# Recycling of Blast Furnace Sludge through Carbochlorination and Direct Reduction

TATA STEEL

### Increasing Material Circularity in Ironmaking

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by

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### Summary

#### **GRAPHICAL ABSTRACT**



Blast furnace (BF) sludge, originating from the blast furnace used for ironmaking, has become a critical waste problem in the steel industry. The captured dust from the blast furnace off-gas is separated based on its size in which low-zinc coarse fraction is returned to the sinter plant, while the middle and fine fractions of the dust containing high zinc (>2%), referred to as blast furnace sludge, are landfilled. The most common practice of landfilling BF sludge globally, including at Tata Steel in IJmuiden, creates a considerable environmental challenge. The heavy metals (Zn, Pb) content burden the circularity of the blast furnace sludge. On the contrary, the high iron and carbon content in the sludge still have an excellent economic value that is important to recover as secondary ironmaking sources. Several metallurgical recycling techniques have been developed to switch the existing landfilling with a more effective, environmentally friendly, and economically viable recycling alternative. Accordingly, this research study aims to provide a viable recycling solution to separate heavy metals from the iron-rich fraction in the BF sludge. Based on the comparative assessment of different recycling technologies, the direct reduction technique has the most potential with high heavy metals removal (>90%) simultaneously with partial self-reduction of iron. Furthermore, adding spent pickling liquor (FeCl<sub>2</sub>) can increase the removal efficiency and selectivity of the heavy metals through carbochlorination reactions. Direct reduction is defined as the reduction process of an element from oxide form to metallic form in the presence of a reducing agent, while carbochlorination is described as the reduction of metal oxides to gaseous metal chlorides in the presence of reducing and chlorination agents.

Experimental methods in this thesis study aim to asses the recycling technique (carbochlorination and direct reduction) from the technical, economic, and environmental points of view for future implementation at Tata Steel in IJmuiden. Four different pellets, varied in size (<3 mm and 3-5 mm), were used in this thesis study. Two of the pellets were added with iron chloride. The thermodynamic analysis concluded that the sample with chloride addition, represented by carbochlorination reactions, has a lower onset temperature and Gibbs free energy change ( $\Delta G^\circ$ ) than the direct reduction-based reactions in

terms of heavy metals (Zn, Pb) removal. The addition of chlorides shows a selective carbochlorination reaction represented by the 99% removal of Pb at 800°C followed by 98% removal of zinc at 1000°C, leaving an iron-rich clean residue free of heavy metals. Based on SEM-EDS analysis, up to 72% of Pb and 66% of Zn were found in the secondary dust generated from the multi-stage carbochlorination at 800°C and 1100°C, respectively, indicating a possibility of producing a separate Pb-bearing and Zn-bearing secondary dust. Therefore a recycling flowsheet based on the double-step carbochlorination was formulated for further assessment. The material balance calculation shows that 88% of Pb and 26% of Zn end up in the Pb-bearing dust from 1<sup>st</sup> carbochlorination at 800°C, and 62% of Zn end up in the Zn-bearing dust from 2<sup>nd</sup> carbochlorination at 1000°C. In addition, 78% of C and 85% of Fe remained in the heavy metals-free (iron-rich) residue as the main recycling product. The cost-benefit analysis of the recycling process estimated a profit of ~210 €/ton from the best-case scenario (marketable recycling product) and a  $\sim$ 250 €/ton loss from the worst-case scenario (unmarketable product). Life cycle assessment (LCA) shows that processing 1 ton of BF sludge pellets through selective carbochlorination produces between 0.3 to 1.3 tons of CO<sub>2</sub>-eq, which depends on the energy sources. In addition, the associated environmental cost considering all the impact categories is between  $\sim$ 100 to ~230 €/ton of BF sludge. The proposed recycling flowsheet for Tata Steel in IJmuiden is to provide a sequential carbochlorination in a connected rotary kiln, incorporated with a dust-capturing system, to produce clean iron-rich residue and zinc-bearing dust as new secondary marketable products. In conclusion, the recycling of blast furnace sludge through a novel selective carbochlorination is favorable (with some limitations) based on the technical, economic, and environmental perspectives.

Keywords: blast furnace sludge, carbochlorination, direct reduction, heavy metals

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I hope this thesis work will bring benefits and impacts to Tata Steel in IJmuiden in the future, and I hope you will enjoy reading this report.

Delft, October 2022

Muhammad Dzikri Ahira Soefihara

## Introduction

**B** last furnace sludge (BF sludge) has been a critical issue in the iron and steelmaking industries. In recent years, different recycling routes have been studied to increase the circularity of the sludge since the most common end-of-life treatment is landfilling [1, 2, 3, 4, 5, 6, 7]. Hence, this thesis study aims to comprehensively assess the most suitable process to recycle blast furnace sludge at Tata Steel in IJmuiden, including a comparative study of different recycling methods followed by further experimental research of one of the most potential routes. In this chapter, a general overview of the research topic is discussed. This chapter starts with information on the production process at Tata Steel in IJmuiden (Section 1.1) followed by the blast furnace off-gas treatment (Section 1.2) as the source of the blast furnace sludge. The subsequent section explains the characteristics and properties of the blast furnace sludge (Section 1.3), followed by the relevance of this research project (Section 1.4) to the steel industry, especially to Tata Steel in IJmuiden.

### 1.1. Tata Steel in IJmuiden

Tata Steel in IJmuiden is one of Europe's leading ironmaking and steelmaking companies. The company is located in IJmuiden, the Netherlands, and is part of Tata Steel Group. The plant produces around 7 million tons of rolled steel annually with different product specifications [8]. The typical production flowsheet of steel via blast furnace route is given in Figure 1.1.



Figure 1.1: Integrated steel production via blast furnace route. Modified from [9].

At Tata Steel in IJmuiden, steel is produced via the blast furnace route, schematically shown in Figure 1.1, in which the input of the raw materials are processed in the blast furnace to produce molten iron, followed by the steelmaking process through basic oxygen furnace [10]. The production process at Tata Steel in IJmuiden starts with feed preparation, including a mix of pelletizing and sintering iron ore. Cokes from the coking plant are then added with sintered/pelletized iron ore feed for the blast furnace (BF). In the BF, iron ore is reduced with the presence of cokes as a reducing agent and blown with hot air to produce metallic iron. Metallic or pig iron is then transported to the basic oxygen furnace (BOF) for the steelmaking process. Steel scrap is also added as an additional input for the BOF. During the process, oxygen is injected to reduce the carbon content of the pig iron. The liquid steel from the BOF follows the continuous casting process and is sent to the hot and cold strip mills producing coil (slabs/billets). The final thickness of the coil is between 1 to 25 mm [8]. The last step of the production process in IJmuiden is the coating, including galvanizing with an organic and metallic coating to protect and increase the corrosion resistance of the steel. In summary, the products of Tata Steel in IJmuiden are hot-rolled coil (HRC), cold-rolled coil (CRC), and coated steel, mainly used in the construction, vehicle, and packaging industry. A summary of the production performance, including the environmental aspect, of Tata Steel in IJmuiden is given in Table 1.1.

Indicators	Unit	2015	2017	2018	2019
Crude steel production	Mt	6.92	6.81	6.85	6.62
CO <sub>2</sub> emission	Mt	12.73	12.98	12.86	12.31
Fresh water consumption	M <sup>3</sup> /t steel	4.49	4.81	4.90	4.93
Waste generated	kt	321	227	193	218
Waste disposed to landfill	kt	57	34	43	42
Waste intensity	t/t	0.0082	0.0050	0.0063	0.0063
Waste re-used, recycled	kt	254	187	143	170

Table 1.1: Performance data of Tata Steel in IJmuiden [8].

### 1.2. Blast Furnace Off-gas Treatment

The blast furnace produces flue gas or off-gas during the ironmaking process. The leaving gas typically contained around 8 to 12 kg of dust per ton produced pig iron [3]. The schematic flow of the blast furnace off-gas treatment at Tata Steel in IJmuiden is given in Figure 1.2.



Figure 1.2: Flowsheet of blast furnace off-gas treatment at Tata Steel in IJmuiden. Data are from 2015 (dry basis) [3].

The off-gas is cleaned through a dry cleaning process (dust bag) followed by wet cleaning using a Bischoff washer (scrubber) in which, in the end, different size fractions of the dust are collected [4]. The first cleaning step is through a dust bag, and the coarse fraction containing a low amount of zinc is collected and recycled back internally within the steel production process. The fine fraction is then sent to the wet cleaning step. In this stage, the cleaned off-gas is released, and the flue dust is sent to the thickener for solid-liquid separation. Subsequently, the underflow is sent to the first cyclone to separate the dust into a fine (<20  $\mu$ m) and a coarse fraction (>20  $\mu$ m) [3]. The fine fraction is then sent to the next cyclone to further separate the dust into sizes under and over 10 µm. Each dust fraction is collected separately based on size and zinc content throughout the off-gas treatment cycle. The coarse fractions contain less zinc than the fine fractions, as 60% zinc is concentrated in the zinc-rich dust fraction (see Figure 1.2). Due to the current limitation of the blast furnace to process high zinc-bearing input, the medium and high zinc dust fractions are currently landfilled in the IJmuiden site [2, 3, 4]. In contrast, the low zinc fraction is recycled internally in the sinter plant. The term "Blast Furnace Sludge or BF Sludge" is referred to the high-zinc fractions of the landfilled dust, which is explained further in the next section. In 2019, the total zinc-bearing dust, including BF sludge, generated from the steel industry was between 48 to 72 million tons, which accounts for 3-4% of the total steel production [5].

### 1.3. Blast Furnace Sludge

The wet cleaning stage of the blast furnace off-gas includes several separation steps by hydrocyclones. The mass balance of zinc throughout the hydrocyclones at Tata Steel is given in Figure 1.3. It can be seen that the coarse fraction, with low zinc content, is sent to the sinter plant corresponds to 54 tons per day. The remaining fractions of the dust, as much as 24 tons and 22 tons per day, are stored internally or landfilled. Zinc input to the blast furnace is kept at 125 g/ton of iron ore hence only allowing the low zinc fraction to be reintroduced to the ironmaking process [3].



Figure 1.3: Zinc mass balance throughout the hydrocyclones at Tata Steel in IJmuiden [4].

This research study will be focused on the blast furnace sludge, which can be referred to as the zincrich filter cake. A recycling solution is urgently needed to prevent waste from ending in landfills. Based on the gas treatment flowsheet, zinc is concentrated in smaller sizes and is primarily sourced from the BOF during the steelmaking process [4]. In BOF, steel scrap is introduced as an input containing Zn from the steel galvanizing process. The dust generated from the BOF is sent to the sinter plant, combined with the raw iron ore, and subsequently enters the blast furnace. As mentioned earlier, zinc is the burden for the dust to be reintroduced to the BF. High zinc content can cause problems to the operations of the blast furnace [6, 7, 11]. Consequently, only low zinc fractions are allowed to be put back into the process while the rich zinc filter cake is stored onsite. Zinc can destroy the furnace lining (wear), decrease the lifetime of the lining, and create a problem of bursting gas during the tapping [3, 4, 12]. Zinc has a low boiling point of 910°C and is concentrated in the off-gas during the ironmaking process [4]. Zinc is commonly attached to the surface of the lining, known as zinc disintegration, and the layers of zinc can create a scaffold. Therefore, the blast furnace dust with high zinc content cannot be directly recycled to the ironmaking process prior to the removal of zinc and other heavy metals to meet the input criteria of BF. The existing treatments of blast furnace sludge in IJmuiden, such as landfilling and transporting to a third party, are not economically favorable due to the valuable contents of iron-carbon left in the dust [13]. On the other hand, the current internal recycling of dust from BF and BOF also creates undesirable circulating loads of heavy elements such as zinc and lead. Moreover, the storage of high-zinc fractions in IJmuiden has become a critical environmental threat as the heavy metals (Pb, Cd) may contaminate the soil and groundwater. The existing Third Dutch National Waste Plan (LAP3) may limit the allowance of landfilling the BF sludge in due time [14].

As discussed in the previous section, the burden of the blast furnace sludge to be recycled in the blast furnace is the zinc and other heavy metals content, including lead and cadmium. Studies on the composition of zinc-bearing materials, including blast furnace sludge, have been done extensively. The presence of different zinc phases in the BF sludge also needs to be considered, as it is related to the efficiency of the recycling methods. Based on previous studies, zinc oxide (ZnO) was soluble in alkaline lixiviant, while zinc ferrite ( $ZnFe_2O_4$ ) and zinc sulfide (ZnS) were resistant to leaching [2, 3, 15]. Another research shows that the zinc phases in the steelmaking dust were mainly formed as zinc ferrite, hardystonite ( $Ca_2ZnSi_2O_7$ ), and zinc chloride ( $ZnCl_2$ ) [5]. The composition (only most influential elements) of zinc-bearing materials from several studies, mainly from the blast furnace dust/sludge, is presented in Table 1.2. In addition, the zinc phases found in the zinc-bearing materials from some literature are listed in Table 1.3.

No.	Source	Zn	Fe	С	Pb	Cd	Ref.
1	BF <sup>1</sup>	4.0	24	36	0.5	0.02	[3]
2	BF <sup>1</sup>	5.6	24	31	0.4	<0.02	[6]
3	BF <sup>1</sup>	2.0	41	19	0.1	-	[16]
4	BF <sup>1</sup>	7.3	29	38	1.4	0.02	[2]
5	BF <sup>1</sup>	9.5	36	14	-	-	[17]
6	BF <sup>1</sup>	3.9	9	-	0.2	-	[18]
7	BF <sup>1</sup>	1.6-8.1	15-37	-	1-2	-	[19]
8	BF <sup>1</sup>	3.9	27	36	0.6	-	[4]
9	BF <sup>1</sup>	0.02	42	19	0.01	-	[11]
10	BF <sup>1</sup>	7.8	24	-	-	-	[5]
11	BOF <sup>2</sup>	4.4	51	1	0.1	<0.02	[20]
12	BOF <sup>2</sup>	4.1	54	5	0.1	-	[3]
13	BOF <sup>2</sup>	2.8-6	41-62	-	-	-	[21]
14	BOF <sup>2</sup>	6.7	55	-	-	-	[22]
15	BOF <sup>2</sup>	2.7	48	-	0.2	-	[23]
16	BF <sup>1</sup> +BOF <sup>2</sup>	4.6	44	7	-	-	[5]
17	EAF <sup>3</sup>	4.7	52	-	0.1	-	[11]
18	Gahnite <sup>4</sup>	35.7	-	-	-	-	[24]
19	EAF <sup>3</sup>	12.2	37	-	1.7	0.01	[25]
20	EAF <sup>3</sup>	24.2	34	-	1.8	-	[26]
21	BF <sup>1</sup>	6.2	35	40	1.6	-	[27]
22	BOF <sup>2</sup>	0.5	83	3	-	-	[27]
23	HOKS⁵	1.2	57	2	0.2	-	[27]
24	BF <sup>1</sup>	1-5.3	16-34	34-60	0 1-1	-	[28]

 Table 1.2: Zinc-bearing wastes composition generated from different processing routes.

<sup>1</sup>Blast Furnace

<sup>2</sup>Basic Oxygen Furnace

<sup>3</sup>Electric Arc Furnace

<sup>4</sup>Gahnite ( $ZnAl_2O_4$ )

<sup>5</sup>Historical Oxychalk Sludge

No.	Source	ZnO	ZnS	$ZnFe_2O_4$	ZnCO <sub>3</sub>	ZnSO <sub>4</sub>	ZnCl <sub>2</sub>	Ca <sub>2</sub> ZnSi <sub>2</sub> O <sub>7</sub>	Ref.
1	BF <sup>1</sup>	46.0	53.0	-	-	-	-	-	[3]
5	BF <sup>1</sup>	61.0	7.2	0.6	-	30.5	-	-	[17]
6	BF <sup>1</sup>	-	17.0	5.0	78.0	-	-	-	[ <mark>18</mark> ]
8	BF <sup>1</sup>	33.3	66.7	-	-	-	-	-	[4]
11	BOF <sup>2</sup>	60.0	-	40.0	-	-	-	-	[ <mark>20</mark> ]
12	BOF <sup>2</sup>	47.0	-	53.0	-	-	-	-	[3]
16	BF <sup>1</sup> +BOF <sup>2</sup>	-	-	>0	-	-	>0	>0	[ <mark>5</mark> ]

Table 1.3: Distribution of zinc phases in the sludge from BF and BOF.

<sup>1</sup>Blast Furnace

<sup>2</sup>Basic Oxygen Furnace

Zinc content in the zinc-bearing materials is substantial in determining the suitable and efficient recycling treatment. The zinc phases would also be influential since different phases will react differently under specific treatments. Table 1.2 shows that zinc content in the materials originating from the blast furnace is between 0.02 to 9.5%. From the BOF, the dust typically contains zinc from 0.5 to 6.7%. Iron is the dominant element in the dust from both BF and BOF. Gahnite or zinc aluminate is a zinc-bearing material different from the BF and BOF dust as it has a significantly higher zinc content of 35.7% and originated from the zinc or brass industry [24]. HOKS is referred to old sludge in the landfill. In terms of heavy metals, Pb content ranges from 0.01 to 2%, while a relatively small amount of less and equal to 0.02% for Cd content, as presented in Table 1.2. Based on Table 1.3, The zinc inside the dust originating from BF and BOF mainly formed in ZnO and ZnS, as the highest amounts found are 61% and 66.7%, respectively. The other zinc phases found are zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>), zinc carbonate (ZnCO<sub>3</sub>), and zinc sulfate (ZnSO<sub>4</sub>). The materials listed in Table 1.2 are the sample used in past studies for different experimental recycling routes to process the zinc-bearing materials, including BF sludge, which will be discussed comprehensively in the next chapter.

### 1.4. Relevance of the Project

As discussed in the previous section, BF sludge contains zinc and heavy metals that have a detrimental effect on the blast furnace. Moreover, the current landfilling of BF sludge is harmful to the environment. Three past master thesis research were conducted at TU Delft on treating blast furnace sludge from Tata Steel in IJmuiden between 2015 and 2019. The first research by Verburg in 2015 [4] concluded that ammonia leaching is insufficient to extract Zn (69% extraction rate) from the BF sludge due to the presence of ZnS. The second research by Feenstra in 2016 [3] shows a good removal of Zn (86%) through roasting, but 32% of Zn was concentrated in the gas phase during roasting process, which needs further treatment and complicates the overall recycling process. Feenstra also conducted leaching following the roasting treatment, resulting in a high zinc extraction of up to 100% as ZnS was converted to leachable ZnO due to roasting. Through microwave-assisted leaching, the third and most recent research by Kempke in 2019 [2] resulted in a 61% extraction of Zn, which was also considered low. The research done by Verburg (2015)[4] and Kempke (2019) [2] were still far below the targeted extraction of Zn, which was set to 80%. The complicated process of Feenstra (2016), which incorporated roasting and leaching, resulting in the split of Zn fractions to the gas phase and solid residue, was also not viable for further implementation at Tata Steel in IJmuiden.

This thesis study will focus on finding a solution for recycling the blast furnace sludge from Tata Steel in IJmuiden. The basic concept of BF sludge recycling is to separate the heavy metals from the ironrich residue, summarized in Figure 1.4. The new secondary product from BF sludge valorization is expected to have sufficient criteria for the subsequent processing routes. The iron-rich residue is aimed to be processed internally in IJmuiden, and the heavy metal residue will be transported to the relevant industry. Based on Figure 1.4, the research questions were formulated to find the most suitable and efficient recycling methods, proven by subsequent experimental works to replace the existing landfilling of BF sludge at Tata Steel in IJmuiden. The research questions were defined sequentially, as given in Figure 1.5.



Figure 1.4: Schematic representation of the thesis project's flow for recycling/waste valorization of BF sludge.



#### **Research Questions**

Figure 1.5: Research questions formulated in this thesis study.

Based on Figure 1.5, the first objective is to define the most appropriate recycling technique through a literature study, followed by experimental work to determine the optimum condition of the selected recycling technique. The final part will be the comprehensive feasibility assessment and the creation of the final recycling flowsheet for Tata Steel in IJmuiden. The research questions will be answered in sequence throughout this report. The following chapter (Chapter 2) briefly explains the comparative study of the alternative routes in recycling zinc-bearing wastes, especially BF sludge, which correspond to the samples provided in Table 1.2 and Table 1.3. The subsequent chapters consist of the materials and methods (Chapter 3) as the framework based on the most preferred and potential recycling route, carried out through various experimental studies. At the end of the report, the research questions are answered in the conclusions and recommendations (Chapter 5). This thesis study aims to comprehensively produce and assess the best recycling route for treating hazardous BF sludge for future implementation at Tata Steel in IJmuiden or other steel industries, as one of the environmental issues that has to be resolved.

 $\sum$ 

### Literature Review

he content of this literature study is based on state-of-art technologies in recycling zinc-bearing materials/wastes, including blast furnace sludge. The recycling methods are generally divided into recycling at high temperatures, called the pyrometallurgical process, and recycling in the aqueous solution referred to as the hydrometallurgical process. The studies on pyrometallurgical and hydrometallurgical recycling routes are explained extensively in Section 2.1 and Section 2.2, respectively. A comparative study between each recycling method is provided in Section 2.3 to select further an adequate route for experimental study in the treatment of blast furnace sludge from Tata Steel in IJmuiden. The discussion on chloride metallurgy as one of the fundamentals in heavy metals separation is provided in Section 2.4.

### 2.1. Pyrometallurgical Process

The pyrometallurgical process is the treatment of materials involving chemical reactions at high temperatures [29]. Recycling the dust generated from the steel industries through pyrometallurgy primarily aims to volatilize zinc and other heavy metals (Pb, Cd), thus producing iron-rich fractions (partly metallic iron) that can be reintroduced or recycled in the ironmaking process. The following pyrometallurgical recycling options are classified based on the operating temperature, which starts at the lowest with the roasting (Subsection 2.1.1), followed by direct reduction (Subsection 2.1.2) and smelting (Subsection 2.1.3) as the reacting temperature increases.

#### 2.1.1. Roasting

Roasting is a metallurgical process consisting of reactions between gas and solid particles at high temperatures [30]. This technique often aims to convert sulfide ores to oxides. It was reported in a study that zinc sulfide was converted to b-type and alpha-type as an intermediate product of zinc oxide before being reduced to zinc in the gas phase [31]. In the case of dust recycling, the main idea of roasting is to oxidize the particular zinc phases that are difficult to dissolve through the hydrometallurgical route. Hence, roasting is often combined with a subsequent extraction process, such as leaching. As discussed before, zinc sulfide and zinc ferrite are the phases found in the dust originating from BF and BOF that are resistant to leaching. Research on roasting was done by Feenstra (2016) [3] that processed a sample of mixed dust from BF and BOF as the composition given in Table 1.2 No. 1 and 12, respectively. The research aimed to transform zinc ferrite ( $ZnFe_2O_4$ ) and zinc sulfide (ZnS) to leachable zinc oxide (ZnO) through roasting. Sodium carbonate ( $Na_2CO_3$ ) was added to decompose zinc ferrite particularly. The reactions of roasting are shown in the below equations [3].

$$2 ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2 ZnO_{(s)} + 2SO_{2(g)}$$

$$(2.1)$$

$$Na_{2}CO_{3(s)} + ZnFe_{2}O_{4(s)} \longrightarrow ZnO_{(s)} + 2NaFeO_{2(s)} + CO_{2(g)}$$
(2.2)

The best result of the research was achieved by roasting the mix of BF and BOF samples at 860°C for 1 hour. This experiment resulted in the 87% removal of zinc [3]. Zinc content was lowered from 4% to 0.8% in the solid residue. Another treatment with the sample consisting only of BF dust has a lower

removal rate of zinc (70%). However, roasting creates an additional waste stream as 32% of zinc was lost to the gas phase together with 96%, 96%, and 71% of carbon (C), cadmium (Cd), and lead (Pb), respectively. This additional waste containing zinc and other heavy metals needs further treatment along with the remaining zinc in the residue, complicating the overall recycling process. Nevertheless, a higher roasting temperature induces a better decomposition of zinc ferrite and zinc sulfide. However, more zinc will also be lost in the gas phase, as illustrated in the stability diagram of Fe-Pb-ZnO in Figure 2.1 as zinc formation occurs at around 400°C with low partial CO pressure.



Figure 2.1: Stability diagram of iron, lead, and zinc oxides [32].

#### 2.1.2. Direct Reduction

The direct reduction technique is a standard ironmaking process to convert iron oxides/ores to iron (electron gain), called DRI (direct reduced iron), with the presence of a reducing agent at an elevated temperature (below the melting point) [29]. In this case, carbon is directly in contact with iron oxides to produce metallic iron in an endothermic reaction. This technique has been long-established to treat zinc-bearing materials from industrial wastes. In recycling dust from the steel industry, direct reduction aims to remove oxygen from metallic oxide with the presence of C, producing (partly) reduced iron in the solid residue and removing heavy metals (Zn, Pb, Cd) to the gas phase at a temperature between 800 to 1200°C. This section briefly discusses the direct reduction techniques at the research and industrial level, including carbothermic and aluminothermic processes, direct reduction in a furnace, microwave-assisted direct reduction, and the existing integrated industrial-based direct reduction (Rotary/Waelz Kiln, Rotary Hearth Furnace, Primus, Solumet).

#### **Carbothermic and Aluminothermic Reduction**

Carbothermic and aluminothermic based experiments were done by Mardones (2012) [24] in recycling gahnite as zinc-bearing material containing 35.7% of zinc. In principle, the carbothermic process uses carbon (C) as the reducing agent, while aluminum (Al) is the reducing agent in the aluminothermic process. The main principle of zinc reduction is based on the Ellingham Diagram, as given in Figure 2.2. Both aluminum and carbon equilibrium lines are below the zinc formation line, leading to more negative Gibbs free energy change ( $\Delta G^\circ$ ), indicating a more spontaneous reaction to promote ZnO reduction. From the experiments by Mardones (2012) [24], high removal of zinc was achieved by carbothermic and aluminothermic reduction, in which 99.9% and 99.98% removal rates of zinc were obtained, respectively. The experiments were done for 1 hour with an argon (Ar) gas flow of 3 L/min. The temperatures were set to 1300°C for the carbothermic reaction and 1200°C for the aluminothermic reaction. The results are consistent with the Ellingham diagram, in which Al<sub>2</sub>O<sub>3</sub> and CO formation are more favorable than zinc oxide formation at temperatures higher than 1000°C. The underlying equilibrium reactions for carbothermic zinc reduction are given in the below reactions [24].

$$ZnO \cdot Al_2O_3(s) + C(s) \Longrightarrow CO_{(g)} + Zn_{(g)} + Al_2O_{3(s)}$$
(2.3)

$$1.5 ZnO \cdot Al_2O_3(s) + Al(s) \Longrightarrow 2 Al_2O_{3(s)} + 1.5 Zn_{(q)}$$

$$(2.4)$$

A critical thing to mention is that the high removal rate of zinc in treating gahnite might vary and not be relevant in recycling zinc-bearing materials from BF or BOF. Compared to gahnite, the low amount of zinc in the dust from BF and BOF might result in different behavior through the aluminothermic, and carbothermic reactions as other more thermodynamically less stable metals may reduce.



Figure 2.2: Ellingham Diagram [33].

#### **Direct Reduction in Shaft Furnace**

Direct reduction at the research level in a furnace was conducted by Zhu et al. (2021) [5]. The sample used for this treatment was a mix of BF and BOF dust, as the composition given in Table 1.2. In addition, coke was added as the reducing agent and bentonite was used as a binder in pelletizing the sample prior to heat treatment. A direct reduction experiment was carried out in a shaft furnace with 100 grams of dried pellets. The temperature varied from 1323°K (1050°C) to 1473°K (1250°C), and the reaction times were set from 10 to 50 minutes. As a result, zinc and heavy metals were reduced and concentrated in the off-gas throughout the reduction process, leaving the iron in the solid fraction. High zinc removal close to 100% was achieved at a temperature up to 1473°K (1250°C) after 30 min of reduction, as given in Figure 2.3. It can be seen that more than 90% of zinc was removed from the reactions at 1473K and 1423 for at least 30 minutes. Zhu (2021) [5] also concluded that the 3D diffusion model controls the kinetics of zinc removal, as the model equation is expressed in the below equation.

$$G(\alpha) = [1 - (1 - \alpha)^{\frac{1}{4}}]^2$$
(2.5)

The study study also reported that the highest zinc removal was obtained in the smallest pellets with a diameter of 12 mm. It concluded that a bigger diameter reduces the diffusion rate of zinc. In the sample, zinc was found in the form of zinc ferrite ( $ZnFe_2O_4$ ), hardystonite ( $Ca_2ZnSi_2O_7$ ), and zinc chloride ( $ZnCl_2$ ). Based on thermodynamic calculations,  $ZnCl_2$  could be volatilized at over 1005°K (732°C) while the  $ZnFe_2O_4$  and  $Ca_2ZnSi_2O_7$  could be removed at a temperature higher than 1180°K (907°C). The reduction reactions of zinc phases reported in the study are expressed below [5].

$$Ca_2ZnSi_2O_{7(s)} + CO_{(g)} \rightleftharpoons 2CaSiO_{3(s)} + CO_{2(g)} + Zn_{(g)}$$
(2.6)

$$ZnFe_2O_{4(s)} + 4CO_{(g)} \implies 2Fe_{(s)} + 4CO_{2(g)} + Zn_{(g)}$$
 (2.7)



Figure 2.3: Zinc removal of direct reduction in a shaft furnace at different temperatures and retention times [5].

#### Carbochlorination

Another research was done by Hamann et al. (2021) [6] in recycling the BF sludge through direct reduction with the addition of spent pickling acid (FeCl<sub>2</sub>), which is referred to as carbochlorination. The sludge composition of the samples originating from the blast furnace is given in Table 1.2, and the experiment overview is given in Figure 2.4. The idea of carbochlorination was to remove the zinc and other heavy metals in chloride forms, thus producing iron-carbon compounds as a new secondary source.



Figure 2.4: Schematic overview of carbochlorination experiment done by Hamann et al. (2021) [6].

The experiment was conducted in a horizontal tube furnace with a flowing 400 L/h nitrogen gas. The sample was heated at a temperature ranging from 650°C to 1000°C for 1 to 60 minutes. As the reaction involves chlorides from spent pickling acid, the chlorination-based reactions (carbochlorination) for the metal oxide (zinc, iron, and lead) contained in the sample are given in the Gibbs standard free energy graph in Figure 2.5. As shown in Figure 2.5, zinc ferrite, zinc oxide, and lead oxide are thermodynamically favorable to be converted into chloride-based gas at temperatures higher than 800°C.

However, some amount of iron chloride might be lost to the gas during chlorination-based reduction. This research also showed that the removal rate of zinc, lead, and cadmium increases with temperature, between 600°C to 1000°C, as shown in Figure 2.6. It can be seen that 100% of zinc and lead removal was achieved with a tiny amount of iron lost in the gas. In summary, the amount of zinc, lead, and cadmium in the processed BF sludge was reduced from 56 g/kg, 4 g/kg, and 0.02 g/kg to 0.7 g/kg, 0.02 g/kg, and 0.008 g/kg, respectively [6].



Figure 2.5: Gibbs free energy change of carbochlorination at different temperatures of (a) zinc, lead and (b) iron [6].



Figure 2.6: The removal rate of (a) zinc, (b) lead, (c) cadmium, and (d) iron through carbochlorination [6].

#### **Microwave-Assisted Direct Reduction**

Microwave-assisted direct reduction technique was studied by Ye et al. (2021) [11]. The research compared conventional and microwave-assisted direct reduction for BF and EAF dust treatment. The

sample used in this research was the mix of BF and EAF dust (0.12% - 0.57% Zn), as each BF and EAF dust composition is given in Table 1.2. The flowsheet of the experiments is given in Figure 2.7. The experiment was started by pelletizing the mixed BF and BOF dust samples as the samples were differentiated into homogeneous and core-shell composite pellets. As mentioned in the paper, the impedance matching of the sample influences microwave absorption. Thus, the core-shell (EAF dust as the shell and BF dust as the core) sample is prepared to reduce reflection loss. Since BF dust has higher carbon content, the impedance matching degree is lower than EAF dust due to the non-magnetic properties of carbon. Next, the direct reduction was conducted in a microwave tube furnace and a conventional tube furnace at 1050°C for 15 min with injected 0.2 L/min nitrogen gas. Prior to analysis, the samples were further processed through ball milling and magnetic separation.



Figure 2.7: Experimental flowsheet of conventional and microwave-assisted direct reduction [11].

Reactions that occurred during the reduction of the samples, including the Gibbs Free Energy and onset temperature, are also mentioned in the report. The reactions are shown in Equation 2.8 to Equation 2.15 [11]. The reaction shows that zinc was initially formed as zinc ferrite and zinc oxide, as given in Equation 2.8, 2.9, 2.10, and 2.11. The experiment results, including the lead and zinc removal, residual iron content, and iron metallization degree, are given in Figure 2.8.

$$ZnO_{(s)} + C_{(s)} \Longrightarrow CO_{(g)} + Zn_{(g)}$$
(2.8)

$$ZnO_{(s)} + CO_{(g)} \Longrightarrow CO_{2(g)} + Zn_{(l)}$$
 (2.9)

$$3 ZnFe_2O_{4(s)} + C_{(s)} \Longrightarrow 2 Fe_3O_{4(s)} + CO_{(g)} + 3 ZnO_{(s)}$$
 (2.10)

$$3 ZnFe_2O_{4(s)} + CO_{(g)} \Longrightarrow 2 Fe_3O_{4(s)} + CO_{2(g)} + 3 ZnO_{(s)}$$
 (2.11)

$$2 \operatorname{PbO}_{(s)} + C_{(s)} \rightleftharpoons \operatorname{CO}_{2(g)} + 2 \operatorname{Pb}(I)$$

$$(2.12)$$

$$PbO_{(s)} + CO_{(g)} \rightleftharpoons CO_{2(g)} + Pb_{(l)}$$
(2.13)

$$Zn_{(l)} \rightleftharpoons Zn_{(g)}$$
 (2.14)

$$Pb_{(l)} \Longrightarrow Pb_{(a)}$$
 (2.15)

Based on Figure 2.8, a high lead removal percentage was achieved through microwave-assisted reduction of more than 95% ( $C_1$  and  $C_2$ ) and 90.5% for conventional reduction ( $C_3$ ).  $C_1$  and  $C_3$  are samples with core-shell structures, while  $C_2$  is a standard homogenized sample. Low zinc removal was obtained for conventional reduction (30.9%), while microwave-assisted reduction resulted in high zinc removal above 90%. The low removal of zinc in  $C_3$  was due to the slow heat transfer in the conventional microwave. This heat transfer also resulted in the low iron metallization degree of the  $C_3$  sample. On the other hand, all experiments resulted in high residual iron content, in the range of 58.1% to 70.6%. The experiment results by Ye et al. (2021) [11] indicate that the promising technique of microwave-assisted reduction as it could remove a high percentage of Zn and Pb from the BF and EAF dust along with the high iron metallization degree of more than 90%.



Figure 2.8: Experimental results of the microwave-assisted (C1 and C2) and conventional direct reduction (C3) [11].

#### Rotary/Waelz Kiln

Direct reduction in the rotary kiln has been well-established in the industry, with a high removal rate of zinc up to 94% [5, 11, 34]. Around 83% of EAF dust is recycled through this process, with the capacity ranging from 100 to 350 kt/year. [34]. The typical input for Rotary Kiln or Waelz Kiln is pelletized mix of dust, binder, pulverized coal, and water. At a temperature of 1100 to 1200°C, the reduction of metal oxides starts to occur, while zinc and alkali metals will be selectively volatilized. The reactions in the waelz kiln occurred in the bottom area (reduction) and upper area (oxidation), with a counter-current movement of the input and injected hot air in a rotating chamber, as illustrated in Figure 2.9. The flowsheet of the waelz kiln in the industry is given in Figure 2.10.



Figure 2.9: Reactions involved in the waelz kiln [34].



Figure 2.10: Flowsheet of EAF dust recycling in waelz kiln [34].

Rotary Kiln has the advantage of a relatively straightforward process of low environmental pollution and has been widely used in treating EAF dust with high zinc content (>16%) [34]. The problem of the rotary or waelz kiln is the ring formation on the furnace lining due to the adhesion of elements with a low melting point as the kiln rotated during the process. The ferrous product (90% DRI) of waelz kiln typically contains 0.2-2% of Zn, 0.5-1% of Pb, and 0.1-0.2% of Cd, while the dust could contain up to 66% of ZnO [34]. The need for a high percentage of Zn input for rotary kiln burdens the use of rotary kiln for blast furnace sludge as BF sludge typically contains <8% of zinc, as given in Table 1.2.

#### **Rotary Hearth Furnace (RHF)**

The rotary hearth furnace is similar to the rotary kiln, based on the direct reduction with coal addition. Compared to the rotary kiln with limited use for EAF dust (high zinc), RHF has been widely used to treat BF, and BOF dust with the final product of the direct reduced iron (DRI) containing up to 95.8% of Fe, <0.004% of Zn with almost no lead found [34]. The report by Wang et al. (2021) [34] also showed that at a temperature of 1230°C and a carbon/oxygen (in reducible oxide) ratio of 1.0, the zinc removal rate could be achieved up to 95%. RHF could also produce a high grade of DRI with up to 90% of metallization degrees and high zinc (63.4%) secondary dust. The flowsheet of the RHF plant of Rizhao Steel in China is given in Figure 2.11.



Figure 2.11: Flowsheet of RHF plant in Rizhao Steel, China [34].

Based on Figure 2.11, the input for the RHF is pelletized mixed of EAF dust (can be from BF and BOF dust) with binder and coal. Drying and reduction of the sample occur inside the furnace, while mechanical collision will create pulverization of the sample due to circumferential movement of the furnace. The hot gas is blown in the counter-current movement of the sample, as illustrated in Figure 2.12. The zinc will be volatilized as a gas phase and collected by waste gas treatment in the form of dust. The production capacity of RHF is between 10 to 520 kt/year, with the feed limited to dust containing below 5% of Zn due to the high zinc content might cause zinc oxide blockage [34]. However, in practice, RHF can treat zinc-bearing dust/sludge that contains more than 5% zinc, primarily found in EAF dust.



Figure 2.12: Schematic diagram of the reduction process in RHF [34].

Burdens for the RHF plant are high initial investment costs and the high production capacity needed for economic feasibility. The simple process of RHF, along with high-quality DRI and high zinc removal, indicates a promising solution for the treatment of blast furnace dust. RHF has been widely developed with some adjustments by several companies. The RHF-based technologies include FASTMET<sup>®</sup> (by Kobe Steel), INMETCO (by International Metals Reclamation Company, Inc.), DRyIron<sup>™</sup>, ITmk3 (by Kobe Steel and Steel Dynamics), HI-QIP, and COMET (by Centre for Research in Metallurgy (CRM)) which some of the technologies have been established and commercialized [35].

#### **Primus (Paul Wurth)**

Primus by Paul Wurth is limited or more suitable for recycling dust containing more than 5% of zinc from BF, BOF, or EAF [34]. Primus is a reduction process in a multi-stage compartments/hearth furnace consisting of the drying zone, heating zone, and reduction zone, starting from the upper part of the furnace where the materials are fed, as given in Figure 2.13. In the drying zone, water is removed from the dust, followed by removing impurities with high vapor pressure in the heating zone. Subsequently, the reduction of metal oxides occurs in the reduction zone at the bottom of the furnace, with the iron metallization degree could reach up to 98% [34]. The gas leaving the furnace is collected in the bag filter and oxidized to collect the heavy metals in oxide form.



Figure 2.13: Schematic overview of the primus process [34].

The typical input for the primus process is a mix of EAF dust and coal. During the reduction, zinc and lead are recovered in the off-gas leaving iron-rich fractions referred to as DRI. Research on a pilot scale shows that zinc and lead removal rates can reach 96% and more than 90%, respectively [34]. In addition, the secondary dust contains up to 55% of zinc oxide. The Primus process's operating temperature is around 1000°C to 1100°C, which is lower than the RK and RHF. Another advantage of the Primus process is directly mixing samples without necessary granulation. Important things to mention are that the evaporation of alkali compounds can cause furnace corrosion, and the design of a multi-hearth compartment lowers overall productivity [34].

#### Solumet

Solumet is a recycling company located in Quebec, Canada, that processes metal-bearing wastes, including BF dust, using dedicated sinter strands to produce a valuable metal referred to as sinter cake prior to direct reduction, with a capacity of 25 kt/year [36]. The treatment principle of Solumet is a direct reduction to remove zinc and other heavy metals from the BF sludge/dust. The raw materials are mixed with carbon and combusted with a gas flame at the entrance of a tunnel-shaped furnace. Most of the operational data, including the temperature, are undisclosed. The main burden for this option is that the cost and permit for transporting wastes from the Netherlands to Canada might become problematic. The construction of a new plant close to IJmuiden is considered a preferable solution for BF sludge recycling from Tata Steel.

#### 2.1.3. Smelting

In principle, smelting is an extraction process (energy-intensive) requiring higher temperature than roasting and direct reduction, which reduces and melts the ores as input materials to produce refined metal. In the case of dust recycling, the target of smelting is to produce an iron-rich fraction, removing the impurities to the slag while releasing the zinc and other heavy metals into the off-gas [37]. Two-step dust recycling, HIsarna, electric smelting reduction furnaces, coke-packed bed processing, and other integrated industrial smelting routes that have been widely developed for the treatment of EAF, BF, and BOF dust are discussed in the following sections.

#### Two-step Dust Recycling (2sDR)

2sDR is a recycling technique supported and funded by EIT Raw Materials that treats EAF dust through calcination (oxidizing) followed by smelting reduction [38]. The flowsheet of the 2sDR process is given in Figure 2.14. The sample preparations of 2sDR are pelletizing ( $<5 \mu$ m) and drying (to humidity below 6%) of EAF dust. In the calcination process, halogens and lead are accumulated in the gas phase at 1100°C. The clinker dust is then transported to the EAF for the smelting reduction process with the addition of coal. The zinc product will be generated in the off-gas, while metallic fractions and slag are produced through the reduction process.



