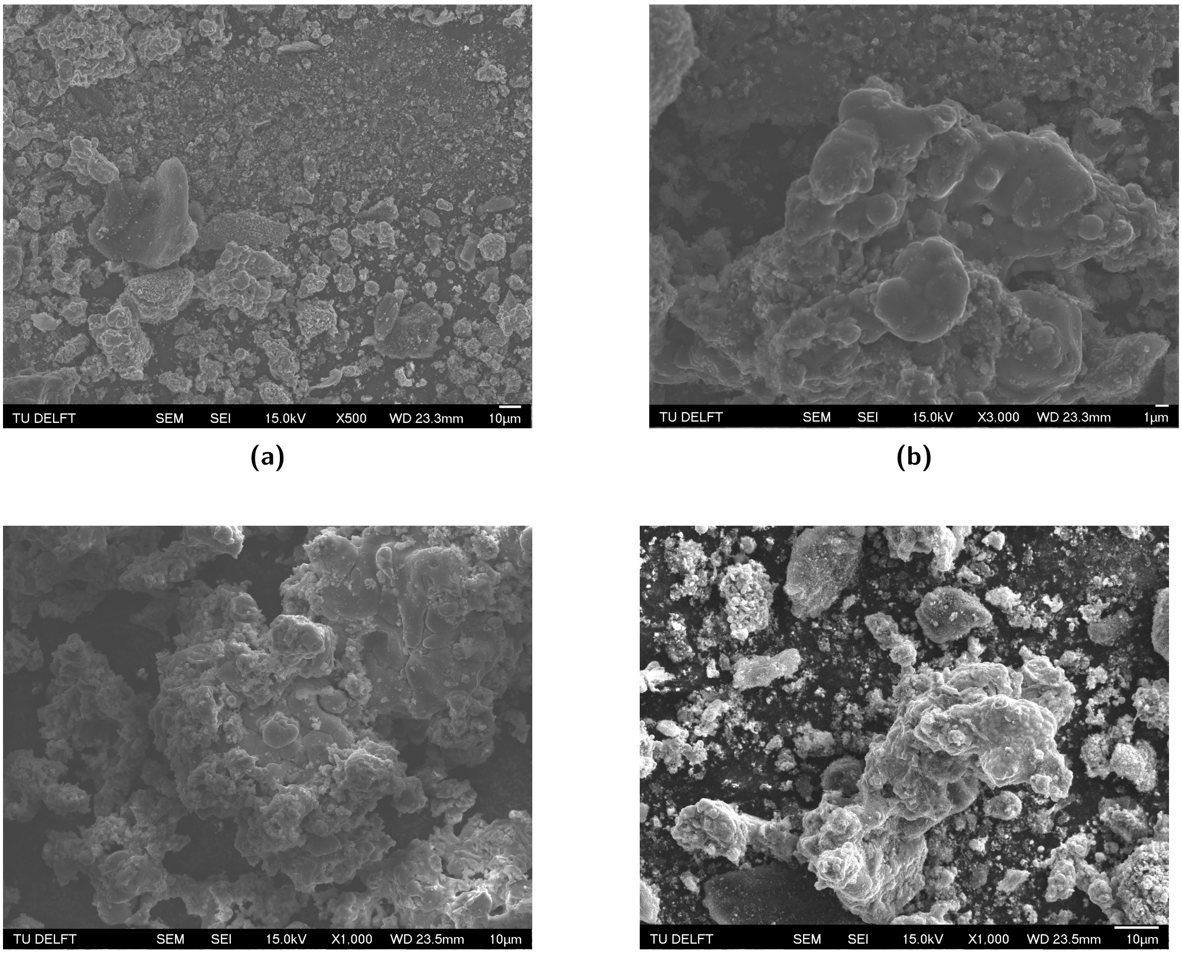
The blue particle is of interest here, being a nearly pure ZnS particle. These can be found abundantly in any of the mixes containing goethite after 2-10 minutes of treatment at high temperature. These cannot be found in the mixes of BOF dust and BF dust, even though the BF dust has ZnS as the dominant zinc mineral. In the BF dust, these ZnS particles are more dispersed throughout the sample, just like all the untreated samples are more homogeneous in particle composition. Take as a comparison the SEM picture of goethite in the Initial Characterisation section, Figure 7-1b. The particles are all very similar looking, and are more homogeneous. By extension, it means that the different shapes and sizes of particles are not native to the dusts, but instead form upon thermal treatment.

