Selective Removal of Zinc From BF High Zinc Filter Cake

Conversion of a Waste Stream into a Recyclate

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Geoscience and Engineering & Material Science and Engineering

Selective Removal of Zinc From BF High Zinc Filter Cake

Conversion of a Waste Stream into a Recyclate

MASTER OF SCIENCE THESIS

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Abstract

At Tata Steel IJ muiden a part of the blast furnace dust is not recycled to prevent too high zinc levels in the blast furnace. Blast furnace dust is first separated from the off-gas into dry dust and sludge. The dry dust is collected in a dust bag and is directly transported to the sinyter plant. Then the sludge is separated by size through hydrocyclones in the water treatment plant. There are three fractions separated from the sludge. The smallest size fraction or the zinc rich fraction, the hydrocyclone cut size for this fraction is 10 μ m and is stored on site as hazardous waste. The two other fractions are zinc low and zinc middle (or zinc third step) and the zinc middle fraction used to be recycled based on the zinc balance in the blast furnace. However since the beginning of 2015 zinc levels in the blast furnace do not allow the zinc middle fraction to be recycled, which results in more hazardous waste that is dumped.

Over the past years research is conducted in order to find a treatment for the stored high zinc blast furnace dust. The aim of a treatment process is the removal of heavy metals and to recycle carbon and iron species from the dumped material. It is expected that the high zinc blast furnace sludge can be recycled when it is treated by hydrometallurgical processing. Before a treatment is selected a literature study is conducted that is focussed on existing hydrometallurgical processes that treat iron or steel making waste. Based on this literature study an ammoniacal leaching process is selected. Ammoniacal lixiviants are selective towards zinc over iron and its compounds, ammonia can be recycled and it is not yet used to treat this type of waste.

The high zinc filter cake is analyzed at the CRC and ANA laboratories at Tata Steel IJ muiden. It is confirmed that both ZnO and ZnS (wurtzite) are present, however over 2/3 of the zinc is present on ZnS. ZnS has to be oxidized to ZnO before zinc dissolution can take place as the zinc ammine complex $(Zn(NH_3)_4^{2+})$.

Laboratory experiments are conducted with the selected ammoniacal treatment, three lixiviant types are studied: $NH_3-(NH_4)_2CO_3$, NH_3-NH_4Cl and $NH_3-(NH_4)_2SO_4$. From the studied parameters the highest zinc removal (69%) is reached at 30 °C, with $NH_3-(NH_4)_2SO_4$ and 20 L/h O₂. It is found that without the addition of an oxidant (O₂) the zinc removal decreased with only 10%. This indicates that the oxidation of ZnS is likely to be influenced by other elements like lead present in the high zinc filter cake. The pH is not controlled in these experiments, it is only monitored. It is found that the pH is not directly related to the reaction rate (kinetics).

The dissolution of zinc shows a waving trend for all three lixiviant types. Zinc hydroxide formation and precipitation occurs in the same pH range as the stability of $\text{Zn}(\text{NH}_3)_4^{2+}(s)$. When the pH in the reactor is outside the insoluble pH range of $\text{Zn}(\text{OH})_2$, then the removal of zinc will increases when the pH decreases further away from the insolubility range.

In future research the influence of other elements, present in the material, on the leaching mechanisms should be studied. And the mechanism responsible for zinc dissolution needs to be unraveled. PARC (Phase Recognition and Characterization) analysis can identify in what crystal structures zinc can be found.

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Chapter 1

Introduction

Steel making starts with the production of hot metal. During this process the iron oxides are reduced, impurities such as silicon, sulfur and phosporus are removed and hot metal is produced. An illustration of the iron and steel production flowsheet is given in Figure 1-1. The illustration shows what charge is needed for the blast furnace and the basic oxygen furnace. At Tata Steel IJmuiden the final product of steel making is rolled and coated steel. Figure 1-2 shows the main features of a blast furnace [1]. At the top of the furnace is charged with coke, slag formers and iron bearing feed like pellets, sinter and lumps of iron ore. Slag formers can be limestone, burnt lime, BOF slag, olivine and dolomite. The charge descends under the influence of gravity while carbon monoxide that is generated at the bottom travels upward, creating a counter-current movement.



Figure 1-1: Flowsheet illustration of iron and steel making [1]

The gas that leaves the blast furnace has a temperature about 160° C and is sent to a power plant [1]. Before the off gas can be used at the power plant it is cleaned. At Tata Steel

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Figure 1-2: Blast furnace iron making [1]

IJmuiden the off gas travels through a dry dust catcher then a wet cleaning step, the Bischoff washer. The Bischoff washer catches the dust and cools the off gas. Dry dust is referred to as flue dust, or grofstof as it is referred to in Figure 1-3. The flue dust is sent to the sinter plant. Blast furnace sludge leaves the blast furnaces and is transported to the water treatment plant by pipe or channel, where it is collected by the thickeners. In the water treatment plant the sludge is separated into three fractions. The zinc rich, zinc middle and zinc poor fractions leave the treatment plant as a filter cake. Zinc rich filter cake and the zinc middle fraction are stored on site. In Figure 1-4 it gives the simplified zinc cycle at IJmuiden.

Recycling of blast furnace dust is done in order to recycle the resources iron and carbon. Zinc inside the blast furnace can create scaffolds, destroy the lining and can cause gas blow out during tapping of the hot metal. In the best case blast furnace off gas could be recycled without recycling zinc. This means somewhere in the process there is an output needed. Next to zinc in raw materials and blast furnace dust, a large amount of zinc enters the steel making through galvanized steel scrap fed to the basic oxygen furnace. The steel making dust is currently recycled to the sinter plant. In the current situation a part of the zinc leaves the process as landfilled zinc rich blast furnace dust. The zinc compounds present in the (high zinc) blast furnace dust are zinc oxide (ZnO) and zinc sulfide (ZnS).



Figure 1-3: A simplified representation of flue dust leaving the blast furnace with the blast furnace off gas [2]

The presence of ZnS makes the blast furnace dust at IJmuiden unique. In literature published on removal of heavy metal from blast furnace dust other zinc is found in other zinc compounds. Treating zinc-bearing blast furnace dust is researched for many years. However recycling this material is not a common practice yet. Technical challenges of turning the BF sludge from a waste stream into a recycling stream are mainly based on material properties. These properties are the extremely small particle size; presence of heavy metals; the type of zinc compounds; the low zinc concentration versus the high concentration of iron.

To find a process that can deal with these material properties of the blast furnace dust both hydrometallurgical and pyrometallurgical processes have been researched over time. In this thesis based on a literature review a process to treat blast furnace dust is designed to selectively remove zinc and create a residue ready for recycling.

1-1 Motivation

In general landfilling of a waste stream is postponing what actually needs to be done. In the end landfilled material has to be relocated/contained safely or processed and so landfilling is basically storing the issue. Storing or landfilling **those amounts** of hazardous waste has environmental consequences if the material is not removed or strickly managed. With longterm storage of hazordous material containment is an issue, there cannot be any leakage or spills. And when the storage is filled, there will be need of new storage. As can be concluded, there is enough reason to find an alternative for storing or landfilling high zinc blast frunace dust.

To find an alternative for landfilling high zinc dust at the IJmuiden site is getting more important based on reasons from economical, environmental and social perspective. From an economical point of view the landfilled material contains over 70% of secondary carbon and iron that can be re-fed to the blast furnace. Environmetal reasons to develop a possible process for zinc rich dust are based on the hazards that come with landfilling heavy metals containing waste. The social and political motivation comes from ever stricter regulations of landfilling (hazardous) waste.



Figure 1-4: A schematic overview of the zinc cycle at IJmuiden

This research is part of a project at Tata Steel IJmuiden to find a solution for the zinc related issues on site. The properties of high zinc blast furnace dust and a treatment process are the focus during this research.

1-2 Research aim and objectives

The current situation of the landfilled high zinc blast furnace dust is described in the introduction, another option than landfilling is required for the high zinc dust in order to prevent any future problems with the landfill and to create a recycle of secondary raw materials. From this, the main research question is stated as:

Is the leaching treatment a selective and effective process to separate zinc from the high zinc blast furnace dust, in order to create a secondary resource for the blast furnace?

To get a better understanding of the propesed leaching process the main research question is supported by subquestions:

- 1. What is the controlling step in the leaching reaction of zinc (ZnS and ZnO)?
- 2. What mechanism explains the dissolution and precipitation of zinc?
- 3. How is the lixiviant recyclable?



Figure 1-5: A schematic representation of the relation between research question and objectives

4. What is the recovery limit to recycle the leaching residue?

The aim of this research project is to transform the high zinc BF dust into a low zinc secondary resource, mainly consisting of iron and carbonaceous species by alkaline leaching. Hereby is contributed to Tata Steel's project on heavy metal removal from iron and steelmaking dust. In order to answer the stated research questions objectives are listed below which support the aim of this research:

- 1. Conduct a literature study that shows what research is done so far and what type of process is worth researching. A literature review is written for Tata Steel IJmuiden.
- 2. Develop a concept process based on the literature study and test the concept by laboratory experiments.
- 3. Evaluate results from the laboratory experiments and discuss why the concept should or should not be further tested on.

In Figure 1-5 the relation between the research question and the set aims is shown.

It is hypothesised that ammoniacal leaching of high zinc blast furnace dust results in selective removal of zinc, leaving a residue that can be used as a secondary resource for the blast furnace.