Figure 2.14: Production flowsheet of Two-step Dust Recycling (2sDR) [39].

Another research of 2sDR by Wegscheider et al. (2015) [40] mentioned that chlorides and fluorides would be removed during calcination, leaving ZnO (with high evaporation temperature) in the clinker dust. The reactions of zinc and iron are given in the below reactions [40]. It is shown that ZnO is captured in the filter from the off-gas in the form of ZnO.

$$ZnO_{(s)} + CO_{(g)} \Longrightarrow Zn_{(g)} + CO_{2(g)}$$
(2.16)

$$Zn_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons ZnO_{(s)}$$
 (2.17)

$$Fe_{3}O_{4(s)} + CO_{(g)} \Longrightarrow 3FeO_{(l)} + CO_{2(g)}$$

$$(2.18)$$

The study by Wegscheider et al. (2015) [40] shows that 99% Fe and 0.004% Zn were found in the metallic fraction from the reduction process. 2sDR process offers a good separation of zinc, other heavy metals, and iron, leading to a high purity of each output fraction [40]. In addition, 73% Zn was contained in the filter dust. However, Wegscheider et al. (2015) [40] research mentioned that some Zn was lost from the calcination process due to the formation of zinc-halide compounds. This study shows a similar technique to the carbochlorination experiments performed by Hamann et al. (2021) [6] which the heavy metals were released in the form of chlorides during the calcination at 1100°C. Therefore if 2sDR is used for recycling the BF sludge, with lower Zn content than EAF, it is more likely that the majority of zinc and other heavy metals might be removed during calcination as reported in several direct reduction-based experiments [5, 6, 11, 34]. This 2sDR process has developed from an established lab to pilot scale testing [39].

#### HIsarna

HIsarna is a new ironmaking (smelting-reduction) technology developed by Tata Steel, which can also recycle zinc-bearing wastes. The research on recycling using HIsarna simulation was carried out by

Strijker (2020) [27] for the treatment of BF dust, BOF dust, and historical oxychalk sludge (HOKS). The experiment was conducted in a horizontal tube furnace and thermogravimetric analysis (TGA) furnace, as a HIsarna simulation, at 1000°C, 1300°C, and 1500°C in a controlled atmosphere. The idea of the experiment was to reduce iron oxide while concentrating zinc and other heavy metals in the secondary dust, which is similar to the direct reduction concept in Rotary Kiln or Rotary Hearth Furnace. The atmospheric conditions were set to inert with nitrogen gas and varied to a condition with 50%CO-50%CO<sub>2</sub> to compare the reduction behavior. The experiment concludes that at 1000°C, 94-95% of zinc was lost to the gas. Besides, at 1300°C, all the carbon and zinc were lost entirely to the gas in an inert (N<sub>2</sub>) and 50/50 CO/CO<sub>2</sub> atmosphere. Zinc and other heavy metals concentration in the residue after the reactions at 1000°C in an inert atmosphere of two different mixtures are presented in Figure 2.15. Based on Figure 2.15, zinc and lead were utterly lost after 20 minutes in both samples. Another treatment at a temperature between 1300-1500°C in the TGA furnace resulted in 97-98% of iron content in the DRI. The author also measured the secondary dust composition generated from the direct reduction using SEM-EDS which the dust contains up to 60% of zinc. Based on this research, zinc content in the secondary dust is sufficient as input to the zinc smelter, with the acceptance range of Zn between 55-75% [27]. HIsarna technology was started on a pilot scale for primary production while the use for zinc recovery from industrial wastes was carried out in a project called Reclamet [41].



Figure 2.15: Concentrations of elements in (a) HOKS/BF (80:20) sample and (b) BOF/BF (76:24) sample as a function of time during the reduction in HIsarna simulation at 1000°C under N<sub>2</sub> gas [27].

#### Electric Smelting Reduction Furnace (ESRF)

The ESRF technique was introduced by Taiwan's KATEC RnD and Japan's JP Steel Plantech to extract valuable metals from industrial solid waste [34]. ESRF requires electrical energy to melt the materials under very high temperatures completely. A mixture of sintered dust with limestone and coke is fed to the furnace for smelting. Zinc and other heavy metals will be concentrated in the gas phase and captured by a bag filter. The zinc removal through ESRF technology is between 65 to 82% [34]. The final product of pig iron and slag with low zinc and low lead contents from the ESRF process can be reintroduced to the iron production cycle. The flowsheet of typical ESRF is given in Figure 2.16. The main disadvantages of ESRF are the high energy cost from high-temperature heating by electrical energy and the difficulty of recycling the generated heat.



Figure 2.16: Schematic flowsheet and reduction reactions of ESRF [34].

#### **Coke-packed Bed Process (CBP)**

The coke-packed bed process is another recycling option for industrial zinc-bearing waste, including EAF dust [34]. Similar to ESRF, CBP requires a very high temperature to entirely reduce and melt all metal oxides at a temperature above 1550°C. The schematic of the CBP process is given in Figure 2.17.



Figure 2.17: Schematic of coke-packed Bed Process (CBP) proces [34].

Based on Figure 2.17, a mix of EAF dust and coked is injected into the furnace from the upper tuyere. At the same time, hot air is blown from the bottom, creating an opposite flow with the input materials falling, forming a reduction area. Ishiwata et al. (2001) [42] conducted an experimental study on recycling EAF dust containing 27.7% zinc and 3.22% lead using the CBP process. The experiment resulted in high zinc and lead recovery in the secondary dust containing 60% zinc and 6% lead. Moreover, the iron-rich residue contains low zinc and lead with 0.005% and 0.001%, respectively. The result indicates an excellent separation of iron-rich fraction and zinc-rich secondary dust. However, similar to ESRF, the CBP process requires a high amount of heat with difficulty in heat reutilizing, leading to high operating costs. At the same time, zinc might also be deposited on the top wall of the furnace [34]. In summary, the CBP process has been commercially established for BOF dust recycling by Kawasaki Steel Corp. with a metal production capacity of 200 tons/day [43]. For the EAF dust treatment, pilot plant tests resulted in >99% recovery of zinc and lead in the secondary product containing 60% Zn and 6.2% Pb [43].

#### **DK Recycling**

DK Recycling is a recycling company in Duisburg, Germany, that treats ferrous wastes, including BF sludge, to produce pig iron with a 450 kt/year production capacity through an integrated sinter plant and blast furnace [44]. The secondary dust will be generated from the blast furnace containing 65-68% zinc and 1-2% lead. The production flowsheet of DK Recycling is given in Figure 2.18. Since DK Recycling is carried out in a blast furnace, zinc content in the input has a detrimental effect on the reduction process, such as refractory loss or lining problems. Blast furnace sludge from Tata Steel in IJmuiden was used for the recycling process in DK Recycling between 1999 and 2007 [36]. As mentioned in the internal memo by Honingh (2021) [36], the deliveries of the BF sludge from Tata Steel ended due to the low iron content of the BF sludge in the new feedstocks. The termination might be due to the economic conditions that need to be achieved by DK Recycling to compromise with the negative impact of zinc contained in the BF sludge. Another report by Xiao (2021) [45] mentioned that the charge to send BF sludge from Tata Steel in IJmuiden to DK Recycling is considered expensive, with the problem of cross-border permit.

#### Oxycup

The Oxycup plant has been developed since 2011 at TISCO in China to treat dust and sludge wastes as self-reducing bricks combined with steel scrap [47]. TISCO was the client of Küttner GmbH in the construction of Oxycup plant. Küttner GmbH also developed an Oxycup shaft furnace for ThyssenKrupp Steel in Duisburg, Germany, constructed in 2004. The plant at TISCO can process 600 Kt/year of brick containing sludges/dust and 100 kt/year of steel scrap. The main features of the technology are brick manufacturing and the Oxycup shaft furnace to melt and reduce the brick. The sludges/dust input



Figure 2.18: DK Recycling flowsheet [46].

contains a significant amount of carbon, as given in Table 1.2, which can induce a self-reducing behavior during the high-temperature treatment. Laboratory tests showed that iron's completed reduction (100% metalization) was achieved at 1400°C [47]. The layout of the Oxycup plant is given in Figure 2.19. Scrap, agglomerates containing sludges (bricks), and coke are mixed as input to the shaft furnace while the gas from the furnace is recirculated for heating. The hot metal produced from the TISCO plant through the Oxycup process treating BOF and BF dust contains 94.23% metallic iron with 3.79% carbon and 1.39% silicon [47]. However, the report did not mention the recovery and removal of zinc and other heavy metals as the main objective of Oxycup was to produce metallic iron.



Figure 2.19: Oxycup plant layout [47].

#### RecoDust

RecoDust is the technological breakthrough to process low zinc-bearing materials, as an alternative for the waelz-process, which can only be economical with a high zinc content of over 20% [48]. The flowsheet of RecoDust is given in Figure 2.20. The main principle of RecoDust is the suspension smelting of iron and the separation of the zinc and heavy metals in the gas phase inside the flash reactor at 1700-1900°C injected with an oxygen burner. The zinc leaving the flash reactor is oxidized, creating zinc oxide through several cooling steps followed by dust capturing in a bag filter. On the other hand, the iron-rich slag is treated through dry slag granulation in a rotating disk. RecoDust offers the process without the necessity of additives (self-reduction), but the dust must be dry and less than 1 mm. The results of the RecoDust experiment show low zinc (<1.5%) found in the slag in the range of 0.14-1.36%, as given in Table 2.1. In summary, the advantages of the RecoDust process are high product quality with no requirements for dust pre-treatment and has been implemented in a pilot plant with a capacity of up to 300 kg/h [48]. However, the operating temperature is very high compared to similar smelting alternatives, and the slag needs additional recycling treatment.

 Table 2.1: Experimental results of zinc content in

 the input and slag from the RecoDust process [48].

Sample	%Fe Input	%Zn Input	%Zn Slag
Dust 1	51.5	5.5	0.14
Dust 2	51.5	5.1	0.11
Dust 3	45.1	10.3	0.14
Dust 4	42.8	8.6	0.21
Dust 5	45.2	10.3	0.59
Dust 6	44.1	13.8	1.17
Dust 7	37.3	9.9	1.36



Figure 2.20: Flowsheet of Recodust process [48].

### 2.2. Hydrometallurgical Process

The hydrometallurgical technique extracts metals of interest by leaching or selective dissolution in an aqueous solution followed by recovery, or purification [49]. This section discusses various leaching methods using different lixiviants (reagents) in recycling zinc-bearing wastes to dissolve the zinc and other heavy metals, producing an iron-rich precipitate/residue. The principle of leaching is to obtain/-dissolve zinc compounds in an equilibrium state under different conditions in particular solutions. The diagram to predict the phase stability in an electrochemically controlled system is called Pourbaix Diagram or potential-pH diagram [50]. The equilibrium phase refers to the phase of particular elements that will be formed, such as a precipitate (solid) or ions in a solution. In this section, different types of lixiviant for the hydrometallurgical process are discussed extensively, including ammonia (Subsection 2.2.1), acid (Subsection 2.2.2), and alkaline (Subsection 2.2.3) based lixiviant.

#### 2.2.1. Ammonia Leaching

Verburg (2015) [4], Feenstra (2016) [3], and Kempke (2019) [2] conducted research based on leaching with ammonia and ammonium salts to recycle blast furnace sludge from Tata Steel in IJmuiden (see Table 1.2 No. 1, 8, and 4). These three research were master thesis projects from TU Delft in collaboration with Tata Steel. three different types of 0.5-2 M ammonia-based lixiviant  $(NH_3-(NH_4)_2CO_3, NH_3-NH_4CI, and NH_3-(NH_4)_2SO_4)$  were used by Verburg (2015) [4] for leaching at temperatures in the range of 20-60°C with the addition of oxygen. The principle of this leaching was based on the Pourbaix Diagram of zinc in an ammonia solution, as given in Figure 2.21. Based on Figure 2.21, zinc can be dissolved with ammonia in the range of pH 8-11. The underlying leaching reactions of zinc dissolution are given in Equation 2.20 [4].

$$ZnO + 2NH_4^+ + 2NH_3 \implies Zn(NH_3)_4^{2+} + H_2O$$
 (2.19)

$$ZnS + 2O_2 + 4NH_3 \Longrightarrow Zn(NH_3)_4SO_4$$
(2.20)



Figure 2.21: Pourbaix diagram of Zn in ammonia-based solution [4]. The blue region indicates the pH range (8-11) in which zinc is dissolved.

Based on the experiment results from Verburg (2015) [4] using three different ammonia-based reagents, 69% of zinc removal was achieved (highest removal) through leaching at 30°C with  $NH_3-(NH_4)_2SO_4$  and oxygen addition. The presence of ZnS hindered leaching efficiency even with the addition of oxygen. This study did not achieve the target of 80% zinc recovery. Feenstra (2016) [3] conducted research on leaching with ammonia (5M) and ammonium sulfate (2M) at 30°C following roasting pretreatment, as previously explained in the pyrometallurgical section. The results showed that 84% of zinc was extracted after 30 minutes, and the remaining 16% was leached after 90 minutes. The low extraction rates of zinc (<60%) were obtained with the sample without roasting pre-treatment. The study concluded that the leaching was effective with the roasted sample due to the conversion of ZnS to leachable ZnO [3].

The research by Kempke (2019) [2] was done through microwave-assisted leaching with oxygen and oxidants. The tests were carried out using ammonium carbonate and ammonium sulfate at 40°C, 5-watt microwave power, 20 L/h oxygen, and three variations of oxidants (FeCl<sub>3</sub>, Fe(OH)<sub>3</sub>, and KMnO<sub>4</sub>). The resulting extraction rate of zinc, lead, and cadmium (highest results) were 61% and 42%, and 83%, respectively, from the microwave-assisted leaching with ammonium sulfate and FeCl<sub>3</sub> oxidant. Besides, the author mentioned that most sulfur comes from the blast furnace, which creates a metal sulfide compound, including zinc sulfide. Based on the results from the test by Kempke (2019) [2], a target of 80% extraction of zinc was also not achieved.

Another study with ammonia/ammonium leaching but without oxygen addition was done by Rodriguez et al. (2020) [22] to recycle BOF dust, as given composition in Table 1.2 No. 14. The lixiviants used were ammonium chloride (NH<sub>4</sub>Cl), ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), and the mixture of these three. The temperature was set to 60°C, and the leaching was done for 3 hours. The experiment results are given in Figure 2.22. Based on Figure 2.22, the highest leaching efficiency was around 70% using a mix of ammonium chloride 1.5 M with ammonia 1.5 M. In addition, the residue after leaching contains 1.8 to 5.5% of zinc. The author concluded that the zinc content in the residue is above the acceptance limit for subsequent production process in a blast furnace at ArcelorMittal Bremen, Germany [22].


Figure 2.22: Leaching efficiency with different ammonia based lixiviants [22].

#### IntraCycle Process

IntraCycle is proposed as an economical hydrometallurgical recycling route of BF sludge based on the past three master theses done at TU Delft (see Subsection 2.2.1). The process has been developed in order to process 30 kt of produced BF sludge annually in IJmuiden [51]. The idea of IntraCycle is to introduce a low-cost BF sludge treatment of around 45  $\in$ /ton, below the cost of landfilling in 2015, through oxidative and low-temperature leaching. The primary process was adapted from the research by Verburg (2015) [4] and Kempke (2019) [2], which use ammonia-based lixiviant (e.g., (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) to selectively remove zinc and other heavy metals from the BF sludge. The flowsheet of IntraCycle is given in Figure 2.23.



Figure 2.23: IntraCycle flowsheet developed by Tata Steel in IJmuiden [51].

Two leaching steps were proposed to obtain the high efficiency of heavy metals dissolution. The pregnant leach solution will be sent to the purification step to precipitate heavy metals through pH adjustment via ammonia distillation or precipitation via sulfidation. On the other hand, the iron-rich residue will be recycled back to the sinter plant as secondary raw materials for ironmaking. Roasting pre-treatment could be implemented within the IntraCycle recycling process to improve leaching efficiency by converting zinc sulfide and zinc ferrite to leachable zinc oxide [3]. The result of the IntraCycle studies (see <u>Subsection 2.2.1</u>) shows a low zinc removal of 60-70% through ammonia-based leaching, and more than 80% through leaching with roasting pre-treatment [51]. It was concluded that the combination of roasting and leaching could effectively remove heavy metals. However, as mentioned in <u>Subsection</u> 2.1.1, zinc was split into gas and solid residue during roasting, complicating the overall process. In summary, IntraCyle has the advantages of relatively low operating cost, mild leaching intensity, and a closed-loop lixiviant circulation but is limited to 70% of heavy metals removal (without roasting pre-treatment).

#### **UBC-Chaparral**

The UBC-Chaparral process is an integrated hydrometallurgical route developed by Dreisinger et al. (1990) [52] from the University of British Columbia. This technique aims to recycle EAF dust containing 20.5% Zn produced by Chaparral in Texas, USA. The flowsheet of the UBC-Chaparral process is given in Figure 2.24.



Figure 2.24: UBC-Chaparral process flowsheet [1].

Based on Figure 2.24, the primary process of the UBC-Chaparral is the leaching of zinc with ammonia, followed by heavy metal precipitation and zinc precipitation. The materials are washed before zinc leaching to remove chloride compounds, followed by lime leach in acetic acid solution to extract CaO with partial PbO and CdO, producing a zinc-rich residue and pregnant leach solution. The residue is further leached with ammonia, followed by zinc precipitation to produce zinc carbonate. On the other hand, the pregnant leach solution is sent to the cementation process to precipitate lead and cadmium, then circulate back into the system. The liquid solution after heavy metals precipitation is processed through resin treatment to produce the final iron-rich residue. The leaching of zinc in the UBC-Chaparral process is based on the following reactions [52].

$$ZnCO_3 + 4 NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + CO_3^{2-}$$
(2.21)

$$ZnO + 2 NH_4^+ + 2 NH_3 \Longrightarrow Zn(NH_3)_4^{2+} + H_2O$$
(2.22)

Based on this process, leaching with a mix of 4M NH<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> at room temperature for 2 hours resulted in the incomplete dissolution of zinc (41.5%). The low extraction of zinc is mainly due to the presence of zinc sulfide. The overall results of the UBC-Chaparral process are a 55-60% recovery of Pb as cement, 55-60% Zn recovery, and 80-85% Cd recovery. The authors calculated the economic value of the UBC-Chaparral plant, including net operation cost between \$15-\$60 per ton of treated dust and the capital cost of \$4.5-5.5 million.

#### 2.2.2. Acid Leaching

Luo et al. (2022) [17] conducted research to recycle blast furnace dust using HCI and NaCI. The sample contained 9.5% zinc, as given in Table 1.2 Ref No. 5. The leaching conditions were varied with 2-6 pH, at 30-90°C, 0-4 M NaCI, 0-1 M HCI, 1:4-1:8 solid/liquid, and 1-4 hour leaching time. The

thermodynamic analysis prior to leaching experiments was modeled using the Pourbaix diagram of zinc stability in a Zn-S-Cl-H<sub>2</sub>O and Fe-Cl-H<sub>2</sub>O system at 25°C and 100°C, as given in Figure 2.25.



Figure 2.25: Pourbaix diagram of Zn-S-Cl-H<sub>2</sub>O at (a) 25°C, (b) 100°C, and Fe-Cl-H<sub>2</sub>O at (c) 25°C, (d) 100°C (d) [17].

Figure 2.25 shows the equilibrium state of zinc ions under different temperatures, pH, and potential. Zinc is stable in the acidic region at a CI concentration equal to zero, and the stability is lowered when reaching pH 4 as the temperature changes to 100°C. Moreover, increasing redox potential increases the stability area of zinc ions, and more CI<sup>-</sup> was concluded to extend the area of free zinc ions [17]. Regarding iron, the stability of the ions is shifted to low pH as the temperature is lowered to 25°C while increasing redox potential leads to a smaller Fe ions stability area. Based on the results of the experimental works, the highest zinc extraction of 93.2% was achieved with leaching using 3M NaCl and 0.25M HCl for 2 hours at 70°C, pH 4, 1:4 s/l. The effects of the varied parameters on the leaching efficiency are given in Figure 2.26.



Figure 2.26: Zinc and iron leaching efficiency under different (a) pH, (b) temperature, (c) NaCl concentration, (d) s/l ratio, (e) HCl concentration, and (f) leaching time [17].

Another leaching experiment with chlorine-based lixiviant was done by G. Van Weert (1993) [19]. The sample was the blast furnace sludge from Hoogovens (now Tata Steel) in IJmuiden, which the composition is given in Table 1.2 No. 7. The pressured leaching tests were done in an autoclave using spent pickling acid consisting of 1-17 g/L HCl and 30-191 g/L FeCl<sub>2</sub> with and without the addition of NaOH. The temperature was set to 140°C, with an  $O_2$  addition of 1000 kPa for 60 min. The results from the experiments are given in Table 2.2. Based on Table 2.2, high zinc and lead extractions were obtained with or without adding NaOH. Moreover, the leaching residue contains a small amount of zinc (min. 0.09%) and lead (min. 0.06%), indicating a very efficient dissolution. An important thing to mention is that the pressurized leaching with chloride might create a severe and corrosive leaching condition with abundant foam due to the carbon content in the dust, complicating the process. Additional treatment for the leaching solution is also needed to extract or precipitate further the zinc and lead in oxide form separately.

Results	Test 61	Test 68	Test 69	Test 70	Test 71
Dust (g)	154	170	170	163	163
Acid (g)	227	158	158	201	201
NaOH 1M (ml)	0	0	75	0	110
Final pH	0.63	0.71	1.08	0.67	1.01
%Zn sol.	96	94.4	95.3	95.2	96.9
%Pb sol.	90	90.9	90.3	89.1	90.6
%Zn in residue	0.21	0.19	0.16	0.14	0.09
%Pb in residue	0.11	0.06	0.06	0.07	0.06
%Fe in residue	30.4	15.8	16.6	25.7	26.1

Table 2.2: Extraction rate of zinc, lead, and residue composition from high-pressure leaching tests [19].

Another acid leaching was done by Mardones (2012) [24] using three different types of lixiviants: sulfuric acid ( $H_2SO_4$ ), hydrochloric acid (HCI), and nitric acid ( $HNO_3$ ), to extract zinc from gahnite (see Table 1.2 No. 18). As explained in the previous section, gahnite contains a large amount of zinc (35%) compared to the typical zinc-bearing dust generated from the ironmaking and steelmaking process. The leaching tests were done in different conditions (atmospheric and pressurized leaching). The atmospheric leaching with 4M of each three lixiviants at 90°C for 120 minutes resulted in no amount of zinc being leached. For pressurized leaching, the pressure was set to 30 to 38 atm and a higher temperature of 140-285°C for 90 min. The pressurized leaching with sulfuric acid and nitric acid resulted in 2.6% to 22.2% extraction of zinc. In conclusion, both atmospheric and pressured leaching with sulfuric acid, nitric acid, and hydrochloric acid were not efficient in extracting zinc from gahnite [24].

Several studies reported the high leaching efficiency of zinc using sulfuric acid. Steer and Griffiths (2013) [53] achieved more than 98% of zinc dissolution, but 47% of iron was leached together with zinc. The high iron dissolution reported might be due to extensive leaching time (24 h) with high  $H_2SO_4$  concentration [1]. Andersson et al. (2017) [54] reported a 95% leaching recovery of zinc, leaving a high-iron rich residue with 91% iron recovery. In this case, the leaching was done in 10 minutes at 80°C, while a longer leaching time was reported leading to a higher dissolution of iron. However, the sample used in this study contains a low amount of zinc of only 0.44%, which might contribute significantly to a high leaching efficiency. In addition, the study did not report lead and cadmium behavior during leaching.

Leaching with organic acid has been studied by Steer and Griffiths (2013) [53] to treat BF sludge. The authors conducted leaching experiments using different types of carboxylic acids, including propanedionic, prop-2-enoic, citric, ethanoic, ethanedioic, and benzoic acids. The principle of leaching reactions with organic acid is given in the below equations.

$$2 \text{RCOOH} + \text{ZnO} = (\text{RCOO})_2 \text{Zn} + \text{H}_2 \text{O}$$
 (2.23)

$$6 \text{ RCOOH} + \text{Fe}_2 O_3 = 2 (\text{RCOO})_3 \text{Fe} + {}_3 \text{H}_2 \text{O}$$
 (2.24)

This study resulted in high zinc extraction along with co-dissolution of iron. The highest zinc extraction was achieved through leaching with propanedioic with 93.9%. However, 18.5% iron was lost in the solution. The extraction rates of zinc and iron with different lixiviants mentioned in this study are summarized in Figure 2.27. The author also compared the leaching results with other strong acid lixiviants. As mentioned in the report, iron dissolution was mainly affected by the pH and followed the Bronsted-Lowry theory which carboxylic acids donate a proton to the iron oxide as expressed in Equation 2.24. Moreover, Fe<sub>2</sub><sup>+</sup> ion is stable in low pH, which is in acidic conditions, as illustrated in the Pourbaix Diagram of iron (see Figure 2.25).



Figure 2.27: Zinc and iron extraction rates using different 1 M carboxylic lixiviants and other strong acids [53].

#### SIDMAR Process

ArcelorMittal initiated the SIDMAR process in collaboration with KU Leuven, Belgium, in developing a recycling route for BF sludge based on oxidative leaching with HCI [1]. The flowsheet of SIDMAR is given in Figure 2.28, which the sludge is added from the bottom of the reactor.



Figure 2.28: SIDMAR process recycling flowsheet [1].

The idea of the SIDMAR process is to obtain a high leaching efficiency even with the presence of ZnS in the dust, which requires oxidative and highly acidic conditions (pH < 0.25) to be dissolved [1]. The process could achieve 95% zinc and 92% lead leaching efficiency. However, 32-49% of iron was lost in the solution. Therefore, two ion exchangers are used to separate zinc and lead chlorides from the filtrate, and the solution is recirculated in the reactor for another iron precipitation. SIDMAR process has already been submitted as a patent and was estimated to cost USD 125 per ton of dry solids [1].

#### **AMAX process**

AMAX Inc. has developed a leaching process with HCl to treat EAF dust [1]. First, the dust is leached with HCl, followed by liquid-solid separation to remove the residue. Next, the solution is oxidized with chlorine gas with lime addition to precipitate iron. Subsequently, the solution is sent to the solvent extraction process with D2EHPA or Cyanex 272 for purification, followed by electrowinning to produce a zinc cathode. The spent solution is then recycled back to the HCl plant. The leaching could extract 88% of zinc and 48% of iron [1]. The author also mentioned that increasing the HCl concentration to 200 g/l could increase zinc extraction to 93%. However, the solid residue from solid-liquid separation is not explained further on which elements it contains and what would be the following processing option. The flowsheet of AMAX is given in Figure 2.29.



Figure 2.29: AMAX recycling process of EAF dust [1].

#### **Terra Gaia Process**

Terra Gaia Environmental Group Inc. has established a recycling route for EAF dust based on  $FeCl_3$  leaching [1]. The process flowsheet can be seen in Figure 2.30. Based on Figure 2.30, the process starts with mixing  $FeCl_3$  and EAF dust in an atmospheric pressure tank. Hydrolyzing the solution will produce HCl to extract zinc and lead oxide. The iron-rich slurry is then sent to an autoclave and heated to 140°C for 30 minutes to convert the slurry to crystalline residue before filtering. Then the filtering takes place in a thickener, followed by brine washing to produce hematite as a residue. Meanwhile, the lead can be recovered from the solution through cementation with iron, and zinc is recovered from the filtrate by solvent extraction followed by purification steps.



Figure 2.30: Terra Gaia recycling process [1].

The lab test work of Terra Gaia has processed EAF dust with 11-27% Zn and 1.1-3.8% Pb. The experimental tests were done using ferric-chloride acid at 140 and 170°C for 45, 90, and 180 minutes by McElroy (1994) [55]. The experiments resulted in zinc and lead extraction of up to 99.3% and 99.5%, respectively, while the leaching residue contains 0.45% Pb. The calculated operating cost for this recycling route was USD 194/ton dust for 20kt ton/year capacity [55].

## INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> Integrated Process

INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> is an integrated pyrometallurgical and hydrometallurgical process to treat zincbearing dust, including EAF dust, developed by Engitec [15]. INDUTEC process is a smelting reduction process that produces pig iron and zinc oxide fume containing Pb, Cd, and Ag. Accordingly, the EZINEX is a complete hydrometallurgical route, including chloride leaching, purification, electrowinning, and crystallization, which treat zinc oxide produced from INDUTEC process. The flowsheet of the INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> Integrated Process is given in Figure 2.31.



Figure 2.31: Flowsheet of INDUTEC®/EZINEX® process [15].

The first step of EZINEX is leaching to dissolve all the zinc and heavy metals using ammonium chloride (NH<sub>4</sub>CI) at 70-80°C in neutral pH, which will dissolve zinc oxide entirely. Hence, the undissolved zinc ferrite residue is returned to the INDUTEC process. The pregnant leach solution is sent to the cementation process to precipitate heavy metals, including lead and cadmium. The typical cement composition is 63-75% Pb, 3-8% Zn, <0.5% Cd. The last step of EZINEX is the electrowinning of purified zinc solution to produce zinc cathode at a temperature above 65°C with high current densities (300-400 A/m2) in the pH of 6-7 by adding ammonia solution. The deposition time is around 24-48 hours. The cathode and anode reactions (Equation 2.25 to 2.27) have a 94-98% efficiency [15]. After electrowinning, the following step is carbonation and crystallization to remove chlorides, fluorides, calcium, and magnesium to avoid unwanted crystallization of salts during the process. Then, the solution is recycled back to the INDUTEC process. The reactions involved in the electrowinning step are mentioned below. It is shown that the end products of the electrowinning are metallic zinc and generated alkali chlorides.

$$Cathode : Zn(NH_3)_2Cl_2 + 2e^- \longrightarrow Zn + 2NH_3 + 2Cl^-$$
(2.25)

Anode: 
$$2 \operatorname{CI}^- + \frac{2}{3} \operatorname{NH}_3 \longrightarrow 2 \operatorname{HCI} + \frac{1}{3} \operatorname{N}_2 + 2 \operatorname{e}^-$$
 (2.26)

$$Cell : Zn(NH)_{3}Cl_{2} + \frac{2}{3}NH_{3} \longrightarrow Zn + \frac{1}{3}N_{2} + 2NH_{4}Cl \qquad (2.27)$$

In general, INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> is suitable for recycling the BF sludge due to the pyrometallurgical step's high-temperature treatment, which can remove all of the zinc and heavy metals to be further processed in the next leaching step. The last purification step of cementation and electrowinning could also produce a high percentage of zinc in the final product and be purely separated from the heavy metals (Pb, Cd). The product quality of INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> is given in Figure 2.32. The pilot plant with 500 t/y zinc production from EAF dust was built in 1993 and developed into an industrial plant with an improved 2000 t/y zinc production the following year [15].



Figure 2.32: Product quality of INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> process [15].

#### Carbon Iron Valorization (CIROVAL<sup>™</sup>)

CIROVAL<sup>™</sup>is a newly developed technology by Paul Wurth treating BF sludge through oxidized leaching at low temperatures [28]. The sludge is leached with hydrochloric acid to dissolve zinc and lead under the oxidized condition at 55°C. Subsequent filtration produces an iron-rich residue. The liquid solution containing zinc and heavy metals is then neutralized with lime at pH 8-9, followed by filtration. Experimental work of the CIROVAL <sup>™</sup>process dealt with a sample of BF sludge (see Table 1.2 Ref No. 24) resulted in an iron-carbon recovery of 85% with <0.3% Zn and 0.1% Pb. The final Zn/Pb by-product contained 20% Zn and 5% lead. The process offers simplicity and low investment cost. However, the final zinc product might not be sufficient for the zinc smelter industry, needing additional treatment. In addition, the research did not report sample that contains zinc compounds with higher resistivity to leaching (e.g., zinc sulfide and zinc ferrite), which might make the dissolution more difficult. The effluent or liquid waste generated from the recycling process also needs further treatment. The CIROVAL<sup>™</sup>is typically capable of treating 20-25 kt per year of BF sludge with 2-3% Zn content. The flowsheet of CIROVAL<sup>™</sup>is given in Figure 2.33.



Figure 2.33: CIROVAL™ process flowsheet [28].

Piezanowski et al. (2015) [28] calculated the economic perspectives of processing BF sludge with CIROVAL<sup>™</sup>in various production capacities. The cost function graph is given in Figure 2.34. It was shown that the operating cost decreases significantly with higher capacity and is still lower than the

maximum dumping cost with the lowest production capacity option. A pilot test in treating BF sludge from Tata Steel in IJmuiden through the CIROVAL<sup>™</sup> process was done in 2016. However, the saltwater filtrate still contains a high amount of heavy metal, which needs further treatment [51].



Figure 2.34: The economic perspective of CIROVAL™ process [28].

#### **Modified Zincex Process**

Modified Zincex Process is an integrated hydrometallurgical route including atmospheric leaching, purification, solvent extraction, and electrowinning, developed by Técnicas Reunidas, S.A. in Madrid, Spain. The flowsheet of the Modified Zincex Process is given in Figure 2.35.



Figure 2.35: Flowsheet of Modified Zincex Process [56].

According to the flowsheet studied by Díaz and Martín (1994) [56], Modified Zincex Leaching started with the leaching process in atmospheric and mild conditions using sulfuric acid to dissolve zinc oxide. The next step is solution purification by precipitation impurities of iron and aluminum. Next, the organic extraction using a cationic exchanger (D2EHPA) was carried out to extract the zinc, followed by zinc stripping. The last step is electrowinning and melting to produce a zinc ingot. The electrolyte from the

electrowinning is recycled back to the stripping process as a circular circuit. The reactions of zinc that occurred throughout the Modified Zincex Process are given in the below equations [56].

$$Dissolution: ZnO + 2H^{+} \Longrightarrow Zn^{2+} + H_{2}O$$
(2.28)

$$Extraction: 2 RH + Zn^{2+} \Longrightarrow R_2 Zn + 2 H^+$$
(2.29)

$$Stripping : R_2Zn + 2H^+ \Longrightarrow 2RH + Zn^{2+}$$
(2.30)

$$Electrowinning: Zn^{2+} + H_2O \Longrightarrow Zn + 2H^+ + \frac{1}{2}O_2$$
 (2.31)

Experimental results of the Modified Zincex Process at atmospheric leaching with  $H_2SO_4$  0.5 M at 40°C for 1 hour in pH 2 treating EAF dust containing 22-37% Zn and 0.5-8% Pb resulted in 67-90% zinc recovery [56]. The process offers high zinc recovery efficiency with high selectivity towards zinc and heavy metals and is environmentally friendly. However, the process is more suitable for high zincbearing input (EAF dust), which the process might not be efficient for BF sludge. In addition,  $H_2SO_4$  is not selective to lead, which might stick in the residue and circulate back to the ironmaking process.

#### 2.2.3. Alkaline Leaching

Alkaline leaching using sodium hydroxide (NaOH) to extract zinc from EAF dust was done by Dutra et al. (2006) [25] and Chairaksa-Fujimoto et al. (2016) [26]. Dutra et al. (2006) [25] conducted the leaching experiments in four conditions: conventional leaching, pressure leaching, leaching following microwave treatment, and leaching under ultrasonic agitation. The sample composition is given in Table 1.2 Ref 19. The zinc recovery of leaching under conventional and pressure leaching is given in Figure 2.36. The zinc recovery was between 30-74% and 40-55% for conventional and pressure leaching, respectively. Pressure leaching was reported to lower the recovery due to zinc ferrite precipitation. EAF dust leached in 6 M sodium hydroxide solution at 90°C following microwave oven resulted in the highest zinc recovery of 60.4% for 240 minutes. This study showed that zincite (ZnO) was easily dissolved through conventional leaching, while zinc ferrite was resistant to leaching, leading to low zinc recovery below 75% [25].



Figure 2.36: Zinc recovery with conventional leaching (left) and pressure leaching (right) under different NaOH concentrations and temperatures [25].

A different approach to alkaline leaching was conducted by Chairaksa-Fujimoto et al. (2016) [26] by introducing pre-treatment of EAF dust prior to leaching. The sample composition is given in Table 1.2 No. 20. EAF dust was reacted with CaO at 1100°C for 5 hours to convert zinc ferrite to leachable zincite prior to alkaline leaching. Subsequently, the leaching treatments were varied with 0.5 to 2 M NaOH at between 25°C to 70°C for up to 6 h. The leaching efficiency of the pre-treated and raw samples from alkaline leaching is given in Figure 2.37. Based on Figure 2.37, it can be seen clearly that "CaO treatment" could improve the zinc leaching efficiency significantly up to 100% compared to the leaching efficiency of the untreated sample with only close to 50%. The results of this study are similar to the results by Feenstra (2016) [3] which high zinc dissolution was achieved after thermal treatment of the samples. The high leaching efficiency of the treated sample was also due to the conversion

of zinc ferrite and zinc chloride to leachable zinc oxide, as expressed by the phases analysis of zinc abundance of the raw and treated sample in Figure 2.38.



Figure 2.37: Leaching efficiency Zn, Ca, and Fe of pre-treated and raw samples under alkaline leaching condition of 2 M NaOH at 70°C and 1:300 S/L ratio [26].

It can be seen that only ZnO was available in the CaO-treated sample. In addition, the study reported that the leach residue only contains 0.36% of zinc and 27.6% Fe. However, the study did not measure the loss of zinc and other metals during the CaO treatment, as the zinc content decreased from 24.24% to 15.99%. Some amount of zinc and other heavy metals might be concentrated in the gas phase, which could complicate the whole recycling process, as this was also the burden for the roasting research by Feenstra (2016) [3].



Figure 2.38: The zinc phase distribution of CaO treated and raw samples [26].

# 2.3. Comparative Study on the Recycling Process

This section consists of the overall summary and comparative discussion on the pyrometallurgical and hydrometallurgical routes provided in the previous section. The comparative study aims to find the most suitable recycling solution for treating blast furnace sludge from Tata Steel in IJmuiden. The comparative assessment is based on technical, environmental, and economic aspects.

#### 2.3.1. Comparative Study on the Pyrometallurgical Route

Compared to the hydrometallurgical route, the pyrometallurgical route has been widely used in the industry to treat zinc-bearing wastes, including blast furnace sludge [34]. As discussed in Section 2.1, pyrometallurgy offers a high percentage of zinc and heavy metals removal through roasting, direct reduction, or smelting. This route can remove zinc compounds, including the phases resistant to leaching (e.g., ZnS, ZnFe<sub>2</sub>O<sub>4</sub>), as a hindrance to the hydrometallurgical route. Regarding route simplicity, the direct reduction of the sludge/dust resulted in good quality products for direct use in the relevant industry, consisting of only an iron-rich fraction as the residue and a zinc-rich fraction (containing heavy metals) from off-gas filtering. The high carbon content of dust, especially from the blast furnace (see Table 1.2), could promote a self-reducing behavior for direct reduction without the need for a reducing agent (cokes) [5, 6]. Besides the advantages of the pyrometallurgical route, the limitation lies within the minimum zinc content based on the economic perspective. Some pyrometallurgical techniques mentioned in the previous chapter requires a high percentage of zinc input with specific input tonnage. For example, Rotary/Waelz Kiln is mainly used to recycle dust with more than 15% zinc, commonly contained in EAF dust [34]. Moreover, pyrometallurgy involving a high-temperature furnace requires a substantial initial capital investment, commonly used to extract high-grade ores [57]. Consequently, blast furnace sludge from Tata Steel in IJmuiden with low zinc content (1.5-8%) is limited to particular pyrometallurgical techniques to achieve a positive economic benefit. Some established smelting-based technology, such as ESRF and CBP, requires significant energy to melt the input materials entirely [34]. The slag is then generated as a byproduct that needs additional waste treatment. Sample preparation for the pyrometallurgical route discussed in Section 2.1 is given in Table 2.3. More detailed information, including the used equipment and best operating parameters and results, is given in Appendix A.

No.	Technique	Advantages	Disadvantages	Ref.
1	Roasting	High Zn, Pb, Cd removal	32% zinc was lost to gas, Leaching needs to follow after roasting	[3]
2	Carbothermic	High Zn removal	Gahnite difference to BF/BOF/EAF Dust	[24]
3	Aluminothermic	High Zn removal	Gahnite difference to BF/BOF/EAF Dust	[24]
4	Direct Reduction	High Zn removal,	Coke addition for low C-containing dust	[5]
		Direct Input for BF		
5	Carbochlorination	High Zn, Pb, Cd removal,	Chlorides addition	[ <mark>6</mark> ]
		Profitable cost-benefit modeling		
6	Microwave-Assisted	High Zn, Pb removal,	Low %Fe in Residue,	[11]
		Without reducing agent	Complex Installation	
7	Rotary/Waelz Kiln	High Zn removal,	Economical for >15% Zn input,	[34]
		Industrially proven,	High maintenance costs	
		Well established,		
		Less pollution		
8	Rotary Hearth Furnace	High Zn removal	High investment costs,	[34, 35]
		Industrially proven,	Limited to <5% Zn input,	
		Capable of treating BF, BOF, EAF Dust	High capacity needed	
9	Primus	High Zn removal,	Low productivity,	[34]
		No sample pre-treatment,	Limited to >5% Zn input,	
		Capable of treating BF, BOF, EAF Dust	Direct input for BF/EAF	
10	2sDR	High %Zn in secondary dust (Cl/Fl free),	2 stage process,	[38, 40]
		High %Fe in residue	Producing slag	
11	ESRF	High Zn removal,	Energy-intensive,	[34]
		Not producing waste gas	Producing slag	
12	Coke-packed Bed	High Zn Removal,	Energy-intensive,	[34, 43]
		High %Zn in dust,	Producing slag	
		No sample pre-treatment		
13	HIsarna	High Zn, Pb removal,	HIsarna is aimed for primary ironmaking,	[27, 41]
		High %Zn in dust,	Require dust circulation	
		No reducing agent		
14	DK Recycling	High %Zn in dust,	Minimum %Fe input,	[36, 44, 45]
		Industrially proven	Expensive, Cross Border Permit	
15	Solumet	Undisclosed data	Undisclosed data,	[ <mark>36</mark> ]
16	Oxycup	High %metallization,	Focus on the DRI,	[47, 58]
17	Recodust	No reducing agent	Very high operating temperature,	[38, 48]
			Producing slag	

Table 2.3: Advantages and disadvantages of the pyrometallurgical technologies.