The formation of wurtzite during the reduction of these industrial waste dusts cannot be found within literature, despite the extensive research on these dusts. Han and colleagues [73] describes a similar formation of wurtzite under controlled conditions, in which fine wurtzite particles grow from zinc oxide in the presence of iron oxide and S_2 gas. Following a similar logic, consider the following reactions for the formation of wurtzite out of $CaSO_4$ and ZnO:

Reaction	T_{onset}	$\Delta G^{1000\,°C}$	ΔH	
$CaSO_4 + C \longrightarrow CaO + SO_{2(g)} + CO_{(g)}$	850 °C	−65 kJ	>0	(7-8a)
$2\,C + 2\,SO_{2(g)} \longrightarrow S_{2(g)} + 2\,CO_{2(g)}$	<0	−254 kJ	<0	(7-8b)
$2\,ZnO + 1.5\,S_{2(g)} \longrightarrow 2\,ZnS + SO_{2(g)}$	<0	−27 kJ	<0	(7-8c)
$2\,ZnO + S_{2(g)} + C \longrightarrow 2\,ZnS + CO_{2(g)}$	<0	−243 kJ	<0	(7-8d)

SO_2 gas forms upon reaction of $CaSO_4$ with carbon, as shown by Kuusik and colleagues [74], reaction equation 7-8a. Sulphur gas can form from SO_2 gas, as described by Araki and colleagues [75], shown in reaction equation 7-8b. The third and fourth reactions are described as a forming mechanism of ZnS from S_2 gas by Han and colleagues, and show how zinc oxide can form fine growing particles of ZnS [73]. In their work, they describe that the ZnS form small, fine particles that grow with time. Thermodynamic calculations have shown that this reaction speeds up considerably with carbon, however it is possible without. To further investigate the growth, and see whether it complies with the information from Han and colleagues, consider Figure 7-13, where 4 SEM images are shown. In the first image, Goethite 60% after 5 minutes, 3 out of the 4 particles described earlier can be observed, only the $CaSO_4$ missing. The second image, Figure 7-13b, is zoomed in on the big particle with ZnS outcrops in the center of the first image. Three interesting observations can be made using these 2 images. There is a large carbon source, providing the carbon and the CO needed in these reactions. Additionally, just above and underneath the ZnS outcrops, iron bearing particles can be observed, most likely the donators of the zinc in the form of ferrite. The ZnS particle therefore grows on top of the iron particle, and indeed forms fine, growing crystals in the form of the outcrops. All elements are present in close vicinity save for the S_2 gas, but being a gas it will be present if formed regardless. Kinetically, it can therefore be stated that the formation of the ZnS particles, involving mostly solid-gas reactions, is much quicker than the direct reduction of ZnO with carbon, a solid-solid reaction. The reduction of ZnO with CO is not favourable as shown in reaction equation 7-1l, explaining the wurtzite intermediate over direct ZnO reduction.

Another proof for this reaction mechanism is found in the filter dust. For the 33% mix dust sample of 1 hour, steelwool was placed near the gas outlet inside the furnace, and used a condensation site for zinc and sulfur vapour. The dust captured with this steel wool was analysed with SEM-EDS, and the particles found contained large quantities of elemental sulfur, others contained elemental zinc and zinc oxide. Thus, it seems that SO_2 can indeed be further reduced to S_2 gas. The boiling point of sulphur is at 445 °C, the melting point around



(a) **(b)**

(c) **(d)**

Figure 7-13: SEM images highlighting specific ZnS particles. The ZnS particles shown are average for the composition, in size and in location. Note that as the retention time in the hot zone of the furnace increases, the ZnS particles become smaller after 5-10 minutes, and are very small after 30 minutes. Top pictures are Goethite 60% after 5 minutes, bottom left Goethite 80% after 30 minutes, bottom right 33% mix at 1300 °Cafter1minute.