1-3 Thesis outline

In this section the set up of the thesis is explained, Figure 1-6 showes the outline. First the project and its research questions is introduced, followed by a chapter on the project background where the project is discussed in more detail. Then in Chapter 3 the literature study and its result are given. Followed by Chapter 4 where the leaching concept from literature is tested by conducted laboratory experiments. The results are given and discussed in Chapter 5. In Chapter 6 conclucions and recommendations are found.



Figure 1-6: A schematic representation of the thesis outline is given

The scope of this project is focused on a treatment of the zinc rich filter cake, in order to prevent the need of storing or landfilling it.

This project is a small part of a bigger project to limit the recycle of zinc in the steel and iron making. However, it does not mean there is experimented with steel making dust from the oxygen converter.

The formation of zinc compounds that are found in the high zinc filter cake lies outside the scope of this project. Why ZnS (wurtzite) is found and how it is formed will not be discussed.

Chapter 2

Project Background

Zinc is naturally part of the raw materials fed to the blast furnace and it enters the blast furnace through recycling streams within the ironmaking and steelmaking plants. Zinc levels have to be controlled, since it has detrimental effects on the blast furnace lining, burden properties and the operation of making pig iron (Yang, 2014). Limiting zinc into the blast furnace is achieved by decreasing the zinc percentage in the recycling streams: the steel converter dust and the blast furnace dust that are recycled to the sinter plant.

In this chapter the origin of blast furnace dust is discussed, where zinc is found at the Tata IJmuiden site and how this Msc thesis project is part of the solution to the removal of heavy metals from recycling streams.

2-1 Zinc cycle at the site Tata Steel IJmuiden

Zinc is a circulating element in the production of hot metal and steel. Iron ore fed to the blast furnace is the source of zinc in hot metal production, for steel zinc coated scrap is the source. Basic oxygen furnace dust (oxykalkslik) is the main internal source of zinc to the overall zinc cycle at IJmuiden. This is found in the scheme of the zinc cycle at the IJmuiden site in Figures 2-1 and 2-2. Oxykalkslik is sent to the sinter plant, through the sinter this dust is fed to the blast furnace where zinc leaves in the pig iron, slag or dust. In 2014 around 110 kton of converter dust is recycled to the sinter plant, over 450 tonnes of zinc is recycled with this dust to the blast furnace through sintering [17].

In the blast furnace, again dust is formed that leaves together with the off gas at the top of the blast furnace. Blast furnace dust is separated from the off gas in two stages. First the coarse fraction is collected in a dry dust catcher and at a second cleaning stage the fine fraction is collected by wet separation (Bisschoff washer). Dry dust is recycled to the blast furnace through the sinter plant, this dust is referred to as the low zinc fraction. The blast furnace sludge is sent to the water treatment plant, where the sludge is separated in high zinc, middle and low zinc fractions. Through the zinc rich blast furnace sludge around 100 g/thm (ton hot metal) of zinc leaves the zinc cycle.

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Zn-balans IJmuiden AP2010-11 - bij inzet van alle Zn-rijke reststoffen behalve Filterkoek Zn-rijk door sturing Zn in schrot Getallen zijn tonnen Zn per jaar

Figure 2-1: The zinc cycle at the IJmuiden site between iron and steel making processing steps, for 2010 - 2011



TATA STEEL



In Figure 2-1 the zinc cycle at the IJmuiden site from the year 2010- 2011 is given, where the numbers indicate tonnes of zinc/year. Figure 2-2 gives the number of tonnes zinc that are circulated in the process in the year 2014. Between 2010 and 2014 the zinc cycle is changed, for example zinc input through scrap is increased as well as the amount of zinc that leaves the cycle by blast furnace dust middle and high zinc, which is stored. In 2014 the zinc circulated

back to the sinter plant from blast furnace dust is decreased and room is created for higher zinc input through galvanised scrap.

2-2 The blast furnace zinc cycle

As mentioned in the previous section, zinc is not only present in the blast furnace as it recycles through the entire iron and steel making plant. Zinc in blast furnace charge feeds the internal zinc cycle. Most zinc leaves the cycle stored as high zinc dust.

In the blast furnace process, numerous complex physical and chemical processes take place, which are correlated [18]. Elements that enter the blast furnace can have both negative and positive influences on the iron making process. The complex reactions that elements undergo inside the furnace and the effects of an element on the iron making process should be critically assessed. Zinc, a heavy metal like lead and cadmium, is a minor element in the blast furnace feed and it is considered a key element affecting the production of pig iron.

Compounds in the feed that contain zinc are oxides (ZnO), ferrite (ZnO.Fe₂O₃), silicates $(2ZnO.SiO_2)$ and sulphides (ZnS) [3]. Circulation of zinc in the furnace can be devided into reduction, vaporisation, condensation and oxidation. The volatile character of zinc, makes ZnO easily reduced at temperatures higher than its melting point of 690 K. As it vaporizes in the lower furnace zones at temperatures between 1190 and 1275 K, the zinc evaporates and moves back to the upper zones of the blast furnace as shown in reaction 2-1. The reduction of other zinc compounds is given in reactions 2-2 and 2-3. Zinc is gassified between 1173 to 1373 K, at the same time temperature in that zone decreases and more coke is consumed [3]. Condensation of zinc on particles or lining occurs when the surrounding temperature is below the boiling point of zinc. When gaseous zinc gets in contact with water vapour and carbon dioxide it is oxidized back to ZnO. Zinc deposits on anything with a large surface area like the fine particles of the refractory lining of the upper part of the blast furnace shaft. Zinc is deposited on the lining surface, in the cracks and pores, a process known as zincdisintegration. Zinc-disintegration results in the deposition of carbon where ZnO acts as a catalyst and swelling in pores or cracks, deposited zinc oxide can melt and resolidify which brings a different thermal expansion than the surrounding lining.

$$ZnO(s) + [C] \rightleftharpoons Zn(g) + CO(g) \tag{2-1}$$

$$ZnO.Fe_2O_3 + 2CO \rightleftharpoons Zn(g) + 2FeO + 2CO_2 \tag{2-2}$$

$$ZnO.SiO_2 + CO \rightleftharpoons Zn(g) + SiO_2 + 2CO_2 \tag{2-3}$$

$$2Zn(g) + H_2O(CO_2) \rightleftharpoons 2ZnO(s) + H_2(CO)$$
(2-4)

Layered zinc-zinc oxide structures and ore-coke layers cemented with zinc can form on blast furnace lining, and these structures are referred to as scaffolds. As a result the blast furnace work volume, gas distribution and burden descending behaviour are affected. When the

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Figure 2-3: A simplified figure of the zinc present in a BF [3]

formation of scaffolds is not ressolved it could have serious concequences to the iron making process and workflorce safety: sudden drop of scaffolds may cause solidification of slag, destruction of tuyeres or sudden zinc release in the tapped slag and hot metal, leading to ZnO fumes exhausted in the casthouse.

Small particles with large surface areas moving upward can get zinc deposited on them and these particles either move with the burden or they travel with the off gas to the gas cleaning stage where the particles are called blast furnace dust. In Figure 2-3 the reactions of reduction, oxidation and circulation of zinc in the blast furnace are given.

It is mentioned how the recycling of iron, and especially steel making dusts increase the zinc percentage in the blast furnace feed, dusts and sludge. The limit of zinc intake depends on each individual blast furnace process. Esezobor and Balogun (2006) [3] have found that, according to the materials balance, for most iron making plants it has 15 - 27% of overall zinc released from the blast furnace through flue dust; 45 - 70% of zinc left in sludge at the off gas cleaning; 5 - 10% of zinc in hot metal and 5% with the blast furnace slag. This leaves 10 - 15% of zinc that is deposited on the blast furnace lining (refractory materials lined in side the BF). The zinc cycle is affected by many and complex factors: top pressure, hydrogen concentration, gas flow rate, heating profile of materials, type of charge and so on.

2-3 High zinc blast furnace dust

High zinc blast furnace dust is stored on site at Tata Steel IJmuiden. To get a better understanding of this complex material the characteristics and origin are presented in this section.

2-3-1 Origin and flow path

Zinc vapour reacts with CO or $CO_2(g)$ to ZnO in the upper part of the blast furnace when the surrounding temperature is below the boiling point of zinc [3]. A part of the newly formed zinc oxide descends back to the high temperature zone, the zinc particles that are carried up by the off gas may form build ups in the lining. Reoxidized zinc particles can form as well. Zinc oxide is also precipitated on particles traveling upward, when they do not recycle the particles end up in the gas cleaning system. Material collected in the dry collection of this system is referred to as dust and the material collected at the wet cleaning stage as sludge. The zinc rich sludge is originally part of the blast furnace dust that is exhausted together with the off gas. In the next part of this section the difference between high zinc blast furnace dust and blast furnace sludge or dust is explained.



Figure 2-4: Schematic water treatment plant, based on the water treatment flow sheet

From 1980 the gas cleaning system at IJmuiden is based on a closed water flow sheet, since 1983 the dust is separated into a zinc rich and a zinc poor fraction [19]. After the dust is separated by wet separation from the blast furnace off gas, it is sent as a sludge to the water treatment plant. The blast furnace sludge contains 2 g/L suspended solids. In the water treatment plant the sludge is separated by size using hydrocyclones and de-watered by filtration. Zinc tends to occur in the small particle size range, since the zinc rich fraction upper size lies below 10 μ m. A schematic representation of the water treatment plant is given in Figure 2-4.