Based on Table 2.3, most pyrometallurgical techniques can remove high amounts of zinc, more than 90%. The direct reduced iron or the iron-rich residue contains a high amount of metal iron which can be directly sent to the sinter plant or even blast furnace. In addition, most technologies have been widely used to treat zinc-bearing dust. As discussed in Section 2.1, parameters influencing the behavior of the reduction process are retention time, temperature, reducing agent, and reducing environment. In principle, the pyrometallurgical treatment aims to promote a reduction process of iron and separate the zinc and heavy metals in the gas phase. Based on this mechanism, coke or coal is needed as a reducing agent to reduce iron oxide. In addition, the reducing environment of either injected with inert gas, CO, or oxygen-enriched air is necessary to convert carbon to CO and promote a direct reduction process. However, the self-reduction behavior could occur in the BF sludge, which contains a high amount of C, and does not need a reducing agent. The iron reduction process starts at a temperature

of more than 1000°C for around 60 minutes, based on the literature discussed in Section 2.1. Based on the comparative assessment in Table 2.3, direct reduction has a higher removal rate than roasting and requires less energy than smelting. Direct reduction operates at a sufficiently high temperature to produce (partly) metallic iron at a compromising temperature and energy demand. Hence, direct reduction produces less waste than smelting without that generates slag. As discussed, BF sludge from Tata Steel contains a large amount of carbon compared to the dust from EAF and BOF. Initial carbon content can lead to self-reduction behavior of the materials without the need for coke or reducing gas (CO) which has been shown effective in producing high-grade (partly) metallic iron and zinc-rich secondary dust [6, 11, 27]. In addition, the direct reduction technique can be improved with chlorine addition resulting in a carbochlorination mechanism. Rotary Kiln, RHF, 2sDR, and ESRF have some burdens, as mentioned in Table 2.3, due to high investment cost, limited %Zn input, slag production, and complexity. The summary of the removal efficiency of each pyrometallurgical route is shown in Figure 2.39. Some technologies have undisclosed data for zinc and lead removal. Each process is associated with the technological readiness levels (TRLs), which have been mentioned previously in the discussion.



Figure 2.39: Removal efficiency, TRL level, and operating temperature of different pyrometallurgical routes.

Based on the graph Figure 2.39, each method's nomination of the TRL level was based on the 9-level classifications [59], provided in Appendix A. TRL 4 is equivalent to the lab scale experiment, which is associated with the direct reduction test in a lab scale furnace based on the literature. TRL 6 represents the pilot lab test achieved for technology such as RecoDust. The highest TRL 9 means the technology has reached commercialization and well-established technology, shown by the rotary kiln, rotary hearth furnace, and some smelting-based technologies. These TRL 9 technologies are developed for processing high zinc-bearing wastes such as EAF dust. In addition, smelting-based technologies are energy-intensive and require a high initial investment cost. TRL 4 of direct reduction offers some potential with the same/maximum level of heavy metals removal as the TRL 9 technologies with less energy and cost, thus having some flexibility to recycle low zinc-bearing wastes such as blast furnace sludge. In addition, the zinc content in the secondary dust produced from some processes is shown in Figure 2.40. It is shown that high-level zinc concentrate can be produced and directly sent to the zinc smelting industry without necessary pre-treatment. In summary, the treatment of BF sludge from Tata Steel in IJmuiden complies with the direct reduction technique with or without additives, based on

the technical (high removal rate and product quality), economic (feasible for poor zinc-bearing wastes), and environmental perspectives (no slag produced) compared to other pyrometallurgical techniques.



Figure 2.40: Zn content in the dust generated from some of the pyrometallurgical processing [27, 34, 40, 44, 47, 48]

#### 2.3.2. Comparative Study on the Hydrometallurgical Route

The hydrometallurgical route is commonly used to extract low-grade ores leading to relatively low initial investment [57]. Based on the discussion in Section 2.2, the hydrometallurgical route involves several steps, including leaching and purification, to selectively separate zinc in an aqueous solution from ironrich fraction as the residue. Based on the studies, the lixiviant and pre-treatment prior to leaching is the dominant factor in achieving the high extraction of zinc. Leaching using hydrochloric acid showed high extraction (>90%) of zinc, while leaching with ammonia [2, 4, 22, 52], alkaline [25], alkaline [12], sulfuric acid [24], and nitric acid [24] resulted in poor zinc extraction. Prior to leaching, roasting and pre-treated dust samples resulted in zinc extraction of up to 100% [3, 15, 26]. The most influential factor affecting zinc extraction is the presence of phases resistant to leaching, such as zinc sulfide and zinc ferrite [2, 3, 4, 15, 25, 52]. Oxidative leaching and oxidant addition are insufficient to promote the zinc extraction rate. The high extraction of the pre-treated samples is due to the conversion of zinc sulfide and zinc ferrite to leachable zinc oxide. Pressurized leaching in an autoclave showed excellent zinc and lead extraction rate using hydrochloric acid at 97% and 91%, respectively [19]. Another study using HCI combined with NaCl showed high zinc extraction, up to 93%. One research has shown a good range of zinc extraction (67%-90%) through alkaline leaching in the Modified Zincex Process with excellent zinc extraction. The excellent extraction of the Modified Zincex Process is due to the several steps of purification of zinc through solvent extraction and electrowinning.

In terms of the residue, only integrated INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> and CIROVAL<sup>™</sup> process resulted in high %Fe of 94% and 85%, respectively. The necessity of complex integrated recycling steps is the burden for recycling zinc-bearing wastes through hydrometallurgy. The generated liquid waste needs further treatment otherwise might contaminate the groundwater and soil. As mentioned before, the presence of undissolved zinc phases hinders the flexibility of the lixiviant and the dependence on the thermal pre-treatment. Although high-pressure leaching could result in high extraction, the high carbon content inside the blast furnace sludge could create foam during oxidation and complicate the leaching process. A summary of the advantages and disadvantages of the hydrometallurgical process is given in Table 2.4. More detailed information on the operating parameter and used equipment are given in Appendix A. The nature of the hydrometallurgical route of treating low-grade ores provides the flexibility of the zinc content on the input. The disadvantages are primarily due to the low extraction rate of zinc and the high probability of iron dissolution with a higher concentration of the lixiviant. Moreover, the hydrometallurgical process requires integrated extraction and purification steps.

No	Technique	Lixiviant	Advantages	Disadvantages	Ref.
1	Intracycle (Oxidative Leaching)	$NH_3 - (NH_4)_2SO_4$	Regenerative lixiviant High Zn extraction (after roasting) Mild leaching intensity	Low Zn extraction ZnS not dissolved Microwave power was not effective Oxidants was not effective	[2, 3, 4, 51]
2	Ammonia Leaching	$NH_4CI + NH_3$	Regenerative lixiviant High selectivity	Low Zn extraction	[22]
3	UBC-Chaparral	NH <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Regenerative lixiviant Integrated process ZnS and ZnO dissolved	Low Zn extraction Zinc ferrite not dissolved Complexity	[52]
4	Chlorination	HCI + NaCI	High Zn extraction Suitable to process BF sludge	Corrosive Low %Fe in residue Iron loss during leaching	[17]
5	Pressure Leaching	HCI + FeCl <sub>2</sub>	High Zn,Pb extraction Usage of spent pickle liquor Suitable to process BE sludge	Corrosive Severe foaming	[19]
6	CIROVAL™	HCI	Integrated process Suitable to process BF sludge High %Fe in residue	Low %Zn in precipitate (20%) Corrosive Severe foaming	[28]
7	INDUTEC <sup>®</sup> /EZINEX <sup>®</sup>	NH <sub>4</sub> Cl	Integrated pyro-hydro routes High selectivity High purity output	Complexity Thermal pre-treatment Zinc ferrite not dissolved	[15]
8	Pressure Leaching	HNO <sub>3</sub>	-	Low Zn extraction	[24]
9	Pressure Leaching	H <sub>2</sub> SO <sub>4</sub>	-	Low Zn extraction	[24]
10	Modified Zincex Process	H <sub>2</sub> SO <sub>4</sub>	High Zn extraction Industrially proven Integrated process	Complex process Limited to high zinc bearing waste	[56]
11	High Temperature Leaching	$H_2SO_4$	High Zn extraction High iron in solid residue	Longer leaching time leads to high iron dissolution	[54]
12	Organic Acid Leaching	Carboxylic	High Zn extraction	Wide variations on Zn extractions Co-dossolution of Fe	[53]
13	SIDMAR	HCI	High Zn and Pb extraction	Co-dissolution of Fe	[1]
14	AMAX	HCI	High Zn extraction	Co-dissolution of Fe	[1]
15	Terra Gaia	HCI	High Zn extraction	Complex process	[1, 55]
16	Alkaline Leaching	NaOH	-	Low Zn extraction Zinc ferrite not dissolved	[25]
17	Alkaline Leaching	NaOH	High Zn extraction Low %Zn in residue	Zinc lost during CaO treatment 2 step process	[26]

Table 2.4: Advar	ntages and disad	vantages of the l	nydrometallurgical	technologies
	nages and disau	vaniages of the i	ryurumetanurgicai	iconnoiogica.

Regarding maturity, most hydrometallurgical techniques are still at the research level or associated with TRL 4. The limited extraction efficiency hinders the upscaling of the hydrometallurgical recycling using alkaline and ammonia-based lixiviants. High extraction efficiency through chloride-based lixiviant has to be compensated by the necessity to sustain from the highly corrosive environment. The summary of the TRL level associated with the lixiviant used in the hydrometallurgical process is shown in Figure 2.41. High level of TRL is shown by INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> (Reduction + NH<sub>4</sub>CI) and Modified Zincex Process with a high extraction rate of Zn. The main reason is introducing the reduction step prior to leaching in INDUTEC<sup>®</sup>/EZINEX<sup>®</sup> and integrated extraction-purifications steps in Modified Zincex Process, which makes these two recycling routes exceptional from other techniques. Some of the reported zinc and iron content in the residue after leaching is shown in Figure 2.42. The iron content ranges from 30% to around 90%, while the zinc content is between 0.025% to 5.5%.

#### 2.3.3. Preferred Methodology for the Treatment of BF Sludge

Based on the pyrometallurgical route, the most suitable method for recycling BF sludge is carbochlorination together with direct reduction, while for the hydrometallurgical route, leaching with hydrochloric acid is preferred. Both routes showed high extraction or removal rates of zinc and heavy metals. Moreover, high purity of the output fractions could be achieved, including the iron and zinc-rich fractions. In terms of process complexity, carbochlorination offers a more straightforward route as selective heavy metals removal can be accumulated in the off-gas while producing a clean iron-rich residue. The residue can be directly recycled to the BF or sinter plant, and the secondary dust can be sent to the zinc smelter.

On the other hand, leaching with hydrochloric acid needs subsequent purification or cementation to refine the zinc and iron residue further. In addition, higher iron content was obtained in the iron-rich residue (99%) from direct reduction than the iron content in the leaching residue (94%) from hydrochloric leaching. Leaching could be insufficient for the dissolution of zinc ferrite, even with hydrochloric acid.



Figure 2.41: Zn extraction and TRL level of hydrometallurgical routes.

The high carbon content on the BF sludge also benefits the direct reduction to induce self-reduction behavior. At the same time, high carbon creates a problem for the hydrometallurgical route due to foaming occurrence during oxidative leaching conditions. More pyrometallurgical routes have been widely used in the industry than the hydrometallurgical route, which is mostly still at the research/development level. From the environmental point of view, the generated liquid waste from the leaching is more challenging to process than the generated off-gas from the pyrometallurgical route. However, the high-temperature treatment of the pyrometallurgical route might generate more carbon emissions and need more energy than a low-intensity hydrometallurgical route. The idea of treating BF sludge from Tata Steel in IJmuiden is to build an internally economically viable, technically proven, and efficient recycling plant. The comparison of the hydrochloric acid leaching and the chlorination - direct reduction, or carbochlorination, as the most suitable methods is given in Table 2.5.

Assessment	Carbochlorination and Direct Reduction	HCI Leaching
Technical	High zinc removal (Up to 100%),	High zinc extraction rate (100%),
	High Fe metallization degree (Up to 96%),	High-quality iron residue (94% Fe),
	High-quality secondary dust (Up to 73% Zn),	Complex process (leaching-refining),
	Simple process (One step),	High initial carbon might complicates leaching,
	High initial carbon content for self-reduction,	Requiring highly acidic and oxidative condition
	Selective removal of heavy metals (Zn, Pb)	
Environmental	Off-gas generation,	Liquid waste generation,
	Energy-intensive process,	Extra additives/reagents for purification,
	Needless of reducing agents (reduce emission),	Less energy intensive
Economic	High investment cost,	Low investment cost,
	Industrially proven,	Primarily conducted on a research scale
	Widely used and developed	

Table 2.5: Comparison of carbochlorination and direct reduction with HCI leaching with respect to the recycling of BF sludge.

Based on Table 2.5, the pyrometallurgical route through carbochlorination and the direct reduction is considered more suitable for treating BF sludge from Tata Steel in IJmuiden due to the capability of removing all zinc phases and other heavy metals, high-quality output, process simplicity, and less generated secondary wastes. Therefore, the objective to create a rich iron residue and zinc-rich secondary dust could be achieved effectively. Although direct reduction needs a high investment cost, a study by Hamann et al. (2021) [6] illustrated that implementing a direct reduction plant in the recycling the BF sludge was economically profitable, as shown in Figure 2.43. Based on Figure 2.43, the recycling profit scenario was between 20 to 62 EUR per ton of processed BF sludge. The calculation already assumed the saleable quality DRI and secondary zinc-rich dust as the sources of revenue.



Figure 2.43: Cost-benefit analysis of carbochlorination-based recycling of BF sludge [6].

Carbochlorination and direct reduction involve underlying reactions of the elements in the blast furnace sludge. The thermodynamic assessment is essential to understand and define reactions at specific temperatures, including iron reduction, zinc, and heavy metals volatilization. The thermodynamic assessment of the reactions involved in the direct reduction of iron and heavy metals (Zn, Pb), studied by Ye et al. (2021) [11], is given in Table 2.6. Zinc and lead oxides could evaporate and react with carbon and carbon monoxide starting at more than 900°C. In summary, the recycling route by direct reduction is thermodynamically feasible, which has been technically proven and suitable for treating the BF sludge from Tata Steel in IJmuiden.

Table 2.6: The reaction involves in direct reduction of mixed BF-EAF dust [11]

No.	Reaction	T <sub>onset</sub> (°C)
1	$C_{(s)} + CO_{2(g)} \Longrightarrow 2CO_{(g)}$	705.1
2	$Fe_3O_{4(s)} + O_{(s)} \implies {}_3FeO_{(s)} + CO_{(a)}$	680.5
3	$Fe_3O_{4(s)} + CO_{(a)} \implies 3 FeO_{(s)} + CO_{2(a)}$	606.9
4	$Fe_3O_{4(s)} + 4CO_{(g)} \implies 3Fe_{(s)} + 4CO_{2(g)}$	873.4
5	$FeO_{(s)} + C_{(s)} \Longrightarrow Fe_{(s)} + CO_{(q)}$	718.6
6	$FeO_{(s)} + CO_{(q)} \implies Fe_{(s)} + CO_{2(q)}$	665.1
7	$3 ZnFe_2O_{4(s)} + C_{(s)} \implies 3 ZnO_{(s)} + 2 Fe_3O_{4(s)} + CO_{(q)}$	286.7
8	$ZnO_{(s)} + C_{(s)} \Longrightarrow Zn_{(q)} + CO_{(q)}$	955.9
9	$ZnO_{(s)} + CO_{(a)} \Longrightarrow Zn_{(l)} + CO_{2(a)}$	937.6
10	$Zn_{(l)} \rightleftharpoons Zn_{(q)}$	904.4
11	$Pb_{(l)} \Longrightarrow Pb_{(g)}$	1733.3

Based on the discussion, the pyrometallurgical technique of direct reduction and hydrometallurgical technique of HCI leaching could effectively separate zinc and heavy metals with high quality of produced iron-rich fraction. Direct reduction is preferred with its high efficiency in removing zinc and heavy metals and the high quality of produced iron-rich residue (DRI) and secondary zinc fraction. The direct reduction has an advantage over the composition of blast furnace sludge due to its carbon content to promote self-reduction behavior. Based on the environmental perspective, the generated off-gas from direct reduction is more straightforward to process than the liquid waste from the hydrometallurgical route. However the integrated combination of pyrometallurgy and hydrometallurgy is needed to achieve a full circularity. The direct reduction technique has been widely used in treating blast furnace dust, an industrially proven, thermodynamically feasible, and economically viable recycling process. In conclusion, as primarily referred to research by Zhu et al. (2021) [5], Hamann et al. (2021) [6], and Ye et al. (2021) [11], direct reduction complies excellently with the technical, environmental, and economic perspectives.

## 2.4. Chloride Metallurgy

Chlorination is one of the essential techniques in the metal extraction process in both pyrometallurgy and hydrometallurgy due to its high reactivity nature [60]. Some of the most common chlorination agents are ( $CI_2$ ) gas, HCI, ferric chloride, and other alkali-based chlorides. The chemistry of the chlorination reactions is based on the dissociation of metal oxides or sulphides, creating the extraction of the metals in chloride forms. The primary reactions of the metal chlorination, depending on the chlorination agent, are shown in the equations below.

$$MeO + Cl_2 \iff MeCl_2 + \frac{1}{2}O_2$$
 (2.32)

$$MeS + Cl_2 \implies MeCl_2 + S \tag{2.33}$$

$$MeO + HCI \implies MeCl_2 + H_2O \tag{2.34}$$

$$MeS + HCI \implies MeCl_2 + H_2S$$
(2.35)

$$MeO + Me'Cl_2 \iff MeCl_2 + Me'O$$
(2.36)

$$MeS + HCI \implies MeCl_2 + Me'S$$
(2.37)

Metals are generally present in the oxide form (MeO) and sulfide form (MeS) for chlorination. One of the critical features of the metal chlorides is that they are generally very volatile in low temperatures, which differs from one another [61]. This feature leads to good selectivity in the metal separation via volatilization at a specific temperature utilizing the difference in the vapor pressure. The vapor pressure and the phase transformation temperature of metal chlorides are shown in Figure 2.44 and Figure 2.45, respectively.



Figure 2.44: Vapor pressure of various metal oxides and chlorides at increasing temperature [62].



Figure 2.45: Phase transformation temperature of metal chlorides [61].

Based on Figure 2.44, it can be concluded that at a small range of elevated temperatures, heavy metals (Zn, Pb, Cd) can have a greater extent to be converted to the gaseous chloride phase as the vapor pressure rapidly increases. The chlorine-based extraction has been widely used to treat different kinds of wastes, such as zircaloy scrap, slag containing niobium (Nb) and tantalum (Ta), copper converter slag, and steel industrial dust [60]. One example is the treatment of EAF dust and BF sludge, explained in the previous sections using FeCl<sub>2</sub> as a chlorination agent. In terms of pyrometallurgy, the basic concept of chlorine metallurgy extraction is based on the different boiling points of metals. Based on Figure 2.45, it can be seen that heating at different temperatures can trigger the volatilization of some metals in the form of chloride for further selective separation. In the case of blast furnace sludge, initial carbon content and the addition of chloride will trigger the carbochlorination reactions that will volatilize the heavy metals in the form of chlorides, along with the partial reduction of iron oxides [6, 63]. The mechanism of carbochlorination reactions is given in Equation 2.38 which the presence of carbon and chlorination gas will reduce and convert the metals oxide to gaseous metal chlorides together with the production of CO gas.

$$MeO + C + Cl_2 \Longrightarrow MeCl_2 + CO$$
(2.38)



# **Experiments**

This chapter explains all the materials used and experiments conducted in the thesis. The methods include thermodynamic modeling, experimental lab work, software simulation, material characterizations, data analysis, and assessment. The materials used for the experiment are explained in Section 3.1, followed by a brief explanation in Section 3.2 on all the methods conducted in this thesis.

# 3.1. Materials

Four different samples of blast furnace sludge were provided by Tata Steel in IJmuiden. The samples were all in pellets and different in size. Each sample was mixed with 0.5% bentonite from Cebo Holland B.V., and two of four samples were added with 4.63% FeCl<sub>2</sub>.4H<sub>2</sub>O from Merck KGaA. The amount of added bentonite and iron chloride was based on weight percentage. Pellets 1 and 2 have a diameter between 3.15-5 mm, while pellets 3 and 4 have a diameter of less than 3.15 mm. The samples were dried for 24 h at 105°C to remove all the remaining moisture. The list and pictures of the samples are given in Table 3.1 and Figure 3.1, respectively.

Table 3.1:	Samples	used for	the	experiment.
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Sample	Size	Additives	Moisture
1	3.15-5 mm		29%
2	3.15-5 mm	FeCl <sub>2</sub>	30%
3	<3.15 mm	FeCl <sub>2</sub>	30%
4	<3.15 mm	-	28%



Figure 3.1: Photos of BF sludge pellets.

# 3.2. Experiment Methods

In general, the experiment methods consist of modeling, laboratory tests, material characterizations, and final assessments of the recycling of BF sludge through carbochlorination and direct reduction.

The experiment methods were done in sequence following the order of the research questions given in Figure 3.2. The solid flow/line represents the sample, and the dashed flow represents the data used in the subsequent methods. The research was started with the FactSage simulation to create a model before starting the experiments and predict the results of the planned laboratory tests. Next, the results from the model (thermodynamic analysis) were used as the parameters for the subsequent lab tests. The first laboratory experiment was a thermogravimetric analysis (TGA) to perform carbochlorination and direct reduction reactions in the BF sludge at four different temperatures. Furthermore, the lab works were upscaled using a sizeable horizontal tube furnace with higher capacity and the additional set-up for a dust-capturing system. The raw and reacted samples were then analyzed by various analytical techniques. This thesis report also incorporated supplementary data from the research by Dr. Peter Beentjes from Tata Steel in IJmuiden. In the last stage of this thesis study, material balance, economic assessment, and life cycle assessment were formulated to thoroughly assess the whole recycling route. The final output of this thesis study is to propose the in-depth recycling flowsheet of BF sludge for future implementation at Tata Steel in IJmuiden.



Figure 3.2: Flowsheet of the experimental works conducted in this thesis project.

## 3.2.1. Thermodynamic Analysis

The carbochlorination and direct reduction modeling were performed using FactSage 8.1 provided by Tata Steel Europe for the thermodynamic analysis. The models were based on the reaction and equilibrium and modules in FactSage. The database used for the calculations were FactPS and FTOxid, the most common databases for minerals and metals reaction modeling. The thermodynamic analysis was further divided into three sections. Two sample conditions (as initial composition) were given in each thermodynamic calculation to represent the carbochlorination and direct reduction mechanism. Carbochlorination was represented by a sample with chloride addition, while the sample without chloride addition represented a direct reduction.

#### **Onset Temperature Measurement**

The onset temperature was calculated to predict at which temperature the reactions involved in the BF sludge will start (spontaneous) related to the change in the Gibbs free energy change ( $\Delta G^\circ$ ). The Gibbs free energy was calculated with a temperature increment of 25°C, from 0 to 1600°C, and the onset temperature was defined when the Gibbs free energy change reached a negative value, referring to spontaneous reaction.

#### **Stability of the Reactions**

Based on the reaction module, the Gibbs Free Energy ( $\Delta G^\circ$ ) was calculated for all the relevant reactions in the range of 0 to 1600°C. This calculation aimed to define the favorability of the reactions at elevated temperatures and compare the reactivity of the elements in the BF sludge related to the Gibbs free energy change value.

#### **Equilibrium Composition**

The equilibrium composition was calculated based on the equilibrium module to predict the product in liquid, solid, and gas phases through a thermal treatment simulation of the BF sludge from 0 to 1600°C.

#### 3.2.2. Carbochlorination and Direct Reduction of BF Sludge

Based on Figure 3.2, the carbochlorination and direct reduction tests were done using two furnaces. TGA furnace used for the small-scale experiment focus on mass alteration during the thermal treatment and further calculation on heavy metals (Zn, Pb) removal rate. The second furnace was a horizontal tube furnace for a big-scale experiment focusing on generating secondary dust.

#### **TGA Furnace**

Netzsch STA 049 TGA/DSC furnace was used for the thermal treatment (carbochlorination and direct reduction) and connected to Julaba as the liquid cooling system and Brooks 0152 as the gas input controller. The experiments in the TGA furnace were conducted at 800, 1000, 1200, and 1400°C. Each sample between 100-200 mg was put in a crucible, placed next to a reference crucible inside the furnace, and heated at 40°C/min starting from room temperature. The isothermal heating at each temperature variation was done for 60 minutes. The Argon and nitrogen gas were injected at 20 ml/min each during the experiment in an inert atmosphere. The sample was then cooled through the water cooling system attached internally. Each variation was done twice to ensure the data's reproducibility. The schematic drawing of the TGA/DSC furnace is shown in Figure 3.3.



Figure 3.3: TGA/DSC furnace schematic drawing. Modified from Netzsch STA 409 brochure.

#### **Horizontal Tube Furnace**

The upscaled carbochlorination and direct reduction experiments were carried out at a horizontal tube furnace at Tata Steel Europe in IJmuiden. This experiment aimed to replicate the multistage removal of zinc and other heavy metals through three continuous stages of thermal treatment. Each sample (only samples 1 and 2) used in this experiment was around 10-20 grams. The nitrogen gas was injected at 200 L/hour during the experiment to ensure an inert atmosphere. At the end of the tube, dust-capturing media are placed on top of the cavity. Either a glass filter or alumina plate was used as the dust-capturing media. The thermal treatment was done continuously, starting at room temperature and increasing to 800, 950, and 1100°C. The dust-capturing media was placed at the start of the heating (from room temperature to 800°C) and was maintained for 30 minutes during isothermal heating. Then the filter was replaced with the new one, and the temperature was increased to 950°C and held again for 30 minutes isothermally at 950°C. The last step was replacing the filter with the new one, and the temperature was increased to 1100°C and held for 30 min isothermally. Next, the sample was cooled down in an inert atmosphere. The experiment was then repeated for a different dust-capturing media (glass filter or Al plate) to ensure reproducibility. The schematic drawing of the horizontal tube furnace is shown in Figure 3.4.



Figure 3.4: Horizontal tube furnace schematic drawing.

#### 3.2.3. Material Characterization

Various material characterization techniques were done to measure the samples from each experiment. The analysis was aimed to measure the overall composition and provide an in-depth analysis of each sample, such as the mineralogy, microstructure, and phase analysis.

#### Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

ICP-OES analysis is used for the chemical composition measurement at the analytical laboratory (PA ANA) of Tata Steel Europe in IJmuiden. First, around 50 mg of the sample is leached using nitric acid and slowly heated to oxidize any metallic compounds in the sample to prevent damage in a later step of the digestion. Then the crucibles are heated up to 150°C to evaporate the remainder of the nitric acid with a heat lamp. When the sample is dried, it is heated to a glowing temperature with a Bunsen Burner to expel all nitric oxide vapors. The sample is then further heated at 1000°C with the addition of 1 g sodium carbonate and 0.5 g sodium tetraborate in an electric oven to disintegrate and dissolve oxidic compounds in the molten salts. After cooling to room temperature, the melt is dissolved in hydrochloric acid and transferred to a volumetric flask.

Reference samples are also analyzed through the same procedure using the same batch of chemicals to validate the measurement. These reference samples are known by composition and compared to the reference data. When the results of the reference samples are within the standard deviation, then the digestion process and the measurement are considered reliable.

After the digestion process, the measurement is done using ICP-OES, in which the dissolved samples are nebulized and heated to about 10000°K in a plasma (gas exited with electromagnetic energy). This mechanism causes electrons of the respective atoms to shift to a higher orbital. When the electrons fall back to the original orbital, the energy difference is converted into photons which can be measured in wavelength (which is uniquely based on the type of atom) and intensity (which is uniquely based

on the concentration). The intensities are then compared to known calibration solutions, which have the same matrix as the samples, to exclude matrix effects (e.g., more difficult atomization of a solution with a higher content of dissolved materials). Measurements are checked by comparing the found concentration of the reference materials to the certified values and are corrected for blank measurements. After correction for dilution (sample weight and final volume of sample solution, possible further dilution if measurements are above calibration), the mass percentage of the found elements can be calculated.

#### X-ray Diffraction (XRD)

Quantitative XRD analysis was done at Ceramics Research Centre (CRC), Tata Steel Europe in IJmuiden. XRD patterns were recorded using Bruker D8 Endeavor Diffractometer (CoK $\alpha$ -radiation) equipped with a positive, sensitive detector. Quantitative determination of phase proportions was also performed by Rietveld analysis. The refinement was done on the assumption of pure phases. Unit cell parameters, background coefficients, preferred orientations, profile parameters and phase proportions were refined using the TOPAS software package for Rietveld refinement.

#### X-ray Fluorescence (XRF)

XRF analysis was done in the MSE department at TU Delft. The instrument used in the measurements was Panalytical Axios Max WD-XRF spectrometer, and data evaluation was done with SuperQ5.0i/Omnian software. Omnian 4kw 27he was used as a database for quantitative analysis. The composition result (oxides) of each sample was further normalized to 100%.

#### **ELTRA Analyzer**

ELTRA instrument is used for the carbon (C) and sulfur (S) measurement at the analytical laboratory (PA ANA) of Tata Steel Europe in IJmuiden. The sample is heated in a furnace with the addition of oxygen. Carbon and sulfur then react with oxygen to form  $CO_2$  and  $SO_3$  gas, detected by an IR cell.

#### Wet Chemical Analysis

This analysis was done at ANA Lab in IJmuiden to measure the chlorine content in the sample. In a nickel crucible,  $2.5 \pm 0.05$  grams of sample was mixed with 1 gram of potassium carbonate and 10 grams of sodium peroxide. Then the mix was covered with 1 gram of sodium peroxide. The sample is heated in the nickel crucible on top of a burner until the sample has melted. Then the sample was leached using water at 90°C for 2 hours, followed by filtration. Next, the solution was neutralized with nitric acid, and added 1 ml of hydrogen peroxide. Silver nitrate was later added to the solution to precipitate silver chloride. In the final step, quantitative measurement was done via titration with ammonium thiocyanate, indicated by the change of color.

#### Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS)

SEM-EDS (JEOL JSM 6500 F) characterizations were done in the MSE department at TU Delft. The analysis was performed using a secondary electron image, 10 mm working distance, and 20.0 kV accelerating voltage. The SEM image was further analyzed using EDS mapping and point measurement for quantitative composition results.

#### 3.2.4. Economic Assesment

The economic assessment was calculated based on the cost-benefit analysis using data from the literature study and experimental results. The cost components were associated with each process and input/consumables within the whole recycling flowsheet. The benefit components were based on the saleable output from the recycling process and the existing cost paid by Tata Steel Europe from landfilling BF sludge. The calculations were divided into best-case and worst-case scenarios depending on each component's minimum or maximum price and the marketability of the final products from the recycling process. The cost-benefit analysis did not include the capital expenditure for the recycling plant. The items that were included in the calculation of the cost-benefit analysis are provided as follows:

#### Benefit:

1. Landfilling cost of BF sludge

2. Marketable products

#### Cost:

- 1. Operating cost of each recycling process (including fuels/energy and maintenance)
- 2. Consumables for each recycling process
- 3. Waste treatment

## 3.2.5. Life Cycle Assessment (LCA)

The goal of LCA is to measure the environmental impact of BF sludge recycling through direct reduction and the consequences associated with the impacts. The LCA was performed according to ISO 14040:2006 about the framework of LCA, which divides the assessment into four sequential interconnected steps. The framework of LCA is shown in Figure 3.5. The assessment starts with goal and scope definition as the baseline, followed by inventory analysis for the input data and boundary of the system. Then the impact will be calculated based on the inventory data. In the last step, all the output from each step was interpreted as related to the consequences of the environmental impacts.



Figure 3.5: LCA framework according to ISO 14040:2006.

4

# **Results and Discussion**

This chapter explains the results and discussion of the research methods in detail. The discussion starts with the characterizations of the four different raw BF sludge in Section 3.1, as the sample used in this research, followed by the analysis of the thermodynamic aspect in Section 4.2. The subsequent discussion (Section 4.3) explains the effect of varying parameters from the TGA experiment, focusing on the removal of heavy metals. The lead and zinc removal behavior, as one of this thesis's main interests, is explained in Section 4.4. Next, the experimental results in the horizontal tube furnace, focusing on the secondary dust, are discussed in Section 4.5. Material balance was calculated in Section 4.6, based on all the experimental results to further measure the economic feasibility (Section 4.7) and the life cycle assessment (Section 4.8). The final proposed recycling flowsheet for future implementation at Tata Steel Europe in IJmuiden, considering all the aspects discussed in this thesis, was formulated in the last section of this chapter (Section 4.9).

# 4.1. Characterization of the Raw BF Sludge

The raw BF sludge pellets were analyzed through five different characterization techniques. The first analysis was carried out with ICP-OES to measure the composition of each sample, in weight percent (wt%), of the BF sludge. Carbon (C) and sulfur (S) content were measured differently by the Eltra analyzer while chlorine was measured by XRF. The composition of each sample is shown in Table 4.1.

 Table 4.1: Composition (wt%) of the raw BF sludge pellets (samples 1 to 4). The analysis was done through ICP-OES, Eltra analyzer (for C and S), and XRF (for Cl).

Sample	Size (mm)	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	v	Zn	Si	CI	Other
1	3.15-5	0.03	40.65	1.65	0.01	24.65	0.63	0.10	0.56	1.11	0.09	0.02	2.83	2.70	0.13	24.85
2	3.15-5 (+ FeCl <sub>2</sub> )	0.02	38.95	1.59	0.01	24.75	0.57	0.10	0.51	1.06	0.08	0.02	2.60	2.60	2.10	25.05
3	<3.15 (FeCl <sub>2</sub> )	0.02	38.00	1.63	0.01	25.15	0.58	0.09	0.49	1.04	0.08	0.02	2.48	2.48	2.22	25.72
4	<3.15	0.02	40.80	1.63	0.01	24.45	0.62	0.10	0.51	1.10	0.09	0.02	2.77	2.77	0.14	24.97

The composition of each sample was the average of the duplicate analysis by ICP-OES, Eltra (for C and S), and XRF (for CI) to ensure reproducibility. Based on Table 4.1, each sample used in experiments has an identical content for each element (except CI) since the only differences between the samples are the size and the addition of iron chloride (FeCl<sub>2</sub>). The other content Table 4.1 is referred to as the oxygen content as ICP-OES measured the metals in elemental form, not in the oxide form. The highest element present in the pellets was carbon (38-40.8%), followed by iron (24.45-25.1%). Zinc, lead, and cadmium content are between 2.48-2.77%, 0.49-0.56%, and 0.01%, respectively.

Another analysis for every sample was carried out using XRF at TU Delft. XRF results (wt%) are shown in Table 4.2, in which the composition was based on the average of the duplicate analysis. The overall composition in Table 4.2 was also normalized to 100%, considering the addition of C content from Table 4.1. The average composition of BF sludge between 2020 to 2021 [64] from the internal analysis at Tata Steel in IJmuiden is also provided in Table 4.2 for comparison. Based on Table 4.2, the initial CI sample for samples without iron chloride addition (samples 1 and 4) was between 0.13 to 0.14%.

Meanwhile, the samples with iron chloride addition (samples 2 and 3) have CI content between 2.1 to 2.22%. The content of most elements measured in the BF sludge samples is relatively identical to the average 2020/2021 composition.

Table 4.2: XRF quantitative (wt%) measurement of raw BF sludge pellets of samples 1 to 4. Carbon content was incorporated
from Table 4.1 and the total composition was normalized to 100%.

Compound	Sample 1	Sample 2	Sample 3	Sample 4	Average 2020/2021 [64]
С	40.65	38.95	38.00	40.80	39.58
Fe <sub>2</sub> O <sub>3</sub>	36.48	37.28	38.01	36.20	37.07
SiO <sub>2</sub>	6.30	6.03	6.05	6.31	5.26
ZnO	5.43	5.06	5.08	5.45	4.14
$AI_2O_3$	3.48	3.27	3.25	3.43	2.65
CdO	0.01	0.01	0.01	0.01	0.02
CaO	2.27	2.18	2.26	2.29	2.93
SO <sub>3</sub>	2.22	2.16	2.16	2.26	1.66
MgO	1.16	1.11	1.09	1.24	0.99
PbO	0.69	0.67	0.67	0.68	0.86
K2O	0.54	0.54	0.56	0.60	1.04
TiO <sub>2</sub>	0.20	0.25	0.22	0.17	0.16
$P_2O_5$	0.17	0.16	0.17	0.17	0.15
MnO	0.14	0.14	0.14	0.14	0.14
CI	0.13	2.10	2.22	0.14	
$V_2O_5$	0.05	0.04	0.04	0.04	
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.01	0.01	
Rb <sub>2</sub> O	0.02	0.02	0.02	0.02	
SrO	0.01	0.01	0.01	0.01	
Bi <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.01	0.01	
Total	100.01	100.03	100.05	100.04	96.64

The difference in the measured content of ICP-OES (Table 4.1) and XRF (Table 4.2) is mainly due to the form of measured metals. The metals from XRF were based on the oxides form, while the ICP-OES was based on the elemental form. The carbon, iron, zinc, lead and cadmium content from both ICP-OES and XRF are within the range of the BF sludge composition found in some literatures, according to Table 1.2. Furthermore, XRD analysis was done for samples 1 and 2 to measure the available phases in the BF sludge, especially the ratio between each zinc phase. The results of the XRD analysis for samples 1 and 2 are shown in Figure 4.1 and Figure 4.2, respectively.



Figure 4.1: Recorded and fitted X-ray pattern along with phase proportions (wt%) of sample 1. Silicon was used as a standard...



Figure 4.2: Recorded and fitted X-ray pattern along with phase proportions (wt%) of sample 2. Silicon was used as a standard.

Based on the XRD patterns, ZnO was found as zincite, and ZnS was found as wurtzite and sphalerite in both samples. The quantitative analysis was measured by adding silicon (as standard) followed by the proportion of each phase. The pattern for quantitative calculation is shown in blue, and the original pattern is shown in red. Each phase content provided in Figure 4.1 and Figure 4.2 still includes silicon (Si) which was further recalculated without Si for the precise quantitative analysis in wt%. It was found that the zinc phases (after recalculation) consists of 0.2% ZnO and 0.3% ZnS in sample 1 and 0.4% ZnO and 0.3% ZnS in sample 2. Therefore the ratio of ZnO/ZnS was between 2/3 to 4/3, which is slightly different from the past analysis done by Feenstra (2016) [3] that mentioned the ratio of 1 (ZnO/ZnS) in the BF sludge originating from Tata Steel Europe in IJmuiden. The last analysis was performed using SEM-EDS to understand the distribution of the elements on a micrograph. The sample was milled and placed on carbon tape to prepare for the measurement. The elemental mapping of sample 1 is shown in Figure 4.3.



Figure 4.3: SEM-EDS analysis of as received sample 1 (no chloride addition). The mapping show selected element of (b) iron, (c) sulphur, (d) oxygen, (e) carbon, and (f) zinc.

Based on Figure 4.3, iron, sulfur, oxygen, and zinc were indicated as the most abundant element in the BF sludge, as shown by the distinguished color distribution in the image. The light, irregular, and cloud-like particles is the dust particle, as the biggest one measured is located in the center, while the

dark background is referred to as carbon tape. High iron and oxygen concentrations in the mapping indicate the initial form of iron as oxide. In addition, oxygen and sulfur are dispersed densely through the image, as most minerals in the BF sludge were either in sulfide or oxide form. The elemental mapping of sample 2 is shown in Figure 4.4. Based on Figure 4.4, chlorines (light blue) were found and concentrated in the same area as iron (green), indicating the iron chlorides mixed with the sample. One interesting finding was the concentrated oval and elongated zinc (yellow) area in the image's left part, in which dense sulfur (purple) was found in the same place. This finding justifies the presence of ZnS as one of the influential phases in the BF sludge. Other elements were also detected in the mapping analysis, such as calcium and silicon, which were not included in Figure 4.3 and Figure 4.4. The pellet's morphology is generally irregular, and some were found in a globular shape.



Figure 4.4: SEM-EDS analysis of as received sample 2 (chloride addition). The mapping show selected element of (b) iron, (c) sulphur, (d) oxygen, (e) chloride, and (f) zinc.

# 4.2. Thermodynamic Analysis

Carbochlorination and direct reduction were chosen as the processing technique studied in this thesis for the recycling of BF sludge. In principle, the heavy metals (Zn, Pb) removal of the sample without chloride addition (samples 1 and 4) is represented by the direct reduction as the underlying mechanism. On the other hand, the carbochlorination reactions govern the heavy metals (Zn, Pb) removal in the sample with chloride addition (samples 2 and 3). Meanwhile, direct reduction of iron oxide occurs in the BF sludge with and without chloride addition. The thermodynamic analysis starts with the list of all the possible reactions involved in the thermal treatment model of the BF sludge (Subsection 4.2.1). The calculation of the Gibbs free energy change of all the involved reactions is provided in Subsection 4.2.2, subsequently. The final equilibrium composition of the carbochlorination and direct reduction reactions is given in Subsection 4.2.3.