115 °C, hence why at the end of the quenching zone it condensates in the filter. Low amounts of SO_2 gas were found on the gas analyser, indicating that not all is reacted with carbon.

Over time, the ZnS particles decrease in size again, allowing the zinc to vapourise. In the 30 minute samples, no ZnS fine particles can be found in case of excess carbon. Only in Goethite 80%, being short on carbon, one ZnS outcrop could be identified, shown in Figure 7-13c. The XRD showed that large amounts of ZnS have formed over the course of the treatment, and these can indeed be identified in SEM pictures after 5 minutes. In the 30 minutes however, these have mostly disappeared.

No mechanism could be identified in the process of this study for ZnS reduction and subsequent zinc metal vapourisation. In literature, often a hydrogen or oxygen source is used to achieve this, however, neither are present within the mixes. Using thermodynamic calculations, several possible reductants were investigated, including CO and CaO. Additionally, the potential substitutes were investigated, such as FeO. None of these proved to be favourable, often achieving the reverse reaction.

7-4 Mechanistic and Kinetic Investigations Overview

At this point, it is worth it to revisit the mechanism detailed in the preceeding part of this chapter, and make some last remarks on the reactions and the kinetics of the zinc removal from the sample. A large variety of reactions is proceeding simultaneously, and competing mechanisms are available. Therefore, a short recap is in order.

It can clearly be stated that carbon is needed to effectively reduce the zinc out of the sample, and in case the dust does not contain any carbon source, such as goethite, that zinc is not vapourised. Thus, the sample to be thermally treated is only self-reducing when there is a carbon source, for example when creating a mix of BF dust and goethite. It was estimated that about 30% BF dust in a sample of goethite is roughly stoichiometric, and 7% for BOF dust. However, since these are underestimations, more carbon is needed for full reduction and effectively vapourising all the zinc. However, using excess carbon in the feed material can potentially disrupt the thermal balance of the furnace, which must be accounted for when adding these dusts to HIsarna.

A summary of the reaction mechanism can be seen in the following equation,

$$\mathrm{ZnO \cdot Fe_2O_3 \xrightarrow{CO} Fe_3O_4 + ZnO \xrightarrow{S_2,\,C} ZnS \longrightarrow Zn_{(g)}} \tag{7-9}$$

This shows the three identified zinc minerals, and it shows that in order to reduce zinc ferrite it has to pass through all of them. Additionally, zinc oxide can also be reduced by carbon directly to zinc metal. The first step is cracking the franklinite using carbon, which is favourable over 700 °C with solid carbon and happens relatively quick after entering the furnace. This reaction, as well as the reduction of other iron oxides including magnetite, haematite, and wüstite, are a source of CO to other reactions happening in the furnace. The demand for CO from the iron oxide reduction levels off after all iron oxides are reduced to wüstite, as the reduction of wüstite with CO is not feasible over 600 °C according to reaction equation 7-1f.

After the zinc ferrite has been reduced to zinc oxide, the zinc oxide reacts with sulfur gas, to form wurtzite. This reaction is fast, being a solid-gas reaction, and is thermodynamically favourable at any temperature. The formation of ZnS seems to peak between 5-10 minutes, and is possible complete at this stage of the reaction. The wurtzite grows in fine particles on top of zinc donating iron particles.

The sulfur gas forms as a result of 2 subsequent reactions. First, the $CaSO_4$ reacts with carbon to form SO_2 gas, which then reacts with the carbon further to form S_2 gas. This then reacts with the zinc oxide to form zinc sulphide. Evidence of this reaction has been found in particles in the filter dust, which were almost pure sulfur.

The ZnS particles decay over time, releasing the zinc in the form of zinc metal that can escape the sample. How this mechanism works and what intermediates are formed could not be determined within this research, however it can be concluded that it does decay. SEM images at different retention times show that the particles become smaller after roughly 10 minutes, and the XRF and XRD show that the zinc gets removed effectively from the sample. However, the reaction is slow and takes time, being almost completed after 30 minutes of treatment at 1000 °C.