The water after filtration is sent to the biological water treatment and the zinc rich filter cake is stored on site, the zinc middle fraction is either sent to the sinter plant or is stored. After the sludge is treated, the zinc rich filter cake has 60% solids and a zinc content of 2

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Figure 2-5: Mass and zinc balance in the hydrocyclones based on 100 t/day of dust [2]

to 8%. In the water treatment plant a zinc poor fraction is separated out as well, which is recycled to the sinter plant. The zinc, lead and cadmium content of the three separated blast furnace sludge fractions from June 2014 to December 2014 is shown in Figure 2-6. In this figure the blue, red and black lines are respectively the rich, middle and poor fractions. The fluctuations are caused by the hydrocyclones and blast furnace charge. When the zinc, lead or cadmium level changes parallel in all three size fractions then the fluctuation is caused by the change in blast furnace charge. And when the zinc, lead or cadmium level in the middle fraction is higher than in the rich fraction then the hydrocyclones do not work properly.

In Figure 2-5 the distribution of dust to either the low, middle or high zinc fraction is given and it is based on a dust inflow of 100 t/day. The high and middle fraction are responsible for the uptake of around 90% from the zinc inflow. The amount of zinc stored with the high and middle fractions depends on the efficiency of the hydrocyclones and blast furnace charge.



Figure 2-6: The amount of cadmium, lead and zinc in the three flue dust fractions; the zinc low, zinc middle and zinc high fraction. Data is based on Tata Steel's sampling system.

Around 40% of the solid particles that travel with the top gas is sent to the water treatment plant and the rest is separated from the gas in the first (dry) gas cleaning stage. Figure 1-3

shows the path of the top gas after leaving the blast furnace. The Zn-middle fraction will no longer be recycled as shown in the figure due to the zinc percentage in this fraction and the maximum intake of zinc in the blast furnace.

In a research done by Hoogovens R&D department [20], fines from the sludge settling pond and particles that are caught in foam on the water are sampled and analyzed. The content of the two products is examined using point count analysis (PCA), the C-reactivity, microscopy (OVL) and SEM-EDS analysis. After characterization ZnS is found in the particles (< 0.3 μ m) that are trapped in foam. Boudouard carbon is found as the biggest portion of carbon bearing species in both the foam (> 99%) and the sludge (> 70%). Also more recent studies confirm the presence of zinc sulphide as the main zinc-bearing phase in BF sludge. J.L.F Najorka [21] states in a report on de-zincing BF zinc-rich sludge, that ZnS is the zinc-bearing phase. XRD analysis done by the MSE department at the TU Delft in 2014, found zinc sulphide (wurtzite) in BF zinc-rich filter cake, see Table 2-1.

2-3-2 Material storage in landfill

High zinc blast furnace dust is stored on site since 1980. Due to the limit on blast furnace dust recycling the middle zinc fraction is now stored as well. From the water treatment plant the high and middle zinc fractions are transported by trucks to the storage site, and the material still holds up to 30 - 40 % water after it leaves the water treatment plant.

Constant surveillance for possible threads to health, safety and the environment like leakage from the storage to groundwater or soil is needed. In the past a part of the filter cake coming from water treatment are sold to external parties, but this activity stopped a few years ago. Drivers of new processes are based on environmental policies, raw material price and limitations on increasing productivity. Storage of the dust is a downstream process, by recycling the stored material upstream costs on blast furnace raw materials are decreased.

2-3-3 Material characteristics

M.K. Jha et al. [22] and Herck et al. [5] show that most of the researched blast furnace dust or sludge is a mixtures of oxides discharged from the top of a blast furnace. It is stated that the two most commonly identified zinc phases in steel and ironmaking dusts are zincite (ZnO) and zinc ferrite ($Zn_xFe_{3-x}O_4$) [9].

Zinc bearing species in the blast furnace at IJmuiden are (mainly) sulphides. The reason why sulphides are the main zinc compound in the iron making dust instead of oxides, ferrite $(Zn_xFe_{3-x}O_4)$ or franklinite $(ZnFe_2O_4)$ is not yet understood.

As Figure 2-6 shows, the lead and cadmium levels in the zinc rich fraction are like the zinc, higher than in the other dust fractions. The zinc-rich fraction is sampled and analysed. Based on these results and literature, possible-processing routes can be designed and tested on laboratory scale. Tables 2-1, 2-2 and 2-3 respectively show results of a XRD and two separate conducted total chemical analysis of the zinc rich blast furnace dust. The material consists of between 4 - 5% zinc, 35% carbon and 35% iron. Zinc, iron and carbon are the elements of interest. The concept process, designed based on the literature review, that transforms high

Compound name	Compound formula	$\mathbf{Percentage}\%_w$
Hematite	Fe_2O_3	17.11
Magnetite	Fe_3O_4	4.15
Wüstite	FeO	0.52
Würtzite	ZnS	1.97
Zinc oxide	ZnO	0.3
Calcium carbonate	$Ca(CO_3)_2$	19.17
Gypsum	$Ca(SO_4)(H_2O)_2$	0.78
Graphite	С	4.59

 Table 2-1:
 Quantitative XRD analysis on the BF Zinc rich fliter cake, conducted at CRC laboratorie, Tata Steel IJmuiden

Table 2-2: Elements present in the BF zinc rich filter cake, analysis conducted by CRM

Element	T_{Fe}	С	Zn	CaO	SiO_2	Al_2O_3	$^{\rm Pb}$	\mathbf{S}	Cl	LOI	SUM	Moisture
%	25.71	35.1	4.27	5.02	5.76	3.06	0.71	1.66	0.04	3.06	84.4	34.4

Table 2-3:	Total chemical	analysis on	the BF	zinc rich	filter	cake,	conducted	at ANA	laboratorie
Tata Steel	IJmuiden								

Compound or Element	%
CO_2	2.69
Met Fe	1.0
FeO metal	2.0
C	35.6
S	1.7
$GLV1000 (CO_2 + C)$	38.5
MgO	1.42
Al_2O_3	2.87
SiO ₂	5.70
P_2O_3	0.15
K ₂ O	1.44
CaO	4.87
TiO ₂	0.17
MnO	0.13
Fe ₂ O ₃	35.1
ZnO	4.91
PbO	0.62

zinc dust into a resource stream is focused on the removal of zinc and recovery of iron and carbon containing compounds.

The type of compounds that are found in the blast furnace zinc rich dust can indicate from which origin the blast furnace dust originates, from the feed or altered compounds. For example the fact that iron is mostly found in hematite means that it originates from the feed, and the compounds MgO, CaO, K_2O , Al_2O_3 and SiO_2 are used in slag formers. The zinc sulphide occurs a s wurtzite, the crytal structure that forms under high temperature and it can hold iron ((Zn,Fe)S).

Point	0 - k	Mg - k	Al - k	Si - k	S - k	K - k	Ca - k	Fe - k	Mo-k	Zn - k
1.2	11.88	0.99	2.96	5.88	8.77	4.05	4.44	39.09	-	21.94
1.5	19.44	2.40	4.06	7.15	6.85	3.84	3.51	33.97	-	18.77
2.2	21.72	2.20	4.18	8.46	2.57	2.38	2.18	34.98	4.02	17.32
2.3	27.83	2.11	4.63	7.36	4.90	4.00	2.22	33.73	-	13.21
2.4	24.81	1.75	3.75	7.06	3.79	3.56	2.59	34.72	3.62	14.34
2.6	21.84	1.60	4.25	8.13	4.34	3.23	4.58	39.66	-	12.18
5.4	30.34	1.80	4.23	6.33	10.48	3.53	-	27.71	-	15.08

Table 2-4: Elements foun	d together with zinc,	SEM-EDS analysis at MSI	E, TU Delft
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A batch of high zinc blast furnace filter cake, as it is received from the water treatment plant, was dried and used in analysis at TU Delft. Next to XRF and XRD analysis, SEM (Scanning Electron Microscopy) analysis was conducted on the dried filter cake in order to get a better understanding of the material properties. In Figures 2-7, 2-8, 2-9 and 2-10 SEI (Scanning Electron Imaging) the scale of the images is 10 μ m, these images show the diversity in size of the particles. From point analysis with SEM-EDS it is found that the zinc compounds cannot be found as pure particles, when zinc is found it always occurs with multiple elements. Table 2-4 is an overview of a few points where zinc is detected, iron is always present > 27 %, zinc content lies between 12 - 22 % and other elements (Al, Si, K and Ca) are present in each measurement. The images where the point measurements come from are given in the appendix.



Figure 2-7: Secondary Electron Image, sample analysis at MSE TU Delft

All SEI figures are scaled the same, especially in Figure 2-8 and 2-10 is shown how bigger particles are completely covered by smaller particles.



Figure 2-8: Secondary Electron Image, sample analysis at MSE TU Delft



Figure 2-9: Secondary Electron Image, sample analysis at MSE TU Delft



Figure 2-10: Secondary Electron Image, sample analysis at MSE TU Delft

2-4 Removal of heavy metals project at IJmuiden

From the start of the water treatment plant operation, the high zinc fractions have been the focus of research projects to find an alternative to storing high zinc dust on site in a landfill. Due to economical reasons, enough room on site and less strict regulations concerning hazardous waste in the past, researched processes are not (yet) implemented on site.