## 4.2.1. Main Reactions Involved in the Self-reduction of BF Sludge

The main reactions involved in the model were derived from the compounds found in the sample from the XRF analysis (see Table 4.2). The reactions involved were further reviewed with the list of other possible reactions related to the BF sludge in some relevant literature [6, 11]. In general, the primary mechanism of the reactions in this thermodynamic modeling of BF sludge was carbochlorination and direct reduction. Carbochlorination is referred to as chlorination with the presence of a chlorination agent (FeCl<sub>2</sub>) and carbon which convert the oxides to gaseous metal chlorides [6]. Direct reduction is defined as the reduction process of an element from oxide form to metallic form in the presence of a reducing agent (carbon) [5]. Since the sample has a significant initial carbon content, the direct reduction can also be referred to as self-reduction, meaning adding a reducing agent is unnecessary. In the reduction process, the oxidation number of the metal decrease, represented by electron gains.

In the case of this thermodynamic model, except for iron, the final form of the reduced metal is gas. The reduction of oxides with carbon monoxide (CO), referred to as indirect reduction, and some side reactions (Bouduard, dissociation) were also considered in the model. The general form of direct reduction of hematite ( $Fe_2O_3$ ), direct reduction of heavy metals removal, carbochlorination, and indirect reduction are shown in the following equations.

$$Fe_2O_{3(s)} + 3C_{(s)} \Longrightarrow 2Fe_{(s)} + 3CO_{(a)}$$

$$(4.1)$$

$$MO_{(s)} + C_{(s)} \rightleftharpoons M(g) + CO_{(g)}$$

$$(4.1)$$

$$(4.2)$$

$$MO_{(s)} + FeCl_{2(l)} + C_{(s)} \Longrightarrow MCl_{2(g)} + CO_{(g)} + Fe_{(s)}$$

$$(4.3)$$

$$MO_{(s)} + CO_{(g)} \Longrightarrow M_{(g)} + CO_{2(g)}$$

$$(4.4)$$

M, MO, and MCl<sub>2</sub> denote the metal oxide, gaseous metal, and metal chlorides, respectively. The reactions from the samples without chloride (samples 1 and 4) were based on direct reduction of all the available oxides, while the samples with chloride (samples 2 and 3) were mainly governed by carbochlorination. The direct reduction or self-reduction of iron oxides to metallic iron is expected to coincide with the heavy metals removal through either direct reduction or carbochlorination, depending on the presence of chloride. The indirect reduction is expected to occur inconsequentially with or without chloride, as CO will be produced from either direct reduction or carbochlorination. The onset temperature was measured for each reaction using FactSage 8.1 in the range from 0 to 1600°C. The calculations assume the ideal mixing of the compounds in the sample under an inert atmosphere without the addition of reducing gases or varying oxygen partial pressure. The possible direct reduction, side, carbochlorination, and indirect reduction reactions in the high temperature treatment of the BF sludge model are provided in Table 4.3, Table 4.4, Table 4.5, and Table 4.6, respectively.

Table 4.3: Possible direct reduction-based reactions involved in the high temperature treatment of BF sludge.

Direct Reduction	T <sub>onset</sub> (°C)	Ref.
ZnO(s) + C(s) = Zn(g) + CO(g)	975	[11]
$1/4 \operatorname{ZnFe}_2O_4(s) + C(s) = 1/4 \operatorname{Zn}(g) + CO(g) + 1/2 \operatorname{Fe}(g)$	1275	[11]
ZnS(s) + CaO(s) + C(s) = Zn(g) + CaS(s) + CO(g)	1000	[31]
PbO(s) + C(s) = Pb(g) + CO(g)	775	[11]
PbS(s) + CaO(s) + C(s) = Pb(g) + CaS(s) + CO(g)	950	[ <mark>31</mark> ]
CdO(s) + C(s) = Cd(g) + CO(g)	600	[ <mark>65</mark> ]
$1/2 \operatorname{SiO}_2(s) + C(s) = 1/2 \operatorname{Si}(g) + CO(g)$	n/a	[ <mark>65</mark> ]
$1/3 \operatorname{Al}_2 O_3(s) + C(s) = 2/3 \operatorname{Al}(g) + CO(g)$	n/a	[ <mark>65</mark> ]
CaO(s) + C(s) = Ca(g) + CO(s)	n/a	[ <mark>65</mark> ]
MgO(s) + C(s) = Mg(g) + CO(g)	n/a	[ <mark>65</mark> ]
$K_2O(s) + C(s) = 2 K(g) + CO(g)$	825	[ <mark>65</mark> ]
$1/2 \operatorname{TiO}_2(s) + C(s) = 1/2 \operatorname{Ti}(g) + CO(g)$	n/a	[ <mark>65</mark> ]
$1/5 P_2O_5(s) + C(s) = 2/5 P(g) + CO(g)$	1150	[ <mark>65</mark> ]
MnO(s) + C(s) = Mn(g) + CO(g)	n/a	[ <mark>65</mark> ]
$3 \operatorname{Fe}_2 O_3(s) + C(s) = 2 \operatorname{Fe}_3 O_4(s) + CO(g)$	325	[ <mark>66</mark> ]
$Fe_{3}O_{4}(s) + C(s) = 3 FeO(s) + CO(g)$	700	[11]
FeO(s) + C(s) = Fe(s) + CO(g)	725	[11]

Table 4.4: Possible side reactions involved in the high temperature treatment of BF sludge.

Side Reactions	T <sub>onset</sub> (°C)	Ref.
$\overline{FeCl_2(I) = FeCl_2(g)}$	1050	[63]
$C(s) + CO_2(g) = 2 CO(g)$	725	[5, 6, 11]
$MgFe_2O_4(s) = MgO(s) + Fe_2O_3(s)$	725	[67]
$CaCO_3(s) = CaO(s) + CO_2(g)$	875	[68]

Carbochlorination	T <sub>onset</sub> (°C)	Ref.
$\overline{ZnO(s) + FeCl_2(l) + C(s)} = ZnCl_2(g) + CO(g) + Fe(s)$	725	[6]
$1/4 \operatorname{ZnFe}_2O_4(s) + C(s) + 1/4 \operatorname{FeCl}_2(l) = 1/4 \operatorname{ZnCl}_2(g) + CO(g) + 3/4 \operatorname{Fe}(s)$	700	[ <mark>6, 69</mark> ]
$ZnS(s) + CaO(s) + C(s) + FeCl_2(l) = ZnCl_2(g) + CaS(s) + CO(g) + Fe(s)$	775	[ <mark>63</mark> ]
$PbO(s) + FeCl_2(I) + C(s) = PbCl_2(g) + Fe(s) + CO(g)$	525	[6]
$PbS(s) + CaO(s) + C(s) + FeCl_2(l) = PbCl_2(g) + CaS(s) + CO(g) + Fe(s)$	700	[ <mark>63</mark> ]
$CdO(s) + FeCl_2(I) + C(s) = CdCl_2(g) + Fe(s) + CO(g)$	250	[ <mark>63</mark> ]
$1/2 \operatorname{SiO}_2(s) + C(s) + \operatorname{FeCl}_2(l) = 1/2 \operatorname{SiCl}_4(g) + CO(g) + \operatorname{Fe}(s)$	1425	[ <mark>63</mark> ]
$1/3 \operatorname{Al}_2O_3(s) + C(s) + \operatorname{FeCl}_2(l) = 2/3 \operatorname{AlCl}_3(g) + CO(g) + \operatorname{Fe}(s)$	1275	[ <mark>63</mark> ]
$CaO(s) + FeCl_2(I) + C(s) = CaCl_2(g) + Fe(s) + CO(g)$	925	[6]
$MgO(s) + FeCl_2(I) + C(s) = MgCl_2(g) + Fe(s) + CO(g)$	1100	[ <mark>63</mark> ]
$K_2O(s) + C(s) + FeCl_2(l) = 2 KCl(g) + CO(g) + Fe(s)$	25	[ <mark>63</mark> ]
$1/2 \operatorname{TiO}_2(s) + C(s) + \operatorname{FeCl}_2(l) = 1/2 \operatorname{TiCl}_4(g) + CO(g) + \operatorname{Fe}(s)$	1175	[ <mark>63</mark> ]
$1/5 P_2O_5(s) + C(s) + 3/5 FeCl_2(l) = 2/5 PCl_3(g) + CO(g) + 3/5 Fe(s)$	1025	[ <mark>63</mark> ]
$MnO(s) + FeCl_2(I) + C(s) = MnCl_2(g) + Fe(s) + CO(g)$	850	[ <mark>63</mark> ]

Table 4.5: Possible carbochlorination-based reactions involved in the high temperature treatment of BF sludge.

Table 4.6: Possible indirect reduction-based reactions involved in the high temperature treatment of BF sludge.

Indirect Reduction	T <sub>onset</sub> (°C)	Ref.
$\overline{ZnO(s) + CO(g)} = Zn(g) + CO_2(g)$	1325	[11]
$1/4 \operatorname{ZnFe}_2O_4(s) + CO(g) = 1/4 \operatorname{Zn}(g) + CO_2(g) + 1/2 \operatorname{Fe}(g)$	1350	[ <mark>5</mark> , 11]
ZnS(s) + CaO(s) + CO(g) = Zn(s) + CaS(g) + CO2(g)	1450	[31]
$PbO(s) + CO(g) = Pb(g) + CO_2(g)$	885.85	[11]
$PbS(s) + CaO(s) + CO(g) = Pb(s) + CaS(g) + CO_2(g)$	1350	[31]
$CdO(s) + CO(g) = Cd(g) + CO_2(g)$	450	[ <mark>65</mark> ]
$1/2 \operatorname{SiO}_2(s) + \operatorname{CO}(g) = 1/2 \operatorname{Si}(g) + \operatorname{CO}_2(g)$	n/a	[ <mark>65</mark> ]
$1/3 \operatorname{Al}_2O_3(s) + \operatorname{CO}(g) = 2/3 \operatorname{Al}(g) + \operatorname{CO}_2(g)$	n/a	[ <mark>65</mark> ]
CaO(s) + CO(g) = Ca(g) + CO(s)	n/a	[ <mark>65</mark> ]
$MgO(s) + CO(g) = Mg(g) + CO_2(g)$	n/a	[ <mark>65</mark> ]
$K_2O(s) + CO(g) = 2 K(g) + CO_2(g)$	950	[ <mark>65</mark> ]
$1/2 \operatorname{TiO}_2(s) + \operatorname{CO}(g) = 1/2 \operatorname{Ti}(g) + \operatorname{CO}_2(g)$	n/a	[ <mark>65</mark> ]
$1/5 P_2O_5(s) + CO(g) = 2/5 P(g) + CO_2(g)$	n/a	[ <mark>65</mark> ]
$MnO(s) + CO(g) = Mn(g) + CO_2(g)$	n/a	[ <mark>65</mark> ]

In all the reactions table, onset temperature is referred to as temperature when the reaction is spontaneous or occurring, based on the starting point of negative Gibbs free energy change ( $\Delta G^{\circ}$ ). Zinc was assumed to be present in the form of zinc oxide (ZnO), zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>), and zinc sulfide (ZnS), which is based on the literature study provided in Table 1.3 and the XRD analysis. The initial lead form in PbS and PbO was based on the XRD and XRF analysis of the as-received sample. Possible side reactions in Table 4.4 were based on the phases found from the XRD analysis, and the possible mechanism occurred during the high-temperature treatment of BF sludge, such as volatilization of excess iron chloride and Bouduard reaction (reactions involving CO, CO2, and C). Indirect reduction reactions in Table 4.6 are assumed to be less likely due to the absence of CO gas injection, leading to a more positive Gibbs free energy change compared to the direct reduction and carbochlorination reactions.

Based on Table 4.5, the carbochlorination of zinc in all phases has an onset temperature between 700 to 775°C, far lower than the onset temperature of direct reduction (975 to 1275°C). This low Tonset means the carbochlorination reactions forming the zinc chloride  $(ZnCl_2)$  are more favorable than direct reduction forming the gaseous zinc (Zn). Similar behavior is also shown for the carbochlorination of other heavy metals such as lead (Pb) and cadmium (Cd). Considering the heavy metals, Cd has the lowest temperature, followed by Pb and Zn, indicating the order of the reactions in the model. Direct reduction of iron (FeO to Fe) has an onset temperature of 725°C, showing the possibility of simultan-

eously occurring with the heavy metals removal. Some other reactions have 'n/a' onset temperature meaning the Gibbs free energy change remains positive from 0 to 1600°C. Thus, it is expected, for example,  $SiO_2$  and CaO to stay in the solid residue during the high-temperature treatment. The significant advantage of the sample with chloride, governed by the carbochlorination reactions, is that the removal of heavy metals is expected to start at a relatively lower temperature, compared to similar reactions based on the direct and indirect reduction, leading to less energy required.

#### 4.2.2. Thermodynamics of the Direct Reduction and Carbochlorination

Thermodynamics of the reaction can be expressed by the Gibbs free energy change ( $\Delta$ G) as a driving force, which is the negative value meaning the reaction can occur spontaneously [33]. Gibbs free energy change depends on the enthalpy ( $\Delta$ H), absolute temperature (T), and entropy ( $\Delta$ S), defined in the below equation.

$$\Delta G = \Delta H - T \Delta S \tag{4.5}$$

Enthalpy is the heat of reaction or energy, which the negative value means an exothermic reaction or or the system releases heat to its surroundings. Positive value refers to an endothermic reaction or energy transfer from the surroundings to the system. Entropy is an indicative measure of the state of disorder of a particular system. Solid has a highly ordered state, while gas has a highly disordered state; therefore, a big positive enthalpy change can be illustrated by the reaction of a solid system forming a gas. In the case of the carbochlorination and direct reduction, as the main mechanism for the heavy metals removal representing the sample used in this study, Gibbs free energy change for each reaction listed in Table 4.3 and Table 4.5, was further calculated at a temperature between 0 to 1600°C. The result depicts the ease of reduction were balanced based on the stoichiometry of 1 mol carbon (C). The result depicts the ease of reduction of the metal oxides in the BF sludge, focusing on carbochlorination and direct reduction as the prevailing reactions. Gibbs free energy change ( $\Delta G^{\circ}$ ) was plotted against temperature, and the slope is defined by entropy change ( $\Delta S$ ). The plot for iron oxide reduction is shown in Figure 4.5.



Figure 4.5: Gibbs free energy changes in the reduction of iron oxide.

The thermodynamic modeling in Figure 4.5 is consistent with the order of iron ore reduction in the blast furnace, which starts with the most negative reactions energy from hematite ( $Fe_2O_3$ ) direct reduction, followed by the magnetite ( $Fe_3O_4$ ), and wustite (FeO) direct reduction [66]. The Gibbs energy plot for other oxides in the BF sludge aims to compare the ease of reduction between carbochlorination and direct reduction, especially on the heavy metals (Zn, Pb, Cd) removal. The Gibbs free energy plot for lead and cadmium removal is shown in Figure 4.6. The open notation represents the reactions with chlorides (carbochlorination). For lead and cadmium, the carbochlorination reactions are more favorable at up to 1000°C, and after that, the direct reduction is expected to be more dominant. On the other hand, the carbochlorination reactions are more favorable than the direct reduction for all the zinc phases at each

temperature up to 1600°C. The main difference is mainly related to the volatility of the zinc in chloride form. The vapor pressure of zinc increases tremendously with a slight temperature change at the earlier stage than lead and cadmium, as expressed in Figure 2.44 [61].



Figure 4.6: Gibbs free energy changes of carbochlorination (filled symbol) and direct reduction (open symbol) of (left) lead, cadmium, and (right) zinc.

The Gibbs free energy change for other oxides is shown in Figure 4.7. Most elements have positive Gibbs free energy, indicating non-spontaneous reactions within the temperature range provided, and the oxides are thermodynamically very stable. The addition of chloride creates a significant effect as it converts reactions for Si, Al, Ca, Ti, and Mg to a spontaneous reaction or negative Gibbs free energy starting at a different temperature over 1000°C. The order of the removal reactions follows the onset temperature provided in Table 4.3 and Table 4.5, beginning with the formation of KCl with the lowest Tonset, followed by CaCl<sub>2</sub>, PCl<sub>3</sub>, MgCl<sub>2</sub>, TiCl<sub>4</sub>, AlCl<sub>3</sub>, and SiCl<sub>4</sub>. It indicates that these impurities might be lost along with the heavy metals to the gas phase during the carbochlorination mechanism.

In general, carbochlorination reactions with more negative Gibbs free energy change are more favorable than direct reductions. In addition, Gibbs free energy change of other impurities present in BF sludge is more positive and has a lower Tonset than Zn, Pb, and Cd compounds, meaning the removal of these three heavy metals is more likely to happen in the first place, especially for the carbochlorination, together with the direct reduction of iron ore.



Figure 4.7: Gibbs free energy changes of carbochlorination (filled symbol) and direct reduction (open symbol) of other oxides contained in the BF sludge.

### 4.2.3. Thermodynamic Modeling of Equilibrium Compositions

Equilibrium composition aimed to predict the result of the thermally treated blast furnace sludge at temperatures between 0 to 1600°C. The calculations were based on the equilibrium module FactSage 8.1. FactPS and FTOxid were used as the databases for the calculation. The input composition (wt%) was based on the average of XRF analysis at TU Delft (see Table 4.2), differentiated into two conditions, the sample without chloride addition (samples 1 and 4) and the sample with chloride addition (samples 2 and 3). The equilibrium results were labeled Reaction 1 or "-1," referring to the sample without chloride addition, and Reaction 2 or "-2," referring to a sample with chloride addition. In general, the input for each compound was in wt% with the selected option of the most stable phase, except for FeCl<sub>2</sub> in the liquid phase. Zinc compounds were assumed to consist of ZnS and ZnO with the ratio defined from the XRD analysis (see Section 3.1). The composition of reactions 1 and 2 are provided below.

Composition 1:

 $\overline{40.8 \text{ C} + 36.83 \text{ Fe}_2\text{O}_3} + 6.15 \text{ SiO}_2 + 2.09 \text{ ZnO} + 3.14 \text{ ZnS} + 3.34 \text{ Al}_2\text{O}_3 + 0.01 \text{ CdO} + 2.24 \text{ CaO} + 1.14 \text{ MgO} + 0.67 \text{ PbO} + 0.56 \text{ K}_2\text{O} + 0.21 \text{ TiO}_2 + 0.17 \text{ P}_2\text{O}_5 + 0.14 \text{ MnO} +$ **0.14 \text{ Cl} + 2.19 \text{ SO}\_3.** 

Composition 2:

 $\overline{40.8 \text{ C} + 36.83} \text{ Fe}_2\text{O}_3 + 6.15 \text{ SiO}_2 + 2.09 \text{ ZnO} + 3.14 \text{ ZnS} + 3.34 \text{ Al}_2\text{O}_3 + 0.01 \text{ CdO} + 2.24 \text{ CaO} + 1.14 \text{ MgO} + 0.67 \text{ PbO} + 0.56 \text{ K}_2\text{O} + 0.21 \text{ TiO}_2 + 0.17 \text{ P}_2\text{O}_5 + 0.14 \text{ MnO} + 2.15 \text{ Cl} + 2.19 \text{ SO}_3.$ 

The products of the calculations were selected as gas and solid. The equilibrium composition of the gas product is shown in Figure 4.8. The open symbol represents the equilibrium composition of the sample without chloride (composition 1), and the filled symbol represents the sample with chloride (composition 2). The results of the equilibrium composition are presented in wt%.



Figure 4.8: Equilibrium composition of gas produced at a temperature ranging from 0 to 1600°C for (a) CO and CO<sub>2</sub>, (b) other compounds, (c) zinc compounds, (d) lead, and cadmium compounds.

Based on Figure 4.8, the model predicts that 30% of carbon monoxide will be produced at 1600°C, significantly increasing from 600 to 900°C. The amount of carbon monoxide overcomes carbon dioxide, indicating a high favorability of direct reduction over indirect reduction. Chloride addition has an insignificant influence on carbon monoxide or carbon dioxide production. The simulation produces up to 3.8% of Zn(g), which increases consistently with temperature. The addition of chloride significantly triggers the formation of new compounds of zinc, such as KZnCl<sub>3</sub>, and ZnCl<sub>2</sub>, which start at around 700-800°C and fluctuate with increasing temperature. Up to 0.6% of Pb in the gas is produced, which increases consistently with temperature from both composition models. The addition of chloride also promotes the formation of PbCl and PbCl<sub>2</sub>, starting at around 700-800°C. Since Cd content in the initial sample is very low, cadmium in gaseous form was only produced at around 0.01% at 600°C, from both models, with no further increase in the content at increasing temperatures to 1600°C.

Furthermore, Figure 4.8 shows that around 0.78% of FeCl<sub>2</sub> is lost to the gas phase at 1200 and 1300°C from composition model 2. The formation of several gases (excluding Zn, Pb, and Cd) generally increases as temperature rises, especially at a temperature higher than 1200°C. This mechanism is related to the high onset temperature of the impurities in the BF sludge beside the heavy metals. The addition of chlorides triggers the formation of 3 additional compounds (MgCl<sub>2</sub>, CaCl<sub>2</sub>, and MnCl<sub>2</sub>), which were not available from the composition model 1. Based on this simulation, chloride addition through a carbochlorination reaction is expected to volatilize the heavy metals (Zn and Pb) in the chloride form. In addition, the formation of chloride compounds is expected to occur at a relatively lower temperature than the elemental gas. This result is consistent with the previous discussion as the carbochlorination reaction has a lower Gibbs free energy change or is more favorable than the direct reduction. The equilibrium composition of the gas could replicate the composition of the secondary dust generated from the thermal treatment of BF sludge through carbochlorination and direct reduction mechanism. The other result of the equilibrium calculations was the formation of compounds in the solid phase, as shown in Figure 4.9.



Figure 4.9: Equilibrium composition of the solid produced at a temperature ranging from 0 to 1600°C for (a) iron and carbon, (b) zinc, (c) lead and cadmium, and (d) other compounds.

Based on Figure 4.9, the iron oxide was converted to Fe<sub>3</sub>C at 900°C, which above 900°C, carbon and Fe<sub>3</sub>C content become relatively constant at around 25% and 23%, respectively. This equilibrium indicates a sufficient initial amount of carbon for the direct reduction of iron oxide. On the other hand, zinc content, represented by ZnS(s), decreased as temperature increased and was removed entirely from the solid at 1200°C. Zinc content close to zero was achieved at 1100°C for composition model 2 (chloride addition). Composition model 1 has a complete Pb removal at 1000°C, represented by Pb(s), while chloride addition lowers the complete removal of Pb to 800°C (model 2). These modeling results are consistent with the gas equilibrium modeling in Figure 4.8, in which carbochlorination occurs at an earlier temperature than direct reduction, meaning a lower temperature for the heavy metals removal. The equilibrium content of compounds other than iron and heavy metals is included in the modeling, which shows a wide variety of compounds of mixed elements in BF sludge. In summary, carbochlorination reactions are thermodynamically more favorable than the direct reduction in terms of the heavy metals removal with a more negative Gibbs free energy, lower onset temperature, and lower temperature for the complete removal of heavy metals (Zn, Pb, and Cd).

# 4.3. Effects of Parameters Variation of the TGA Experiments

Thermogravimetric analysis (TGA) was carried out with varying parameters to define the optimum conditions for the heavy metals removal. The varying parameter from the experiment using a TGA furnace includes thermal temperature, pellets size, and chloride addition which will be discussed extensively in this section.

#### 4.3.1. Effects of Reacting Temperature on the Residual Mass

As mentioned in the previous chapter, the TGA experiments were done at four different temperatures, starting from 800°C up to 1400°C with 200°C intervals. In each experiment, the mass of the sample during the thermal treatment was measured continuously. The results of the mass alteration (TGA graph) during the heating and the residual mass at each variation are shown in Figure 4.10.



**Figure 4.10:** TGA graph of all samples from the thermal treatment up to (a) 800°C, (b) 1000°C, (c) 1200°C, and (d) 1400°C. The holding time of the isothermal heating was 60 minutes.

Based on Figure 4.10, sample 1, 2, 3, and 4 corresponds to the black, yellow, blue, and green curve, respectively. Samples 2 and 3 are the samples with chloride addition. From all the graphs, it can be seen that a significant mass change occurred at the non-isothermal heating, especially at higher temperatures. For the sample reacted up to 800°C, significant weight loss continues at the isothermal heating. Meanwhile, there was only a slight reduction of residual mass during the isothermal heating for samples heated up to 1000, 1200, and 1400°C. As the maximum temperature increases, the sample's residual mass becomes smaller, which means more elements are released into the gas phase. It is expected that the most abundant compound in the gas was carbon monoxide (CO), as the FactSage calculation estimated, up to 23% of CO will be produced from either direct reduction or carbochlorination when the BF sludge is reacted at between 800°C to 1400°C (see Figure 4.8). Another weight's loss would be from the volatilization of zinc, lead, and cadmium which could contribute around 5% in total within the range of 800 to 1400°C, also based on FactSage simulation (see Figure 4.8). The residual mass in each temperature for every sample is shown in Figure Figure 4.11. The data shown are the average of the duplicate analysis for every variation.



Figure 4.11: Residual mass of sample 1, 2 (+ FeCl<sub>2</sub>), 3 (+ FeCl<sub>2</sub>), and 4 at varied TGA reacting temperatures. The holding time of the isothermal heating was 60 minutes.

Based on Figure 4.11, it can be seen that with increasing temperature, the residual mass becomes lower. However, as the temperature increased, the curve became flattened, or the influence of the increasing temperature on the residual mass became less significant. Hence, the residual mass's most notable difference was from the heating at 800°C and 1000°C. Another highlight is that the sample with chloride additions (samples 2 and 3) has a lower residual mass than those without chloride additions (samples 1 and 4). This difference is mainly due to carbochlorination reactions being thermodynamically more favorable than the direct reduction in terms of the heavy metals removal, leading to an increased weight loss.

#### 4.3.2. Effects of Reacting Temperature on the Metals Removal

Each solid residue left after thermal treatment at 800, 100, 1200, and 1400°C was analyzed using ICP-OES to measure the composition. The metal removal was calculated through the ratio of the amount of the metal leaving the sample and the initial metal's amount using Equation 4.6.

$$\% Metal Removal = \frac{(f x F) - (c x C)}{f x F} x 100\%$$
(4.6)

In Equation 4.6, F is the sample's initial mass, with f being the metal's initial content (in wt%). C is the final mass of the solid residue after thermal treatment, and c is the metal content in the residue (wt%). The metal removal was calculated for the iron (Fe), carbon (C), zinc (Zn), and lead (Pb) of each sample which is shown in Figure 4.12. The results are the average of the duplicate analysis for every variation. Based on Figure 4.12, reacting the sample at 1000°C led to a high removal rate of Zn and Pb, up to 98 and 99%, respectively. Furthermore, up to 98% of Pb has already been removed at 800°C from the
samples with chloride addition (samples 2 and 3). Meanwhile, only 37% (sample 1) and 31% (sample 4) of Pb were removed at 800°C from the sample without chloride addition. The removal rate results mean that the carbochlorination reaction could lower the temperature required for the complete removal of Pb compared to the direct reduction. This result is consistent with the thermodynamic analysis, in which, at 1200°C, zinc and lead were removed entirely from the solid equilibrium composition (see Figure 4.9). On the other hand, up to 12% of iron was lost to the gas phase, measured from sample 1 reacted at 1200°C. The iron loss might be due to the excess FeCl<sub>2</sub> as it was converted to the gaseous form as a side reaction during the heating, supported by the thermodynamic modeling of gas equilibrium composition (see Figure 4.8). There is also an increasing trend of carbon removal, up to 21%, as carbon was consumed for direct reduction or carbochlorination reactions of heavy metals removal and iron ore reduction, producing carbon monoxide.



Figure 4.12: Removal rate of (a) zinc, (b) lead, (c) carbon, and (d) iron from TGA experiments.

#### 4.3.3. Effects of the Pellets Size on Zinc and Lead Removal

The influence of the pellets size on the Zn and Pb removal can be measured by comparing the difference of the removal from sample 1 (3.15-5 mm) with sample 4 (<3.15 mm) and sample 2 (3.15-5 mm) with 3 (<3.15), disregarding the effect of chloride addition. Based on Figure 4.12 (a), the difference in zinc removal between sample 1 and sample 4 (represented by the open notation) is small, similar to the difference between sample 1 and sample 3 (represented by the filled notation). For lead removal, based on Figure 4.12 (b), the difference between sample 1 and sample 1 and sample 4 is also small, similar to the difference between sample 2 and sample 3. In general, a small sample (diameter <10 mm) could increase the diffusion rate from the inner core to the bulk, increasing the removal rate of heavy metals [5]. In this case, for the zinc and lead removal at 800°C, sample 1 has a slightly higher removal than sample 4, and sample 2 has a slightly higher removal than sample 3. Based on this result, a bigger sample diameter with a larger surface area could provide more contact for the reactions in which the size was sufficiently small not to burden heavy metals removal. In addition, Zhu (2020) [5] reported a reduced removal rate of zinc when the sample size was increased from 12 mm to 18 mm, which is far greater than the diameter of the pellets used in this study.

#### 4.3.4. Effects of Chloride Addition on the Reacted BF Sludge

The effect of chloride addition can be seen from the comparison of samples 1 and 4 with samples 2 and 3 since the effect of pellets size was minimal or can be neglected, based on the previous discussion. The comparison is referred to as a comparison between carbochlorination (sample with chloride addition) and direct reduction (sample without chloride addition) as the primary mechanism for removing heavy metals. The influence of chloride based on the zinc and lead concentration on the reacted sample is expressed in Figure 4.13.



Figure 4.13: Concentration of (a) zinc and (b) lead in the sample reacted at four different temperatures. The sample without chloride consists of samples 1 and 4, and the sample with FeCl<sub>2</sub> consists of samples 2 and 3.

The filled symbol in Figure 4.13 represents the sample with chloride (samples 2 and 3), while the open symbol represents the sample without chloride (samples 1 and 4). The average initial content of each metal (Zn and Pb) is shown as a horizontal dashed line. Based on the thermodynamic calculations, chloride addition in ferric chloride (FeCl<sub>2</sub>) led to a carbochlorination mechanism that is thermodynamically more favorable than direct reduction, such as a lower onset temperature and increasing the ease of heavy metals removal. This simulation is consistent with the result shown in Figure 4.13, as the zinc and lead content in the solid residue for the sample with chloride addition are lower than the sample without chloride at every reaction temperature. The most significant difference was the zinc and lead content from the sample reacting at 800°C.

The influence of FeCl<sub>2</sub> or carbochlorination reaction becomes insignificant when the reaction temperature increases to 1000, 1200, and 1400°C. Moreover, zinc content in the residue (without FeCl<sub>2</sub>) reacted at 800°C was higher than the initial content as the temperature was insufficient for the direct reduction to remove the zinc, especially for the most stable phases, such as zinc sulfide. More thermodynamically unstable phases such as PbO, PbS, and CdO were removed at 800°C while zinc remained in the sample. Further comparison is shown in Figure 4.12, showing that the sample with additional chloride has a higher zinc removal rate at 800°C than the sample without chloride addition. For Pb removal, the more considerable difference can be seen as samples with chloride addition has a removal rate of close to 100%. In contrast, the samples without chloride only have a removal rate below 40%.

#### 4.3.5. External Data from Research by Tata Steel

As discussed in Chapter 3 (see Figure 3.2), supplementary data was provided in parallel with this thesis work from the experiments done by Dr. Peter Beentjes, a researcher from Tata Steel Europe in IJmuiden. The sample used in the experiment was the same sample (<3.15 mm) used in this thesis report. Sample 1 (sample 3 in TGA experiment) is referred to as the sample without chloride addition, and sample 2 (sample 4 in TGA experiment) is the sample with chloride addition. The experiments were conducted at five different reaction temperatures (500, 850, 950, 1100, and 1166°C). The atmospheric conditions were varied using nitrogen, air, and HCl gas. Some experiments were done through double-step thermal treatment, with the first thermal treatment fixed at 500°C. The experiment's results on the heavy metals content of the reacted sample are shown in Figure 4.14. Each sample was analyzed through XRF at Tata Steel in IJmuiden after the thermal treatment.



Figure 4.14: Equilibrium carbon (C), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), Fe metallic, lead oxide (PbO), and zinc oxide (ZnO) content in the reacted sample at different temperatures and atmospheric conditions.

Double-step thermal treatments in Figure 4.14 were denoted by the arrow showing the atmospheric conditions provided in the legend box information. The plot in the graph was based on the latest reaction temperature. The initial content for C, Fe<sub>2</sub>O<sub>3</sub>, Fe metallic, PbO, and ZnO, represented by horizontal dashed line was based on the initial content of sample 1. The open symbol depicts sample 1 (without chloride), and the filled symbol represents sample 2 (with chloride). In general, ZnO was removed entirely from the sample at 1100°C. At 850°C, atmospheric conditions rich in air (square notation) resulted in the ZnO content above the initial content of sample 1 (0%) and sample 2 (6%). Carbochlorination led to a higher zinc removal over direct reduction at 850°C for every variation, as each filled symbol has a lower zinc content than its respective open symbol. However, at 950°C, the direct reduction resulted in a higher zinc removal than carbochlorination. This mechanism at 950°C contradicts the result at 850°C and the results from the TGA experiments, which concluded that carbochlorination has a higher removal rate of zinc. In principle, carbochlorination and direct reduction are based on the presence of carbon as the reducing agent. The formation of heavy metals gas is stoichiometrically related to carbon consumption, shown below reaction.

$$ZnO(s) + \mathsf{FeCl}_2(l) + C(s) = \mathsf{ZnCl}_2(g) + CO(g) + Fe(s)$$
(4.7)

$$ZnO(s) + C(s) = Zn(g) + CO(g)$$
(4.8)

Based on Figure 4.14 at 950°C, C content in the reacted sample without chloride (open yellow triangle and open purple rhombus) is lower than most of the sample with chloride (filled symbol). The low C content in the sample without chloride indicated a higher formation of gaseous zinc through direct reduction resulting in a lower amount of ZnO left in the sample reacted at 950°C, compared to the sample with chloride addition. This finding needs further research to measure the mechanism behind

the carbon consumption related to the carbochlorination and direct reduction reactions. Regarding the Pb removal, the results are consistent with the thermodynamic and TGA results, which through carbochlorination, led to a lower content of PbO at each variation. The most considerable influence can be seen at 850°C, in which most of the samples with chloride addition have PbO content close to zero, showing similar results to a 98% Pb removal from the TGA experiment conducted at 800°C. Figure 4.14 also shows that Fe (metallic) content was increased along with increasing temperature, with the highest being 22% in sample 1 reacted at 1166°C.

#### Iron Metallization Degree

The metallization degree was further calculated by the ratio of the metallic iron mass divided by the mass of the total iron. The content of the metallic iron and the oxide is provided in Figure 4.14. The calculation for the iron metallization using the formula given in Equation 4.9.

$$\% Metallization = \frac{Mass Fe_{(metallic)}}{Mass Fe_{(oxide)} + Mass Fe_{(metallic)}} x 100\%$$
(4.9)

The results of the iron metallization degree are shown in Figure 4.15. The highest metallization (39%) was achieved in the sample (open red circle notation) reacted at 1166°C. The metallization degree shows an increasing trend as the reacting temperature increases, starting at 950°C. In general, the iron metallization degree of the samples with chloride addition is lower compared to the sample without chloride addition, as some amount of carbon was also consumed for the carbochlorination reactions. Figure 4.14 also shows that the carbon consumption of the sample without chloride, representing the direct reduction mechanism, is more significant than its respective sample with chloride addition, representing the carbochlorination mechanism. The kinetics of the direct reduction and carbochlorination mechanism were not measured in this study which might be related to the degree of carbon consumption for heavy metals removal and iron ore reduction.



Figure 4.15: Iron metallization degree of reacted BF sludge at different temperatures and atmospheric conditions.

## 4.4. Zinc and Lead Removal Behaviour

In this section, the mechanism of zinc and lead removal is further discussed. The analysis was based on the SEM-EDS characterization and reactions occurrence for the reacted sample 1, representing the direct reduction mechanism, and sample 2, representing carbochlorination, from the TGA experiments.

#### 4.4.1. Zinc and Lead Occurrence in Reacted BF Sludge

The previous discussion concluded that at a reacting temperature over 1000°C, there is no further removal of zinc and heavy metals as it has already finished at 1000°C. Based on this finding, it is expected that no zinc and lead were found at the solid residue reacted after 1000°C. Therefore the

SEM-EDS analysis aimed to check the occurrence of zinc and lead in the solid residue reacted at 800 and 1000°C from the TGA experiments of sample 1 (without chloride) and sample 2 (with chloride). The SEM picture and EDS point analysis for samples 1 and 2 reacted at 800°C are shown in Figure 4.16.



Samplo	Point -	Point Content (%)										
Sample	FUIIL	С	0	Mg	AI	Si	S	К	Са	Fe	Zn	CI
	1	91.26	7.54			0.46	0.75					
1	2	77.53	17.83		0.54	0.85	0.38	0.22	0.14	2.13	0.38	
	3	88.77	9.39			0.42	0.55		0.14	0.73		
	4	87.23	9.19		0.54	0.78	0.67	0.27	0.13	1.19		
	5	79.11	16.7	0.11	0.34	0.64	0.42	0.15	0.1	1.99	0.34	
	6	61.78	11.58	0.14	0.92	1.51	0.24	0.22	2.3	18.54	2.78	
	7	36.84	34.54	0.67	1.97	3.15	0.64	0.28	0.52	18.01	3.37	
	8	86.02	13.23			0.15	0.51		0.09			
	1	62.28	15.19	1.03	1.16	3.04	0.75		4.03	10.39	2.13	
	2	47.1	15.5	1.31	3.95	5.54	1.13	0.47	2.53	18.25	3.51	0.4
	3	49.75	12.21	0.7	1.65	2.96	2.38	0.13	1.42	21.28	7.52	
2	4	64.32	26.08	0.23	0.81	0.93			0.35	6.76	0.52	
	5	81.07	15.11			0.4	0.61	0.14	0.34	2.33		
	6	51.13	32.66	0.38	0.94	1.23		0.11	1.36	10.9	0.89	0.4
	7	26.41	41.23	12.72	0.4	9.51			0.47	9.26		

Figure 4.16: SEM-EDS analysis of samples (a) 1 and (b) 2 reacted at 800°C.

Based on Figure 4.16, zinc was detected at some points in samples 1 and 2, indicating that the remaining zinc was still left in the residue after being reacted at 800°C. On the other hand, lead was not detected in sample 1. Based on the ICP-OES analysis, the lead remained in the sample heated at 800°C for the sample without chloride addition, indicating the lead content is beyond the EDS detection limit. The majority of element detected was due to the carbon tape as the sample was placed on carbon tape. The second most detected element was oxygen indicating the metals in the BF sludge were present in the oxide form. Referring to the FactSage simulation at 800°C and XRD analysis of the raw BF sludge, zinc is present in two phases: zinc oxide (ZnO) and zinc sulfide (ZnS). These two thermodynamically stable compounds in the BF sludge are indicated by the detection of zinc, oxygen, and sulfur, based on the several points analysis, with the highest Zn content measured on points 7 (sample 1) and 3 (sample 2).

SEM-EDS analysis for the samples reacted at 1000°C is shown in Figure 4.17. Based on all the measurements, zinc was not detected in samples 1 and 2. The most dominant element (besides carbon) is iron, as measured in points 7 (sample 1) and point 5 (sample 2). Chloride was not found in sample 2, which indicates that the carbochlorination or direct reduction of the heavy metals removal was finished when the sample was reacted at 1000°C. In addition, TGA results (see Figure 4.10) concluded that there was no further significant reduction in residual mass when the reacting temperature was increased to more than 1000°C, meaning the most dominant reaction occurring at 800° and 1000°C is carbochlorination or direct reduction of heavy metals removal.



Comple	Point -				Conte	nt (%)			
Sample	POIN	С	0	Mg	Al	Si	S	Са	Fe
	1	84.96	12.33		0.23				2.48
	2	76.76	12.72	0.25	0.53	0.9	0.26	0.42	8.03
	3	76.7	13.67			0.87			8.76
	4	82.53	10.2		0.81	0.55	0.3	0.18	5.43
1	5	87.5	9.09		0.21	0.28	0.58		2.17
	6	72.44	22.05		0.66	1.43		0.17	2.92
	7	64.43	12.2		1.07	1.47		1.33	19.49
	8	81.49	13.83	0.17	0.37	0.55	0.2	0.17	3.22
	9	80.25	16.46		0.39	0.53			2.37
	1	75.4	9.78	0.48	1.41	2.25	0.35	1.55	8.79
	2	82.27	11.01	0.41	0.98	1.3	0.43	0.74	2.86
	3	76.6	13.62	0.19	0.4	0.72	0.16	0.51	7.8
2	4	84.62	8.5		0.21	0.28	0.17	0.12	6.1
	5	48.17	8.52	0.24	0.41	0.7		0.35	41.61
	6	77.25			0.73	1.31	2		18.71
	7	58.76	22.07	0.5	0.74	3.69	0.33	1.69	12.23

Figure 4.17: SEM-EDS analysis of sample (a) 1 and (b) 2 heated at 1000°C.