A last consideration for the mechanism is to check whether it holds at higher temperature. To that end the 1300 °C runs were performed. It turns out that most of the observations are similar, but that the time needed to reach the endstate is reduced considerably. The 33% mix held no zinc anymore after 5 minutes of treatment, whereas this would take 20 minutes at 1000 °C. Similarly, ZnS particles could be identified after 1 minute in this sample. For goethite, it was verified that the zinc ferrite would not crack at 1300 °C, and XRF confirmed that only a small amount of the zinc has left the goethite after 5 minutes. This amount is similar to the 30minute sample at 1000 °C. Therefore, it can be concluded that the mechanism holds at the higher temperature.

Chapter 8

Conclusions and Further Recommendations

HIsarna is a promising new innovation in the steel industry, and has been shown to have the potential to replace traditional iron smelters in the future. An important aspect of the HIsarna lies in its higher tolerances for gangue elements. This can unlock new feed streams, and possibly even waste streams currently being landfilled. Additionally, it is possible to enrich the flue dust with zinc by using feed materials with high zinc fractions. Such a flue dust could be fed to the zinc smelters, recovering zinc metal.

To investigate the optimisation of this zinc enrichment in the flue dust, research is being done in the ReclaMet project. One of the aspects is the inclusion of waste dusts. Effectively and efficiently feeding these into HIsarna for zinc enrichment requires a solid foundation of their behaviour at high temperatures.

This thesis focuses on providing that foundation, specifically for three dusts, goethite, Blast Furnace (BF) dust, and Basic Oxygen Furnace (BOF) dust. These dusts were subjected to thermal shock experiments, and the products were characterised in depth.

A literature study was conducted to investigate which alternative waste streams are available for HIsarna to aid the zinc enrichment of the flue dust. First, the restrictions HIsarna imposes on these dusts were investigated. Important is that the alternative streams do not hamper the iron quality of the product or the productivity of HIsarna. Large additional wear and tear on the furnace is unacceptable, as this would reduce the longevity of the furnace. Lastly, a new feed stream material must contain sufficient iron and zinc.

For the inclusion of many interesting streams, there are still challenges to overcome. As an example, slag wastes generally hold significant iron and zinc content to serve as a feed material. Due to their large, often fluctuating, lime and silica contents, slag quality could deteriorate, and more research is needed to prevent that. Another interesting material for inclusion in HIsarna are copper flue dusts, after recovery of the copper content. Copper poses a challenge to the hot metal quality, and as such cannot be present in large amounts in the feed stream. A pre-processing step is needed to scrub the copper from the flue dusts, after which these form an interesting alternative for feeding into HIsarna.

Iron-bearing sludge wastes from the zinc smelters face a similar problem. Their iron and zinc content are ideal, and they contain very few gangue elements that would compromise the above restrictions. Especially goethite and jarosite are of interest. Their copper contents are too high at the moment, however, after copper recovery these would be ideal candidates. This is currently already being investigated, and it is likely that this will be solved quickly.

Other zinc-bearing sources are unlikely, as they often suffer from low collection rates, are often contaminated with other materials, or already have a high zinc fraction. In the latter case, it is more efficient to recycle to the zinc smelters directly.

Galvanised steel scrap is a suitable option for zinc enrichment in HIsarna. It contains virtually no gangue elements if it is pure scrap, consists mostly of iron and has a significant zinc fraction. A challenge to overcome is the current collection system, which means that the composition is often not know. EOL scrap suffers from this by-and-large, as separation techniques are not accurate enough to separate types of steel. EOL scrap can carry gangue elements that could harm HIsarna, including oil and plastics, however with sufficient pre-processing this should not be a problem.

A solution for the unknown composition of EOL scrap or other types of steel scrap is to treat them in the Electric Arc Furnace (EAF) first. EAF dust is often recycled internally until a concentration of zinc is reached that does not allow for further processing. At that point, the dust is discarded. This dust holds significant potential for zinc enrichment of HIsarna flue dust. Recycling the scrap first into the EAF and then recycling the EAF dust after a certain zinc fraction threshold is reached into HIsarna would allow for more efficient and effective zinc recovery.