Figure 2-11: Simplified flow sheet of a RHF operation

Recent developments in the steel industry combined with future change in environmental policies concerning hazardous landfill, have made the high zinc waste stream a hot topic. Future processes to deal with high zinc dust are RHF (Rotary Hearth Furnace), HIsarna, Hydrometallurgical route or a combined hydro-pyrometallurgical route. In a RHF the blast furnace dust is reduced, first the dust is agglomerated before it is charged. The RHF flow sheet is shown in Figure 2-11. HIsarna is a new iron making process designed by joint industry partners, sintering or pelletizing is no longer needed.

The overall objective of the new research project (Converting Waste to Resource) is to convert heavy metal bearing waste streams into iron and carbon resources. The aim is to reduce the amount of landfill disposal, minimize the zinc load in the blast furnace and develop a cost effective bleeding stream. In order to recycle the waste, heavy metal removal is targeted at 80% by hydrometallurgucal selective leaching, combined processing routes are developed when the target is not reached. The objective of this thesis is to find a selective and efficient leaching process to treat the blast furnace high zinc filter cake from Tata Steel IJmuiden.

The company Paul Wurth has joined the current project on converting high zinc blast furnace dust into a resource. Parallel to this Msc thesis study of a selective leaching route, Paul Wurth has tested there own acidic leaching route called CIROVAL.

As is described in the literature review, ammoniacal leaching is not yet studied for high zinc blast furnace dust. The ammoniacal leaching route is the focus for this thesis project.

2-5 Summary

Zinc is an impurity element of iron and steel making processes and it is mainly caught in the recycled iron and steel making dusts.

Due to the hazardous effect of zinc on the blast furnace, a part of the blast furnace dust is stored on site which is a temporarely solution that cannot conitnue for much longer.

Both for the iron production and environment, a way out of the process for zinc is favoured. If zinc can be removed from the recycling dusts, less hazardous material has to be stored and more secondary iron and carbon species can be recycled.

Chapter 3

Literature Review: Removal of Zinc

This chapter provides an overview of the hydrometallurgical processes for removal or recovery of zinc from waste streams during iron and steel making. The discussed processes are divided by the type of lixiviant: acidic or ammoniacal. For each discussed process the selectivity, efficiency and environmental impact are considered. Treatment of zinc-bearing raw materials originating from iron and steel making is studied. Some of the processes are designed for another type of feed than iron or steel making waste. Waste streams from steel or iron making are dusts or sludges originated from processes in the iron and steel industry (e.g. BOF, EAF or BF sludge/dust). They are mentionted because of the mineralogical similarity of the zinc species (e.g. ZnS, ZnO). Recycling of flue dust and sludge originating from iron or steel making is not a common practice in the industry yet. Material properties of the waste, economics and plant implementation of a optional treatment are the challenges faced by iron and steel industry with changing a waste stream (e.g. BOF, EAF or BF sludge/dust) into a secondary resource. Based on the review, process requirements and characteristics of the material, a hydrometallurgical method (leaching) to treat the BF zinc-rich filter cake is suggested and this is further studied through laboratory research. The main purpose of the proposed method is to selectively remove the zinc, leaving iron in the solid phase, and if possible remove cadmium and lead. If the removal of zinc is sufficient, the solid residue can be recycled to the blast furnace as a secondary resource and the liquid phase should be enriched enough with zinc in order to extract it.

3-1 Acidic leaching of zinc

From literature acidic leaching is the most common treatment for removal of heavy metals from blast furnace dusts. It is also the most studied method in a research project Uitloogonderzoek from the former Royal Hoogovens. The Uitloogonderzoek was project of De Koninklijke Hoogovens between the years 1977 and 1987. They researched other options than storage of dusts and sludges originated from the iron and steel production.

3-1-1 Hydrochloric acid based lixiviant

Leaching treatments with hydrochloric acid for iron and steel maing wastes are further devided in chemical; oxidative and pressure leaching.

Chemical leaching of zinc

C.P. Heijwegen and W. Kat from the Environmental Control Department of the former Royal Hoogovens, have written an article [4] on the removal of zinc from three main zinc containing waste streams at the Royal Hoogovens site. The selected waste streams are blast furnace wet dust, fine primary BOF wet dust and secondary dry dust. The average chemical composition of the studied materials is given in Figure 3-1b. Secondary dry dust is the same material as the blast furnace high zinc fraction, the raw material in this research project. The secondary dry dust particle size distribution is given in Figure 3-1a.



Figure 3-1: In a) the particle distribution is given of the seconary dry dust, b) shows the chemical composition of the zinc - bearing waste streams [4]

Blast furnace wet dust is treated with concentrated hydrochloric acid, where retention time, pH and solids concentration are the tested parameters. Temperature was kept at 50 ° C, while the wash water was charged with flue dust. The reached zinc recovery was > 70% and 40 - 50 % for lead with pH 2 - 3 for 20 minutes of leaching and a solid concentration of 5 $\%_w$. Removal of zinc and lead from BOF wet dust through HCl leaching is not efficient. Upscaling the leaching treatment with HCl lixiviant is found to be an issue due to economics and the complexity of process chemistry. The best results were with a combination of leaching agents

HCl and NaCl, at 95 °C and oxygen injection. Leaching yields of both zinc and lead reached 70 - 80 %. A treatment that is effective for the processing of secondary dry dust is during this study assumed to be the same as for blast furnace wet dust. no recovery or yield is noted.

Removal of zinc with HCl leaching did not reach the desired recovery for any three the zinc containing waste streams. Selectivity, or the loss of iron, is not mentioned in the article except for the entire dissolution of the BOF sample. The studied lixiviant cannot be regenerated. In the analysis of feed and residue the species of zinc or the influence of different species of zinc on the recovery and efficiency of the process are not studied.

Oxidative acidic leaching of zinc

Hydrochloric acid is often used in the Uitloogonderzoek. The objective of Uitloogonderzoek was to develop a hydrometallurgical process for the treatment of zinc containing waste streams. In the beginning of the project parallel tests are done using HNO_3 , HCl and H_2SO_4 with and without the oxidant O_2 (g) [23]. In a report written on the parallel tests [24] hydrochloric acid had the best leaching results. The parameters set for the highest zinc recovery on leaching zinc from BF dust are pH=3, $50^{\circ}C$ for 60 minutes and the leaching efficiency for zinc was 98%, for lead 90 % and iron loss is 1 %. From the reports written in 1977 and 1978 the zinc compound are assumed to be ZnO and Zn_2SiO_4 . However in a report from 1983 [25] the addition of oxygen to HCl leaching could increase the zinc recovery to be over 95% while the negative side effect was 20-25% loss of iron. If oxidation is necessary for high recovery of zinc, this indicates ZnS to be present. Oxidation of sulfur is needed, before zinc can be dissolved through leaching. From analyses done during the Uitloogonderzoek a note written on the phase analysis suggests that zinc is present as ZnO, Zn_2SiO_4 and ZnS. None of the reports written in the Uitloogonderzoek discuss the reactions occuring in their conducted leaching experiments. The BF sludge characteristics have changed over time due the change of production conditions in the blast furnace.

In a research by P. van Herck et al. [5] a hydrometallurgical process to treat blast furnace sludge is discussed under both acidic and oxidizing conditions. This article is one of the few to suggest the presence of wurtzite in the blast furnace sludge. Experiments conducted under oxidizing conditions during leaching had a higher zinc recovery. Lead and zinc are removed in order to recycle the carbon and iron back to the blast furnace, as is the Tata Steels aim. The oxidizing agent iron(III)chloride (FeCl₃) was used to improve the leaching ability of zinc as a function of pH to recovery of 96%, instead of 78% with a 40% HCl solution. The recovery of lead improves as wel with the addition of FeCl₃ to 94%. For the best recoveries pH values should be below 1.5, together with a redox potential above 650 mV and a retention time of 2 hours. Figure 3-2 shows the leaching efficiency of both lead and zinc under oxidizing acidic conditions. The leaching efficiency decreases rapidly when the pH increases, for zinc at a pH over 3 and for lead over 2.

In a series of pilot scale tests, the oxidizer FeCl₃ is replaced by sodium hypochlorite (NaOCl) and the leaching solution is re-circulated. The pH value and the redox potential are the same as in the laboratory scale experiments. Recoveries were slightly lower than for the laboratory tests and the zinc recovery reached is 95% and lead 92% was recovered.



Figure 3-2: The leaching efficiency of zinc and lead using HCl and $FeCl_3$ lixiviant [5]



Figure 3-3: The pilot plant for treating BF flue dust [5]

Particle size (mm)	Element (%)							
	Zn (%)	Fe (%)	Cu (%)	S (%)	Acid insolubles (%)			
0.212-0.106	57.87	0.98	-	29.32	11.83			
0.106-0.075	59.97	0.16	-	30.15	9.72			
0.075-0.045	60.14	0.09	0.05	30.93	8.79			

Figure 3-4: Sphalerite concentrate composition [6]

In acidic leaching a variety of oxidation agents can be selected for oxidizing sphalerite. In the research by C. Uçar [6], sphalerite is leached in a HCl liquor with NaClO₃ to oxidize the sulfur from S^{2-} to S^{0} , as given in Equation 3-1.

$$2ZnS + 2NaClO_3 + 4HCl \rightleftharpoons 2ZnCl_2 + S + Na_2SO_4 + 2H_2O + CL_2(g)$$
(3-1)

In the sphalerite concentrate iron is present, with low quatities as shown in Figure 3-4. The highest zinc recovery of > 99 % from sphalerite concentrate, is found at 60°C, 1 M HCl, 1 M of NaClO₃ and a particle size of 45-75 μ m [6]. The dissolution of sphalerite in acidic leaching processes is explained by the shrinking core model.