#### 4.4.2. Zinc and Lead Removal Mechanism

Thermodynamic modeling and TGA experiments have shown that zinc and lead could be removed through carbochlorination or direct reduction. Based on the direct reduction mechanism (sample without chloride addition), thermodynamic modeling shows that zinc, represented by the ZnS in the solid, could be removed or volatilized entirely at 1200°C, as shown in Figure 4.9. On the other hand, based on the results from TGA experiments, the temperature needed for the complete removal is 1000°C (see Figure 2.3), lower than the thermodynamic modeling. Regarding lead (Pb) removal, TGA experimental results show the same reacting temperature required with the thermodynamic modeling for the complete removal, which is at 1000°C. The zinc and lead removal through direct reduction reactions are shown in the following equations.

$$PbO(s) + C(s) = Pb(g) + CO(g)$$
 (4.10)

$$PbO(s) + C(s) = Pb(g) + CO(g)$$

$$PbS(s) + CaO(s) + C(s) = Pb(g) + CaS(s) + CO(g)$$
(4.10)
(4.11)

$$ZnO(s) + C(s) = Zn(g) + CO(g)$$
 (4.12)

$$ZnS(s) + CaO(s) + C(s) = Zn(g) + CaS(s) + CO(g)$$
(4.13)

In principle, zinc and lead oxide are reduced with the presence of carbon, forming lead and zinc metals in gaseous form. On the other hand, zinc and lead sulfide are reduced with CaO and C, then the calcium bond with sulfur forming calcium sulfide (CaS). Zinc and lead are converted to gaseous form and removed from the solid. Carbon monoxide is also formed as part of the direct reduction reactions. For the second removal mechanism through carbochlorination (sample with chloride addition), thermodynamic modeling shows that the complete removal of zinc and lead could be achieved at 1200°C and 800°C, respectively. In addition, a low amount of zinc (<0.5%) remained in the sample reacted at 1100°C

from the thermodynamic model. The TGA experimental results show that the complete removal of zinc and lead occurred at reacting temperatures of 1000°C and 800°C, respectively. The carbochlorination mechanism on the zinc and lead removal is shown in the following equations.

$$PbO(s) + \mathsf{FeCl}_2(l) + C(s) = \mathsf{PbCl}_2(g) + Fe(s) + CO(g)$$
(4.14)

$$PbS(s) + CaO(s) + C(s) + FeCl_2(l) = PbCl_2(g) + CaS(s) + CO(g) + Fe(s)$$
 (4.15)

$$ZnO(s) + \mathsf{FeCl}_2(l) + C(s) = \mathsf{ZnCl}_2(g) + CO(g) + Fe(s))$$
(4.16)

$$ZnS(s) + CaO(s) + C(s) + \mathsf{FeCl}_2(l) = \mathsf{ZnCl}_2(g) + CaS(s) + CO(g) + Fe(s)$$
(4.17)

Based on the above equations, zinc, and lead, in the initial form of oxide and sulfide, are reduced to a metallic form which then the presence of FeCl<sub>2</sub> as chlorination agent converts the lead and zinc to gaseous chloride form. Thermodynamic modeling and TGA results confirmed that lead and zinc could be removed at earlier temperatures through the carbochlorination mechanism compared to direct reduction. Carbochlorination reactions have a lower onset temperature and more negative Gibbs free energy leading to a more thermodynamically favorable than direct reduction. Considering all the compounds in the BF sludge, the carbochlorination-based mechanism on all the compounds, including the direct reduction of iron oxide and the side reactions, are summarized in Figure 4.18.



Figure 4.18: Summary of the reactions involved in the reacted sample at 800°C (red zone) and 1000°C (blue zone) based on the carbochlorination mechanism. The reaction's location indicates the zone in which the reactions occur.

The graph in Figure 4.18 is the TGA curve at 800°C combined with the TGA curve at 1000°C (see Figure 4.10) from sample 2 (with chloride addition), representing the mass alteration with respect to the carbochlorination reactions. The highlighted reactions in green are the heavy metals removal reactions which are the main focus of this thesis study. This summary was made based on the thermodynamic analysis and the results of the TGA experiments related to at which temperature the reactions started occurring and at which temperature the reactions were finished. In Figure 4.18, The carbochlorination of cadmium and lead occurred in the red zone, which finished at 800°C, as lead and cadmium were removed entirely from the sample reacted at 800°C. Most of the reactions, including carbochlorination of zinc, direct reduction of iron oxide, volatilization of excess iron chloride, Bouduard reaction, and carbochlorination of thermodynamically stable compounds, occurred in both zones (red and blue). The highest thermodynamically stable compounds, such as CaO and MnO, were expected to occur in the blue zone as both have onset temperatures above 800°C.

#### 4.5. Multistage Removal of Lead and Zinc

Based on the previous TGA results, lead could be removed at 800°C while zinc required reacting temperature of 1000°C. From this finding, the multistage removal experiment of zinc and lead was conducted at Tata Steel (IJmuiden) in a horizontal tube furnace with 3-step continuous thermal treatment for samples 1 (without chloride) and 2 (with chloride). The sample was heated to 800, 950, and 1100°C (each for 30 minutes), and the dust was collected at each reacting temperature. The multistage removal goal was to selectively remove zinc and lead in separate dust fractions generated from a different heating stage. Based on the ICP-OES analysis (see Figure 4.12), lead could be removed at 800°C, followed by the completed removal of zinc at 1000°C. Therefore, the secondary dust (from the off-gas) generated at 800°C is expected to have a higher lead content than zinc. In contrast, the dust generated at 1100°C is expected to have a higher zinc content than lead since most lead should have already been removed at 800°C. From the experiments, the generated dust was analyzed using SEM-EDS. The SEM pictures and EDS analysis of the dust generated at 800, 950, and 1100°C from sample 1 is shown in Figure 4.19.



Duct	Point -	Content										
Dust	Point -	С	0	S	CI	к	Zn	Pb	Cd	Al	Fe	
	1	35.63	2.53	0.42	2.86	0.35	0.89	8.96	1.11	44.06	3.18	
	2	39.07	3.02	0.38	2.35	0.42		7.75		43.41	3.59	
	3	42.34	12.35	0.41	4.89	0.69		14.36	1.04	17.57	6.35	
	4	35.05	6.34		12.32	3.05		7.56	11.44	20.45	3.8	
	5	27.5	14.39	0.62	5.87	0.29	1.48	7.43	5.04	29.2	8.19	
A	6	22.57	32.06		3.55					11.71	30.11	
	7	33.9	26.18		16.35					14.34	9.24	
	8	43.81	27.57	0.18	0.31			1.18		2.12	24.82	
	9	13.02	57.42	0.23	0.78					17.22	11.32	
	Average	32.54	20.21	0.37	5.48	0.96	1.18	7.87	4.66	22.23	11.18	
	1	55.67	26.26		0.65		10.15	7.28				
	2	8.53	16.71	0.7	2.34	1.42	48.08	22.21				
	3	5.55	15.94	0.63	1.73	0.83	50.98	24.34				
P	4	5.08	14.35	0.58	1.67	0.84	54.96	22.53				
D	5	3.87	7.82		1.23	0.59	66.01	20.48				
	6	36.84	28.33		1.14	0.33	21.64	11.72				
	7	5.31	13.61	0.65	1.72	0.7	56.26	21.75				
	Average	17.26	17.58	0.64	1.5	0.78	44.01	18.61				
	1	9.29	22.9		0.97	0.28	62.12	4.43				
	2	5.37	15.99		1.78	0.42	65.48	10.95				
	3	5.01	14.24		1.5	0.56	68.31	10.37				
	4	17.9	25.12		1.25	0.18	48.93	6.63				
С	5	67.01	32.99									
	6	19.73	18.92	0.25	0.94	0.21	54.41	5.55				
	7	33.95	28.92		0.72	0.19	30.28	5.93				
	8	15.42	24.08		1		53.64	5.86				
	Average	21.71	22.89	0.25	1.17	0.31	54.74	7.1				

Figure 4.19: SEM-EDS analysis of dust generated from sample 1 after reacting at (a) 800, (b) 950, (C) 1100°C.

In Figure 4.19, The number indicates the point or area (in purple color) measured by EDS, and the average composition for each dust from several measurements (point/area) was provided in the last column in the table. Carbon (32%) and aluminum (22.23%) are the primary elements (besides oxygen) in dust generated at 800°C. It is also shown that a small zinc concentration was only found in points 5 and 8. In addition, the average amount of lead (7.87%) was significantly higher than zinc (1.18%), indicating a good removal selectivity of lead over zinc at 800°C. Cadmium was also found to be up to 11% as it is one of the most susceptible elements to chlorination in BF sludge. Although sample 1 was the sample without chloride addition, the initial chloride content (0.5%) is sufficient to also trigger carbochlorination of heavy metals, as CI was detected in the EDS results. In the dust generated at 950°C, up to 24% of Pb was found. On the other hand, a high amount of Zn, up to 66%, was also detected, as the most dominant element in the dust, meaning an improved selectivity of zinc over the

lead from reacting at 950°C. Increasing the heating to 1100°C, the generated dust has a relatively similar composition to the dust generated at 950°C with a slight increase in the average Zn content (54%) and a decrease in average Pb content (7.1%). The SEM-EDS analysis of the generated dust from sample 2 reacted at 800°C is shown in Figure 4.20. The average content of Pb and Zn is 44% (highest 72%) and 17.49% (highest 51%), respectively. This result indicates the high selectivity of lead removal over zinc, similar to the analysis of the dust generated at 800°C from sample 1.



Moncurement				Con	tent			
Measurement	0	Cl	К	Fe	Zn	Pb	Na	S
Area A	2.35	24.93	1.56	0.52	7.88	58.65	1.48	1.03
Spectrum 65	0.42	21.19	1.42	0.42	1.97	71.76	0.04	0.46
Area B	5.55	30.97	1.64	2.50	21.82	30.11	3.60	1.64
Spectrum 21	6.05	30.51	1.28	4.09	51.48	1.74	2.83	0.95
Spectrum 20	1.44	24.11	2.53	0.32	2.36	66.69	0.55	1.33
Spectrum 61	4.57	31.49	2.01	2.38	34.47	8.20	11.41	1.89
Spectrum 60	0.00	23.13	1.24	0.31	2.43	70.18	0.27	1.50
Average	2.91	26.62	1.67	1.51	17.49	43.90	2.88	1.26

Figure 4.20: SEM-EDS analysis of dust generated from sample 2 after reacting at 800°C.

A high amount of zinc was detected in the dust generated at 950°C from sample 2, as shown in Figure 4.21. The average zinc content is comparable to the average lead content detected from the EDS analysis. The analysis highlights that the chloride content is high in dust generated at 950°C from sample 2, indicating the addition of chloride in the sample and the increase of the chloride-based metal formation due to carbochlorination as the prevailing mechanism.



Maacuramont				Con	ntent			
Measurement	0	Cl	К	Fe	Zn	Pb	Na	S
Area A	10.74	28.07	7.79	3.64	23.97	17.27	4.59	1.34
Spectrum 43	16.49	24.63	4.82	9.71	38.41	0.21	3.64	0.94
Spectrum 35	1.79	19.54	6.23	1.05	4.68	62.41	0.81	0.00
Average	9.67	24.08	6.28	4.80	22.35	26.63	3.01	0.76

Figure 4.21: SEM-EDS analysis of dust generated from sample 2 after reacting at 950°C.

The last analysis of the dust generated at 1100°C is shown in Figure 4.22. The average zinc content (57%) in the generated dust is far more significant than the average lead content (6.94%), indicating that a more considerable portion of zinc was removed from the sample, which is left at the solid residue reacted at 950°C. Furthermore, up to 66% of Zn was detected in the dust (point 1). In summary, the dust generated from reacted sample 1 and sample 2 has a similar trend in which the zinc/lead content ratio increases with the reacting temperature. This result indicates that there is a possibility to concentrate

lead in the secondary dust generated at 800°C followed by the removal of zinc at 1100°C through a carbochlorination or direct reduction mechanism.



Content										
С	0	Al	Cl	К	Fe	Zn	Pb	S		
2.76	8.24		10.71	1.51	4.09	65.7	6.6	0.41		
7.76	23.25		11.54	1.92	3.54	52				
7.12	23.19		10.19	1.19	3.12	47.91	7.28			
6.78	14.7		10.71	1.1	4.47	62.24				
6.1	17.34		10.78	1.43	3.81	56.96	6.94	0.41		
	C 2.76 7.76 7.12 6.78 6.1	C         O           2.76         8.24           7.76         23.25           7.12         23.19           6.78         14.7           6.1         17.34	C         O         Al           2.76         8.24           7.76         23.25           7.12         23.19           6.78         14.7           6.1         17.34	C         O         AI         Cl           2.76         8.24         10.71           7.76         23.25         11.54           7.12         23.19         10.19           6.78         14.7         10.71           6.1         17.34         10.78	C         O         Al         Cl         K           2.76         8.24         10.71         1.51           7.76         23.25         11.54         1.92           7.12         23.19         10.19         1.19           6.78         14.7         10.71         1.1           6.1         17.34         10.78         1.43	C         O         Al         Cl         K         Fe           2.76         8.24         10.71         1.51         4.09           7.76         23.25         11.54         1.92         3.54           7.12         23.19         10.19         1.19         3.12           6.78         14.7         10.71         1.1         4.47           6.1         17.34         10.78         1.43         3.81	C         O         Al         Cl         K         Fe         Zn           2.76         8.24         10.71         1.51         4.09         65.7           7.76         23.25         11.54         1.92         3.54         52           7.12         23.19         10.19         1.19         3.12         47.91           6.78         14.7         10.71         1.1         4.47         62.24           6.1         17.34         10.78         1.43         3.81         56.96	C         O         Al         Cl         K         Fe         Zn         Pb           2.76         8.24         10.71         1.51         4.09         65.7         6.6           7.76         23.25         11.54         1.92         3.54         52           7.12         23.19         10.19         1.19         3.12         47.91         7.28           6.78         14.7         10.71         1.1         4.47         62.24         4.11		

Figure 4.22: SEM-EDS analysis of dust generated from sample 2 after reacting at 1100°C.

The ratio of Zn/Pb in the secondary dust generated from samples 1 and 2 through continuous reacting temperature is shown in Figure 4.19. As discussed previously, the ratio of Zn/Pb is low at 800°C, which increased further as the reaction temperature was increased to 1100°C, with a ratio up to 8. This result is consistent with the thermodynamic analysis and the ICP-OES results from TGA experiments which shows that lead could be removed at an earlier temperature, followed by zinc at a higher temperature. However, at reacting temperature of 950°C, the secondary dust generated from sample 1 has a higher Zn/Pb ratio than the dust generated from sample 2. This result indicates a more favorability of direct reduction over carbochlorination. On the other hand, carbochlorination reactions are more favorable at 800 and 1100°C as the dust generated from sample 2 has a higher Zn/Pb ratio than the secondary dust from sample 1. Nevertheless, the EDS analysis only indicates the available compounds in the sample, which in this case is represented by Zn/Pb ratio. Further bulk analysis through ICP-OES is required to measure the overall composition of the secondary dust.



Figure 4.23: Zn/Pb ratio of the secondary dust generated from multistage reduction. The ratio at each reacting temperature was based on the average of SEM-EDS point analysis.

### 4.6. Mass and Material Balance of the Recycling Flowsheet

The discussion from the previous sections led to a substantial advantage of carbochlorination over the direct reduction mechanism for heavy metals removal. In addition, the multistage removal experiment indicates that a selective carbochlorination reaction can take place to concentrate lead and zinc in

separate secondary dust through double-step removal. Hence, the material balance was calculated based on the idea of the double-step carbochlorination, first to remove lead, followed by zinc removal in the second-stage reduction. Based on the previous discussion, the temperature for the first-stage carbochlorination was set to 800°C for the complete removal of lead, producing lead-bearing dust. The temperature for the second carbochlorination was set to 1000°C to produce zinc-bearing dust. The final product will be the heavy metals-free (HMF) residue with partial metallization of iron. The calculation for the material balance was based on a dry basis due to the high variations of the moisture in the BF sludge originating from Tata Steel Europe in IJmuiden. The material balance calculation is conducted for the general recycling flowsheet proposed by Tata Steel, as shown in Figure 4.24, based on 2-stage carbochlorination in two separate rotary kilns.



Figure 4.24: Double-step carbochlorination recycling flowsheet.

In principle, mass balance calculation is based on the conservation of mass. The amount of material entering the system should equal the amount of material leaving the system. The general formula of mass balance is shown in Equation 4.18. The basis flow rate of the calculation is kt/year.

$$\frac{dm}{dt} = \sum_{i} \dot{M}_{i} - \sum_{o} \dot{M}_{o} \qquad \frac{|kt|}{[year]}$$
(4.18)

Based on Figure 4.24, the conservation of mass is shown in the equations inside the box, representing the system during each recycling step. The recycling process starts with sample preparation or pelletizing. The initial input for pelletizing is the BF sludge mixed with binder and iron chloride. The pellets are then sent to the first rotary kiln for carbochlorination at 800°C. Complete lead and partial zinc removal occur in this process, and the removed metal chlorides will be concentrated to the off-gas. Then the solid residue is sent to the second rotary kiln to remove the remaining zinc and concentrate the zinc in the secondary dust at 1000°C. The final product will be the heavy metal clean residue as a new secondary raw material for the input in the ironmaking or steel-making processes. The initial input of BF sludge (dry basis) is 20 kt/year as the actual capacity in Tata Steel in IJmuiden. The first process is pelletizing BF sludge by adding bentonite (0.5%) and iron chloride (4.6%). The content of bentonite and iron chloride was based on the total input of BF sludge, the exact same amount added in the sample used in this thesis study. During the pelletizing process, it is assumed that 10.6% of the feed is lost as fines referred to the study about pelletizing of iron ore concentrates [70]. For the first carbochlorination at 800°C, the residual mass of the residue will be 86%.

Input/Output	Amount	Unit	Remarks
Flue Dust (input)	20	kt/year	Dry basis (Tata Steel capacity).
Bentonite	0.5%	per input BF sludge	Binder (Added in sample).
Iron Chloride	4.6%	per input BF sludge	Added in sample 2 and 3.
			Stoichiometry for carbochlorination
Fines Dust	10.6%	per total input	Loss during pelletizing [70].
Residual Mass at 800°C	86%	per total input	TGA experiment (Sample 2).
Residual Mass at 1000°C	72%	per total input	TGA experiment (Sample 2).
Gas Produced at 800°C	0.67	kt/year	Carbon removed is converted to CO gas.
Gas Produced at 1000°C	1.57	kt/year	Carbon removed is converted to CO gas.

Table 4.7: Initial data for mass and material balance calculation	on.
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For the second carbochlorination at 1000°C, the residual mass will be 72% based on the initial input in the first rotary kiln. Thus, the further mass reduction of the solid through the second rotary kiln will be 14%. The residual mass from both carbochlorination processes in the rotary kiln was based on the TGA results of sample 2 (see Figure 4.10), which is the sample with chloride addition, representing the carbochlorination mechanism. Gas produced at 800°C and 1000°C was based on the conversion of carbon removed to carbon monoxide, as thermodynamic modeling shows that CO will be produced in the equilibrium gas composition (see Figure 4.8) from the carbochlorination reactions. Carbon removal was measured initially from ICP-OES analysis of sample 2 reacted at 800°C and 1000°C. The amount of each input and output was then calculated based on the mass balance equation in section 4.6. The result is illustrated through a Sankey diagram, as depicted in Figure 4.25.



Figure 4.25: Mass balance diagram of the recycling flowsheet.

Figure 4.25 shows that the final product from the carbochlorination-based recycling is heavy metalsfree residue (HMF) which accounts for 13.5 kt/year (67.5%) from the input of 20 kt/year BF sludge. The generated secondary zinc-bearing and lead-bearing accounts for 1.05 kt/year and 2.05 kt/year, respectively. The off-gas was assumed to consist of carbon monoxide (CO) as the product of the carbochlorination reactions from the thermodynamic modeling which all the carbon consumed/removed is converted to carbon monoxide (CO). The further calculation was conducted for the material balance considering the composition of each input and output in the whole recycling route of the blast furnace sludge. The material balance principle is given in Equation 4.19.

$$\frac{dm}{dt} = \sum_{i} \dot{F}_{i} f_{i} - \sum_{i} \dot{C}_{o} c_{o} - \sum_{i} \dot{T}_{o} t_{o} \qquad \frac{[kt]}{[year]}$$
(4.19)

Based on Equation 4.19, F and f are the mass of the input/feed and the concentration of the metal in the input, respectively. C and T represent the mass of the concentrate/product and tailing/by-product, while the c and t show the metal concentration in the respective output. In general, the amount of metal in the input should equal its respective amount in the output. The initial known compositions for the calculation are BF sludge pellets (A), bentonite (B), and iron chloride (C). Solid residue (G) and HMF (I) composition are based on the ICP-OES analysis from the TGA experiments at 800°C and 1000°C of sample 2. The composition of the BF sludge, lead-bearing, and zinc-bearing dust was further calculated using the material balance equation. Some adjustment was made in the calculation using the content for BF sludge sample 3, representing the sample with chloride addition similar to sample 2 but with a smaller diameter. Nevertheless, the effect of the pellets size was insignificant, as discussed in the previous section.

Some elements (Si, Al, Cl, P) for material balance calculation were based on the XRF result from a similar larger-scale experiment (same sample) done by Dr. Peter Beentjes at Tata Steel Europe in IJmuiden in parallel with this thesis project. The material balance for carbon, iron, zinc and lead are shown in Figure 4.26. Material balance for other elements is provided in Appendix C. In Figure 4.26, the distribution of carbon, iron, zinc, and lead in each output is shown in a separate pie chart. It is shown that most iron (85%) and carbon (78%) end up in the HMF residue, which can also be referred to as recovery. Most of the zinc is concentrated in the zinc-bearing dust (62%), while some amount of zinc (26%) is lost in the lead-bearing dust. Most of the lead (88%) was already removed into the lead-bearing dust from the first carbochlorination. The ratio of zinc in the Zn-bearing dust and lead in the Pb-bearing dust is also referred to as recovery, meaning the ratio of the metals in the respective product.



Figure 4.26: Material balance of (from the inner to outer layer) carbon, iron, zinc, and lead. The percentage shows the distribution of the elements in each recycling process output.

## 4.7. Economic Assessment of the Recycling Process

The economic assessment of the complete recycling route through carbochlorination was calculated with a simple cost and benefit analysis. This calculation was based on the balance between the returns and the costs associated with the input, output, and recycling process. The basis of the calculation was 20 kt/year of BF sludge with the throughput discussed in the material balance section (Section 4.6). The criteria and the associated cost or return are shown in Table 4.8. The price was based on the study from some literature and further checked by the people from the relevant department of Tata Steel Europe in IJmuiden. The price of each item was adjusted within the range provided as the minimum and maximum scenarios.

No	ltom	Cost (€/t)		Returns (€/t)		Source		
NO	Rom	Min	Max	Min	Max	Course		
1	BF Sludge	-	-	70	170	Internal Data		
2	Bentonite	120	140	-	-	Adjustment from 2021 Average Price US [71]		
3	Iron Chloride	-	100	-	-	Internal Discussion, [6]		
4	Pelletizing	15	25	-	-	[72]		
5	Rotary Kiln #1	32	150	-	-	[6, 73]		
6	Pb-bearing dust	-	300	-	-	Internal Discussion		
7	Rotary Kiln #2	22	100	-	-	[6, 73]		
8	Zn-bearing dust	-	-	-	720	[6, 74]		
9	HMF Residue	-	50	-	100	Internal Disussion, [6]		

Table 4.8: Items and the associated cost or returns in the recycling process of BF sludge.

In Table 4.8, The return for the BF sludge was the cost avoided for the landfilling based on the existing practice on Tata Steel Europe in IJmuiden. Since recycling will prevent landfilling costs, the cost of landfilling BF sludge was associated with the potential return. Bentonite's price is based on the US average price in 2021, which was further adjusted based on the discussion with the people from Tata Steel. The pelletizing cost was based on a report from India regarding the ironmaking industry [72]. The minimum cost was adjusted from the maximum cost mentioned in the report since, in the actual condition, the induration step is not needed during pelletization. The actual rotary kiln operating cost of between 54 to 250 EUR was based on the report by Andersson (2019) [73], and Hamann et al. (2021) [6]. Since RK#1 and RK#2 is a continuous carbochlorination process at 800 to 1000°C, the cost was adjusted based on the ratio of 0.6 for RK#1 (heating from room temperature to 800°C) and 0.4 for RK 2 (heating from 800 to 1000°C).

For the spent pickling, it was assumed that the maximum cost from the scenario on purchasing the chloride from external companies [6], and the other scenario of zero cost was assumed that the chloride could be used from the spent pickling waste from the internal production at Tata Steel. The generated lead-bearing dust was assumed to be landfilled, with the maximum cost assumed to be 300 EUR as the landfilling cost. Zinc-bearing dust might contain up to 60% Zn (based on SEM-EDS, see Figure 4.19), which is marketable to the zinc smelter with a price around 720 EUR [6, 74]. The final product of HMF residue can be associated with a cost if the quality is insufficient for input to the ironmaking process [6]. Based on Table 4.8, the calculations for the economic assessment were finalized with two scenarios. The best-case scenario is the balance between the maximum returns and the minimum cost. In contrast, the worst-case scenario is derived from the balance between the minimum returns and the maximum costs. The calculated best-case and worst-case scenarios are shown in Figure 4.27.

The best-case scenario has a potential profit of  $\sim$ 210 EUR/ton of processed BF sludge. On the other hand, the worst-case scenario resulted in a loss of  $\sim$ 250 EUR/ton of processed BF sludge. This loss is higher than the cost of landfill, which is not a good option from an economic point of view to replace the current landfilling. However, the worst-case scenario assumed that the return was only generated from the landfill cost of BF sludge which is very unlikely to happen since the recycling of the BF sludge aims to produce a new secondary product which, in this case, the zinc-bearing dust and HMF residue were expected to meet the criteria of saleable product which the experimental results have proved.

Therefore the best-case scenario would be more representative of the economic assessment, which depends on the actual price for the implementation within the range provided in this study.



Figure 4.27: Economic assessment of the BF sludge recycling based on best-case and worst-case scenarios.

## 4.8. Life Cycle Assessment (LCA)

The life cycle assessment in this study aims to measure the environmental impact of BF sludge recycling through carbochlorination. The baseline in defining the goal of the LCA is within the context of the 3P, planet, people, and prosperity [75]. These three interconnected aspects are the foundation for determining the sustainability of the recycling process through LCA. These three aspects are further classified into six sectors for articulating sustainable development, as shown in Figure 4.28. In this thesis, the LCA focuses on the environment, energy, and materials aspects, given in the top part of Figure 4.28. The steps for the LCA, starting from the goal definition until data interpretation, are discussed in the following subsection.



Figure 4.28: Six major aspects in sustainability analysis by Ashby [75].

#### 4.8.1. Goal and Scope Definition

Based on Figure 4.28, in the case of LCA of this thesis study, the focus will be on the top three aspects: materials, energy, and environment. The materials are related to the input and output in the recycling process. Energy is based on the carbochlorination process in the rotary kiln as the primary process for recycling BF sludge. Later, the environmental aspect, such as the emissions, is further discussed in the last step before data interpretation of the impact calculations. As mentioned in the previous section, the LCA aims to quantify the carbochlorination environmental impact and the associated shadow costs (environmental price). The scope of this LCA will be based on the gate-to-gate framework, in which the recycling started with the BF sludge as an intermediate product and then converted to a new secondary product for use in the ironmaking industry. In this case, the production process of BF sludge (wet and dry cleaning processing steps) and other production processes for bentonite and iron chloride were not involved in the calculations.

For the environmental impact categories, the focus was set on the global warming potential (GWP) in the unit of  $CO_2$ -eq and further converting the impacts, including other impact categories, to the environmental price. Environmental price or shadow cost is referred to as the price that indicates the social costs (loss of economic welfare) of particular environmental impacts [76]. The functional unit (FU) of the LCA in this thesis was based on the impact per ton of processed BF sludge through carbochlorination. In summary, the method for the LCA calculation was the life cycle impact assessment (LCIA) method using the software OpenLCA. LCIA means calculating the impacts by a standardized unit which will be explained further in the following subsection.

#### 4.8.2. Inventory Analysis

The inventory analysis includes all the relevant processes for the LCIA calculation. The inventory was based on the material balance, as explained in Section 4.6. The data inventory for the calculation is shown in Figure 4.29.



Figure 4.29: LCA inventory of the recycling of BF sludge.

Figure 4.29 shows the system is based on 1 ton of BF sludge as a functional Unit (dry basis). System boundary includes only the process route of two-step direct carbochlorination. The energy input for each process was based on two papers about the life cycle assessment in the ironmaking industry.

The energy for pelletizing was based on the report by Wei Lv et al. (2019) [77]. The report calculated the energy needed for pelletizing iron ore prior to the ironmaking process. The pelletizing includes four sub-process, including grinding iron concentrates, materials mixing and balling, induration, and cooling-storage of the pellets, with the total direct energy consumption of 793.4 MJ/ton pellet, which 88.1% of the energy used in the induration process. Due to the condition in the case of BF sludge, the only sub-process needed is materials mixing and balling, which accounts for energy equal to 22.3 MJ (2.8%) per ton input (BF sludge).

For the carbochlorination, the energy requirement data was based on the calculation by Nduagu [78]. The calculations were based on the rotary kiln operation to produce DRI from iron ores, representing a similar case to the recycling of BF sludge in both rotary kilns. Based on this process, the energy needed is 21.9 GJ/ton DRI, which has the input of 1.574-ton pellets reacted at 1060°C. The energy was associated with the heat and reductant needed to reduce iron ore. In the case of direct reduction for recycling BF sludge, with the basis of a 1-ton input, the energy needed was adjusted to 13.9 GJ, referring to the energy required to react the BF sludge up to 1000°C. The energy required was not adjusted with respect to the temperature since the temperature difference between the Rotary kiln studied in the paper (1060°C) to the rotary kiln used for carbochlorination (1000°C) is relatively small.

Similar to what has been done for the economic calculation, in which the process in both rotary kilns is sequential, the energy ratio for carbochlorination 1 and 2 was set to 0.6 and 0.4 based on the total energy needed for bringing the temperature up to 1000°C (13.9 GJ). For carbochlorination 1, with the operating parameter 8000°C (heating from room temperature), the adjustment on the energy needed per ton input was set to 8.3 GJ/ton. In comparison, for carbochlorination 2 (heating from 800°C to 1000°C), the energy adjustment was set to 5.6 GJ/ton. Emission from carbochlorination was based on carbon monoxide production as the result of carbochlorination reactions. Only a considerable distance of the material flow was included in the system, which was for transportation by a lorry for landfilling the lead-bearing dust and the supply of bentonite. The end products of the recycling process are the zinc-bearing dust and the heavy metal-free residue (HMF), which is assumed to be transported to the subsequent industry.

#### 4.8.3. Impact Assesment

The impact assessment was calculated using OpenLCA software with three databases used for the data input in the software. The process input and output were derived from Worldsteel 2020 database, while the electricity input was based on the NEEDS (New Energy Externalities Developments for Sustainability) database. The final impact assessment was measured using Recipe H Midpoint provided in the openLCA LCIA database.

#### Worldsteel 2020

Worldsteel 2020 database was developed by the World Steel Association, a non-profit organization based in Belgium. The organization was founded in 1967 with representatives from 85% of global steel industries. One of the activities conducted within the organization was the life cycle assessment (LCA), resulting in the Worldsteel 2020 database. This database is the 7<sup>th</sup> edition of its kind since 1996, which has been updated regularly to ensure the quality of the data representing the steelmaking industry related to its environmental impacts [79]. This work has been done according to ISO 14044: 2006, which was also the LCA's guide in this thesis report. In creating this life cycle inventory, 33 world-leading companies have been involved, including Tata Steel Europe and Tata Steel India. Since the inventory only provides the impact assessment of the sintering and steelmaking process (BOF/EAF), this inventory was used as a source of input and output in the recycling of BF sludge. The items used are shown in Table 4.9. Data were based on the inventory provided in Figure 4.29. For the lead-bearing dust, it was assumed that the dust consists of 0.5 lead (Pb) and 0.5 zinc (Zn) of total Pb-bearing dust, which end up in the landfill (as disposal residual landfill).

#### NEEDS (New Energy Externalities Developments for Sustainability)

NEEDS project provides life cycle inventory for electricity supply in Europe [80]. The data also include transportation methods for goods. In electricity supply, energy sources are the dependent factor contributing to the generated environmental impact for the calculations. In the case of BF sludge recycling, the input data for the calculation, based on the material flowsheet (see Figure 4.29), is shown in Table 4.10.

No.	Input/Output	Flow in Database	Category	Amount (kg)
1	BF Sludge	Iron ore, in ground	Resource/in ground	1000
2	Bentonite	bentonite	Non-renewable material resources	5
3	Iron Chloride	Chloride	Emission to water/unspecified	46
4	Fines	Dust, unspecified	Emission to air/unspecified	111
5	Pb-bearing dust	Disposal	residual material landfill	102
6	Pb-bearing dust	Lead	Emission to soil/industrial	51
7	Pb-bearing dust	Zinc, fume or dust	Emission to soil/industrial	51
8	Off-gas RK#1	Carbon monoxide, fossil	Emission to air	33
9	Zinc-bearing dust	Zinc, lead ore (21.7% Zn, 5.6% Pb)	Resource/in ground	52
10	Off-gas RK#2	Carbon monoxide, fossil	Emission to air	79
11	HMF Residue	HMF Residue	Final Product	673

Table 4.9: Input data from Worldsteel 2020 Database.

Table 4.10: Input data from	n NEEDS Database.
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No.	Input/Output	Flow in Database	Category	Amount	Unit
1	Pelletizing	electricity	electricity/production mix	23.4	MJ
2	Transport (Bentonite)	transport, lorry 16t	transport systems/road	100.0	kg*km
3	Carbochlorination 1	electricity	electricity/production mix	7847.3	MJ
4	Transport (Pb-bearing Dust)	transport, lorry 16t	transport systems/road	10.2	t*km
5	Carbochlorination 2	electricity	electricity/production mix	4474.6	MJ

The amount of energy given in Table 4.10 was the calculated total energy based on the input for the respective process and the energy needed, as discussed in the previous subsection. The electricity mixes for pelletizing and carbochlorination were further divided into six scenarios. The scenarios were based on the sources of energy to generate electricity. The energy distribution was generally classified into BAU, 440 ppm, and renewables. Each classification was divided into 2025 and 2050 outlooks, comprising six scenarios in total. BAU means "business as usual" as the existing practice of electricity supply, which is mainly based on fossil fuels. 440 ppm means the threshold level of carbon dioxide up to 440-gram  $CO_2$  emission per ton of air to adjust the required energy supply. Renewable represents the increase of the energy source portion from renewable sources, such as hydrogen and wind. The electricity mix generally consists of 15 different energy sources, as shown in Table 4.11.

Table 4.11: Electricity supply mixes of NEEDS database [80].

Sources	BA	NU	440p	opm	Renew		
	2025	2050	2025	2050	2025	2050	
Coal	23.6%	26.6%	6.7%	5.8%	10.7%	2.9%	
Lignite	9.2%	9.7%	3.2%	0.0%	1.0%	0.0%	
Gas	19.5%	18.7%	40.6%	41.4%	35.2%	16.7%	
Oil	0.6%	0.6%	0.7%	0.2%	0.5%	0.0%	
Nuclear	24.4%	22.1%	21.6%	24.4%	0.0%	0.0%	
Hydrogen	0.0%	0.0%	0.0%	0.1%	0.0%	0.0%	
Hydro	15.3%	13.4%	17.0%	10.9%	16.3%	19.3%	
Wind	3.7%	4.6%	4.7%	7.0%	22.5%	32.3%	
Solar	0.2%	0.4%	0.2%	0.4%			
PV					3.1%	6.5%	
Solar Thermal					1.0%	1.4%	
Geothermal	0.2%	0.8%	1.3%	4.2%	1.1%	4.5%	
Ocean Energy	0.0%	0.1%	0.1%	2.1%	0.3%	0.5%	
Biomass solid / Waste	2.6%	2.9%	3.0%	2.3%	8.2%	15.8%	
Biogas / DME	0.6%	0.8%	0.7%	1.0%			

#### **ReCiPe H Midpoint**

Recipe H Midpoint is one of the most common databases used for the impact assessment through the LCIA method [81]. This impact assessment translates the emission from the calculations to several impact categories. The impacts can be calculated based on the midpoint and endpoint perspectives as the results. In this study, the midpoint impact category was considered better to assess the resulting environmental impact of the recycling process. The midpoint impact is better to define which process contributes to which impact categories in the data interpretation steps according to the associated flow. On the other hand, endpoint impact is better to represent the exact impact in more general aspects, including human health, ecosystem, and resources. This study's LCIA method is based on the flowsheet in Figure 4.29 and the data provided in Table 4.10 and Table 4.11, the environmental impact was calculated resulting in 18 different impact categories. As the focus of this assessment, the GWP category in the unit of  $CO_2$ -eq is shown in Figure 4.30. In this recycling process, direct reduction in both rotary kilns contributes the most to the  $CO_2$ -eq emissions. The results of the other impact categories are provided in the Appendix C.



Figure 4.30: Global warming potential (GWP) of BF sludge recycling through carbochlorination in six different scenarios.

Based on Figure 4.30, the recycling of BF sludge through carbochlorination could generate between 0.3 to 1.3 tons of  $CO_2$ -eq, depending on the energy sources, per 1 ton of BF sludge input. In a year, a throughput of 20 kt/year of BF sludge from Tata Steel Europe in IJmuiden leads to a generation of CO2-eq emissions between 6 to 26 ktons per year. According to Figure 4.30, replacing fossil fuels with gas and renewable energy could significantly decrease the GWP as depicted by the 440 ppm and renewable scenarios. Further discussion on the impact assessment results, including the associated cost, is provided in the following section.

#### 4.8.4. Interpretation

Data interpretation is further carried out to convert the environmental impacts to the associated shadow costs. This shadow cost represents the loss of economic welfare from the pollutants [76]. CE Delft developed the report, commissioned by the Dutch Ministry of Infrastructure and Environment in 2017, which is applicable in the Netherlands. Based on the report, one application of the environmental prices is to quantify the costs or as a weighing factor from the life cycle impact assessment based on the midpoint or endpoint level. Each impact category has an external cost in the unit of EUR per kg of the respective unit as shown in Table 4.12.

Impact category	Cost	Unit
agricultural land occupation - ALOP	0.0261	€/m2*year
climate change - GWP100	0.057	€/kg CO2-eq.
freshwater ecotoxicity - FETPinf	0.0369	€/kg 1,4 DB-eq.
freshwater eutrophication - FEP	1.9	€/kg P-eq.
human toxicity - HTPinf	0.158	€/kg 1,4 DB-eq.
ionising radiation - IRP_HE	0.0473	€/kg kBq U235-eq.
marine ecotoxicity - METPinf	0.00756	€/kg 1,4 DB-eq.
marine eutrophication - MEP	3.11	€/kg N
natural land transformation - NLTP	0.0261	€/m2*year
ozone depletion - ODPinf	30.4	€/kg CFC-eq.
particulate matter formation - PMFP	69	€/kg PM10-eq.
photochemical oxidant formation - POFP	2.1	€/kg NMVOC-eq.
terrestrial acidification - TAP100	5.4	€/kg SO2-eq.
terrestrial ecotoxicity - TETPinf	8.89	€/kg 1,4 DB-eq.
urban land occupation - ULOP	0.0261	€/m2*year

Table 4.12: Environmental price associated to each midpoint based impact category [76].

Based on Table 4.12 each impact has different shadow cost, which particulate matter formation (PMFP) has the highest price compared to other impact category. More straightforwardly, this shadow cost summarized all the impact categories in one uniform unit for the life cycle assessment. In the end, this shadow cost is beneficial in comparing different routes and combatting the environmental impact by focusing on the impact category with the highest prices. The results of the total environmental prices for the recycling of BF are provided in Figure 4.31. As mentioned in the previous section, the calculation considered all the impact categories in six different scenarios.



Figure 4.31: Calculated total environmental price in six different energy mix scenarios.

Based on Figure 4.31, the environmental costs of recycling per ton of BF sludge are between EUR 100 to 230. It is shown that replacing fossil fuels with renewable energy could reduce the shadow cost by more than half. The four impacts with the highest contributions are climate change (GWP100), ionising radiation (IRP), particulate matter formation (PMFP), and human toxicity (HTP). Based on the assessment, these four aspects depend on the electricity source used in the calculations. GWP was calculated as the carbon emission produced from the energy generation, which clearly shows that the level decreased if the 440ppm and renewables scenario were implemented due to the threshold CO<sub>2</sub> limitation and the use of renewable sources with less carbon emission. Ionising radiation (IRP) refers to the excitation of electrons from the materials, which can cause damage to human DNA if exposed, generated from radioactive materials [76]. The costs of IRP vanished in the renew scenario since nuclear was not involved in the energy mix in this scenario (see Table 4.11).

Particulate matter formation (PMFP) refers to a compound consisting of solid and liquid particles or known as aerosol [76]. This PM is associated to PM variations by size (PM10, PM2.5, PM1) or gaseous compounds such as ammonia, sulfur dioxide, and nitrogen oxides. Similar to GWP, these particulate formations are mainly generated from fossil fuels-based energy such as coals and decreased when the scenario was based on the 440ppm and renewable. The last most contributing aspect, human toxicity (HTP), was measured based on the components or substances that can cause damage to human health due to their natural toxicity [76]. In this case, the HTP was measured from the generation of lead (Pb) in the Pb-bearing dust, categorized as hazardous heavy metals, and measured as a single contributor to HTP. Based on this interpretation, the strategy to further reduce the potential environmental impact caused by this recycling technique is to depend on renewable energy sources and prevent the Pb-bearing dust as the hazardous heavy metal sources from ending up in the landfill.

## 4.9. Proposed Route for the Recycling of Blast Furnace Sludge

In general, the recycling of blast furnace sludge has been theoretically feasible and proved by the complete removal of the zinc and other heavy metals (Pb, Cd) through experimental works. Carbochlorination has been a more favorable mechanism than the direct reduction in terms of heavy metals removal due to its more negative Gibbs free energy change ( $\Delta G^\circ$ ), lower onset temperature, and lower temperature for the complete removal of heavy metals. In addition, the SEM-EDS analysis of the secondary dust generated from the multi-stage carbochlorination indicates the possibility of producing separate Pb-bearing and Zn-bearing dust.