The three waste dusts that were chosen for the research are goethite, BF dust, and BOF dust. These dusts were selected for their high iron and zinc content. Although the provided BOF dust does not contain much zinc, it was investigated because it can hold significant zinc. These dusts were intensively characterised and then subjected to thermal shock treatment at various temperatures and various residence times. The dusts were investigated both individually and mixed.

From the conducted work, the following mechanism pathway the zinc bearing compounds go through was identified, and can be summarised as follows:

$$\mathrm{ZnO\cdot Fe_2O_3} \xrightarrow{\mathrm{CO}} \mathrm{Fe_3O_4} + \mathrm{ZnO} \xrightarrow{\mathrm{S_2,\,C}} \mathrm{ZnS} \longrightarrow \mathrm{Zn_{(g)}} \tag{8-1}$$

The main source of zinc in goethite is zinc ferrite, a compound that needs a good reductant species to decompose. Carbon turned out to be a key component, and was supplied handsomely by the BF dust upon mixing the dusts. After decomposing the $ZnO\cdot Fe_2O_3$ to an iron oxide and zinc oxide, the zinc oxide can be further reduced. This can either be done directly by carbon, yielding zinc metal, or via a zinc sulfide intermediate by reacting with S_2 gas. The zinc sulfide intermediate grows as a fine particle during the treatment, and slowly decomposes over time, releasing the zinc. Therefore, it can be stated that zinc can effectively be liberated from the most common zinc minerals present in the dusts.

An important aspect of adding the zinc-rich feed materials to HIsarna is that they can be vapourised quickly. Large amounts of zinc in the lower parts of the furnace can be detrimental to the quality of the hot metal and to the longevity of the furnace. Therefore, the timescale of the mechanism is important. To that end, it was investigated whether the reaction time can be shortened with an increase in temperature. At 1000 °C, the time needed for full zinc evaporation is between 20 and 30 minutes. At 1300 °C, this was shortened to under 5 minutes. Hence, it lies within reason to assume that at the higher temperatures of the cyclone, most of the zinc will have vapourised quickly enough. Furthermore, the reducing atmosphere within the cyclone will further speed up the reduction.

Mixing the different dusts has a positive effect on the reduction of the oxide species, and by extension on the vapourisation of zinc. The main interaction between the dusts is via the carbon supplied by the BF dust, and the amount of carbon needed to reach full reduction was estimated. The estimations turned out to be reasonable, allowing a prediction of what mix would be ideal. Mixing BF dust into the goethite, 30% of the mix needs to be BF dust to achieve full reduction. For the used BOF dust, this estimation is 7%.

Another benefit of mixing the dusts is that it allows greater control over the composition of the feed material added into HIsarna. This allows, for example, for a reduction of coal requirements. If the iron oxides are reduced by the carbon in the sample, no additional coal is required to achieve this. A similar point can be made for adding materials that include slag materials such as lime and silica. If these are added to the cyclone, less virgin material is needed.

Besides the vapourisation of zinc and the reduction of iron, several other elements played an important role in the process. The dominant species of calcium and sulphur, both of which play a role in the mechanism, is $CaSO_4 \cdot 2\,H_2O$. Early on in the treatment, the calcium sulfate hydrate salts were dehydrated, after which the remaining $CaSO_4$ was reduced to CaO and SO_2. The SO_2 gas was further reduced to S_2 gas, which either left the sample and condensated in the filter dust, or reacted with zinc oxide to form a fine, growing zinc sulfide particle.

Two elements that were effectively reduced and vapourised are cadmium and lead. Cadmium oxide can react with carbon, carbon monoxide, metal iron, or wüstite, to form elemental cadmium vapour. Lead sulfide can react with lime and carbon to form elemental lead. These elements will both condensate in the flue dust, enriching it significantly. High lead concentrations in the flue dust might hinder the roasting process in the zinc smelters, and are as such an element to avoid in the feed material.