Compared to the previous discussed process options, the research by Herck et al. [5] is the only one with a recirculating leaching solution, after the solids are removed by a horizontal belt filter as shown in Figure 3-3. In the Uitloogonderzoek another waste stream, the pickling line acid, was used as the leaching agent. Using two waste streams brings both economic and environmental benefits, while pickling line acid causes processing difficulties of the filtrate.

All treatment processes of Uitloogonderzoek, Herck at al., and by C. Uçar have reached > 95% zinc recovery. However the selectivity of the processes is in question, C. Uçar did not address the selectivity and in Uitloogonderzoek the iron loss varies (1 - 25 %) in the conducted experiments. Zinc species and their influence on the recovery or removal of zinc is rarely mentioned. Herck et al. have mentioned that the presence of ZnS was an option together with ZnO.

Elevated pressure leaching

Pressure leaching of the blast furnace zinc-rich filter cake is studied as part of the Uitloogonderzoek. Hydrochloric acid and pickling line acid (FeCl₂) are both used in this process, Figure 3-5 shows the matching flow sheet.

The pressure and pH are most important in controlling the precipitation of Fe^{3+} . The pressure is brought up to 10 bar using pure oxygen which helps to oxidize all the Fe(II) and Fe(III) and pH in the reactor is kept at 2.8. A high leaching rate is maintained with temperature > 110 °C. After leaching an iron rich filter cake and a zinc-lead rich filtrate remain. The quality of both products is controlled by controlling the pH. High selectivity and efficiency is achieved by two-step leaching In the first step pH value was 2.8 to 3 and in the second step it was set at 2.0 to 2.6. The recovery with the two-step leaching process is 98% for zinc, 94% for lead and 2% loss for iron [7].

In the zinc-lead rich filtrate the high chlorine level is considered as a down side for further processing. And setting up a plant scale leaching experiment was considered however the process control of working with the autoclaves was considered as an issue. Zinc removal in this process is the highest from all the processes that treat zinc bearing waste from iron and steel making processes.



Figure 3-5: The two step leaching process part of the Uitloogonderzoek of [7]

3-1-2 Sulphuric acid based lixiviant

Sulphuric acid can react with other elements or compounds in the feed than the intended zinc oxide. For example CaO in Reaction 3-2 or any other trace of carbonate, increases acid consumption during the leaching process [22].

$$CaO + H_2SO_4 \rightleftharpoons CaSO_4 + H_2O \tag{3-2}$$



Figure 3-6: Sulfuric leaching step is part of a zinc extraction process from blast furnace dust [8]

Figure 3-6 shows the hydrometallurgical processing route of a research on the removal of zinc from blast furnace flue dust to prevent landfilling of the dust [8]. The first step in the processing route is sulphuric acid leaching of the BF dust. Selective leaching is necessary to prevent iron dissolution together with zinc. Sulphuric acid is chosen for its selectivity towards zinc. Over 80% of the zinc present in the flue dust is removed however what type of zinc compounds are present is not discussed. The iron loss was neither mentioned or dicussed.

Sulphuric acid is often part of the solvent extraction/electro-winning (SE) method for extraction of zinc from a filtrate. The first stage of the SE process is diluted sulphuric acid leach to solubilize zinc. Other metals like iron and aluminum also get into solution with the zinc. By carefully raising the pH the insoluble metal hydroxides (Fe(OH)₂ and Fe(OH)₃) are precipitated out of solution [26].

In the Uitloogonderzoek sulfuric acid is used as well in the preliminary conducted experiments, however the recovery, efficiency and selectivity could not compete with the leaching agent hydrochloric acid.

Modified Zincex Process (MZP)

The leaching step in the Modified Zincex process (MZP) uses diluted sulfuric acid and sodium chloride at 40°C and sodium chloride at atmospheric pressure, followed by precipitation of impurities with lime [27]. Secondary zinc resources are fed to the MZP process, for example EAF dust. Diaz and Reuzife first presented the MPZ in a conference paper called 'Coping with Zinc Secondary Materials' (1991): "the Modified Zincex Route". MZP is discussed in several literature reviews for example by J. Steer (2008) [26], Y. Yang (2007) [28] and M.K. Jha (2001) [22].

$$ZnO + H + \rightleftharpoons Zn^{2+} + H_2O \tag{3-3}$$

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After leaching solid-liquid separation of the zinc containing filtrate and solid residue follows, through a thickener and rotary vacuum disc filter. Impurities are removed from the leach solution with addition of lime or limestone. The zinc rich filtrate is sent to the solvent extraction circuit there around 30 g/l zinc is extracted from the filtrate. The main materials treated by the MZP are EAF dust, Wealz oxides and galvanizing ashes. It is one of the few processes that is implemented on an industrial scale in Spain.

To make the process applicable for BF zinc-rich filter cake, there is an oxidizing step needed prior to the sulphuric acid leach to oxidize ZnS. Possibilities to recycle the leachate make MZP an interesting option from environmental point of view.

3-1-3 Other acidic based lixiviants

Steer and Griffiths (2013) [9] have written an article on the leaching of zinc from BF dust slurry by carboxylic acids and non-aqueous solvents. The samples are provided by Tata Steel Strip Products UK. Several types of carboxylic acids with different structures, functionality groups and acid strength were used to investigate the capability of extracting high levels of zinc. Carboxylic acids are partly dissociated weak acids, however by consumption of the anion RCOO⁻ (R is the organic substituent group) it facilitates further dissociation of the carboxylic acid. Reactions 3-4 and 3-5 show the stabilization of and consumption the carboxylate (RCOO⁻) anion.

$$RCOOH + H_2 O \rightleftharpoons RCOO^- + H_3 O^+ \tag{3-4}$$

$$RCOO^- + MO \rightleftharpoons RCOOM + H_2O$$
 (3-5)

 Table 4

 Extraction of zinc and iron using a variety of carboxylic acids at 1 mol/L.

Acid	Formula	рK _a	pН	Extraction	n
				Zinc (%)	Iron (%)
Propanedioic (malonic)	HOOC-CH ₂ -COOH	2.8 ^a 5.7 ^b	1.4	93.9	16.9
Prop-2-enoic (acrylic)	H ₂ C=CH-COOH	4.3	3.3	83.1	8.5
2-Hydroxypropane-1,2,3 tricarboxylic (citric)	СООН НООС-СН ₂ -С-СН ₂ -СООН ОН	3.1 ^a 4.8 ^b 5.4 ^c	1.0	82.6	32.2
Ethanoic (acetic)	H ₃ C-COOH	4.8	2.9	58.1	2.7
Ethanedioic (oxalic)	HOOC-COOH	1.2 ^a 4.1 ^b	0.8	18.5	31.2
Benzoic acid	C _c H _s – COOH	4.2	3.9	37.0	0.1

^a First proton dissociation.

^b Second proton dissociation.

^c Third proton dissociation.

Figure 3-7: The compared carboxilic acids [9]

In Figure 3-7 it is found that the highest recovery was achieved with the prop-2-enoic acid. Zinc and iron extraction is explained from two different perspectives. It is stated that the

zinc extraction follows the Lewis acid/base theory and iron extraction is said to follow the Bronsted-Lowry theory. Iron extraction is mainly affected by pH, as seen in Figure 3-7 and the highest iron extraction occurs with lower pH values.

$$2RCOOH + ZnO \rightleftharpoons (RCOO)_2 Zn + H_2 O \tag{3-6}$$

$$6RCOOH + Fe_2O_3 \rightleftharpoons 2(RCOO)_3Fe + 3H_2O \tag{3-7}$$

When the non-aqueous solvent methylbenzene is added (2:1 water:methylbenzene) the zinc extraction is around 85% and iron loss minimized and this was the highest recovery from all conducted experiments [9]. The feed analysis includes XRD characterization, here the zinc compound ZnO is found. Carboxylic acid lixiviant is shown to be effective and in combination with a non-aqueous solvent selective, towards removing zinc from BF sludge.

The next study is focused on the dissolution of sphalerite. Powder ore containing sphalerite is leached using nitric acid(HNO₃) and hydrogen peroxide(H₂O₂) A.O. Adebayo et al., (2006) [29]. When a sulphide mineral is leached by hydrogen peroxide in an acid medium the reaction is given in Reaction 3-8. If temperature rises sulphur will oxidize to a higher oxidation state such as sulphate. During the experiments conducted in this study elemental sulphur is detected, which supports Reactions 3-9 and 3-10.

$$S^{2-} + 4H_2O_2 \rightleftharpoons SO_4^{2-} + 4H_2O$$
 (3-8)

The dissolution of sphalerite in nitric acid is given in the reactions below:

$$3ZnS + 8HNO_3 \rightleftharpoons 3Zn^{2+} + 6NO_3^- + 3S + 2NO(g) + 4H_2O$$
 (3-9)

$$ZnS + 4HNO_3 \rightleftharpoons Zn^{2+} + 2NO_3^- + S + 2NO(g) + 2H_2O$$
 (3-10)

Extraction of zinc decreased with a decrease in particle size, for the 150 to 100 μ m range the extraction is > 80% while for the 75 to 5 μ m range the extraction was < 55%. The fraction of zinc dissolution from ZnS decreased as the particle size decreased (the surface area increased) and the reason behind this is not mentioned or discussed. Highest recoveries of zinc are reached with 11.4 M HNO₃ and 5.2 M H₂O₂ in the lixiviant. Implementation from environmental or economical perspective is not discussed.