Furthermore, the economic assessment led to a potential profit in implementing the recycling of BF sludge through a carbochlorination mechanism with respect to a marketable product consisting of HMF residue and Zn-bearing dust. In terms of the environmental point of view, the impact could be further reduced by using the required energy from renewable sources and preventing Pb-bearing dust from ending in landfills. Based on the discussion throughout this thesis, carbochlorination is proposed as the mechanism for recycling blast furnace sludge from Tata Steel in IJmuiden based on its favorability from technical, economic, and environmental points of view. The proposed flowsheet of the recycling of BF sludge through carbochlorination is shown in Figure 4.32.

The recycling flowsheet starts with pelletizing of bf sludge with the addition of iron chloride and bentonite, followed by the first carbochlorination at 800°C in rotary kiln 1. The fines could be alternatively circulated back to the system to minimize the loss from the pelletizing. The output from the carbochlorination process in rotary kiln 1 is the solid residue and Pb-bearing dust. The scrubber is attached to the flowsheet to capture the secondary dust in an oxidizing environment before releasing the off-gas from the rotary kiln into the air. This dust containing heavy metals (Pb-bearing dust) is assumed to be landfilled with the alternative of further transporting to the relevant industry to recover the lead through the hydrometallurgical process. The solid residue is sent to the second direct reduction in rotary kiln 2, operating at 1000°C. Similar to the rotary kiln 1, a scrubber is also installed for the rotary kiln 2 as the off-gas treatment. The zinc-bearing dust from rotary kiln 2, assumed to meet the quality of marketable secondary raw zinc materials, is planned to be sent to the zinc smelter. Finally, the heavy metals-free residue can be recycled into the ironmaking process internally in IJmuiden.



Figure 4.32: Proposed flowsheet idea for the recycling of blast furnace sludge at Tata Steel in IJmuiden.

#### 4.9.1. Data Limitation

The discussion throughout the thesis has some limitations in some aspects. The material balance calculation did not include the total composition (100%) of each input and output flow. This limitation on the material balance is due to the analytical method used for the calculation, which was based on ICP-OES. Oxygen content was not measured through ICP-OES, while the elements contained in the as-received and reacted samples most likely formed as oxides. This thesis study did not thoroughly explore the subsequent process for the recycling output, especially for the Zn-bearing dust. The chloride content in the Zn-bearing dust might become a problem for the zinc smelter or require further hydrometallurgical processing for zinc recovery.

For the economic assessment, the cost associated with the item involved in the calculation was mainly based on the literature study and discussion with the people from the relevant department and experience, which still has the potential of some deviations from the actual condition in the industry. In addition, some insignificant costs associated with the recycling process might be missing from the calculation, and a capital expenditure study might be needed to improve the economic model. In terms of the environmental assessment, energy, as the most crucial factor resulting in the environmental impact, needs further investigation to represent the actual energy required for the exact recycling mechanism studied in this thesis. However, in general, the data from the literature used in some aspects of this thesis study have been carefully selected with the highest match to represent the respective discussion. Therefore further experimental work to improve and validate the literature data used in some discussions might be needed to represent the actual case of the recycling process.

5

# **Conclusion and Recommendations**

## 5.1. Conclusions

The conclusions were derived based on the answer to the research questions mentioned at the beginning of this report to finalize this thesis project. The conclusions are as follows:

# What is the most suitable and efficient recycling method to selectively extract or remove heavy metals (Zn, Pb) from BF sludge to obtain a clean secondary iron-rich fraction?

The most suitable route for recycling blast furnace sludge is through carbochlorination. The carbochlorination mechanism is thermodynamically favorable and proven through experimental works showing a high removal rate of heavy metals (Zn, Pb, Cd) at a relatively lower temperature and could produce a heavy metals-free residue along with the partial self-reduction of iron oxides.

# How do the recycling method's operating conditions and parameters influence the process's performance?

The thermodynamic analysis concluded that carbochlorination has a lower onset temperature and the Gibbs free energy change of the heavy metals (Zn, Pb, Cd) removal reactions compared to direct reduction. The addition of chlorides in the sample shows a selective carbochlorination reaction represented by the 99% removal of Pb at 800°C followed by 98% removal of zinc at 1000°C, leaving an iron-rich clean residue free of heavy metals. Based on SEM-EDS analysis, up to 72% of Pb and 66% of Zn were found in the secondary dust generated from the multi-stage carbochlorination at 800°C and 1100°C, respectively, indicating a possibility of producing a separate lead and zinc-bearing secondary dust.

#### How is the feasibility of the recycling process based on the technical, economic, and environmental perspectives?

Thermodynamic analysis has good agreement and consistency with the results from the experimental works. The material balance calculation shows that 88% of Pb and 26% of Zn end up in the Pb-bearing dust from 1<sup>st</sup> carbochlorination at 800°C, and 62% of Zn end up in the Zn-bearing dust from 2<sup>nd</sup> carbochlorination at 1000°C. In addition, 78% of C and 85% of Fe remained in the heavy metals-free (iron-rich) residue as the main recycling product. The economic assessment estimated a profit of € ~210 per ton of BF sludge from the best-case scenario (marketable product) and a loss of € ~250 per ton of BF sludge pellets through carbochlorination could produce between 0.3 to 1.3 tons of CO<sub>2</sub>-eq, which depends on the energy sources. In addition, the associated environmental price (shadow cost) of BF sludge recycling, as one of the impacts standard unit, considering all the impact categories, is between € 100 to 230 per ton of BF sludge.

# What would be the proposed final flowsheet of the BF sludge recycling route at Tata Steel in IJmuiden?

Based on the discussion throughout this thesis study, the final proposed flowsheet for recycling BF sludge is a sequential double-step carbochlorination in two connected rotary kilns with independently attached dust capturing systems, resulting in the final products of clean iron-rich residue and zinc-bearing dust as new secondary marketable products. This novel double-step step carbochlorination has been proposed as a patent with the discovery of concentrating lead and zinc in different fractions. In conclusion, the recycling of blast furnace sludge with this novel double-step carbochlorination is favorable based on the technical, economic, and environmental perspectives that could be implemented or realized in IJmuiden subject to further technical feasibility study.

## 5.2. Recommendations

The recommendation from this thesis study is classified into several aspects. In general, the recommendation focuses on improving the results achieved in this thesis study and the idea of subsequent steps for further upscaling the recycling project. The recommendation is briefly explained in the following subsection.

#### 5.2.1. Optimization of the Heavy Metals Removal and Selectivity

Further research should focus on the selectivity between lead and zinc to produce a cleaner leadbearing and zinc-bearing dust from each carbochlorination. The approach can be made by variating chloride's content concerning the removal efficiency of zinc and other heavy metals during each carbochlorination. Thermodynamic modeling has been made to show the molar ratio of chloride and zinc phases (ZnO and ZnS), given in Figure 5.1. The model indicates that the minimum temperature required for complete zinc removal was 700°C, with at least a molar ratio of 4.5. Increasing the molar ratio above 4.5 does not reduce the temperature needed for complete removal. Lead complete removal at the model's lowest temperature (600°C) was achieved with a minimum molar ratio of 2. Therefore the model indicates that the molar ratio of 4.5 could lead to the lowest temperature possible for the complete removal of zinc and lead, with lead can be selectively removed at 600°C followed by the complete removal of zinc at 700°C. However, this model might deviate from the actual conditions and needs to be validated through extensive experimental study to find the optimum molar ratio of chlorine and zinc phases.



**Figure 5.1:** The plot of temperature required for complete removal of zinc and lead with respect to the molar ratio of Cl and (ZnO + ZnS). The plot shows the earliest temperature to achieve a 100% removal (Pb and Zn) within 600°C to 1000°C.

Furthermore, this thesis study concludes that heavy metals removal occurred at a temperature between 800°C to 1000°C. Therefore, conducting more experiments at a different temperature within the heavy metals removal region would enrich the data accuracy of the exact temperature of the zinc and lead complete removal. Another fundamental aspect is the atmosphere condition which could be improved

by providing a reducing atmosphere with a variation of oxygen partial pressure. This idea might influence heavy metals removal together with the improvement of iron ore reduction.

#### 5.2.2. Bigger Scale Research

Upscaling the experiment with larger samples is essential to mimic the industrial case, especially to have a more representative composition of the generated secondary dust from the carbochlorination. Based on SEM-EDS analysis, the highest content of Pb measured in the Pb-bearing dust is 72%, and Zn in Zn-bearing dust is 66%. This quality is a baseline for the marketability of the by-products from the recycling process subject to further analysis to measure the actual bulk composition. Regarding the HMF residue (clean iron-rich), further research can be carried out to measure the mechanical properties to define the subsequent treatment process within the ironmaking route. More detailed economic assessments can be improved by gathering data from the relevant industry as the base practice. In general, the recycling of the BF sludge through carbochlorination in a research scale conducted in this thesis provides a potential for further study in the broader environment for implementation at Tata Steel in IJmuiden in the future.

#### 5.2.3. Characterization Techniques

The use of ICP-OES in this study has a limitation on the detection limit of some elements, especially cadmium content, which is in the range of 0.01%. Further improvement can be made by replacing ICP-OES with mass spectrometry (ICP-MS) to have a higher detection limit for trace elements such as cadmium. The analysis of the SEM-EDS of the secondary dust generated from the carbochlorination did not intend to represent the actual/bulk composition of the dust but only an indication of the phases present in the dust. Bulk composition analysis is essential to confirm the actual composition of the dust in further study, which heavily depends on the scale of the research to generate a sufficient amount of secondary dust for the analysis.

#### 5.2.4. Technical Aspect on the Recycling Process

Detail mechanism of the technical aspect of carbochlorination is not included in this study. It is crucial for the future to define an efficient way to transfer the materials from the first rotary kiln to the second rotary kiln without any considerable heat loss. Another alternative for kiln replacement is a multi-hearth furnace with different compartments for the first and second carbochlorination. However, the multi hearth compartment must be isolated from one another and independently attached to a separate dust-capturing system to prevent the mixing of Pb-bearing and Zn-bearing dust.

#### 5.2.5. Data Optimization

As mentioned in some discussions in this thesis report, some literature data were used throughout the report, especially for economic and environmental assessment. The assessment model can be improved by incorporating the calculation of heat/energy balance in the carbochlorination reactions that can be used to calculate the energy needed to perform carbochlorination, leading to a more represent-ative economic and environmental assessment. The typical energy balance calculation can be followed thorugh the general equation given in Equation 5.1 [82].

$$\dot{Q}_{\text{net,in}} - \dot{W}_{\text{net,out}} = \sum_{i} \dot{M}_{i} h_{i} = \sum_{o} \dot{M}_{o} h_{o} \qquad \frac{[Joule]}{[year]}$$
(5.1)

In general, the energy for a particular system is given by the balance of the heat added to the system and the work done by the system. Hence, the energy coming out from the system should be equal to the energy coming into the system. The energy to perform the carbochlorination can be measured by the enthalpy (h) of the reactions times the mass (M) of the reducible metals that will take place during the carbochlorination reactions.

# References

- [1] Binnemans, K., Jones, P. T., Fernández, Á. M. & Torres, V. M. (2020). Hydrometallurgical processes for the recovery of metals from steel industry by-products: A critical review. *Journal of Sustainable Metallurgy*, 6, 505–540. https://doi.org/10.1007/s40831-020-00306-2
- [2] Kempke, A. (2019). Sulfur stream identification and selective removal of heavy metals from ironmaking blast furnace dust. [Master Thesis, Delft University of Technology]. http://resolver.tudelft. nl/uuid:a070d733-d9bb-405a-ae1d-3d4a0936159d
- [3] Feenstra, E. (2016). Selective heavy metal removal from blast furnace and basic oxygen furnace flue dust. [Master Thesis, Aalto University]. http://urn.fi/URN:NBN:fi:aalto-201609224194
- [4] Verburg, R. (2015). Selective removal of zinc from bf high zinc filter cake. conversion of a waste stream into a recyclate. [Master Thesis, Delft University of Technology]. http://resolver.tudelft.nl/ uuid:dc2119a4-9dbd-402c-b929-3abaa281199b
- [5] Zhu, D., Wang, D., Pan, J., Tian, H. & Xue, Y. (2021). A study on the zinc removal kinetics and mechanism of zinc-bearing dust pellets in direct reduction. *Powder Technology*, 380, 273–281. https://doi.org/10.1016/j.powtec.2020.11.077
- [6] Hamann, C., Spanka, M., Stolle, D., Auer, G., Weingart, E., Al-Sabbagh, D., Ostermann, M. & Adam, C. (2021). Recycling of blast-furnace sludge by thermochemical treatment with spent iron(ii) chloride solution from steel pickling. *Journal of Hazardous Materials*, 402, 123511. https://doi.org/10.1016/j.jhazmat.2020.123511
- [7] Mustafa, S., Luo, L., Zheng, B.-T., Wei, C.-X. & Christophe, N. (2021a). Effect of lead and zinc impurities in ironmaking and the corresponding removal methods: A review. *Metals*, 11(3). https: //doi.org/10.3390/met11030407
- [8] Sustainability performance at our sites ijmuiden. (2020). Retrieved February 2, 2022, from https: //www.tatasteeleurope.com/construction/sustainability/performance-at-our-sites/ijmuiden
- [9] (EUROFER), T. E. S. A. (2020). What is steel and how is steel made? Retrieved October 14, 2022, from https://www.eurofer.eu/about-steel/learn-about-steel/what-is-steel-and-how-issteel-made/
- [10] Peeters, T. (2016). *Tata steel rnd ironmaking, steelmaking and casting* [[Company Presentation]. Tata Steel Europe].
- [11] Ye, L., Peng, Z., Ye, Q., Wang, L., Augustine, R., Perez, M., Liu, Y., Liu, M., Tang, H., Rao, M., Li, G. & Jiang, T. (2021). Toward environmentally friendly direct reduced iron production: A novel route of comprehensive utilization of blast furnace dust and electric arc furnace dust. *Waste Management*, 135, 389–396. https://doi.org/10.1016/j.wasman.2021.08.045
- [12] Mustafa, S., Luo, L., Zheng, B.-T., Wei, C.-X. & Christophe, N. (2021b). Effect of lead and zinc impurities in ironmaking and the corresponding removal methods: A review. *Metals*, *11*(3). https: //doi.org/10.3390/met11030407
- [13] Mansfeldt, T. & Dohrmann, R. (2001). Identification of a crystalline cyanide-containing compound in blast furnace sludge deposits. *Journal of Environmental Quality*, 30(6), 1927–1932. https://doi. org/10.2134/jeq2001.1927
- [14] National waste management plan. (2020). Retrieved February 2, 2022, from https://lap3.nl/ service/english/
- [15] Maccagni, M. (2016). Indutec<sup>®</sup>/ezinex<sup>®</sup> integrate process on secondary zinc-bearing materials. *Journal of Sustainable Metallurgy*, 2, 133–140. https://doi.org/10.1007/s40831-016-0041-0
- [16] Vereš, J., Lovás, M., Jakabský, Š., Šepelák, V. & Hredzák, S. (2012). Characterization of blast furnace sludge and removal of zinc by microwave assisted extraction. *Hydrometallurgy*, 129-130, 67–73. https://doi.org/10.1016/j.hydromet.2012.09.008
- [17] Luo, X., Wang, C., Shi, X., Li, X., Wei, C., Li, M. & Deng, Z. (2022). Selective separation of zinc and iron/carbon from blast furnace dust via a hydrometallurgical cooperative leaching method. *Waste Management*, 139, 116–123. https://doi.org/10.1016/j.wasman.2021.12.007

- [18] Van Herck, P., Vandecasteele, C., Swennen, R. & Mortier, R. (2000). Zinc and lead removal from blast furnace sludge with a hydrometallurgical process. *Environmental Science & Technology*, 34(17), 3802–3808. https://doi.org/10.1021/es991033I
- [19] Weert, G. V., van Sandwijk, A., Kat, W. & Honingh, S. (1993). The treatment of iron making blast furnace dusts by chloride hydrometallurgy. *Hydrometallurgy: Fundamentals, technology, and innovations* (pp. 931–945). Society for Mining, Metallurgy, Exploration.
- [20] Cantarino, M. V., de Carvalho Filho, C. & Mansur, M. B. (2012). Selective removal of zinc from basic oxygen furnace sludges. *Hydrometallurgy*, 111-112, 124–128. https://doi.org/10.1016/j. hydromet.2011.11.004
- [21] Jaafar, I. (2014). Chlorination for the removal of zinc from basic oxygen steelmaking (bos) byproduct. [PhD Thesis, Cardiff University]. http://orca.cardiff.ac.uk/id/eprint/64052
- [22] Rodriguez Rodriguez, N., Gijsemans, L., Bussé, J., Roosen, J., Önal, M. A. R., Masaguer Torres, V., Manjón Fernández, Á., Jones, P. T. & Binnemans, K. (2020). Selective removal of zinc from bof sludge by leaching with mixtures of ammonia and ammonium carbonate. *Journal of Sustainable Metallurgy*, 6(4), 680–690. https://doi.org/10.1007/s40831-020-00305-3
- [23] Trung, Z. H., Kukurugya, F., Takacova, Z., Orac, D., Laubertova, M., Miskufova, A. & Havlik, T. (2011). Acidic leaching both of zinc and iron from basic oxygen furnace sludge. *Journal of Hazardous Materials*, 192(3), 1100–1107. https://doi.org/10.1016/j.jhazmat.2011.06.016
- [24] Mardones, J. P. (2012). Processing of spinel-bearing compounds for zinc extraction. [Master Thesis, Delft University of Technology]. http://resolver.tudelft.nl/uuid:27b4e2c2-1796-428da5a4-fb7d32990766
- [25] Dutra, A., Paiva, P. & Tavares, L. (2006). Alkaline leaching of zinc from electric arc furnace steel dust. *Minerals Engineering*, 19(5), 478–485. https://doi.org/10.1016/j.mineng.2005.08.013
- [26] Chairaksa-Fujimoto, R., Maruyama, K., Miki, T. & Nagasaka, T. (2016). The selective alkaline leaching of zinc oxide from electric arc furnace dust pre-treated with calcium oxide. *Hydrometallurgy*, 159, 120–125. https://doi.org/10.1016/j.hydromet.2015.11.009
- [27] Strijker, M. (2020). Zinc recovery from steelmaking wastes. [Master Thesis, Delft University of Technology]. http://resolver.tudelft.nl/uuid:46b8a45e-bb3a-440b-ab9d-c4a6f2b6b025
- [28] Piezanowski, L., Raynal, S., Hugentobler, J. & Houbart, M. (2015). Selective hydrometallurgical extraction of zn/pb from blast furnace sludge. 7<sup>th</sup> International Conference on the Science and Technology of Ironmaking, Cleveland, Ohio, USA.
- [29] Yang, Y. (2020). Recycling metallurgy [[Course Materials]. Delft University of Technology].
- [30] Surhone, L., Timpledon, M. & Marseken, S. (2010). *Roasting (metallurgy)*. VDM Publishing. https://books.google.co.uk/books?id=X6GicQAACAAJ
- [31] Huang, C. H., Lin, C. I. & Chen, H. K. (2005). Carbothermic reduction of zinc sulfide in the presence of calcium oxide. *Journal of Materials Science*, 40(16), 4299–4306. https://doi.org/10.1007/ s10853-005-2805-y
- [32] Bodsworth, C. (1994). The extraction and refining of metals (1st ed.). Routledge. https://doi.org/ 10.1201/9780203736722
- [33] Gleeson, B. (2010). 1.09 thermodynamics and theory of external and internal oxidation of alloys. Shreir's corrosion (pp. 180–194). Elsevier. https://doi.org/10.1016/B978-044452787-5.00012-3
- [34] Wang, J., Zhang, Y., Cui, K., Fu, T., Gao, J., Hussain, S. & AlGarni, T. S. (2021). Pyrometallurgical recovery of zinc and valuable metals from electric arc furnace dust – a review. *Journal of Cleaner Production*, 298, 126788. https://doi.org/10.1016/j.jclepro.2021.126788
- [35] Stewart, D. J. & Barron, A. R. (2020). Pyrometallurgical removal of zinc from basic oxygen steelmaking dust – a review of best available technology. *Resources, Conservation and Recycling*, 157, 104746. https://doi.org/10.1016/j.resconrec.2020.104746
- [36] Honingh, S. (2021). Options to prevent landfill of bfsludge [[Memo]. Tata Steel Europe].
- [37] Singh, R. (2016). Chapter 1 introduction. Applied welding engineering (second edition) (Second Edition, pp. 3–5). Butterworth-Heinemann. https://doi.org/10.1016/B978-0-12-804176-5.00001-3
- [38] Rieger, J., Colla, V., Matino, I., Branca, T. A., Stubbe, G., Panizza, A., Brondi, C., Falsafi, M., Hage, J., Wang, X., Voraberger, B., Fenzl, T., Masaguer, V., Faraci, E. L., di Sante, L., Cirilli, F., Loose, F., Thaler, C., Soto, A., ... Snaet, D. (2021). Residue valorization in the iron and steel industries: Sustainable solutions for a cleaner and more competitive future europe. *Metals*, *11*(8). https://doi.org/10.3390/met11081202

- [39] Voraberger, B., Antrekowitsch, J., Auer, M., Pastucha, K., Dieguez-Salgado, U., Fleischanderl, A. & Wimmer, G. (n.d.). 2sdr—an innovative, zero waste two step dust recycling process. Proceedings of the Residue Valorization in Iron and Steel Industry—Sustainable Solutions for A Cleaner and More Competitive Future Europe, Virtual Workshop, ESTEP 2020, Brussels, Belgium, 13 November 2020.
- [40] Wegscheider, S., Steinlechner, S., Pichler, C. A. M., Rösler, G. & Antrekowitsch, J. (2015). The 2sdr process – innovative treatment of electric arc furnace dust. https://doi.org/10.1201/b18853-59
- [41] Kerry, T., Peters, A., Georgakopoulos, E., Dugulan, I., Meijer, K., Hage, J., Offerman, E. & Yang, Y. (2022). Zinc vaporization and self-reduction behavior of industrial waste residues for recycling to the hisarna furnace. *Journal of Sustainable Metallurgy*, *8*, 658–672. https://doi.org/10.1007/ s40831-021-00440-5
- [42] Ishiwata, N., Hara, Y. & Takeda, K. (2001). Total model with zinc and iron reduction kinetics for simulation of a coke packed bed furnace. *Tetsu-to-Hagane*, 87(5), 418–425. https://doi.org/10. 2355/tetsutohagane1955.87.5\_418
- [43] Hara, Y., Ishiwata, N., Itaya, H. & Matsumoto, T. (2000). Smelting reduction process with a coke packed bed for steelmaking dust recycling. *ISIJ International*, 40(3), 231–237. https://doi.org/10. 2355/isijinternational.40.231
- [44] Sassen, K.-J. & Hillmann, C. (2011). The dk process for the recovery of iron and zinc from bof dusts and sludges. Steel Times International. https://www.dk-duisburg.de/wp-content/uploads/ Artikel-Steelmaking-2014.pdf
- [45] Xiao, Y. (2021). *Gec project creating value from by-products* [[Company Presentation]. Tata Steel Nederland Technology BV].
- [46] und Roheisen GmbH, D. R. (2021). *The dk-process*. Retrieved February 19, 2022, from https: //www.dk-duisburg.de/en/dk-process/
- [47] Lemperle, M., Jennes, R. & Cappel, J. (n.d.). Oxycup<sup>®</sup> furnace operation at tisco, china. 6<sup>th</sup> *International Congress on the Science and Technology of Ironmaking.*
- [48] Raupenstrauch, H., Doschek-Held, K., Rieger, J. & Reiter, W. (2019). Recodust—an efficient way of processing steel mill dusts. *Journal of Sustainable Metallurgy*, 5(3), 310–318. https://doi.org/ 10.1007/s40831-019-00216-y
- [49] Free, M. (2013). Introduction. *Hydrometallurgy* (pp. 1–20). John Wiley; Sons, Ltd. https://doi.org/ 10.1002/9781118732465.ch1
- [50] O'Keeke, T. (2001). Pourbaix diagrams. Encyclopedia of materials: Science and technology (pp. 7774–7781). Elsevier. https://doi.org/10.1016/B0-08-043152-6/01399-1
- [51] Xiao, Y. (2020). Intracycle process for heavy metal removal from blast furnace ironmaking residues zinc bleeding from an integrated steelworks [[Report]. Tata Steel Nederland Technology BV].
- [52] Dreisinger, D., Peters, E. & Morgan, G. (1990). The hydrometallurgical treatment of carbon steel electric arc furnace dusts by the ubc-chaparral process. *Hydrometallurgy*, 25(2), 137–152. https: //doi.org/10.1016/0304-386X(90)90035-Z
- [53] Steer, J. M. & Griffiths, A. J. (2013). Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry. *Hydrometallurgy*, 140, 34–41. https://doi.org/10.1016/j.hydromet.2013.08.011
- [54] Andersson, A., Ahmed, H., Rosenkranz, J., Samuelsson, C. & Björkman, B. (2017). Characterization and upgrading of a low zinc-containing and fine blast furnace sludge – a multi-objective analysis. *ISIJ International*, 57(2), 262–271. https://doi.org/10.2355/isijinternational.ISIJINT-2016-512
- [55] McElroy, R. O. & McClaren, M. (1994). Processing of electric arc furnace dust via chloride hydrometallurgy. *Hydrometallurgy '94* (pp. 993–1010). Springer Netherlands. https://doi.org/10.1007/ 978-94-011-1214-7\_68
- [56] Díaz, G. & Martín, D. (1994). Modified zincex process: The clean, safe and profitable solution to the zinc secondaries treatment. *Resources, Conservation and Recycling*, 10(1), 43–57. https: //doi.org/10.1016/0921-3449(94)90037-X
- [57] Anderson, C. (2016). Pyrometallurgy. Reference module in materials science and materials engineering. Elsevier. https://doi.org/10.1016/B978-0-12-803581-8.03609-2
- [58] LI, K.-j., ZHANG, J.-I., LIU, Z.-j., MAO, R. & YANG, T.-j. (2014). Comprehensive evaluation of oxycup process for steelmaking dust treatment based on calculation of mass balance and heat

balance. *Journal of Iron and Steel Research, International*, 21(6), 575–582. https://doi.org/10. 1016/S1006-706X(14)60089-3

- [59] Kota, K. B., Shenbagaraj, S., Sharma, P. K., Sharma, A. K., Ghodke, P. K. & Chen, W.-H. (2022). Biomass torrefaction: An overview of process and technology assessment based on global readiness level. *Fuel*, 324, 124663. https://doi.org/10.1016/j.fuel.2022.124663
- [60] Jena, P. & Brocchi, E. (1997). Metal extraction through chlorine metallurgy. *Mineral Processing and Extractive Metallurgy Review*, 16(4), 211–237. https://doi.org/10.1080/08827509708914136
- [61] Peek, E. (2011). Chloride metallurgy: Process technology development. *Epd congress 2011* (pp. 467–501). John Wiley; Sons, Ltd. https://doi.org/10.1002/9781118495285.ch56
- [62] Han, J., Xu, M., Yao, H., Furuuchi, M., Sakano, T. & Kim, H. J. (2007). Simulating the transformation of heavy metals during coal or sewage sludge combustion. *Journal of Environmental Science and Health, Part A*, 42(2), 217–224. https://doi.org/10.1080/10934520601011395
- [63] Peek, E. (1995). Chloride pyrohydrolysis, lixiviant regeneration and metal separation. [Doctoral Thesis, Aalto University]. http://resolver.tudelft.nl/uuid:4a3ad18d-ff40-4896-8b78-f847bd9e3411
- [64] Ijmuiden bf sludge zn-high samples [[FILRIJIK Year average between 23/2/21 23/2/22]. Tata Steel]. (2021).
- [65] Ryabchikov, I. V., Belov, B. F. & Mizin, V. G. (2014). Reactions of metal oxides with carbon. Steel in Translation, 44, 368–373. https://doi.org/10.3103/S0967091214050118
- [66] Yang, Y., Raipala, K. & Holappa, L. (2014). Chapter 1.1 ironmaking. In S. Seetharaman (Ed.), *Treatise on process metallurgy* (pp. 2–88). Elsevier. https://doi.org/10.1016/B978-0-08-096988-6.00017-1
- [67] Bahgat, M. (2006). Reduction behaviour of mgfe2o4 with the synthesis of fe/mgo nanocomposite. *Mineral Processing and Extractive Metallurgy*, 115(4), 195–200. https://doi.org/10.1179/174328 506X148920
- [68] Galan, I., Glasser, F. P. & Andrade, C. (2013). Calcium carbonate decomposition. Journal of Thermal Analysis and Calorimetry, 111, pages1197–1202. https://doi.org/10.1007/s10973-012-2290-x
- [69] Lee, J.-J., Lin, C.-I. & Chen, H.-K. (2001). Carbothermal reduction of zinc ferrite. Metallurgical and Materials Transactions B, 32, 1033–1040. https://doi.org/10.1007/s11663-001-0092-9
- [70] Vibcze, L. & Cavanagh, R. (1971). Pelletizing of iron ore concentrates with peat moss binder. *Aime Centennial Annual Meeting, New York.*
- [71] Garside, M. (2022). U.s. bentonite average price 2010-2021. Retrieved October 16, 2022, from https://www.statista.com/statistics/248186/average-bentonite-price/
- [72] Gundewar, C., Ram, M., Sutaone, A., Rao, M., Sengupta, A., Banerjee, T., Borkar, S., Bendre, R., Singh, A. & Sumesh, M. (2011). *Iron & steel vision 2020*. Indian Bureau of Mines. https: //ibm.gov.in/?c=pages&m=index&id=790
- [73] Andersson, A. (2019). Recycling of blast furnace sludge within the integrated steel plant: Potential for complete recycling and influence on operation. [Doctoral Thesis, Luleå University of Technology]. http://ltu.diva-portal.org/smash/record.jsf?pid=diva2%3A1344770&dswid=-9853
- [74] Schwartz, M. (2020). Base metals pricing and concentrate contracts. Teck. https://www.teck. com/media/Teck-2020-Modelling-Workshop-April-2.pdf
- [75] Ashby, M. F. (2016). Chapter 2 what is a "sustainable development"? In M. F. Ashby (Ed.), Materials and sustainable development (pp. 27–38). Butterworth-Heinemann. https://doi.org/10. 1016/B978-0-08-100176-9.00002-5
- [76] the Bruyn, S., Ahdour, S., Bijleveld, M., de Graaff, L., Schep, E., Schroten, A. & Vergeer, R. (2018). Environmental prices handbook 2017. CE Delft. https://cedelft.eu/publications/environmentalprices-handbook-2017/
- [77] Lv, W., Sun, Z. & Su, Z. (2019). Life cycle energy consumption and greenhouse gas emissions of iron pelletizing process in china, a case study. *Journal of Cleaner Production*, 233, 1314–1321. https://doi.org/10.1016/j.jclepro.2019.06.180
- [78] Nduagu, E. I., Yadav, D., Bhardwaj, N., Elango, S., Biswas, T., Banerjee, R. & Rajagopalan, S. (2022). Comparative life cycle assessment of natural gas and coal-based directly reduced iron (dri) production: A case study for india. *Journal of Cleaner Production*, 347, 131196. https: //doi.org/10.1016/j.jclepro.2022.131196
- [79] *Life cycle inventory (lci) study, 2020 data release.* (2021). World Steel Association. https://world steel.org/publications/bookshop/life-cycle-inventory-study-report-2020-data-release/

- [80] Gerboni, R., Pehnt, M., Viebahn, P. & Lavagno, E. (2008). Final report on technical data, costs and life cycle inventories of fuel cells.
- [81] Huijbregts, M. A. J., Steinmann, Z. J. N., Elshout, P. M. F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A. & van Zelm, R. (2017). Recipe2016: A harmonised life cycle impact assessment method at midpoint and endpoint level. *The International Journal of Life Cycle Assessment*, 22, 138–147. https://doi.org/10.1007/s11367-016-1246-y
- [82] Altinkaynak, M., Kabul, A. & Kizilkan, Ö. (2015). Exergetic assessment of a rotary kiln for clinker production in cement industry. *International Journal of Exergy*, 16(3), 263–277. https://doi.org/ 10.1504/IJEX.2015.068226



# **Chapter 2 Literature Study**

# A.1. Summary of Pyrometallurgical Route

Detailed information on the various pyrometallurgical routes discussed in this thesis report is provided in Table A.1. The number in Table A.1 corresponds to the literature mentioned in Table 2.3. The results of each pyrometallurgical processing were based on the highest achieved results in the respective study, associated with the most optimum parameters.

# A.2. Summary of Hydrometallurgical Route

Detailed information on the various hydrometallurgical routes discussed in this thesis report is provided in Table A.2. The number in Table A.2 corresponds to the literature mentioned in Table 2.4. The results of each hydrometallurgical processing were based on the highest achieved results in the respective study, associated with the most optimum parameters.

# A.3. Technology Readiness Levels (TRLs)

Technology readiness level criteria used in this thesis was based on the study by Kota et al. (2022) [59] about the technological assessment of biomass torrefaction. The assessment included TRL measurement on a scale from level 1 to level 9 as the development stage of the technology increases. The criteria for each level mentioned in the study by Kota et al. (2022) [59] is provided in the following:

- Level 1: Data formulation.
- Level 2: Data description.
- Level 3: Experimental proof of concept.
- Level 4: Validation in a lab-scale environment.
- Level 5: Upscaling test in broader environment.
- Level 6: Demonstration on a pilot scale.
- Level 7: Simulation of the pilot research
- Level 8: Demonstration on an industrial scale.
- Level 9: Technology has been commercially and industrially validated

TRL labeled for each recycling technique in this report was based on the author's self-evaluation from the literature study. References mentioned in Table 2.4 and Table 2.4 have provided an explicit statement of the development stage for a particular recycling technique. Generally, if the technology is found or referred from a paper based on experimental work (lab scale), the associated TRL is around 3 to 4. Some literature mentioned that the development of the discussed technology had reached a pilot, which then was given a TRL around 6 to 7. More developed technologies on an industrial and commercial scale, such as rotary kiln and rotary hearth furnace, were given the maximum TRL 9.

1					Proces	SS					2	-	â	Resu	lts				S 8
No	Cample	Input					<b>T</b>			Fe	Rem	oval	(%)	Resi	idue (%	)	Off-ga	S	TDI
NO	Sample	Shape	Technique	Technology	Equipment	Additive	(°C)	(min)	Gas Flow	Metalliza tion (%)	Zn	Pb	Cd	Fe	Zn	Pb	Zn	Pb	IKL
1	BF+BOF	Granules	Roasting	Roasting	Box Oven	Na <sub>2</sub> CO <sub>3</sub>	860	60	N <sub>2</sub>	-	87	71	96	-	0.8		5	-	4
2	Gahnite	Milled	Direct Reduction	Carbothermic	Horizontal Tube Furnace	С	1300	60	Ar (3L/min)	-	100	-	-	- 1	-	-	-	-	4
3	Gahnite	Milled	Direct Reduction	Aluminothermic	Horizontal Tube Furnace	Al	1200	60	Ar (3L/min)	-	100	-	-	(=)	-	-	-	-	4
4	BF+BOF	Pellets	Direct Reduction	Direct Reduction	Shaft Furnace	Coke	1250	30	-	61%	99	e.	-	87	0.07	-	7	5	4
5	BF	Granules	Direct Reduction	Carbohlorination	Tube Furnace	FeCl <sub>2</sub>	1000	60	N <sub>2</sub> (400/L)	÷	99	99	70	99	< 0.07	< 0.002	-	2	4
6	BF+EAF	Pellets	Direct Reduction	Microwave- Assisted	Tube Furnace	-	1050	15	$N_2$ (0.2L/min)	94%	91	95	-	71	-	-	-	-	4
7	EAF	Pellets	Direct Reduction	Rotary/Waelz Kiln	Rotary Kiln	Coal	1100- 1200	240- 360	02	80-90	>94	-	-	121	0.2-2	0.5-1	55-58	7-10	9
8	BF+BOF +EAF	Pellets	Direct Reduction	FASTMET, etc.	Rotary Hearth Furnace	Coal	1230	15	CO <sub>2</sub>	75-96	95	-	-	96	< <mark>0.00</mark> 4	0	48-63	-	9
9	BF+BOF +EAF	Raw Mix	Direct Reduction	Primus	Multi Hearth Furnace	Coal	1100	-	Air	90-95	90- 96	>90	-	(-3	-	- 1	-	-	8
10	EAF	Pellets	Smelting	2sDR	Drum Furnace and EAF	Coal	1500	120	Natural Gas+O <sub>2</sub>	-	95	95	-	99	0.004	0.003	73		5
11	BF+BOF +EAF	Sintered	Smelting	ESRF	Electric Furnace	Lime+Coke	>1250	-	Air	-	65-8	-	-	-	-	-	-	-	9
12	EAF	Raw Mix	Smelting	Coke-packed Bed	Shaft Furnace	Coke (Bed)	>1550	170	02	2	95	95	8	(T)	0.005	0.001	60	6.2	9
13	BF+BOF +HOKS	Granules	Smelting	HIsarna	TGA Furnace		1300	20	N <sub>2</sub> CO/CO <sub>2</sub> (50/50)	-	99	99		97- 98			60	2	6
14	BF+BOF	Sintered	Smelting	DK Recycling	Blast Furnace	Coke, Flux	-	-	02	-	-	-	-	>90	-	-	65-68	1-2	9
15	BF	Sintered	Smelting	Solumet	Tunnel Furnace	Coal	-	-	-	-	2	-	-	-	-	-	-	-	9
16	BF+BOF	Brick	Smelting	Oxycup	Shaft Furnace	-	1480- 1530	-	02	99	99	99	-	94	-	-	38	-	9
17	BOF	-	Smelting	Recodust	Flash Reactor		1700	-	Natural Gas+O <sub>2</sub>	-	90		-	(-)	0.1-1.4	-	13.2	-	6

#### Table A.1: Detailed summary of pyrometallurgical processing routes in the recycling of zinc-bearing wastes.

and a second sec		Process										Results						
Pre-			2	Concentrat S/L		Temp		Time		-	Ex	tractio	n (%	5)	Re	sidue	(%)	TRL
Treatment	Technique	Lixiviant	Equipment	ion (M)	Ratio	(°C)	Oxidant	(min)	рН	Pressure	Fe	Zn	Pb	Cd	Fe	Zn	Pb	
Roasting	Intracycle	$NH_3 + (NH4)_2SO_4$	Reactor	0.5-5	132 g/L	30	H <sub>2</sub> O <sub>2</sub> /KMn	30-90	8-11	-	0.05	70,	42	83	-	-	S=0	4
	(Oxidative						$O_4/Fe_2(SO)$					>80						
	Leaching)						Ja/FeCla											
-	Ammonia	NH CI + NH	Reactor	4	200 g/L	60	Air	360	-	-	<20	70	-	-	43-	18-	-	4
	Leaching	NII4CI + NII3	neactor	•	200 6/2	00		500			-20				56	5.5		
Chloride	UBC-	$NH_{2} + (NH4)_{2}CO_{2}$	-	4 + 0.75	-	25	-	120	-	-	-	42	1	44	-	-	-	5
washing and	Chaparral																	
cementation	1																	
-	Chlorination	HCl + NaCl	Flask Reactor	0.25 + 3	1/4	70	-	120	4	-	10	93	-	-	45	<1	-	4
									K-Sarah						0.000			09000
-	Pressure	HCl + FeCl <sub>2</sub>	Autoclave	1-17 g/L +	1/1.3	140	NaOH + $O_2$	60	1	1 MPa	-	97	91	-	30	0.09	0.06	5
	Leaching			30-191 g/L	10404 000000000													
-	<b>CIROVAL</b> <sup>™</sup>	HCl	Reactor	-	-	55	$\checkmark$	-	-	-	-	0 <b>-</b> 0	-	-	85	< 0.3	< 0.1	6
Direct	INDUTEC®/	NH <sub>4</sub> Cl	-	-	-	70-80	-		7	-	-	100	-	-	92-	10-1	-	9
reduction	EZINEX®														94			
-	Pressure	HNO <sub>3</sub>	Autoclave	4	1/40	250	02	90	-	35 atm	-	22	-	F	-	-	-	4
	Leaching																	
-	Pressure	H <sub>2</sub> SO <sub>4</sub>	Autoclave	0.75	1/40	140	02	90	-	38 atm	-	3	-	-	-	-	-	4
	Leaching																	
	Modified	H <sub>2</sub> SO <sub>4</sub>	-	0.5	-	40	-	60	2	-	-	67-90	-	-	-	-		7
	Zincex																	
	Process	- 100 C																
-	High	$H_2SO_4$	-	1	1/10	80	-	10	1-3	-	-	91-95	-	-	91	0.03	-	4
	Temperatur																	
	e Leaching	6 1 1:		4	4/40	25 4 0 0		4.4.40			0.1	105						
-	Organic	Carboxylic	-	1	1/10	25-100	-	1440	-	-	0.1-	18.5-	-	-	-	-	-	4
	Acid										32.2	93.9						
	Leaching	UCI				-		-			22 40	OF	02				-	C
-	AMAY		-	-	-	-	-	-	-	-	32-49	73	92		-	1.57		5
-	AMAX Termo Coio	HCI	Autoalaria			140 175		45 100			48	88-93	06				0.45	5
	reffa Gala	nu	Autociave			140-1/5		42-100				00-99	90-				0.45	Э
	Alkaline	NaOH	Flask Reactor	6	1/20			240				74	-					4
	Leaching	indon	, ask neactor	9	1/20			210				11						
Heating with	Alkaline	NaOH	Flask Reactor	2	1/300	70	-	120	-		-	100	-	-	28	0.36	-	4
			- mon neucloi	-	-1000							100				5.00		

#### Table A.2: Detailed summary of hydrometallurgical processing routes in the recycling of zinc-bearing wastes.

No Sample

1 BF

2 BOF

3 EAF

4 BF

5 BF

6 BF

11 BF

12 BF

13 BF

14 BF

15 EAF

16 EAF

17 EAF

8 Gahnite -9 Gahnite -10 EAF

7 EAF -

-

-

-

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Ca0

Leaching



# **Chapter 3 Experiments**

## **B.1. Bentonite Composition**

Bentonite was supplied by Cebo Holland B.V., the Netherlands and was further analysed internally at Tata Steel in Ijmuiden under reference number of LIMS 200072651. The analysis data was created on 18 June 2021, shown in Table B.1.