Having found answers to all of the subquestions, it is time to take another look at the main research question:

Will the zinc present in an industrial waste dust be reduced and vapourised under thermal treatment, and be removed effectively, efficiently, and selectively?

The answer is more complicated than a simple yes or no. It is dependent on the waste dust, as a carbon source must generally be present to effectively reduce the zinc bearing compounds. If this carbon source is natively present in a waste dust, it can be considered self-reducing. When the reduction is complete, the vapourisation of zinc is quick and efficient, leading to an almost complete removal from the sample. Without a native carbon source, carbon must be added to the dust, otherwise no zinc removal takes place under inert atmosphere.

While zinc can be removed effectively, the efficiency and selectivity are more complicated. The formation of zinc sulfide using sulphur gas presented a competing mechanism to the quicker direct reduction of zinc oxide. This costs time, however, as pointed out earlier, this is not necessarily cause for concern as the decomposition is relatively quick at higher temperatures. The thermal treatment is not selective, and other elements including sulphur, cadmium, and lead were vapourised and rejected to the flue dust in addition to the zinc.

Further research is certainly warranted, as the analysed alternative streams hold potential for inclusion in the HIsarna feed. This would recover the iron and zinc, and would reduce the impact of these waste streams on the environment.

8-1 Future research recommendations

With the fundamental research into the thermal behaviour of alternative feed materials conducted, additional research can be carried out. A good first step would be to investigate whether the mechanism holds under a reducing atmosphere. The timescale of the reactions could be shortened significantly under a reducing atmosphere, and it is worth verifying the mechanism under these conditions.

Closer mimicking of the real furnace conditions would entail using a vertical drop tube furnace. This would allow dropping the dusts through a reducing atmosphere at high temperature into an iron melt. By creating conditions more closely resembling HIsarna, the behaviour of the dusts can be monitored and verified in a closed system. This would further investigate the timescale of the reactions, to see whether the zinc and other gangue elements will reach the iron melt, and if they do, what their effects will be.

A further mechanistic and kinetic study would help identify the bottlenecks of the system and how these can be solved. As indicated earlier, the mechanism at which the zinc sulfide decomposes is unclear. This research can, for example, be done by creating a closed system similar to the one described in the work of Han and colleagues [73]. Creating a controlled environment where the crystals can grow, their decomposition can then be controlled by varying the atmosphere and the temperature. Finding an optimum atmosphere for reduction could then aid in more efficient zinc release and subsequent vapourisation.

As a last example of further research, it can be investigated how the direct reduction of zinc oxide with carbon can be promoted over the formation of zinc sulfide. The direct reduction is more efficient, and will thus lead to quicker vapourisation of the zinc. It is undesirable that zinc reaches the SRV, and as such it is better that it is reduced quicker. It is possible that in a reducing atmosphere, such as a carbon monoxide atmosphere, this already happens. Aside from promoting the direct reduction, the formation of zinc sulphide can perhaps also be suppressed. This can be done by preventing the formation of sulphur gas, or by lowering the amount of sulphur in the feed material.

Appendix A

XRF table values

In this Appendix the XRF values for selected mixtures are displayed. These values are the measured XRF values, corrected for carbon. At the bottom of the table is the Sum before Normalisation displayed, this sum is before the carbon correction. Values are reported down to 0.5%, elements with lower concentrations are omitted from the appendix.

Table A-1: XRF values for the goethite. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

Goethite

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		21.7 %	24.2 %
Fe	55.4 %	59.5 %	58.5 %
Zn	12.0 %	13.4 %	14.5 %
Ca	8.7 %	8.0 %	8.0 %
S	8.4 %	4.8 %	3.9 %
Pb	5.0 %	6.1 %	6.2 %
Si	4.0 %		1.8 %
Cd	5.0 %	1.9 %	1.7 %
Al	1.5 %	1.7 %	1.2 %
Cu	0.8 %	0.8 %	0.8 %
Mn	0.8 %	0.8 %	0.9 %
Na	0.6 %	0.7 %	n.d.
C	0.07%	0.03%	0.04%
before norm.	102.9 %	91.9 %	84.3 %