3-2 Ammoniacal leaching of zinc

Alkaline leaching is known for its selectivity between iron and zinc and the difficulty of leaching zinc ferrite $(ZnFe_2O_4)$.

Selectivity between iron and zinc is one of the main reasons for a process to be applicable for turning the zinc-rich filter cake into a secondary resource. Ammoniacal solutions with ammonium chloride and ammonium carbonate are already used for treating several secondary sources because zinc ammine complexes are formed, leaving iron in the solid phase [22].

During the production of coke from coal in coke-oven batteries raw gas, coal tar and other components are washed away with water. The water is then treated and after the treatment valuable side products are delivered like tar, benzene, sulfur, COG and ammonia (ammonium sulfate) [1]. If ammonia leaching has promising leaching rates, the coking process by-product can be used as a base for the lixiviant.

UBC-Chaparral process described by D.B. Dreisinger et al in 1990 [10] and the EZINEX process are both based on ammoniacal leaching of electric arc furnace dust [30]. Electric arc furnace dust contains more zinc compared with blast furnace dust or sludge. Common zinc bearing species in EAF dust are ZnO, ZnCO₃ and ZnFe₂O₄. The UBC-Chaparral process is designed to detoxify EAF dust and maximize the recovery of metal values, while in the EZINEX process the objective is to recover high-grade zinc cathodes.

UBC - Chaparral process

The UBC-Chaparral process is discussed by D.B. Dreisinger in 1990 [10] and R.L. Nyirenda in 1991 [31]. In Figure 3-8 the complex flowsheet is given of the UBC - Chaparral process. The main process steps are described by R.L. Nyirenda: 1) Chloride removal by washing. 2) Free lime leaching step, to prevent high CO₂ consumption during the zinc leaching step. Calcium acetate (Ca(CH₃COO)₂ is formed. 3) From the calcium acetate formed in the previous step, gypsum (CaSO₄ · 2H₂O) is precipitated by the addition of sulfuric acid. 4) Ammoniacal ammonium carbonate leaching of lime leach residues to solubilize zinc oxide. 5) A clean up leaching step of the zinc leach residue with acetic acid, lead and cadmium are cemented out with zinc oxide. 6) A last cleaning step before disposal of the final residue.

Reactions 3-11 and 3-12 occur during leaching of zinc from the EAF dust. With this process zinc, lead and cadmium recovery were 60%, 60% and 85%. The leaching has been continued for two hours at room temperature and 1.5 L of 4 M $NH_3 - 0.75 M (NH_4)_2CO_3$ solution was used for 600 grams of lime leach residue, which contains around 21% zinc.

$$ZnCO_3 + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + CO_3^{2-}$$
 (3-11)

$$ZnO + 2NH_4^+ + 2NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + H_2O$$
 (3-12)

EZINEX process

The EZINEX (Engitec Zinc Extraction) process that is developed by the Italian company Engitec (M. Olper and M. Maccagni) is summarized by S.R. Rao [30], Y. Yang [28] and many others. Ammonium chloride leaching process is the foundation of the developed EZINEX process. Ammonium chloride - sodium chloride (NH₄Cl - NaCl) solution was used as the lixiviant and the retention time was 1 hour at 70 - 80 o C. Zinc ferrite will not dissolve as ZnO does. Dissolution of ZnO is given in Reaction 3-13. Iron oxides, ferrite and silica have not dissolved. After the leaching step, zinc is cemented out and the zinc metal is produced from the purified zinc amino chloride electrolyte by electrolysis. The anodic oxidation of ammonium chloride to nitrogen is shown in Reaction 3-14 [22].



Figure 3-8: Process flow sheet of the UBC - Chaparral process [10]

EZINEX is designed in order to create high-grade zinc. Impurities that get into solution like Cu, Pb and Cd are cemented out. For the purpose of leaching zinc from BF high zinc filter cake it is not necessary to remove those elements, it even creates a win - win situation if lead and cadmium are leached out with the zinc from the solid residue. Typical zinc concentrations of the leaching solution of EZINEX is 31 - 36 g/L and for the impurities < 5 mg/L.

$$ZnO + 2NH_4Cl \rightleftharpoons Zn(NH_3)_2Cl_2 + H_2O \tag{3-13}$$

$$3Zn(NH_3)_2Cl_2 + 2NH_4OH \rightleftharpoons 3Zn + 2H_2O + 6NH_4Cl + N_2$$
 (3-14)

Sphalerite concentrate

The dissolution reaction of sphalerite in an ammoniacal liquor is given in Reaction 3-15.

In ammonia leaching the oxidation of sulphide minerals is rather complex. The order of extraction as estimated from the reaction potential does not agree with those determined experimentally [32]. A sphalerite (ZnS) concentrate always contains small amounts of other sulfide species like CuFe₂, Cu₂, CuS, CoS, NiS, Sb₂S₃, FeS and FeS₂. Galvanic interaction between different sulphides plays an important role in the oxidation of sphalerite. In 1969 Majima and Peters have found that the oxidation of sulfides in ammonia at elevated temperatures occurs in decreasing order of oxidation: Cu₂S > CuS > CuFeS₂ > Sb₂S₃ > PbS > FeS = FeS₂ = ZnS. M.K. Gosh et al. [14] have studied the effect of other minerals to the dissolution of zinc sulphides.

$$ZnS + 4NH_3 + 2O_2 \rightleftharpoons Zn(NH_3)_4SO_4 \tag{3-15}$$

In the article written by S. Aydogan et al., in 2005 [11] the objectives were to investigate the main factors involving the leaching of sphalerite with oxygen in ammonia solutions. At elevated temperature and pressure leaching of sphalerite is found effective in an ammoniacal solution.

Particle Size	Zn	Cu	S	Fe
(µm)	(%)	(%)	(%)	(%)
-106 +75	65.17	0.01	32.11	0.02
-75 +63	65.04	0.03	32.05	0.06
-63 +45	65.73	-	32.38	-
-45 +38	66.08	-	32.55	-

Figure 3-9: Sphalerite concentrate content by chemical analysis [11]

The catalytic effect of copper during ammonia leaching of sphalerite is known. Various lead compounds are studied for the effect of their presence on the leaching of zinc sulphide. [33] PbS is found to be the lead compound that has the best effect in increasing the zinc recovery from zinc sulphide.

BOS underflow process

At British Steel a method with an ammonium chloride solution is tested to remove over 95% of the lead and zinc from BOS (basic oxygen steelmaking) clarifier underflow slurry [15]. The research started because the treatment of the slurry by hydrocyclones did not result in satisfactory separation. Burrows method [34] was used as an example, a measured amount of BOS clarifier underflow was stirred and heated with a measured amount of ammonium chloride solution. The main process reaction is probably as discussed in the process discussed by Burrows. Leaching conditions are the temperature between 90 and 102° C and a retention time of 4 hours. After 4 hours the residue and filtrate were separated by filtration. The feed analysis is shown in Table 3-1 and in Table 3-2 the overall results of the tested leaching method are given. The zinc source that was found from the raw material is ZnO. This study is set out to be an examination of interest and optimum process conditions are not attempted to define.

Element

 $\overline{\%}$

 Fe_T

70.25

 Fe_{Met}

6.85

Test Name	$\rm NH_4 Cl/H_2 O$	Recovered Fe $\%$ (solid phase)	Removed Zn $\%$ (liquid phase)
1	0.3000	84.15	64.32
2	0.1848	88.73	33.36
3a	0.0986	95.12	10.10
$3\mathrm{b}$	0.0986	87.95	10.85
4	0.1314	90.55	27.20
5	0.4509	86.06	96.90

Table 3-1: BOS clarifier underflow analyzed feed

S

0.081

 K_2O

0.41

С

1.03

 Na_2O

0.41

ZnO

2.69

PbO

0.185

Ρ

0.105

Table 3-2: BOS underflow leaching experiments [15]

3-3 Summary

In order to create a clear overview of the discussed treatments for selective zinc removal they are listed in the table below.