Table B.1: Composition of bentonite added to the BF sludge pellets.

Bentonite	Fe	CaO	MgO	SiO <sub>2</sub>	$AI_2O_3$	TiO <sub>2</sub>	MnO	$P_2O_5$	Na <sub>2</sub> O	K <sub>2</sub> O	Total
%wt	3.3	5.0	3.5	53.2	17.6	0.7	0.1	0.2	2.8	0.8	87.2

## B.2. Iron Chloride (FeCl<sub>2</sub>) Composition

Iron chloride was supplied by Merck KGaA, Darmstadt with the product name "IJzer(II)chloride - tet-rahydraat voor analyse EMSURE®" and item number 103861. The chemical formula of iron chloride is  $FeCI_2 \cdot 4 H_2O$  (iron dichloride tetrahydrate) with the molar mass of 198.83 g/mol.

# $\bigcirc$

# **Chapter 4 Results and Discussion**

# C.1. Raw BF Sludge Analysis

Table C.1: Composition of raw BF sludge pellets from ICP-OES first analysis.

Sample	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	V	Zn
1	0.02	40.80	1.71	0.01	25.40	0.65	0.11	0.59	1.10	0.09	0.02	2.82
2	0.02	39.30	1.64	0.01	25.60	0.59	0.11	0.55	1.02	0.09	0.02	2.71
3	0.02	38.40	1.68	0.01	25.60	0.60	0.10	0.48	1.04	0.08	0.02	2.38
4	0.02	41.00	1.63	0.01	25.10	0.64	0.10	0.44	1.11	0.09	0.02	2.62

Table C.2: Composition of raw BF sludge pellets from ICP-OES second analysis.

Sample	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	V	Zn
1	0.04	40.50	1.59	0.01	23.90	0.60	0.09	0.53	1.11	0.09	0.02	2.84
2	0.01	38.60	1.53	0.00	23.90	0.56	0.09	0.48	1.10	0.08	0.02	2.48
3	0.01	37.60	1.57	0.00	24.70	0.56	0.09	0.50	1.04	0.09	0.02	2.57
4	0.02	40.60	1.63	0.01	23.80	0.60	0.09	0.59	1.08	0.09	0.02	2.92



A servicition Com	-1 -1	the second
Acquisition con		LUION
Instrument	:	IT100LA
Volt	:	20.00 kV
Current	:	
Process Time	:	ТЗ
Live time	:	196.60 sec.
Real Time	:	201.06 sec.
DeadTime	:	2.00 %
Count Rate	:	3286.00 CPS

Figure C.1: EDS signal of mapping of sample 1 given in Figure 4.3.



Figure C.2: EDS signal of mapping of sample 2 given in Figure 4.4.

 Table C.3: XRD quantitative analysis of sample 1 (AR1) and sample 2 (AR2). The composition was calculated with the error based on the pattern shown in Figure 4.1 and Figure 4.2

Measurement code Sample	RD18834 SM-JB2022- AR1	00644-0001	RD18835 SM-JB2022-00 AR2	644-0002							
Mineral name – Chemistry *)	Comp wt%	2 σ wt%	Comp wt%	2 σ wt%							
Sample composition includi	ng standard			WC/0							
Silicon standard	21.3	11	18.0	0.9							
	21.0	1.1	10.5	0.0							
Hematite Fe <sub>2</sub> O <sub>3</sub>	37.2	1.8	32.6	2.4							
Sphalerite ZnS	0.6	0.4	0.4	0.6							
Magnesioferrite MgFe <sub>2</sub> O <sub>4</sub>	9.1	0.9	8.4	0.9							
Corundum Al <sub>2</sub> O <sub>3</sub>	7.4	1.3	19.4	1.3							
Graphite 2H	6.5	2.4	6.5	1.7							
Srebrodolskite Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	1.1	0.8	1.0	0.8							
Calcite CaCO <sub>3</sub>	2.0	0.8	0.3	0.5							
Quartz SiO <sub>2</sub>	0.8	0.9	0.1	0.5							
Wuestite FeO	2.2	0.6	2.2	0.5							
beta NaAlO2	5.3	2.0	5.0	2.0							
gamma NaAlO2	0.0	0.0	0.0	0.0							
Galena PbS	0.2	0.1	0.1	0.1							
Hedenbergite CaFe++Si <sub>2</sub> O <sub>6</sub>	5.3	2.0	4.0	1.9							
Wurtzite ZnS	0.6	0.2	0.5	0.3							
Zincite ZnO	0.5	0.3	0.6	0.5							
Recalculated sample compo	sition without	standard		1							
Hematite Fe <sub>2</sub> O <sub>3</sub>	19.4	0.9	19.2	1.4							
Sphalerite ZnS	0.3	0.2	0.3	0.4							
Magnesioferrite MgFe <sub>2</sub> O <sub>4</sub>	4.8	0.5	5.0	0.5							
Corundum Al <sub>2</sub> O <sub>3</sub>	3.9	0.7	11.4	0.8							
Graphite 2H	3.4	1.2	3.8	1.0							
Srebrodolskite Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	0.6	0.4	0.6	0.5							
Calcite CaCO <sub>3</sub>	1.1	0.4	0.2	0.3							
Quartz SiO <sub>2</sub>	0.4	0.5	0.1	0.3							
Wuestite FeO	1.2	0.3	1.3	0.3							
beta NaAlO2	2.8	1.0	3.0	1.2							
gamma NaAlO2	0.0	0.0	0.0	0.0							
Galena PbS	0.1	0.1	0.0	0.0							
Hedenbergite CaFe++Si <sub>2</sub> O <sub>6</sub>	2.8	1.0	2.4	1.1							
Wurtzite ZnS	0.3	0.1	0.3	0.2							
Zincite ZnO	0.2	0.2	0.4	0.3							
Amorphous	58.9	2.4	52.3	2.5							
Compound	1a	1b	Error	Ave.	Norm.	Compound	2a	2b	Error	Ave.	Norm.
--------------------------------------	--------------	--------------	-------	--------------	--------------	--------------------------------	--------	--------	-------	--------	--------
					40.05	С					38.95
	64 44	64.00	0.40	64 47	40.05	Fe <sub>2</sub> O <sub>3</sub>	60.88	61.22	0.10	61.05	37.28
Fe <sub>2</sub> O <sub>3</sub>	01.11	01.03	0.10	01.47	30.48	SiO <sub>2</sub>	9.99	9.76	0.09	9.88	6.03
SIO <sub>2</sub>	10.80	10.38	0.09	10.62	0.30	ZnO	8.23	8.33	0.08	8.28	5.06
	9.1Z	9.17	0.09	9.14	5.43 2.40	Al <sub>2</sub> O <sub>3</sub>	5.44	5.28	0.07	5.36	3.27
	0.07	0.00	0.07	0.00	3.40	CdO	0.02	0.02	0.02	0.02	0.01
CaO	0.02	0.02	0.00	0.02	0.01	CaO	3.51	3.64	0.06	3.58	2.18
CaO	3.09 2.77	3.70	0.00	3.03 2.74	2.27	SO3	3.53	3.53	0.06	3.53	2.16
503 MaO	3.11	J.12 1 00	0.00	3.74 1.06	2.22	MgO	1.85	1.77	0.04	1.81	1.11
NIGO DhO	2.03	1.00	0.04	1.90	0.60	PbO	1.08	1.11	0.03	1.10	0.67
PDO K2O	1.14	1.10	0.03	0.02	0.69	K <sub>2</sub> O	0.91	0.85	0.03	0.88	0.54
K2O TiO	0.91	0.93	0.03	0.92	0.04	TiO <sub>2</sub>	0.40	0.41	0.03	0.40	0.25
	0.34	0.32	0.03	0.33	0.20	$P_2O_5$	0.26	0.26	0.02	0.26	0.16
F <sub>2</sub> O <sub>5</sub> MpO	0.20	0.31	0.02	0.29	0.17	MnO	0.23	0.23	0.01	0.23	0.14
	0.24	0.24	0.01	0.24	0.14	CI	3.44	3.42	0.05	3.43	2.10
V-O-	0.22	0.21	0.01	0.21	0.15	V <sub>2</sub> O <sub>5</sub>	0.06	0.07	0.06	0.06	0.04
$v_2 O_5$	0.00	0.00	0.01	0.00	0.00	Cr <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.02	0.02	0.01
Rh <sub>2</sub> O	0.00	0.02	0.01	0.02	0.01	Rb <sub>2</sub> O	0.03	0.03	0.03	0.03	0.02
SrO	0.03	0.03	0.01	0.00	0.02	SrO	0.02	0.02	0.00	0.02	0.01
BiaOa	0.02	0.02	0.00	0.02	0.01	Bi <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.02	0.02	0.01
ZrO₀	0.02	0.02	0.00	0.02	0.01	ZrO <sub>2</sub>	0.02	0.02	0.02	0.02	0.01
NiO	0.02	0.02	0.00	0.02	0.01	NiO	0.02		0.02	0.02	0.01
Total	100.00	100.00	0.01	100.01	100.02	BaO	0.04		0.04	0.04	0.02
Total	100.00	100.00		100.01	100.01	Total	100.00	100.00		100.03	100.03

 Table C.4: Composition (%wt) of raw BF sludge pellets (sample 1 and 2) from XRF analysis. The notations 'a' and 'b' represent the first and second analysis, respectively. The average composition was calculated with further normalization incorporating C content from ICP-OES analysis of the respective sample.

 Table C.5: Composition (%wt) of raw BF sludge pellets (sample 3 and 4) from XRF analysis. The notations 'a' and 'b' represent the first and second analysis, respectively. The average composition was calculated with further normalization incorporating C content from ICP-OES analysis of the respective sample.

Compound	3a	3b	Error	Ave.	Norm.						
С					38.00	Compound	4a	4b	Error	Ave.	Norm.
Fe <sub>2</sub> O <sub>3</sub>	61.35	61.23	0.01	61.29	38.01	C					40.80
SiO <sub>2</sub>	9.65	9.87	0.09	9.76	6.05	FeoOo	60 94	61 32	0 10	61 13	36.20
ZnO	8.18	8.19	0.08	8.18	5.08	SiO	10.80	10 52	0.10	10.66	6.31
$AI_2O_3$	5.25	5.22	0.07	5.23	3.25	ZnO	Q 21	9.21	0.00	9.21	5 4 5
CdO	0.02	0.01	0.00	0.01	0.01	ALO	5.81	5.21	0.00	5 79	3 43
CaO	3.71	3.59	0.06	3.65	2.26	CdO	0.01	0.02	0.00	0.02	0.40
SO₃	3.45	3.51	0.05	3.48	2.16	CaO	3.85	3.89	0.00	3.87	2 29
MgO	1.78	1.74	0.04	1.76	1.09	SO <sub>2</sub>	3 90	3 75	0.00	3.82	2.20
PbO	1.08	1.07	0.03	1.07	0.67	MaQ	2.04	2 13	0.00	2.02	1 24
K2O	0.92	0.88	0.03	0.90	0.56	PhO	1 18	1 10	0.04	1 14	0.68
TiO <sub>2</sub>	0.35	0.36	0.03	0.36	0.22	K-0	1.10	1.10	0.00	1.14	0.00
$P_2O_5$	0.26	0.28	0.02	0.27	0.17	TiO	0.27	0.29	0.00	0.28	0.00
MnO	0.23	0.23	0.01	0.23	0.14	P <sub>2</sub> O <sub>2</sub>	0.31	0.28	0.02	0.20	0.17
CI	3.55	3.62	0.06	3.59	2.22	MnO	0.24	0.23	0.02	0.23	0.17
$V_2O_5$	0.08	0.06	0.01	0.07	0.04	CI	0.24	0.25	0.01	0.20	0.14
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.02	0.00	0.02	0.01	V <sub>2</sub> O <sub>2</sub>	0.08	0.20	0.01	0.07	0.14
Rb <sub>2</sub> O	0.03	0.03	0.01	0.03	0.02	$Cr_2O_5$	0.00	0.07	0.01	0.07	0.04
SrO	0.02	0.02	0.00	0.02	0.01	Rh <sub>2</sub> O	0.01	0.02	0.00	0.01	0.07
Bi <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.00	0.02	0.01	SrO	0.00	0.00	0.00	0.00	0.02
ZrO <sub>2</sub>	0.02	0.02	0.00	0.02	0.01	BioOo	0.02	0.02	0.00	0.02	0.01
NiO		0.02	0.01	0.02	0.01	NiO	0.02	0.02	0.00	0.02	0.02
BaO	0.02		0.01	0.02	0.01	CeO		0.00	0.01	0.00	0.02
CeO <sub>2</sub>	0.04		0.01	0.04	0.03	Total	100.00	100.00	0.01	100.04	100.04
CuO		0.02	0.01	0.02	0.01		.00.00	.00.00		100.04	
Total	100.00	100.00		100.05	100.05						

## C.2. Thermodynamic Analysis

 $\label{eq:constraint} \mbox{Table C.6: Gibbs free energy change } (\Delta G^\circ) \mbox{ of possible direct reduction reactions in BF sludge (1).}$ 

Temp. (°C)	ZnO	ZnFe2O4	ZnS	PbO	PbS	CdO
0	285936	344431	301218	301218	264416	177053
25	278212	337418	293373	293373	257049	169435
50	270486	330394	285526	285526	249688	161823
75	262763	323364	277680	277680	242336	154218
100	255047	316333	269841	269841	234995	146622
125	247338	309303	262011	262011	227668	139039
150	239640	302276	254192	254192	220355	131468
1/5	231953	295254	246386	246386	213058	123912
200	224278	288240	238595	238595	205//8	100044
225	208068	201233	230010	230010	101270	100044
275	200300	267248	215311	215311	184042	93838
300	193712	260271	207582	207582	176833	86359
325	186105	253305	199870	199870	169641	78897
350	178513	246349	192174	192174	162466	71450
375	170935	239405	184494	184494	155310	64019
400	163371	232473	176830	176830	148171	56604
425	155821	225552	169183	169183	141049	49205
450	148286	218643	161551	161551	133945	41822
475	140764	211746	153935	153935	126858	34454
500	133256	204861	146335	146335	119787	27101
525	125762	197987	138750	138750	112734	19763
550	118282	191125	131181	131181	105696	12440
5/5	102261	184274	123020	123020	98075	2164
625	05021	170606	100000	100000	84680	0///
650	88493	163790	101048	101048	77705	-16711
675	81079	156984	93550	93550	70746	-23964
700	73676	150189	86066	86066	63802	-31204
725	66287	143405	78595	78595	56873	-38430
750	58910	136632	71138	71138	49958	-45644
775	51545	129869	63693	63693	43058	-52845
800	44191	123116	56261	56261	36171	-60033
825	36850	116374	48842	48842	29299	-67209
850	29521	109642	41435	41435	22440	-74372
875	22203	102919	34040	34040	15595	-81524
900	14896	96207	26658	26658	8763	-88663
925	7001 318	09004 82811	19207	19207	1944	102007
975	-6955	76128	4579	4579	-4002	-110012
1000	-14217	69453	-2758	-2758	-18435	-117105
1025	-21468	62788	-10026	-10026	-25203	-124187
1050	-28708	56132	-17089	-17089	-31959	-131258
1075	-35938	49485	-24141	-24141	-38703	-138318
1100	-43157	42847	-31184	-31184	-45434	-145367
1125	-50365	36218	-38216	-38216	-51996	-152406
1150	-57564	29597	-45239	-45239	-58361	-159434
1175	-64752	22985	-52251	-52251	-64712	-166451
1200	-71929	16381	-59254	-59254	-71049	-173458
1225	-79097	9785	-66248	-66248	-77372	-180455
1250	-86255	3198	-/3232	-/3232	-83682	-18/441
12/5	-93403	-3381	-80206	-80206	-89977	-194418
1325	-100541	-9952	-0/1/2	-0/1/2	-90200	-201304
1350	-114788	-23071	-101075	-101075	-105330	-215287
1375	-121897	-29618	-108014	-108014	-108675	-222224
1400	-128997	-36158	-114943	-114943	-112018	-229151
1425	-136087	-42690	-121864	-121864	-115360	-236069
1450	-143168	-49215	-128777	-128777	-118701	-242977
1475	-150239	-55732	-135681	-135681	-122042	-249875
1500	-157301	-62242	-142576	-142576	-125381	-256764
1525	-164354	-68744	-149464	-149464	-128720	-263645
1550	-171398	-75239	-156343	-156343	-132059	-270516
1575	-178433	-81728	-163214	-163214	-135397	-277378
1600	-185459	-88209	-170078	-170078	-138735	-284231

 $\label{eq:constraint} \mbox{Table C.7: Gibbs free energy change } (\Delta G^\circ) \mbox{ of possible direct reduction reactions in BF sludge } (2).$ 

Temp. (°C)	SiO2	AI2O3	CaO	MgO	K2O	TiO2	P2O5	MnO	Fe2O3	Fe3O4	FeO
0	500156	584219	618006	552465	316921	528547	258682	474192	71695	148125	111718
25	493792	577188	610285	544636	306652	522137	252722	466550	66184	142541	107724
50	487408	570139	602566	536797	296409	515716	246746	458914	60656	136919	103739
75	481010	563078	594852	528956	286194	509289	240761	451288	55120	131269	99766
100	474602	556011	587146	521115	276008	502859	234773	443674	49579	125598	95805
125	468189	548941	579452	513277	265852	496431	228782	436072	44037	119913	91857
150	461773	541871	571770	505447	255728	490007	222791	428485	38494	114223	87923
175	455357	534804	564102	497624	245636	483588	216803	420913	32950	108532	84003
200	448943	527742	556449	489812	235575	477176	210819	413357	27406	102846	80096
200	442532	520686	548812	482010	225546	470773	204842	405817	21859	97170	76202
250	436126	513638	541101	474220	215550	464370	108873	308203	16309	91510	72320
275	420726	506508	533587	466442	205584	457005	102013	300785	10753	85860	68450
300	423723	100567	526000	458678	105650	451621	186064	383205	5190	80252	6/501
325	420000	400545	518/30	450070	185748	431021	181025	375820	-385	74663	607/1
350	410570	492040	510430	430320	175975	438005	175000	368363	-505	60106	56002
375	404201	403034	503340	435463	166033	432565	160196	360000	11593	63586	53070
400	207042	470000	405940	400400	1660033	402000	162206	252407	17212	63360 E910E	40247
400	39/04Z	47 1040	490019	421100	100221	420233	167200	246000	-17213	50105	49247
425	205155	404004	400310	420000	140439	419910	157599	220607	-22012	32070	40401
430	270017	457590	400029	412371	130003	413009	101027	221220	-20002	47203	410ZZ
475	272510	400009	4/3307	207044	120900	407313	120009	222060	-34290	41930	2/010
500	372310	443093	400902	397044	107505	401020 204755	109020	323900	-40001	30075	20225
525	300205	430758	458462	389401	107595	394755	133998	310015	-45881	31464	30225
550	359911	429834	451038	381//1	97954	388492	128185	309285	-51/55	26321	20434
5/5	353630	422921	443628	374153	88340	382239	122387	301970	-57689	21252	22045
600	34/30/	416018	436234	300549	78752	3/5998	110/31	294670	-63713	16274	18859
625	341113	409127	428854	358957	69191	369767	111123	287385	-69665	11310	15073
650	334866	402246	421488	351378	59656	363546	105533	280114	-75534	6360	11287
0/5	328028	395376	414137	343811	50147	35/335	99959	272858	-81312	1422	7500
700	322398	388510	406799	330250	40662	351134	94403	200010	-87002	-3505	3/10
725	310170	301000	399474	320/13	31203	04494Z	00002	200001	-92056	-0419	-03
750	30990Z	3/4020	392103	321102	22042	330/00	03331 77077	2011/0	-90209	-13323	-3001
115	303/33	30/990	304003 277500	313002	10011	332300 226425	70220	243971	-103902	-10217	-/000
825	201365	35/367	370307	202657	4011	320425	66852	220600	115001	27075	15204
850	291303	347566	363046	290007	-4050	320270	61387	229009	-120673	-27975	-10112
875	200102	340775	355708	293606	21300	307099	55035	215209	126240	37701	22010
900	272867	333003	348561	276232	-29878	301860	50497	208162	-120240	-42553	-26722
925	266728	327221	341336	268778	-38427	295740	45073	200102	_137390	-47308	-30533
950	260597	320458	334123	261334	-46948	280628	30662	103028	-142957	-52238	-34347
975	254473	313703	326021	253001	-55441	283525	34263	186820	-148524	-57073	-38153
1000	248356	306958	319730	246478	-63907	277429	28878	179742	-154092	-61902	-41952
1025	242246	300221	312550	239065	-72346	271341	23505	172667	-159660	-66728	-45743
1050	236143	293493	305380	231662	-80760	265261	18144	165604	-165229	-71551	-49526
1075	230046	286773	298222	224268	-89148	259188	12795	158553	-170800	-76371	-53303
1100	223956	280062	291073	216884	-97511	253122	7458	151513	-176374	-81188	-57071
1125	217873	273359	283935	209510	-105849	247064	2132	144485	-181950	-86004	-60832
1150	211796	266664	276807	202144	-114163	241012	-3183	137468	-187529	-90819	-64586
1175	205725	259977	269688	194788	-122454	234968	-8486	130463	-193112	-95634	-68333
1200	199661	253298	262580	187441	-130721	228930	-13778	123469	-198697	-100449	-72072
1225	193603	246627	255481	180102	-138965	222900	-19060	116486	-204287	-105264	-75804
1250	187551	239964	248392	172773	-147187	216875	-24331	109514	-209880	-110081	-79529
1275	181505	233308	241312	165452	-155386	210858	-29592	102552	-215477	-114899	-83246
1300	175464	226660	234241	158140	-163564	204846	-34842	95602	-221077	-119719	-86956
1325	169430	220020	227179	150836	-171721	198841	-40082	88662	-226682	-124543	-90659
1350	163401	213387	220126	143541	-179856	192842	-45313	81733	-232291	-129369	-94354
1375	157378	206761	213083	136253	-187970	186849	-50533	74814	-237904	-134427	-97966
1400	151361	200142	206047	128974	-196064	180862	-55744	67906	-243522	-140684	-101176
1425	145349	193531	199021	121703	-204137	174881	-60946	61009	-249144	-146945	-104388
1450	139342	186927	192003	114440	-212191	168905	-66138	54121	-254770	-153210	-107595
1475	133341	180330	184993	107185	-220225	162936	-71321	47244	-260400	-159478	-110796
1500	127346	173739	177992	99938	-228240	156972	-76495	40378	-266034	-165750	-113991
1525	121357	167156	170999	92698	-236236	151013	-81660	33521	-271673	-172025	-117180
1550	115372	160579	164014	85466	-244213	145060	-86816	26674	-277317	-178304	-120457
1575	109393	154009	157037	78242	-252171	139112	-91963	19837	-282964	-184587	-123828
1600	103418	147446	150067	71025	-260111	133169	-97102	13011	-289081	-190640	-127195

Temp. (°C)	ZnO	ZnFe2O4	ZnS	PbO	PbS	CdO	SiO2	AI2O3	CaO	MgO	K2O	TiO2	P2O5	MnO
0	161435	36726	176716	97429	139914	52551	375655	460962	493504	427963	192420	404046	134181	349691
25	158084	35905	173246	94281	136922	49308	373665	458262	490158	424508	186525	402010	132595	346423
50	154760	35103	169800	91169	133962	46097	371682	455570	486840	421071	180683	399990	131020	343188
75	151459	34318	166376	88090	131032	42914	369706	452887	483548	417652	174890	397984	129457	339984
100	148181	33548	162975	85042	128129	39756	367736	450213	480280	414249	169142	395993	127907	336808
125	144923	32791	159595	82025	125252	36623	365773	447549	477036	410862	163437	394015	126366	333657
150	141683	32047	156236	79035	122398	33512	363817	444894	473813	407490	157772	392050	124834	330529
175	138462	31314	152895	76071	119567	30421	361866	442248	470611	404133	152144	390097	123311	327422
200	135256	30591	149573	73132	116756	27348	359921	439610	467427	400790	146553	388154	121/9/	324335
225	132066	29877	146267	70217	113965	24293	357982	436981	464262	397459	140996	386222	120291	321266
250	128889	29172	142978	6/324	111192	21254	356048	434360	461113	394141	135471	384300	118/94	318214
2/5	120720	28474	139704	0440Z	106435	16231	354119	431740	457980	390835	129977	382387	115926	3131/8
325	110/3/	27/02	133100	58767	102095	10221	350276	429140	454002	38/255	110076	378587	11/35/	3001/0
350	116305	26416	120066	55953	102370	9242	348362	423041	448669	380981	113668	376698	112802	306155
375	113187	25741	126746	53156	97562	6271	346453	421363	445592	377716	108285	374817	111438	303174
400	110078	25069	123537	50377	94878	3312	344550	418784	442527	374460	102929	372942	109993	300205
425	106979	24401	120340	47614	92207	363	342651	416211	439474	371213	97596	371074	108557	297247
450	103889	23737	117154	44866	89548	-2575	340758	413643	436432	367974	92288	369212	107130	294300
475	100807	23074	113978	42134	86901	-5503	338870	411082	433400	364744	87003	367356	105712	291363
500	97734	22414	110813	39416	84265	-8422	336987	408526	430379	361522	81741	365506	104304	288437
525	94668	21755	107656	36715	81640	-11331	335111	405975	427368	358307	76501	363661	102904	285521
550	91611	21097	104509	34026	79025	-14232	333240	403430	424367	355099	71283	361821	101514	282614
575	88561	20440	101372	31348	76421	-17123	331376	400889	421374	351899	66086	359985	100133	279716
600	85518	19783	98242	28681	73826	-20007	329524	398354	418391	348706	60909	358155	98888	276827
625	82483	19125	95121	26025	71241	-22883	327674	395823	415416	345519	55753	356328	97685	273947
650	79454	18467	92008	23380	68666	-25750	325827	393297	412449	342338	50617	354506	96494	271075
675	76432	17806	88903	20745	66100	-28611	323981	390775	409490	339164	45500	352688	95313	268211
700	73417	17144	85806	18120	63542	-31464	322138	388258	406539	335996	40403	350874	94143	265356
725	70408	16478	82716	15505	60994	-34309	320297	385745	403595	332834	35324	349063	92983	262508
750	6/405	15809	79633	12900	58454	-3/148	318457	383237	400659	329677	30538	34/250	91832	259668
000	61410	10100	70000	7710	52200	-39900	214794	300/32	204907	320327	20175	343453	90092	250030
000	60419 50425	14400	70409	7719 5144	50003	-42000	314/04	375735	201001	323301	21039	243052	09000	254011
850	55455	13/79	67371	2577	48376	-40024	312950	373243	388083	317107	132/3	3410001	87322	2/18383
875	52484	12418	64322	2011	45876	-51242	300204	370754	386079	313077	8081	338270	86216	245580
900	49518	11737	61279	-2216	43384	-54042	307488	368268	383183	310853	4743	336481	85118	242783
925	46557	11051	58242	-4202	40899	-56836	305684	365787	380292	307733	528	334695	84028	239994
950	43601	10362	55211	-6176	38422	-59623	303881	363309	377407	304618	-3664	332912	82945	237211
975	40652	9674	52186	-8139	35952	-62405	302080	360834	374528	301508	-7834	331131	81870	234435
1000	37707	8989	49167	-10091	33489	-65181	300280	358363	371654	298403	-11982	329353	80802	231666
1025	34768	8306	46211	-12033	31033	-67951	298482	355895	368786	295301	-16110	327577	79741	228903
1050	31835	7624	43454	-13964	28584	-70715	296685	353430	365923	292205	-20217	325803	78687	226147
1075	28907	6945	40703	-15885	26142	-73474	294890	350969	363066	289113	-24303	324032	77639	223397
1100	25984	6266	37956	-17797	23706	-76227	293096	348511	360213	286025	-28370	322262	76598	220654
1125	23066	5590	35215	-19699	21277	-78975	291304	346055	357366	282941	-32418	320495	75563	217916
1150	20153	4915	32478	-21592	18855	-81717	289513	343603	354524	279861	-36446	318729	74534	215185
11/5	1/246	4242	29746	-23476	16439	-84454	287723	341154	351686	276786	-40456	316965	73512	212461
1200	14344	3570	27019	-25351	14029	-8/185	285934	338708	348853	273714	-44448	315203	72495	209742
1220	11447	2899	24290	-2/21/	0220	-89911	204147	330200	340025	270040	-484ZZ	313443	7 1484	20/029
1230	5667	1561	18864	-29070	9220	-92032	280575	331388	340382	207502	-52376	300028	60470	204323
1300	2785	894	16154	-32767	4451	-98058	278790	328953	337567	261466	-60238	308172	68484	198928
1325	-92	228	13449	-34602	2071	-100763	277007	326521	334756	258413	-64143	306418	67495	196239
1350	-2965	-437	10748	-36428	-303	-103464	275225	324092	331950	255364	-68032	304665	66511	193556
1375	-5832	-1100	8052	-38247	-2671	-106159	273443	321665	329148	252318	-71905	302914	65532	190880
1400	-8695	-1764	5359	-40059	-5033	-108849	271663	319242	326350	249276	-75762	301164	64558	188209
1425	-11552	-2433	2670	-41864	-7390	-111534	269883	316820	323555	246238	-79603	299415	63589	185543
1450	-14405	-3101	-14	-43662	-9741	-114214	268105	314402	320765	243203	-83429	297668	62625	182884
1475	-17253	-3768	-2695	-45453	-12088	-116889	266327	311985	317979	240171	-87240	295921	61665	180230
1500	-20097	-4435	-5372	-47238	-14429	-119560	264551	309572	315196	237143	-91035	294176	60710	177582
1525	-22935	-5102	-8045	-49016	-16764	-122226	262776	307161	312418	234117	-94817	292432	59759	174940
1550	-25769	-5814	-10714	-49882	-19095	-124887	261001	304752	309643	231096	-98584	290689	58813	172303
1575	-28598	-6576	-13379	-48802	-21421	-127543	259228	302346	306871	228077	-102336	288946	57872	169672
1600	-31422	-7338	-16041	-47724	-23742	-130195	257455	299942	304104	225061	-106075	287205	56934	167047

Table C.8: Gibbs free energy change ( $\Delta G^{\circ}$ ) of possible indirect reduction reactions in BF sludge.

Temp. (°C)	ZnO	ZnFe2O4	ZnS	PbO	PbS	CdO	SiO2	Al2O3	CaO	MgO	K2O	TiO2	P2O5	MnO
0	200369	139836	215651	156073	198558	30179	263663	292045	273824	319975	8674	228443	205718	233523
25	192523	134610	207684	147773	190414	26660	258029	285307	265492	311706	-2768	222620	199935	225753
50	184762	129398	199802	139573	182366	23195	252467	278643	257242	303515	-14087	216874	194190	218065
75	177081	124201	191998	131466	174408	19781	246971	272048	249071	295398	-25292	211199	188486	210453
100	169476	119021	184270	123448	166535	16415	241538	265519	240975	287351	-36387	205593	182822	202912
125	161942	113858	1/6614	115515	158743	13094	236165	259052	232951	279371	-47380	200050	177195	195438
150	154475	108712	169027	107663	151027	9814	230848	252647	224994	271456	-58273	194568	171604	188027
200	14/0/3	103000	161000	99009	125012	00/4	220004	240290	217103	203002	-09074	109140	100040	100070
200	132447	90470	146649	92100 84557	128305	203	215208	233765	209274	233600	-79705	178460	155042	166142
250	125219	88313	139308	76995	120863	-2933	210200	227576	193792	240382	-100953	173195	149591	158954
275	118043	83259	132021	69497	113480	-6038	205019	221434	186134	232748	-111419	167977	144172	151815
300	110917	78221	124787	62061	106156	-9116	199989	215340	178529	225164	-121809	162804	138787	144723
325	103839	73201	117604	54685	98888	-12167	195000	209289	170973	217627	-132127	157675	133434	137676
350	96807	68197	110467	47366	91672	-15193	190051	203281	163465	210135	-142375	152588	128112	130671
375	89818	63210	103377	40102	84507	-18197	185139	197313	156003	202686	-152557	147539	122821	123708
400	82871	58237	96331	32890	77391	-21180	180264	191384	148584	195279	-162676	142529	117560	116784
425	75964	53279	89326	25728	70321	-24143	175423	185492	141208	187911	-172733	137554	112329	109897
450	69095	48336	82360	18614	63296	-27088	170616	179635	133870	180580	-182731	132612	107127	103045
475	62262	43406	75433	11546	56313	-30017	165841	173812	126571	173285	-192672	127703	101952	96228
500	55463	38488	64695	4522	49371	-32931	161096	168021	119308	166025	-202559	122825	96805	89443
525	48097	33583	61085 54961	-2458	42407	-3583Z	150382	162260	104002	158/90	-212393	11/9/5	91085	82088 75062
575	35257	23805	48067	-9399	28768	-30721	147037	150823	07717	144430	-222177	108356	81520	69265
600	28579	18931	41303	-23176	21969	-45697	142410	145144	90581	137289	-241603	103583	76601	62593
625	21927	14065	34566	-30014	15202	-49533	137803	139489	83472	130174	-251249	98832	71739	55946
650	15300	9208	27854	-36822	8464	-53378	133214	133855	76388	123083	-260853	94101	66900	49321
675	8695	4357	21167	-43601	1754	-57233	128643	128243	69328	116013	-270417	89390	62085	42718
700	2111	-488	14501	-50353	-4930	-61100	124088	122649	62290	108965	-279942	84695	57291	36134
725	-4454	-5328	7855	-57080	-11591	-64979	119545	117072	55272	101934	-289433	80016	52518	29567
750	-11002	-10165	1226	-63784	-18231	-68871	115015	111510	48271	94920	-298617	75349	47762	23016
775	-17536	-15000	-5387	-70468	-24851	-72778	110493	105960	41285	87920	-307364	70693	43024	16478
800	-24053	-19831	-11983	-77129	-31450	-76697	105983	100425	34317	80936	-316070	66050	38304	9956
825	-30550	-24656	-18559	-83/65	-38025	-80626	101488	94908	27369	/39/1	-324734	61423	33603	3452
850	-3/028	-29474	-25113	-90374	-445/5	-84501	97007	89409	20442	60101	-333355	50012	28922	-3033
0/0	-43404 10018	-34265	38157	-90957	57601	-00002	92000	03920 78467	6652	53106	350468	02210 47642	24200	-9490 15042
925	-56343	-43891	-44657	-109187	-64086	-96410	83706	73015	-222	46302	-358971	43073	14990	-22376
950	-62752	-48690	-51142	-115150	-70553	-100383	79296	67576	-7080	39421	-367440	38514	10376	-28797
975	-69137	-53478	-57602	-121081	-76991	-104355	74907	62159	-13913	32565	-375864	33977	5784	-35194
1000	-75497	-58255	-64038	-126980	-83401	-108327	70537	56764	-20723	25732	-384244	29459	1213	-41567
1025	-81834	-63022	-70392	-132849	-89783	-112300	66187	51391	-27508	18921	-392582	24962	-3338	-47918
1050	-88147	-67778	-76528	-138687	-96139	-116272	61854	46039	-34270	12133	-400879	20484	-7870	-54245
1075	-94438	-72525	-82642	-144495	-102468	-120245	57540	40707	-41010	5367	-409135	16025	-12382	-60551
1100	-100706	-77261	-88733	-150275	-108771	-124218	53244	35396	-47727	-1378	-417351	11584	-16875	-66835
1125	-106952	-81988	-94803	-156026	-114891	-128191	48965	30105	-54423	-8101	-425528	/162	-21350	-73097
1150	-1131//	-80/05	106000	167449	120801	-132104	44703	24833	67751	-14805	-433007	2/5/	-25806	-79339
1200	125563	-91413	112888	173115	132540	1/0111	40400	14345	7/385	-21400 28151	-441709	6001	-30245	-00000
1200	-131726	-100802	-112000	-178759	-138370	-144085	32015	9129	-80998	-34795	-443033	-10356	-39071	-97941
1250	-137868	-105483	-124845	-184377	-144174	-148059	27817	3930	-87592	-41421	-465859	-14694	-43459	-104102
1275	-143991	-110156	-130794	-189970	-149952	-152033	23634	-1251	-94167	-48027	-473819	-19016	-47831	-110243
1300	-150094	-114820	-136724	-195539	-155706	-156007	19466	-6415	-100723	-54616	-481745	-23323	-52186	-116366
1325	-156178	-119476	-142636	-201084	-160890	-159982	15313	-11562	-107260	-61187	-489638	-27615	-56526	-122470
1350	-162243	-124124	-148530	-206605	-163684	-163957	11174	-16693	-113780	-67740	-497499	-31892	-60850	-128555
1375	-168290	-128764	-154406	-212103	-166465	-167932	7049	-21807	-120281	-74276	-505328	-36154	-65159	-134622
1400	-174321	-133398	-160268	-217581	-169237	-171911	2934	-26908	-126768	-80798	-513128	-40405	-69455	-140674
1425	-180345	-138032	-166122	-223047	-172008	-175900	-1177	-32004	-133249	-87314	-520908	-44652	-73743	-146719
1450	-186352	-142659	-171961	-228492	-174769	-179889	-5276	-37086	-139713	-93814	-528658	-48886	-78017	-152747
14/5	-192342	-14/2/9	-1///83	-233916	-1//519	-183880	-9362	-42153	-146162	-100299	-536380	-53108	-82277	-158/58
1500	-190310	156500	-103591	-23932U 244702	-100209 182080	-10/0/3 101866	-13430	-41200 52245	-102090 150012	-113225	-044072 551737	-0/31/	-00023 00757	-104/53
1550	-204213	-161171	-105000	-244703	-185802	-191000	-11499	-57363	-165510	-110220	-550468	-65703	-90131	-176780
1575	-216426	-165909	-201208	-251945	-188706	-200142	-25874	-62565	-172090	-126378	-567271	-70158	-99356	-182928
1600	-222530	-170643	-207149	-254627	-191601	-204333	-30097	-67756	-178658	-132985	-575048	-74514	-103668	-189054

Table C.9: Gibbs free energy change ( $\Delta G^\circ)$  of possible carbochlorination reactions in BF sludge.

Temp. (°C)	FeCl2	MgFe2O4	CaCO3	Bouduard
0	126870.4	4065	133380.2	124501.6
25	122839.9	4289 2	129289 5	120127 1
50	118003.2	4516 1	125204.4	115726 1
75	115051.6	4733.8	1211/3 5	111304 1
100	1110001.0	4733.0	121143.3	106966
100	107577.1	4934.Z	117094.0	100000
120	107577.1	5111.0	113059.9	102415.7
150	103943.2	5263	109039.3	97956.6
175	100372	5365.3	105035.4	93491.2
200	90009.0	5477	07005 4	09021.9
220	93402.7	5550.9	97005.4	04000.0
250	09990.2	5564.2	93103	00070.0
215	00043.0	0000.0 5510.6	09104.0	73007.4
200	00072 E	5519.0	00219.9 01000 E	66671
323	00073.3 76954 4	5240 7	01290.0	6007 I
350	70004.1	5340.7	77390.2	62207.5
3/5	73075.9	5200.3	73494.7	57747.9
400	70537.2	5025.7	69611.5	53292.7
425	67436.5	4816.7	65740.5	48842.3
450	64372.2	4572.8	61881.4	44397
475	61343.2	4293.7	58034	39957
500	58348.1	3978.8	54198	35522.6
525	55385.7	3627.4	50373.2	31093.9
550	52455.1	3238.6	46559.4	26671.1
5/5	49555.1	2811.2	42756.5	22254.2
600	46684.8	2343.8	38964.3	17843.2
625	43843.3	1834.5	35182.6	13438.3
650	41029.7	1281.2	31411.4	9039.5
675	38243.3	680.9	27650.6	4646.6
700	35483.3	36.2	23899.9	259.8
725	32748.9	-635.1	20159.4	-4120.9
750	30039.5	-1328.4	16428.9	-8495.7
//5	27354.4	-2041.3	12708.3	-12864.6
800	24692.9	-2//1.4	8997.7	-1/22/.6
825	22054.4	-3517.3	5296.9	-21584.0
850	19438.5	-4277.5	1605.9	-20930.9
000	14271.0	-5050.0	-2075.4	-30201.4
900	14271.9	-5655.7	-5740.9	-34021.2
920	0100 0	7427.6	-9400.0	-30900.3
930	6677 4	-7457.0 8252.8	16704 1	47606 7
1000	4195 5	-0202.0	-10704.1	-47000.7
1000	4100.0	-9070.5	-20000	-01924.2
1025	7/1 5	-9900	-23903.3	-50250.2
1030	-3177 5	-10740.0	-21300.1	-64844 2
1100	5505.6	12442.0	34780.7	60140.3
1125	7006.2	13200 /	38382.0	73/31 2
1120	10270.7	14160.0	41069 7	77716.0
1175	10373.7	15026.0	45547.2	91007.5
1200	15006.6	15020.9	-40047.0	-01997.0
1200	17430.7	16770.3	-49119 52683.0	-00273.1
1220	107/0	17647	-52003.9	-90040.0
1230	22051 7	18526.5	5070/ 1	-94009.3
12/0	2/330.3	10/08 3	63330.7	103326
1225	26611 9	20202.1	-03539.7	107577
1350	28860.7	21177.6	60423.4	111823
1375	31113 2	22064.4	72284 6	116065
1400	33342.4	22004.4	75140 5	120302
1400	35557.8	23840.8	77001 /	124535
1420	37750.5	24720.7	80837.2	124333
1475	-300/17 7	-2-7123.1	-83678 2	-13202
1500	-421226	-26507 4	-86514 4	-137200
1525	-44284 6	_27305 R	-80346	_141410
1550	-46433 7	-28283 4	-02173	_145620
1575	-48570 2	-29170	-94995 6	-140835
1600	-50694.4	-30055.3	-97813.8	-154036

**Table C.10:** Gibbs free energy change ( $\Delta G^{\circ}$ ) of possible side reactions in BF sludge.

T(C)	g-CO(g)	g-CO2(g)	g-SiO(g)	g-SiS(g)	g-KCl(g)	g-Zn(g)	g-KZnCl3(g)	g-Cd(g)	g-Pb(g)	g-PbS(g)	g-PbCl(g)
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
200	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.001	3.183	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
400	0.019	3.470	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
500	0.148	3.579	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
600	2.691	12.486	0.000	0.000	0.000	0.000	0.000	0.009	0.000	0.000	0.000
700	8.798	8.742	0.000	0.000	0.003	0.000	0.001	0.009	0.001	0.000	0.002
800	17.913	3.607	0.000	0.000	0.027	0.009	0.147	0.009	0.017	0.006	0.062
900	21.368	0.933	0.000	0.000	0.051	0.082	0.079	0.009	0.108	0.051	0.182
1000	22.420	0.255	0.000	0.000	0.173	0.516	0.022	0.009	0.323	0.203	0.138
1100	22.649	0.079	0.000	0.000	0.235	2.315	0.007	0.009	0.336	0.266	0.063
1200	22.780	0.029	0.000	0.000	0.281	3.785	0.000	0.009	0.334	0.319	0.014
1300	23.086	0.012	0.000	0.016	0.283	3.785	0.000	0.009	0.312	0.346	0.012
1400	24.754	0.006	0.008	0.817	0.289	3.785	0.000	0.009	0.300	0.367	0.005
1500	25.561	0.003	0.067	2.149	0.293	3.786	0.000	0.009	0.532	0.103	0.001
1600	29.176	0.002	0.233	1.199	0.293	3.786	0.000	0.009	0.612	0.011	0.000

Table C.11: Equilibrium gas composition of sample without chloride (composition 1).