Table A-2: XRF values for the BF dust. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

BF dust

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		14.8 %	30.1 %
Fe	35.4 %	39.3 %	40.9 %
Zn	6.2 %	3.8 %	0.3 %
Cd	3.6 %	n.d.	n.d.
Si	3.3 %	3.8 %	5.1 %
Ca	2.3 %	2.6 %	2.7 %
Al	2.0 %	2.4 %	3.2 %
S	1.6 %	1.2 %	1.2 %
Pb	1.6 %	0.8 %	n.d.
K	1.3 %	1.3 %‘	1.3 %
Rb	0.9 %	1.0 %	1.3 %
Mg	0.7 %	1.0 %	1.4 %
Na	0.6 %	0.4 %	0.6 %
C	39.9 %	41.2 %	41.5 %
before norm.	94.4 %	76.8 %	67.5 %

Table A-3: XRF values for the BOF dust. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

BOF dust

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		6.4 %	7.0 %
Fe	85.4 %	90.1 %	91.0 %
Ca	8.1 %	6.4 %	6.3 %
Mg	1.1 %	0.5 %	0.5 %
Si	0.8 %	0.9 %	0.7 %
Mn	1.0 %	1.0 %	1.0 %
Zn	0.7 %	0.5 %	0.2 %
C	2.3 %	0.1 %	0.1 %
before norm.	91.7 %	66.6 %	61.4 %

Table A-4: XRF values for Goethite 40% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

Goethite 40%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		17.9 %	12.2 %
Fe_2O_3	39.3 %	41.2 %	43.7 %
SO_3	7.0 %	4.4 %	6.0 %
ZnO	6.6 %	4.5 %	0.3 %
SiO_2	5.0 %	7.8 %	8.6 %
CdO	3.6 %	n.d.	n.d.
Al_2O_3	2.6 %	4.7 %	5.1 %
PbO	2.0 %	0.6 %	n.d.
MgO	0.8 %	1.5 %	1.7 %
Na_2O	0.7 %	0.5 %	0.3 %
C	25.4 %	26.5 %	25.3 %
before norm.	97.1 %	88.7 %	93.2 %

Table A-5: XRF values for the Goethite 60% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

Goethite 60%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		21.3 %	20.6 %
Fe_2O_3	46.9 %	46.9 %	49.0 %
SO_3	9.6 %	5.9 %	7.6 %
ZnO	7.4 %	6.9 %	1.3 %
SiO_2	4.7 %	8.7 %	9.9 %
CdO	3.8 %	n.d.	n.d.
Al_2O_3	2.4 %	5.4 %	6.1 %
PbO	2.4 %	1.3 %	n.d.
MgO	0.7 %	1.5 %	1.6 %
Na_2O	0.7 %	n.d.	0.7 %
C	18.2 %	11.4 %	12.3 %
before norm.	100.1 %	92.4 %	91.5 %

Table A-6: XRF values for Goethite 80% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

Goethite 80%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		16.0 %	21.9 %
Fe_2O_3	53.6 %	53.6 %	57.7 %
SO_3	12.7 %	4.7 %	6.6 %
ZnO	8.8 %	9.3 %	1.7 %
SiO_2	4.7 %	7.6 %	9.2 %
PbO	3.0 %	1.8 %	n.d.
Al_2O_3	2.4 %	4.3 %	5.6 %
CdO	1.9 %	n.d.	n.d.
MgO	0.8 %	0.6 %	0.7 %
Na_2O	0.8 %	n.d.	0.7 %
C	8.5 %	5.3 %	1.8 %
before norm.	96.8 %	66.6 %	61.4 %

Table A-7: XRF values for BOF 40% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