Lixiviant	Oxidant	Temperature $^o\mathrm{C}$	Feed	Recovery Zn $\%$	Loss Fe $\%$	$_{\rm pH}$
HCl	-	50	BF wet dust	> 70	-	2-3
HCl	O_2 (g)	50	BF dust - ZnO, $Zn_x SiO_y$, ZnS	90 - 98	1 - 25	3
HCl	FeCl ₃ and NaOCl	Room	BF sludge	95 - 96	32 - 49	$<\!\!1.5$
HCl	NaOCl	60	ZnS concentrate	> 99	-	-
$FeCl_2$		>110, 10 bar	BF high Zn dust	98	2	2-3
$H_2SO_4 \ 1 \ M$	-	Room	BF dust	> 80	5	-
H_2SO_4	-	40	EAF dust	-	-	-
Carboxylic acids	-	Ambient	BF dust	85.5	0.1	3.3
HNO_3	H_2O_2	30	Sphalerite	> 80	-	-
$NH_3 (NH_4)_2 CO_3$	-	Room	EAF dust	41.5	-	-
NH_4Cl - $NaCl$	-	70 - 80	EAF dust	31 - 35 g/l	-	-
$NH_3 - (NH_4)_2SO_4$	O_2	120	Sphalerite	55	-	10.80
$\rm NH_4Cl(aq)$	-	90 - 120	BOS underflow	95	14	-

Table 3-3: Overview of discussed processes

3-4 Selected leaching process

The studied processes for treating iron or steel making dust are found to be mostly acidic for BF dust and ammoniacal for steel making dust. As M.K. Jha et al. 3-3 state: the ammoniacal ammonium carbonate solution has been employed for the treatment of steel making flue dusts. Acidic leaching reaches a higher leaching rate than ammoniacal leaching. As removal of zinc through an ammoniacal route is not yet conducted on BF dust and due to the need of a selective treatment for the high zinc blast furnace dust, ammoniacal based leaching is selected for this research. Ammoniacal lixiviants are known for their selectivity and recyclability, these two characteristics apply to the need of recycling a high iron residue with limiting environmental consequences.

Chapter 4

Experiments

In this chapter the material and experimental methodolgy are described in detail. The first section describes materials used in the experiments, and in the following section the set up and experimental procedure together with the characterization methods are given.

4-1 Materials

High zinc blast furnace dust was filtrated in the end stage of the water treatment plant at Tata Steel IJmuiden. From there a filter cake sample was collected for laboratory experiments in this research project. Figure 4-1a shows a piece of dried high zic filter cake from the water treatment plant. After grinding the dried high zinc filter cake looks as shown in Figure 4-1b. experiment.



Figure 4-1: (a) The dried filtercake as received from Tata Steel IJmuiden (b) The ground filtercake, feed for leaching experiment

The cut size in the hydrocyclones is 10 μ m (Figure 2-4) for the high zinc fraction. The filter cake was received dry the material is different from the original wet filter cake. Dried filter cake forms a clump that is no longer able to form a sludge without an additional comminution step. In order to conduct leaching experiments on the dried filter cake it was first manually ground with mortal and pestle. The filter cake was ground until the dust reponds like a fluid. The particle size distribution of the ground filter cake was analysed at the CRC laboratory in IJmuiden with a laser analyzer Mastersizer 2000. In Figure 4-2 the particle size distribution (PSD) curve is given of ground high zinc filter cake and the D₁₀, D₅₀ and D₈₀ are respectively 2, 13 and 81 μ m. Except grinding the material, there is no further physical or chemical treatment conducted on the dried filtercake.



Figure 4-2: PSD diagram of ground filter cake, from CRC laboratory at Tata Steel IJmuiden

For the leaching liquor ammonia (28 $\%_w$ in water, Alfa Aesor) and three types of ammonium salt were used. The three types of ammonium salts are ammonium chloride (ACS reagent >99.5%, Sigma-Aldrich), ammonium carbonate (Meets analytical specification of NF, Sigma-Aldrich) and ammonium sulfate (Molecular Biology Grade >99%, Merck Millipore Corporation). Oxygen gas (99.5% pure) was purged into the leach reactor.

4-2 Experimental set-up and procedure

All the laboratory scale experiments are conducted on the batch filter cake that is received from Tata Steel IJmuiden. The filtercake is dried overnight at 106°C to remove all the residual moist present in the material. After drying the material is ground manually. For all the conducted experiments a stock of material is ground. A sample from the stock of ground filter cake is assumed to represent the characteristics of this material. This sample was analysed with XRD and XRF. The laboratory scale leaching experiments were conducted in a glass reactor, as shown in Figure 4-3a and 4-3b of leaching set up. The reactor is cylindrical shaped. On the reactor a Plexiglas lid is placed with round openings for the stirrer and oxygen purging tube. Through the tube oxygen is purged to the bottom of the reactor and the gas flow rate is monitored by the flow meter in between the gas cylinder and the reactor inflow. The stirrer evenly mixes oxygen through the leached sludge. In order to control the reactor temperature, the reactor is placed into a water bath that was heated by a heating plate.

The water bath is used to control temperature fluctuations that occur due to the leaching

R.A. (Rosa) Verburg



Figure 4-3: (a) Experimental set up (b) Sampling set up

reactions and the water bath acts like a buffer. As shown in Figure 4-3a the reactor is sealed with a lid, however for sampling it had to be lifted in order to reach the leach solution with a pipet and the pH meter as shown in Figure 4-3b. Samples taken from the leaching solution are sent for inductively coupled plasma (ICP) analyses, in the Characterisation section this method is discussed in detail. During experiments the pH meter is kept at the same temperature as the reactor which minimizes stabilizing time of the pH meter. The pH meter could not be kept in the leaching solution due to the alkaline nature of the leach solution. For experiments conducted at 60°C no sampling is conducted and these experiments are conducted multiple times in order to get samples at different leaching time. Samples taken from an experiment at 60° C would not be representative due to the high reaction rate and ammonia evaporation. At the beginning of each experiment the feed and water is added to the empty reactor to reach the desired temperature and the ammonium salt and ammonia solution are added simultaneously in a later stage. As soon as the ammonia-ammonium salt is added, the lid is placed and stirring starts together with oxygen purging. During an experiment samples are taken at set intervals in order to study the leaching behaviour over time. The sample size is limited (< 2 ml) to have nigligible effect on the leaching kinetics when the samples are taken during the experiment. Samples taken from the leach solution are filtrated and after filtration the liquid samples are analysed by ICP at Tata Steel IJmuiden. At the end of an experiment the residue is chemically analysed at Tata Steel and by XRD (MSE group, TU Delft), and leach solution is analysed by ICP. Analyses of samples and leach residue is conducted to find the selectivity and efficiency of the chosen leaching system.

4-3 Characterization

Knowledge of chemical composition, morphology, particle size distribution and other material properties of the feed support understanding of the studied process. Different methods are used for characterization of the feed, samples and residue.

XRD (X-ray diffraction) analysis is conducted on the feed and leach residues at the MSE department of TU Delft. For XRD analysis a Bruker D8 Advance diffractometer is used in combination with Bragg-Brentano geometry and a Lynxeye position sensitive detector. The data is evaluated with Bruker software. Amorphous compounds or compounds where the crystalline structure is altered due to deformation can not be characterized by XRD. From the XRD characterization of both the feed and residues the change of compound type and occurrence is found in the peak hight and shift. The focus in the XRD data is on the zinc species that are found in the residue compared to the feed after each leaching experiment.

The chemical analysis is conducted at Tata Steel IJmuiden and it takes several analyzing steps. First the carbon and sulfur content is determined in an Eltra analyser. A sample is placed in an oxygen flow and burned in a High Fregency induction furnace/oven. Carbon is converted to CO_2 and S to SO_3 the concentrations are measured by infra red detection. Then the XRF analysis is conducted and a sample is weight in a platinum cup on a known flux. The sample is pre-oxidized at 1000° C in a Linn furnace. Most of the carbon is converted to CO₂. The remainder of the sample is dissolved in a flux that is a mixture of Li-tetraboraat and Li-metaboraat. The mixture is poured into a Pt-dish this results in a pearl or glass-like disc on the dish. This disc is analyzed on the rontgen spectrometer (An Axios of PANanalytical). The sample is boiled in hydrochloric acid and CO_2 gas is released, which is captured in a mixture of pyridine and mono-ethanolamine. The mixture turns acidic when it captures CO_2 this acid is titrated with a base (TBAH) and the set up is original (in house) from the Royal Hoogovens period. For the analysis of minor metals as Zn, Pb and Cd a sample is put in a cealed teflon tube that is submurged and unlocked in aqua regia. The aqua regia and the teflon tube are placed in a microwave (CEM Mars 5). After the aqua regia mixture is filtrated the filtrate and residue are analyzed in ICP-OES (iCAP 6300 RADIAL of Thermo Fissher). ICP data is used to plot the recovery, these curves are plotted and fitted with the program Origin Pro 9.

XRD (CRC laboratory, Tata Steel), XRF (CRM) and total chemical analysis results (MLA laboratory, Tata Steel) are respectively given in Tables 2-1, 2-2 and 2-3. The material morphology and occurence of zinc are both studied with scanning electron microscopy and optical microscopy. SEM analysis (SEM-SEI, SEM-BEI and SEM-EDS) is conducted both at Tata Steel and at TU Delft, both with different sample preparation. At Delft the ground filter cake is placed on a sample holder with tape and at Tata Steel the ground filter cake is emulsified with a raisin and then polished as shown Figure 4-4a and 4-4b.



Figure 4-4: (a) Filter cake dust embedded in raison sample for SEM-EDS analysis at Tata Steel, IJmuiden (b) Close up of embedded dust sample

With SEM-BSE (Back scattered Electron Imaging) the contrast in compound specific weight is visible by shades of black to white, a lighter particle or area has a higher molecular weight. SEM-SEI (Secondary Electron Imaging) is used for analysis of the ground filter cakes' morphology. SEM-EDS (Energy Dispersive X-Ray Spectrometry) is an analytical tool that is used for elemental analysis of the sample. The SEM-EDS analysis complements the XRD and chemical analyses based on XRF, LECO and ICP by showing in what composition certain elements occur. In the case of high zinc filter cake zinc is the target element, and ZnS is the compound that is searched for.