Table C.12: Equilibrium gas composition of sample with chloride (composition 2) (1).

T(C)	g-CO(g)	g-CO2(g)	g-SiO(g)	g-SiS(g)	g-MgCl2(g)	g-KCl(g)	g-CaCl2(g)	g-MnCl2(g)	g-FeCl2(g)
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
200	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.002	4.694	0.000	0.000	0.000	0.000	0.000	0.000	0.000
400	0.026	4.737	0.000	0.000	0.000	0.000	0.000	0.000	0.000
500	0.203	4.893	0.000	0.000	0.000	0.000	0.000	0.000	0.000
600	2.586	12.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
700	8.349	8.252	0.000	0.000	0.000	0.000	0.000	0.014	0.029
800	17.987	3.513	0.000	0.000	0.000	0.004	0.000	0.073	0.280
900	21.497	0.912	0.000	0.000	0.000	0.027	0.000	0.222	0.271
1000	22.549	0.249	0.000	0.000	0.002	0.137	0.000	0.223	0.255
1100	22.802	0.077	0.000	0.000	0.013	0.307	0.002	0.234	0.326
1200	22.972	0.029	0.000	0.000	0.165	0.478	0.033	0.241	0.761
1300	23.345	0.012	0.000	0.022	0.715	0.597	0.150	0.245	0.778
1400	25.131	0.006	0.011	1.210	1.250	0.758	0.152	0.247	0.610
1500	26.601	0.003	0.078	2.760	1.763	0.822	0.212	0.243	0.102
1600	30.213	0.002	0.241	1.775	1.490	0.836	0.636	0.192	0.028

Table C.13: Equilibrium gas composition of sample with chloride (composition 2) (2).

	0.000
	0 000
100 0.000 0.000 0.000 0.000 0.000 0.000 0.000	0.000
200 0.000 0.000 0.000 0.000 0.000 0.000	0.000
300 0.000 0.000 0.000 0.000 0.000 0.000 0.000	0.000
400 0.000 0.000 0.000 0.000 0.000 0.000 0.000	0.000
500 0.000 0.000 0.000 0.001 0.000 0.000 0.000	0.002
600         0.000         0.005         0.001         0.009         0.000         0.000         0.002	0.009
700 0.000 0.222 0.061 0.009 0.001 0.000 0.052	0.310
800 0.009 1.874 1.457 0.009 0.005 0.002 0.157	0.646
900 0.085 1.615 1.612 0.009 0.030 0.014 0.311	0.423
1000 0.533 1.387 1.820 0.009 0.088 0.055 0.387	0.209
1100 2.399 1.533 1.427 0.009 0.147 0.116 0.352	0.100
1200 3.057 1.123 0.615 0.009 0.162 0.154 0.319	0.073
1300 3.562 0.392 0.114 0.009 0.203 0.225 0.236	0.031
1400 3.731 0.102 0.017 0.009 0.236 0.294 0.145	0.010
1500 3.782 0.006 0.001 0.009 0.472 0.098 0.075	0.001
1600         3.785         0.001         0.000         0.009         0.582         0.015         0.032	0.000

T(°C)	C(s)-1	C(s)-2	Fe2O3(s)-1	Fe2O3(s)-2	Fe(s)-1	Fe(s)-2	Fe3C(s)-1	Fe3C(s)-2	Fe2SiO4-1	Fe2SiO4-2
0	39.21	38.88	36.56	32.48	0.00	0.00	0.00	0.00	0.00	0.00
100	39.20	38.63	36.43	25.67	0.00	0.00	0.00	0.00	0.00	0.00
200	38.77	38.37	25.10	19.09	0.00	0.00	0.00	0.00	10.39	5.91
300	39.01	38.60	29.75	24.28	0.00	0.00	0.00	0.00	6.25	14.31
400	38.92	38.58	27.62	23.91	0.00	0.00	0.00	0.00	8.75	15.05
500	38.84	38.46	26.53	22.54	0.00	0.00	0.00	0.00	10.22	17.00
600	35.32	35.50	0.00	0.00	17.85	14.82	0.00	0.00	9.68	16.46
700	33.72	34.05	0.00	0.00	20.45	16.80	0.00	0.00	7.12	14.63
800	31.21	31.21	0.00	0.00	25.61	24.07	0.00	0.00	0.00	0.00
900	28.62	28.66	0.00	0.00	0.00	0.00	27.52	26.13	0.00	0.00
1000	28.40	28.45	0.00	0.00	0.00	0.00	26.77	25.35	0.00	0.00
1100	28.46	28.49	0.00	0.00	0.00	0.00	25.15	23.68	0.00	0.00
1200	28.50	28.46	0.00	0.00	0.00	0.00	23.92	23.31	0.00	0.00
1300	28.33	28.28	0.00	0.00	0.00	0.00	24.57	23.63	0.00	0.00
1400	27.39	27.31	0.00	0.00	0.00	0.00	27.24	26.03	0.00	0.00
1500	27.05	26.61	0.00	0.00	0.00	0.00	27.41	27.38	0.00	0.00
1600	25.75	25.32	0.00	0.00	0.00	0.00	23.68	23.56	0.00	0.00

 Table C.14: Equilibrium carbon and iron solid composition of sample without (-1) and with (-2) chloride.

Table C.15: Equilibrium heavy metals solid composition of sample without (-1) and with (-2) chloride.

T(°C)	Pb(s)-1	Pb(s)-2	PbS(s)-1	PbCl2(s)-2	CdS(s)-1	CdS(s)-2	CdCl2(s)-2	ZnS(s)-1	ZnS(s)-2
0	0.00	0.00	0.00	0.00	0.01	0.00	0.01	5.64	5.64
100	0.00	0.00	0.00	0.83	0.01	0.00	0.01	5.64	5.64
200	0.00	0.00	0.00	0.83	0.01	0.00	0.01	5.64	5.64
300	0.00	0.00	0.72	0.83	0.01	0.01	0.00	5.51	5.64
400	0.29	0.00	0.38	0.39	0.01	0.01	0.00	5.64	5.64
500	0.62	0.62	0.00	0.00	0.01	0.01	0.00	5.64	5.64
600	0.62	0.61	0.00	0.00	0.00	0.00	0.00	5.64	5.64
700	0.62	0.35	0.00	0.00	0.00	0.00	0.00	5.64	5.45
800	0.52	0.00	0.00	0.00	0.00	0.00	0.00	5.54	3.62
900	0.28	0.00	0.00	0.00	0.00	0.00	0.00	5.45	3.62
1000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.85	3.02
1100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1200	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1300	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1400	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1500	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1600	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table C.16: Equilibrium other compound solid composition of sample without (-1) and with (-2) chloride.

T(°C)	CaMg(CO3)2 (s)-1	CaMg(CO3)2 (s)-2	CaS (s)-1	CaS (s)-2	CaCl2 (s)-2	KCaCl3 (s)-2	SiO2 (s)-1	SiO2 (s)-2	Mg2SiO4 (s)-1	Mg2SiO4 (s)-2	KAISi2O6 (s)-1	CaAl2Si2O8 (s)-2
0	4.94	2.71	0.00	0.00	1.16	2.21	3.29	5.73	0.00	0.00	0.00	0.00
100	4.95	3.47	0.00	0.00	1.04	1.84	2.92	1.74	0.00	0.00	0.00	0.00
200	5.22	3.47	0.00	0.00	1.04	1.84	0.00	0.00	0.00	0.00	0.00	0.00
300	0.00	0.00	0.00	0.00	1.05	1.84	0.00	0.00	0.00	0.00	1.73	0.00
400	0.00	0.00	0.00	0.00	1.23	2.21	0.00	0.00	0.37	0.15	0.00	0.00
500	0.00	0.00	0.00	0.00	1.38	2.21	0.00	0.00	1.48	1.41	0.00	0.00
600	0.00	0.00	0.00	0.00	1.38	2.21	0.00	0.00	1.48	1.41	0.00	0.00
700	0.00	0.00	0.00	0.00	1.03	0.00	0.00	0.00	0.37	0.15	1.74	0.00
800	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.42	1.06	2.29	8.49
900	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.55	0.48	2.32	8.65
1000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.35	0.02	1.98	9.02
1100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.37	0.00	1.85	9.11
1200	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	1.30	0.00	1.75	9.11
1300	0.00	0.00	0.81	0.29	0.00	0.00	0.00	0.00	1.09	0.00	0.00	9.11
1400	0.00	0.00	2.84	1.41	0.00	0.00	0.00	0.00	0.00	0.00	1.50	5.12
1500	0.00	0.00	1.51	0.91	0.00	0.00	0.00	0.00	1.38	0.20	1.44	6.99
1600	0.00	0.00	2.85	2.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

## C.3. Analysis of the Reacted TGA Samples

Sample	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	V	Zn
01-800	0.02	45.50	1.78	0.00	26.60	0.69	0.11	0.41	1.10	0.10	0.02	2.71
02-800	0.02	43.40	2.00	0.00	28.10	0.72	0.12	0.01	1.24	0.10	0.03	2.29
03-800	0.02	42.80	1.74	0.00	28.10	0.67	0.11	0.01	1.16	0.10	0.03	2.16
04-800	0.02	44.60	2.03	0.00	27.10	0.72	0.11	0.35	1.17	0.10	0.02	2.81
01-1000	0.03	50.60	2.03	0.00	29.90	0.83	0.14	0.01	1.49	0.11	0.03	0.06
02-1000	0.03	48.40	1.89	0.00	33.20	0.76	0.13	0.00	1.27	0.12	0.03	0.06
03-1000	0.03	47.00	2.17	0.00	34.90	0.80	0.14	0.00	1.30	0.12	0.03	0.05
04-1000	0.03	48.70	2.05	0.00	31.50	0.82	0.13	0.00	1.34	0.12	0.03	0.08
01-1200	0.03	50.60	2.25	0.00	33.10	0.85	0.14	0.00	1.45	0.12	0.03	0.08
02-1200	0.03	47.40	2.29	0.00	35.90	0.84	0.14	0.00	1.53	0.13	0.03	0.00
03-1200	0.03	48.80	2.42	0.00	34.40	0.79	0.14	0.00	1.48	0.12	0.03	0.00
04-1200	0.03	48.70	2.46	0.00	33.60	0.90	0.15	0.00	1.53	0.13	0.03	0.00
01-1400	0.03	50.20	2.43	0.00	32.80	0.20	0.12	0.06	1.63	0.13	0.03	0.00
02-1400	0.03	48.30	2.03	0.00	39.40	0.32	0.12	0.03	1.42	0.14	0.03	0.07
03-1400	0.03	49.10	2.23	0.00	35.50	0.22	0.12	0.07	1.46	0.13	0.03	0.05
04-1400	0.04	51.10	2.52	0.00	34.40	0.25	0.13	0.01	1.52	0.13	0.03	0.14

Table C.17: ICP-OES 1st analysis of reacted BF sludge samples.

Table C.18: ICP-OES 2nd analysis of reacted BF sludge samples.

Sample	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	V	Zn
01-800	0.02	44.10	1.83	0.00	26.00	0.64	0.10	0.35	1.23	0.10	0.02	2.99
02-800	0.03	44.10	1.83	0.00	25.90	0.64	0.10	0.01	1.10	0.10	0.02	1.99
03-800	0.02	42.60	1.87	0.00	27.30	0.66	0.11	0.02	1.11	0.10	0.02	2.19
04-800	0.02	43.50	1.87	0.00	26.50	0.66	0.11	0.41	1.17	0.10	0.02	2.97
01-1000	0.03	47.60	2.23	0.00	31.00	0.80	0.13	0.02	1.41	0.12	0.03	0.03
02-1000	0.03	46.10	1.94	0.00	34.30	0.71	0.12	0.02	1.23	0.12	0.03	0.02
03-1000	0.03	45.40	2.93	0.00	32.90	0.77	0.13	0.01	1.24	0.11	0.03	0.04
04-1000	0.03	47.10	1.93	0.00	28.00	0.71	0.11	0.01	1.42	0.11	0.03	0.06
01-1200	0.03	48.10	2.48	0.00	41.50	0.91	0.14	0.00	1.57	0.14	0.03	0.00
02-1200	0.04	49.80	2.77	0.00	35.00	0.77	0.12	0.02	1.44	0.13	0.03	0.00
03-1200	0.04	48.60	2.49	0.00	37.20	0.79	0.13	0.01	1.47	0.13	0.03	0.00
04-1200	0.04	49.70	2.47	0.00	34.10	0.85	0.14	0.01	1.52	0.13	0.03	0.00
01-1400	0.04	50.80	2.45	0.00	35.20	0.22	0.11	0.01	1.59	0.13	0.03	0.00
02-1400	0.04	50.30	2.31	0.00	36.20	0.09	0.11	0.03	1.46	0.13	0.03	0.01
03-1400	0.04	49.80	2.16	0.00	38.50	0.21	0.12	0.01	1.38	0.13	0.03	0.00
04-1400	0.04	49.00	2.72	0.00	35.30	0.14	0.13	0.01	1.55	0.13	0.03	0.00

Sample	Ва	С	Са	Cd	Fe	Mg	Mn	Pb	S	Ti	V	Zn
01-800	0.02	44.80	1.81	0.00	26.30	0.66	0.11	0.38	1.17	0.10	0.02	2.85
02-800	0.02	43.75	1.92	0.00	27.00	0.68	0.11	0.01	1.17	0.10	0.03	2.14
03-800	0.02	42.70	1.81	0.00	27.70	0.66	0.11	0.01	1.14	0.10	0.02	2.18
04-800	0.02	44.05	1.95	0.00	26.80	0.69	0.11	0.38	1.17	0.10	0.02	2.89
01-1000	0.03	49.10	2.13	0.00	30.45	0.81	0.13	0.01	1.45	0.12	0.03	0.04
02-1000	0.03	47.25	1.92	0.00	33.75	0.73	0.12	0.01	1.25	0.12	0.03	0.04
03-1000	0.03	46.20	2.55	0.00	33.90	0.79	0.13	0.01	1.27	0.12	0.03	0.05
04-1000	0.03	47.90	1.99	0.00	29.75	0.76	0.12	0.01	1.38	0.11	0.03	0.07
01-1200	0.03	49.35	2.37	0.00	37.30	0.88	0.14	0.00	1.51	0.13	0.03	0.02
02-1200	0.03	48.60	2.53	0.00	35.45	0.81	0.13	0.01	1.49	0.13	0.03	0.00
03-1200	0.03	48.70	2.46	0.00	35.80	0.79	0.14	0.01	1.48	0.12	0.03	0.00
04-1200	0.03	49.20	2.47	0.00	33.85	0.88	0.14	0.01	1.53	0.13	0.03	0.00
01-1400	0.04	50.50	2.44	0.00	34.00	0.21	0.12	0.03	1.61	0.13	0.03	0.00
02-1400	0.04	49.30	2.17	0.00	37.80	0.20	0.12	0.03	1.44	0.13	0.03	0.04
03-1400	0.03	49.45	2.20	0.00	37.00	0.22	0.12	0.04	1.42	0.13	0.03	0.02
04-1400	0.04	50.05	2.62	0.00	34.85	0.19	0.13	0.01	1.54	0.13	0.03	0.06

 Table C.19: ICP-OES average analysis of reacted BF sludge samples.

Table C.20: Removal rate (%) of zinc, cadmium, lead, iron, carbon, and sulfur of the reacted BF sludge.

-						
Sample	Zn removal	Cd removal	Pb removal	Fe removal	C removal	S removal
01-800	7.74	100.00	37.25	2.18	0.33	8.26
02-800	29.63	100.00	98.15	6.85	4.08	15.58
03-800	24.56	100.00	97.56	5.60	3.69	6.44
04-800	4.69	100.00	31.94	1.12	1.52	2.52
01-1000	98.82	100.00	98.42	6.96	8.99	6.84
02-1000	98.89	100.00	98.61	5.61	12.45	14.68
03-1000	98.68	100.00	98.93	4.18	13.57	13.17
04-1000	98.18	100.00	98.98	10.68	13.76	7.38
01-1200	99.09	100.00	99.58	12.09	18.72	8.56
02-1200	100.00	100.00	98.25	6.65	18.71	8.54
03-1200	100.00	100.00	99.28	7.38	16.66	7.77
04-1200	100.00	100.00	99.09	6.69	18.77	6.18
01-1400	100.00	100.00	96.09	10.25	19.26	5.27
02-1400	99.05	100.00	96.44	4.91	21.19	15.30
03-1400	99.39	100.00	94.77	6.51	17.34	13.24
04-1400	98.31	100.00	98.28	8.17	21.03	9.74

### C.4. External Data from Tata Steel

Table C.21: Experimental data from research by Dr. Peter Beentjes from Tata Steel in IJmuiden.

Na	Identification	Turne	1st	soak	2nd	soak	We	ight	Deceted	Domork
INO.	Identification	туре	Gas	T(°C)	gas	T(°C)	Wet	Dry	Reacted	Remark
1	Raw I	I					14.70	10.60	10.60	No Cl
2	I-500-01	I	air	500			6.70	4.83	5.30	No Cl
3	I-850-03	I	air	850			10.20	7.36	2.90	No Cl
4	I-500-05	I	N2	500			10.20	7.36	7.10	No Cl
5	I-850-07	I	N2	850			13.80	9.95	8.90	No Cl
6	I-1100-11	I	N2	1100			26.70	19.25	14.10	No Cl
7	I-1166-13	I	N2	1166			12.00	8.65	5.80	No Cl
8	I-HCI-23	I	HCI	950			16.40	11.83	9.20	No Cl
9	I-HCI-25	I	HCI	1100			16.00	11.54	8.40	No Cl
10	I-HCI-27	I	HCI	1166			15.00	10.82	7.20	No Cl
11	I-2STEP-17	I	N2	500	N2	825	11.60	8.36	7.50	No Cl
12	I-2STEP-21	I	N2	500	N2	950	10.20	7.36	5.60	No Cl
13	I-2STEP-15	I	air	500	N2	825	11.00	7.93	5.80	No Cl
14	I-2STEP-19	I	air	500	N2	950	11.70	8.44	5.00	No Cl
15	I-2STEP-29	I	air	500	HCI	825	14.90	10.74	9.50	No Cl
16	1-2STEP-33	I	air	500	HCI	950	15.80	11.39	7.50	No Cl
17	I-2STEP-31	I	N2	500	HCI	825	17.30	12.48	11.50	No Cl
18	II-2STEP-35	I	N2	500	HCI	950	17.40	12.55	9.90	No Cl
19	Raw II	II					12.80	8.80	8.80	
20	II-850-04	Ш	air	850			8.10	5.57	3.30	
21	II-500-06	II	N2	500			9.00	6.19	6.10	
22	II-850-08	II	N2	850			9.60	6.60	6.00	
23	II-950-10	II	N2	950			11.30	7.77	6.40	
24	II-1100-12	II	N2	1100			21.60	14.85	11.10	
25	II-1166-14	II	N2	1166			9.90	6.81	5.00	
26	II-HCI-24	II	HCI	950			10.90	7.49	6.50	
27	II-HCI-26	II	HCI	1100			12.00	8.25	6.40	
28	II-HCI-28	II	HCI	1166			12.40	8.53	6.30	
29	II-2STEP-18	II	N2	500	N2	825	9.70	6.67	6.20	
30	II-2STEP-22	II	N2	500	N2	950	8.80	6.05	4.90	
31	II-2STEP-16	II	air	500	N2	825	10.20	7.01	5.80	
32	II-2STEP-20	II	air	500	N2	950	9.90	6.81	5.10	
33	II-2STEP-30	II	air	500	HCI	825	12.30	8.46	7.90	
34	II-2STEP-34	II	air	500	HCI	950	13.50	9.28	7.60	
35	II-2STEP-32	II	N2	500	HCI	825	12.70	8.73	8.10	
36	II-2STEP-36	II	N2	500	HCI	950	12.30	8.46	7.30	

No.	AI2O3	С	CaO	CdO	CI	Fe2O3	met.Fe	MgO	MnO	P2O5	PbO	S	SiO2	TiO2	ZnO
1	2.90	43.34	2.59	0.01	0.08	37.00	0.52	1.15	0.15	0.15	0.69	1.22	6.12	0.16	3.92
2	3.67	29.01	3.34	0.02	0.00	46.58	0.31	1.47	0.19	0.19	0.86	1.54	7.78	0.21	4.86
3	4.93	0.05	4.62	0.00	0.00	67.06	0.31	1.97	0.28	0.28	0.74	1.45	11.23	0.26	6.83
4	2.92	43.11	2.65	0.01	0.00	37.29	0.41	1.16	0.15	0.15	0.69	1.17	6.18	0.16	3.92
5	3.01	42.12	2.67	0.00	0.00	38.14	1.26	1.20	0.16	0.15	0.20	1.24	6.35	0.17	3.33
6	2.67	33.06	2.39	0.00	0.00	33.98	19.61	1.08	0.14	0.14	0.00	1.01	5.66	0.15	0.12
7	2.69	30.49	2.41	0.00	0.00	34.20	22.03	1.06	0.14	0.14	0.00	1.03	5.66	0.15	0.00
8	2.95	36.74	2.62	0.00	0.02	37.41	9.75	1.18	0.15	0.15	0.00	1.17	6.22	0.16	1.46
9	3.07	34.73	2.74	0.00	0.02	38.97	11.36	1.23	0.16	0.16	0.00	0.82	6.52	0.17	0.04
10	3.25	29.98	2.88	0.00	0.02	41.47	12.90	1.31	0.17	0.17	0.00	0.83	6.84	0.18	0.01
11	2.98	42.93	2.65	0.00	0.00	37.96	0.58	1.19	0.15	0.15	0.29	1.14	6.26	0.17	3.55
12	2.79	35.48	2.48	0.00	0.00	35.17	15.22	1.11	0.15	0.14	0.00	1.08	5.86	0.16	0.37
13	3.61	31.69	3.24	0.00	0.00	46.10	0.30	1.44	0.19	0.18	0.25	0.79	7.63	0.20	4.38
14	3.59	24.01	3.19	0.00	0.00	45.85	12.43	1.45	0.19	0.18	0.01	0.70	7.63	0.20	0.57
15	3.09	40.79	2.75	0.00	0.00	39.60	0.30	1.24	0.16	0.16	0.28	0.89	6.55	0.17	4.03
16	3.67	26.63	3.29	0.00	0.00	47.06	6.98	1.49	0.20	0.19	0.00	0.84	7.78	0.20	1.66
17	2.98	42.71	2.65	0.00	0.00	37.96	0.30	1.20	0.16	0.15	0.38	1.18	6.28	0.17	3.88
18	3.36	35.80	2.96	0.00	0.00	43.31	2.79	1.37	0.19	0.17	0.02	1.06	7.13	0.19	1.65
19	2.81	41.34	2.47	0.01	1.40	39.02	0.63	1.10	0.15	0.14	0.11	1.11	5.98	0.16	3.58
20	4.67	6.08	4.09	0.00	0.00	65.97	0.31	1.82	0.32	0.24	0.06	1.11	10.01	0.27	5.04
21	2.83	41.69	2.52	0.01	1.26	38.90	0.41	1.10	0.15	0.14	0.20	1.01	6.05	0.16	3.57
22	2.85	41.64	2.52	0.00	0.42	39.52	1.35	1.11	0.17	0.15	0.03	1.06	6.09	0.16	2.94
23	2.66	35.82	2.38	0.00	0.21	36.80	11.80	1.05	0.15	0.14	0.00	0.99	5.69	0.15	2.16
24	2.63	32.91	2.31	0.00	0.01	36.78	17.29	1.02	0.17	0.14	0.00	0.93	5.63	0.15	0.04
25	2.62	33.29	2.31	0.00	0.00	36.23	17.42	1.02	0.15	0.13	0.00	0.98	5.57	0.15	0.14
26	2.81	40.56	2.50	0.00	0.14	39.19	3.30	1.11	0.16	0.14	0.02	1.07	5.99	0.16	2.86
27	2.87	37.19	2.52	0.00	0.02	39.85	8.38	1.13	0.17	0.15	0.00	0.88	6.15	0.16	0.51
28	2.92	34.83	3.08	0.00	0.01	40.43	9.90	1.15	0.16	0.15	0.00	0.72	6.24	0.17	0.23
29	2.88	41.74	2.56	0.00	0.46	40.05	0.50	1.14	0.17	0.15	0.04	1.00	6.14	0.17	3.02
30	2.72	37.28	2.37	0.00	0.13	37.11	10.20	1.05	0.17	0.14	0.00	0.99	5.78	0.15	1.92
31	3.21	35.61	2.85	0.00	0.43	44.66	0.30	1.26	0.18	0.17	0.09	0.57	6.86	0.18	3.65
32	2.99	32.55	2.67	0.00	0.14	41.73	9.35	1.19	0.18	0.15	0.00	0.63	6.39	0.17	1.85
33	2.86	42.23	2.50	0.00	0.13	39.64	0.30	1.12	0.15	0.15	0.25	0.83	6.10	0.16	3.59
34	3.21	36.59	2.85	0.00	0.12	44.53	0.29	1.27	0.18	0.16	0.05	0.72	6.85	0.19	3.00
35	2.84	42.07	2.52	0.00	0.44	39.69	0.30	1.11	0.16	0.15	0.08	1.07	6.06	0.16	3.35
36	3.06	39.39	2.68	0.00	0.07	42.30	0.30	1.19	0.17	0.16	0.05	0.81	6.51	0.17	3.15

Table C.22: Experimental results from research by Tata Steel in Ijmuiden.

No.	Fe2O3	met.Fe	Iron Metallization Degree (%)
1	37.00	0.52	1.39
2	46.58	0.31	0.67
3	67.06	0.31	0.46
4	37.29	0.41	1.08
5	38.14	1.26	3.20
6	33.98	19.61	36.59
7	34.20	22.03	39.18
8	37.41	9.75	20.67
9	38.97	11.36	22.58
10	41.47	12.90	23.73
11	37.96	0.58	1.52
12	35.17	15.22	30.20
13	46.10	0.30	0.64
14	45.85	12.43	21.33
15	39.60	0.30	0.75
16	47.06	6.98	12.92
17	37.96	0.30	0.78
18	43.31	2.79	6.05
19	39.02	0.63	1.60
20	65.97	0.31	0.47
21	38.90	0.41	1.05
22	39.52	1.35	3.31
23	36.80	11.80	24.28
24	36.78	17.29	31.98
25	36.23	17.42	32.47
26	39.19	3.30	7.76
27	39.85	8.38	17.38
28	40.43	9.90	19.68
29	40.05	0.50	1.22
30	37.11	10.20	21.55
31	44.66	0.30	0.67
32	41.73	9.35	18.30
33	39.64	0.30	0.75
34	44.53	0.29	0.66
35	39.69	0.30	0.74
36	42.30	0.30	0.71

 Table C.23: Metallization degree from research by Dr. Peter Beentjes from Tata Steel in IJmuiden.









Figure C.4: EDS signal of mapping of reacted sample 1 (top) and sample 2 (bottom) at 1000°C given in Figure 4.17.

#### C.6. Multistage Removal of Lead and Zinc





Figure C.5: EDS signal of mapping of dust generated at 800°C from sample 1 given in Figure 4.19.



Figure C.6: EDS signal of mapping of dust generated at 950°C from sample 1 given in Figure 4.19.



Figure C.7: EDS signal of mapping of dust generated at 1100°C from sample 1 given in Figure 4.19.



Figure C.8: EDS signal of mapping of dust generated at 800°C from sample 2 given in Figure 4.20 (1).



Figure C.9: EDS signal of mapping of dust generated at 800°C from sample 2 given in Figure 4.20 (2).



Figure C.10: EDS signal of mapping of dust generated at 950°C from sample 2 given in Figure 4.21.



Figure C.11: EDS signal of mapping of dust generated at 1100°C from sample 2 given in Figure 4.22.

#### C.7. Material Balance Calculation

Bentonite	%wt (oxide)	conversion scale	%wt (elemental)
Fe	3.34	1.00	3.34
CaO	5.03	0.71	3.59
MgO	3.51	0.60	2.12
SiO2	53.20	0.47	24.87
Al2O3	17.60	0.53	9.31
TiO2	0.73	0.60	0.44
MnO	0.08	0.77	0.06
P2O5	0.16	0.44	0.07

Table C.24: Bentonite composition for material balance calculation.

Table C.25: Solid residue and HMF composition for material balance calculation.

Element	Initial/Raw	Residue After 800	Residue After 1000
Ва	0.02	0.02	0.03
С	38.95	43.75	47.25
Са	1.59	1.92	1.92
Cd	0.01	0.00	0.00
Fe	24.75	27.00	33.75
Mg	0.57	0.68	0.73
Mn	0.10	0.11	0.12
Pb	0.51	0.01	0.01
S	1.06	1.17	1.25
Ti	0.08	0.10	0.12
V	0.02	0.03	0.03
Zn	2.60	2.14	0.04
Si	2.50	2.60	2.60
Al	1.45	1.56	1.71
CI	2.08	0.43	0.26
Р	0.16	0.07	0.07

Table C.26: Gas produced at 800°C and 1000°C based on stochimetry carbon consumption.

Reacting Temperature	800	1000	°C
Carbon Consumed	0.29	0.67	kt/year
Gas Produced (CO)	0.67	1.57	kt/year

#### Table C.27: Mass Balance Calculation (in kt/year).

ltem	Flue Dust	Bentonite	Iron Chloride	Fines	Pellets	Pb-bearing dust	Solid Residue	Zn-bearing dust	HMF
Gas (CO)	0.00	0.00	0.00	0.00	0.00	0.67	0.00	1.57	0.00
Solid	20.00	0.10	0.93	2.23	18.80	2.05	16.08	1.05	13.46
Total Weight	20.00	0.10	0.93	2.23	18.80	2.72	16.08	2.62	13.46

Table C.28: Material Balance Calculation.

Item	Flue Dust		Bentonite		Iron C	hloride	Fines		Pellets		Pb-bea	ring dust	Solid F	Residue	Zn-bea	ring dust	HMF	
Element	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year	wt%	kt/year
Ва	0.02	0.00	-	-	-	-	0.02	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.03	0.00
С	40.95	8.19	-	-	-	-	38.95	0.87	38.95	7.32	-	-	43.75	7.04	-	-	47.25	6.36
Ca	1.65	0.33	3.59	0.00	-	-	1.59	0.04	1.59	0.30	0.18	0.00	1.83	0.29	3.48	0.04	1.92	0.26
Cd	0.01	0.00	-	-	-	-	0.01	0.00	0.01	0.00	0.06	0.00	-	-	-	-	-	-
Fe	24.70	4.94	3.34	0.00	28.09	0.26	24.75	0.55	24.75	4.65	6.50	0.13	28.10	4.52	8.52	0.09	32.90	4.43
Mg	0.59	0.12	2.12	0.00	-	-	0.57	0.01	0.57	0.11	0.25	0.01	0.64	0.10	0.42	0.00	0.73	0.10
Mn	0.10	0.02	0.06	0.00	-	-	0.10	0.00	0.10	0.02	0.01	0.00	0.11	0.02	0.12	0.00	0.12	0.02
Pb	0.54	0.11	-	-	-	-	0.51	0.01	0.51	0.10	4.63	0.09	0.01	0.00	0.05	0.00	0.01	0.00
S	1.11	0.22	-	-	-	-	1.06	0.02	1.06	0.20	0.54	0.01	1.17	0.19	1.90	0.02	1.25	0.17
Ti	0.09	0.02	0.44	0.00	-	-	0.08	0.00	0.08	0.02	0.00	0.00	0.10	0.02	0.04	0.00	0.11	0.02
V	0.02	0.00	-	-	-	-	0.02	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.03	0.00
Zn	2.73	0.55	-	-	-	-	2.60	0.06	2.60	0.49	7.01	0.14	2.14	0.34	32.38	0.34	0.04	0.01
Si	2.50	0.50	24.87	0.02	-	-	2.50	0.06	2.50	0.47	2.57	0.05	2.60	0.42	6.49	0.07	2.60	0.35
AI	1.48	0.30	9.31	0.01	-	-	1.45	0.03	1.45	0.27	1.05	0.02	1.56	0.25	1.93	0.02	1.71	0.23
CI	0.54	0.11	0.44	0.00	35.66	0.33	2.08	0.05	2.08	0.39	15.74	0.32	0.43	0.07	3.26	0.03	0.26	0.04
Р	0.17	0.03	0.06	0.00	-	-	0.16	0.00	0.16	0.03	0.94	0.02	0.07	0.01	0.09	0.00	0.07	0.01
Total	77.20	15.44	44.23	0.04	63.75	0.59	76.45	1.70	76.45	14.37	39.49	0.81	82.55	13.28	58.70	0.61	89.03	11.99

#### C.8. Economic Assessment Calculation

No	Itom	kt/voor	Cost (€/t)		Returns (€/t)		Total Co	st (€/year)	Total Returns (€/year)		
NO	item	Ku'year	Min	Max	Min	Max	Min	Max	Min	Max	
1	BF Sludge	1.000	€-	€-	€ 70.0	€ 170.0	€ -	€ -	€ 70,000	€ 170,000	
2	Bentonite	0.005	€ 120.0	€ 140.0	€ -	€-	€ 600	€ 700	€-	€-	
3	Iron Chloride	0.046	€-	€ 100.0	€ -	€-	€ -	€ 4,630	€-	€-	
4	Pelletizing	1.051	€ 15.0	€ 25.0	€-	€-	€ 15,770	€ 26,283	€-	€-	
5	Rotary Kiln #1	0.940	€ 32.4	€ 150.0	€-	€-	€ 30,452	€ 140,979	€-	€-	
6	Pb-bearing dust	0.103	€-	€ 300.0	€-	€-	€ -	€ 30,829	€-	€-	
7	Rotary Kiln #2	0.804	€ 21.6	€ 100.0	€-	€-	€ 17,369	€ 80,410	€-	€-	
8	Zn-bearing dust	0.052	€-	€-	€ -	€ 720.0	€ -	€ -	€-	€ 37,334	
9	HMF Residue	0.673	€-	€ 50.0	€-	€ 100.0	€ -	€ 33,662	€-	€ 67,325	
			Total				€ 64,190	€ 317,493	€ 70,000	€ 274,658	

Table C.29: Economic assessment calculation of BF sludge recycling.

Scenario	€/year	€/year per t
Worst case scenario	-€ 247,493	<i>-</i> € 247
Best case scenario	€ 210,469	€ 210

# C.9. Life Cycle Assesment Calculation

Table C.30: Description of impact category used in the LCA.

Impact Category	Description	Source	Ref.
agricultural land occupation (ALOP)	Land use/change impacting ecosystem	Industrial, residential, agriculture	[76]
climate change (GWP100)	Change of Earth's temperature and weather	Greenhouse gases	[ <mark>76</mark> ]
freshwater ecotoxicity (FETPinf)	Pollutants hazardous to nature	Pesticides, chemicals	[ <mark>76</mark> ]
freshwater eutrophication (FEP)	Excessive nutrients into soil	Waste water	[ <mark>76</mark> ]
human toxicity - (HTP)	Pollutants hazardous to human health	Heavy metals, toxic chemicals	[ <mark>76</mark> ]
ionising radiation (IRP_HE)	Radiation damage to DNA	Radioactive materials	[ <mark>76</mark> ]
marine ecotoxicity (METP)	Pollutants hazardous to nature	Pesticides, chemicals	[ <mark>76</mark> ]
marine eutrophication (MEP)	Nitrogen enriched soil	Agriculture, fertilizers	[ <mark>76</mark> ]
natural land transformation (NLTP)	Land use/change impacting ecosystem	Industrial, residential, agriculture	[ <mark>76</mark> ]
ozone depletion (ODP)	Decrease in thickness of ozone layer	Br, Cl, CFCs, nitrogen substances	[ <mark>76</mark> ]
particulate matter formation (PMFP)	Aerosol (Anthropogenic particulates)	Combustion, mechanical processing	[ <mark>76</mark> ]
photochemical oxidant formation (POFP)	Smog containing ozone (O3)	Combustion, industrial process	[ <mark>76</mark> ]
terrestrial acidification (TAP100)	SO2 and NOx pollutants in soil	Agriculture, fossil fuels	[ <mark>76</mark> ]
terrestrial ecotoxicity (TETPinf)	Pollutants hazardous to nature	Pesticides, chemicals	[ <mark>76</mark> ]
urban land occupation (ULOP)	Land use/change impacting ecosystem	Industrial, residential, agriculture	[ <mark>76</mark> ]

Table C.31: Calculated impact assessment in six different scenarios.

Impact category	2025 BAU	2050 BAU	2025 440 ppm	2050 440 ppm	2025 Renew	2050 Renew	Reference unit
ALOP	16.15	16.88	5.37	4.48	7.18	2.29	m2a
GWP100	1282.75	1274.20	890.60	262.02	744.86	310.61	kg CO2-Eq
FETP	0.64	0.64	0.42	0.36	0.52	0.46	kg 1,4-DCB-Eq
FEP	0.00	0.00	0.00	0.00	0.00	0.00	kg P-Eq
HTP	180.33	180.33	167.84	163.00	164.32	159.42	kg 1,4-DCB-Eq
IRP_HE	1126.19	1012.08	991.53	1135.73	1.27	1.14	kg U235-Eq
METP	0.78	0.78	0.60	0.52	0.68	0.50	kg 1,4-DCB-Eq
MEP	0.54	0.53	0.42	0.26	0.38	0.37	kg N-Eq
NLTP	0.80	0.88	1.04	0.94	1.72	2.62	m2
ODP	0.00	0.00	0.00	0.00	0.00	0.00	kg CFC-11-Eq
PMFP	0.59	0.59	0.43	0.29	0.42	0.35	kg PM10-Eq
POFP	6.77	6.75	6.54	6.08	6.40	6.26	kg NMVOC
TAP100	1.66	1.65	1.25	0.84	1.24	0.93	kg SO2-Eq
TETP	1.03	1.03	1.03	1.03	1.03	1.03	kg 1,4-DCB-Eq
ULOP	3.49	3.60	1.57	1.35	2.18	1.51	m2a

Table C.32: Total environmental price considering all impact categories in six different scenarios.

Impact category	2025 BAU	2050 BAU	2025 440 ppm	2050 440 ppm	2025 Renew	2050 Renew
ALOP	€ 0.42	€ 0.44	€ 0.14	€ 0.12	€ 0.19	€ 0.06
GWP100	€ 73.12	€ 72.63	€ 50.76	€ 14.94	€ 42.46	€ 17.70
FETP	€ 0.02	€ 0.02	€ 0.02	€ 0.01	€ 0.02	€ 0.02
FEP	€ 0.01	€ 0.01	€ 0.00	€ 0.00	€ 0.00	€ 0.00
HTP	€ 28.49	€ 28.49	€ 26.52	€ 25.75	€ 25.96	€ 25.19
IRP_HE	€ 53.27	€ 47.87	€ 46.90	€ 53.72	€ 0.06	€ 0.05
METP	€ 0.01	€ 0.01	€ 0.00	€ 0.00	€ 0.01	€ 0.00
MEP	€ 1.68	€ 1.66	€ 1.29	€ 0.80	€ 1.20	€ 1.16
NLTP	€ 0.02	€ 0.02	€ 0.03	€ 0.02	€ 0.04	€ 0.07
ODP	€ 0.00	€ 0.00	€ 0.00	€ 0.00	€ 0.00	€ 0.00
PMFP	€ 40.75	€ 40.70	€ 29.66	€ 20.06	€ 29.20	€ 23.83
POFP	€ 14.22	€ 14.17	€ 13.74	€ 12.77	€ 13.44	€ 13.15
TAP100	€ 8.97	€ 8.92	€ 6.73	€ 4.52	€ 6.70	€ 5.02
TETP	€ 9.17	€ 9.17	€ 9.15	€ 9.13	€ 9.17	€ 9.12
ULOP	€ 0.09	€ 0.09	€ 0.04	€ 0.04	€ 0.06	€ 0.04
Total	€ 230.24	€ 224.21	€ 184.99	€ 141.89	€ 128.51	€ 95.42