BOF 40%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		5.1 %	−1.2 %
Fe_2O_3	52.9 %	52.7 %	52.7 %
SiO_2	5.0 %	7.9 %	8.1 %
CaO	4.6 %	4.2 %	4.3 %
ZnO	3.8 %	0.7 %	0.1 %
SO_3	2.2 %	1.3 %	0.9 %
Al_2O_3	2.5 %	4.5 %	4.5 %
MgO	1.3 %	1.8 %	1.8 %
PbO	0.8 %	0.0 %	n.d.
Na_2O	0.6 %	0.6 %	0.6 %
C	24.4 %	23.4 %	23.7 %
before norm.	91.6 %	88.5 %	89.9 %

Table A-8: XRF values for BOF 60% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

BOF 60%

Compound	initial	after 10 min	after 30 min
weightloss [wt%]		7.0 %	9.9 %
Fe_2O_3	58.7 %	52.7 %	52.7 %
CaO	5.3 %	5.1 %	5.0 %
SiO_2	3.9 %	7.9 %	8.1 %
ZnO	2.8 %	0.7 %	0.1 %
Al_2O_3	1.9 %	4.5 %	4.5 %
SO_3	1.6 %	1.3 %	0.9 %
MgO	1.3 %	1.8 %	1.8 %
PbO	0.6 %	0.0 %	n.d.
Na_2O	0.6 %	0.6 %	0.6 %
C	24.4 %	23.4 %	23.7 %
before norm.	101.0 %	81.6 %	81.4 %

Table A-9: XRF values for BOF 80% mix. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

BOF 80%

Compound	initial	after 10 min	after 30 min
weightloss [wt%]		6.9 %	9.9 %
Fe_2O_3	73.1 %	73.2 %	52.7 %
CaO	6.9 %	5.8 %	5.0 %
SiO_2	3.0 %	5.7 %	8.1 %
ZnO	1.8 %	n.d.	n.d.
MgO	1.4 %	1.4 %	1.2 %
Al_2O_3	1.1 %	3.2 %	2.7 %
SO_3	0.9 %	0.7 %	0.4 %
PbO	0.3 %	n.d.	n.d.
C	9.8 %	6.3 %	4.1 %
before norm.	94.3 %	77.9 %	58.0 %

Table A-10: XRF values for 33% MIX. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

MIX 33%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		13.8 %	15.7 %
Fe_2O_3	50.6 %	56.2 %	57.2 %
SO_3	7.5 %	4.2 %	5.1 %
CaO	5.9 %	6.4 %	7.7 %
ZnO	5.8 %	4.1 %	1.3 %
SiO_2	4.1 %	7.9 %	
Al_2O_3	2.0 %	4.7 %	5.4 %
PbO	1.7 %	0.6 %	0.1 %
CdO	1.4 %	n.d.	n.d.
MgO	0.8 %	1.4 %	1.9 %
C	16.8 %	10.0 %	7.6 %
before norm.	96.8 %	84.4 %	89.0 %

Table A-11: XRF values for 40% MIX. Initial values in the first column, after 10 minutes and after 30 minutes of treatment respectively at 1000 °C

MIX 40%

Compound	**initial**	**after 10 min**	**after 30 min**
weightloss [wt%]		11.5 %	15.9 %
Fe_2O_3	57.6 %	60.9 %	64.5 %
SO_3	7.6 %	5.7 %	6.4 %
CaO	6.6 %	8.7 %	10.1 %
ZnO	5.8 %	4.2 %	0.6 %
SiO_2	4.1 %	6.4 %	6.4 %
Al_2O_3	1.9 %	3.5 %	4.1 %
PbO	1.7 %	0.9 %	0.1 %
CdO	1.5 %	n.d.	n.d.
MgO	0.9 %	0.6 %	0.6 %
C	10.0 %	5.9 %	2.6 %
before norm.	95.9 %	88.3 %	87.9 %

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Glossary

List of Acronyms

BF	Blast Furnace
BOF	Basic Oxygen Furnace
EAF	Electric Arc Furnace
CCF	Cyclone Converter Furnace
SRV	HIsmelt Smelt Reduction Vessel
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
SEM	Scanning Electron Microscopy
SEM-EDS	Scanning Electron Microscopy - Electron Dispersive X-ray Spectroscopy
TGA	Thermal Gravimetric Analysis
ULCOS	Ultra Low CO_2 Steelmaking