Analysis and characterization of the filter cake is challenged by the small particle size. The forces between particles in the ground material (Van der Waals, electrostatic and adhesive forces) are impossible to break. This causes difficulty in analyzing separate particles in the dust.

Chapter 5

Results & Discussion

In this chapter the tested parameters and outcome of laboratory experiments are given. The results are presented and then the mechanisms that control the outcome of the experiments is discussed. In the first section is explained how XRF and XRD analysis results were combined in order to estimate what part of zinc can be found in ZnS or ZnO. The second section starts with an explaination of studied parameters. And follows up with subsections that are based on a changed parameter. For example in 5-2-1 the effect of ammonium salt type and different temperature is discussed on the outcome of the conducted experiments. The aim of the studied treatment was selectivity between zinc and iron therefore the thrird section is about selectivity. In the last section of this chapter a conceptual flowsheet is given that contains the studied treatment.

5-1 Characterization of zinc species in zinc rich filter cake

In section 2.3 some of the material characteristics of high zinc filter cake were already described. In this section the characterization is used for the estimation of zinc in ZnS and ZnO. The XRD spectrum of the leach feed (ground high zinc filter cake) is shown Figure 5-1. Not all of the zinc characterized in the XRF analysis is found in the quantified XRD analysis. In Table 5-1 the elements are given from both the elemental analysis and the elements found in the characterized compounds from XRD analysis.

In the XRD pattern of ground high zinc filter cake (Figure 5-1) the locations of zinc compounds ZnS, ZnO and $Zn(OH)_2$ are indicated and the main peaks of compounds without zinc. The XRD pattern of the original (untreated) sample is given in the same figure as the patterns of leaching residues for a better comparison between the peak intensity. In the first section where XRD patterns are compared the main non-zinc species are given. And in the following sections only the zinc compounds are indicated in the patterns.

In two ways the unidentified zinc is linked to either ZnO or ZnS. First combining the quatitative XRD and elemental analysis are combined. The second method only uses the elemental analysis by matching all sulfur to the zinc.



Figure 5-1: XRD pattern of ground high zinc filter cake, the position of ZnS, ZnO and $Zn(OH)_2$ peaks is shown.

5-1-1 Method 1

This method for matching zinc to sulfur makes use of both the elemental and quatitative XRD analysis. From XRD analysis is found that both ZnS (würtzite) and ZnO occur in the blast furnace zinc cake.

Table 5-1: Elements (%	\mathcal{W}_w	detected in 2	XRF	and XRD,	ANA	laboratories	Tata	Steel
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Element	C	0	Fe	\mathbf{S}	Mg	Al	Si	P	K	Ca	Ti	Mn	Zn	\mathbf{Pb}	н	Total
$\%_w$ Elemental analysis	36.33	20.70	27.18	1.70	0.86	1.52	2.67	0.07	0.60	3.48	0.10	0.10	3.94	0.58		99.82
$\%_w$ XRD analysis	7.33	16.12	15.38	1.25					9.32				1.56		0.02	50.98

Table 5-2: Zinc characterized in XRD and elemental analysis, ANA laboratories Tata Steel

Compound	$\%_w$ in XRF	$\%_w$ in XRD	$\%_w$ unidentified by XRD
ZnO	4.91	0.30	
ZnS	0	1.97	
Zn	3.94	1.56	2.38
\mathbf{S}	1.70	1.25	0.45
Ο	20.70	16.12	4.58

Table 2-1 gives the compounds found in XRD analysis. For compounds found in XRD and XRF the weight percentage of elements are calculated based on the molar weights. The weight percentages of elements present in XRD and XRF analysis are shown in Table 5-1. In the last column the total characterized weight percentage is given. From XRD analysis $51\%_w$ of the sample could be identified this leaves $49\%_w$ of the sample uncharacterized. A part of zinc is uncharacterized only 1.56% of the 3.95% zinc is found to be either ZnO or ZnS. In Table 5-2

ZnO, ZnS, Zn, O and S found by XRD and XRF are listed. Based on the ratio of ZnS and ZnO detected in XRD analysis, the undetected zinc is assigned to ZnS or ZnO by calculation. Equation 5-1 is determined how much of the undetected Zn goes to ZnO. Table 5-3 gives the result of Zn assigned to ZnO or ZnS together with the necessary S and O to complete the compounds.

$$Zn_{ZnO} = \frac{Zn_{ZnO}}{Zn_{ZnO} + Zn_{ZnS}} \cdot Zn_{undetected}$$
(5-1)

Table 5-3: Of the unidentified zinc in XRD analysis, what part is ZnO or ZnS. And what sulfur and oxygen is needed to bond to zinc for the compounds to excist.

Compound	$\%_w$ Zn	$\%_w$ of O needed	$\%_w$ of S needed	$\%_w$ O available	$\%_w$ S available
ZnO	0.37	0.073	-	4.58	-
ZnS	2.01	-	0.68	-	0.45

The necessary sulfur given in Table 5-3 is more than the sulfur available for ZnS. In the calculation of ZnO and ZnS the available sulfur is assigned to ZnS. This results in $1.37\%_w$ Zn for ZnS and $1.01\%_w$ Zn for ZnO. In Table 5-4 the final values of Zn in ZnO or ZnS are given. Expressed in percentages there is $32\%_w$ of ZnO and $68\%_w$ ZnS found in the material. The total percentage of calculated Zn $(3.94\%_w)$ together with Zn already found in XRD analysis agrees with the percentage of Zn found in XRF analysis. This calculated distribution of zinc in either ZnO or ZnS species is based on the XRD analysis that shows ZnS and ZnO as the zinc species present in the filter cake. The possibility that zinc occurs (hidden) in other crystal structures and small particles cannot be identified with XRD analysis.

Table 5-4: Assign Zn

Compound	$\%_w$ in XRD	$\%_w$ Zn
ZnO _{calculated}	1.21	1.01
$ZnO_{calculated+XRD}$	1.51	1.25
$ZnS_{calculated}$	1.82	1.37
$\text{ZnS}_{calculated+XRD}$	3.79	2.69
Total	5.30	3.94

5-1-2 Method 2

This method is based on the $\%_w$ of sulfur and zinc characterized from elemental analysis by the ANA laboratories at Tata Steel IJmuiden. For now it is assumed that all zinc is bound to sulfur. In elemental analysis 3.94 $\%_w$ zinc and 1.70 $\%_w$ sulfur is characterized (Table 5-1).

Table 5-5 shows that $3.47\%_w$ of the $3.94\%_w$ characterized zinc is bound as ZnS and $0.47\%_w$ as ZnO.

SEM-EDS analysis is conducted in order to identify ZnS particles in the filter cake and to confirm the analysis results from XRD analysis. However after research on the sample shown in Figure 4-4a (CRC laboratory, Tata Steel) and on filter cake dust placed on a sample

Element	$\%_w$
S available	1.70
S in ZnS (S/ZnS)	0.49
Zn for available S	3.47
Zn left for ZnO	0.47

Table 5-5: When all sulfur bonds to zinc

holder (TU Delft) no pure ZnS is detected. It can be stated that zinc probably occurs in other compounds next to pure ZnS and ZnO as found from XRD and XRF characterization. Crystal structures unkown to XRD databases can not be recognized during characterization. In Table 2-4 the point measurements from SEM-EDS analysis show that if zinc is present iron and oxygen represent over 50% of the detected elements. This does not prove that zinc and iron occur in the same crystal structure. And it neither proves that ZnS and ZnO are the only compounds where zinc is found. Accurracy of SEM-EDS point measurements in this sample can be influenced by the particle/grain size of the ground filter cake, the background of a measured point can have an influence on the analysis outcome. For a more detailed and reliable analysis of blast furnace sludge or filter cake microanalysis is needed.

5-1-3 Effect of material treatment

The material received from Tata Steel IJmuiden is after collection dried, then it was kept in a plastic container before it is used in this study. In a study part of the Uitloogonderzoek conducted at the previous Royal Hoogovens a difference in zinc recovery is found between aged (has beeen stored for a while) filter cake and 'fresh' filter cake. The aged filter cake was thought to contain $ZnSO_4$. This is not identified in the dried filter cake that is used in this study.

5-2 Studied parameters

Ammonia lixiviant is chosen for leaching zinc from the high zinc filter cake for its selectivity in forming a complex with zinc over iron. The reaction that is known from literature [10] is the formation of ammonia-zinc complex by the following reaction (5-2). In Figure 5-2 the (thermodynamic) stability, or Eh-pH diagram of the Zn - NH₃ - H₂O system at 25° C is given. The zinc ammine complex $(Zn(NH_3)_4^{2+})$ is soluble in the pH range 8 - 11. Outside the stable region for the zinc ammine complex, zinc hydroxide is stable and insoluble. In acidic solutions zinc is soluble as Zn^{2+} . This stable region of $Zn(NH_3)_4^{2+}$ depends on temperature. With increasing temperature the stability of $Zn(NH_3)_4^{2+}$ shifts towards a slightly more acidic pH region. The stability range of $Zn(NH_3)_4^{2+}$ is indicated (in blue) in all the following curves where the zinc dissolution is plotted, for example Figure 5-4a.



Figure 5-2: Eh - pH diagram of the Zn - NH₃ - H₂O system [12]

$$ZnO + 2NH_4^+ + 2NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + H_2O$$
 (5-2)

Reaction 5-2 shows that zinc oxide leaching is not a redoc reaction under oxidative ammoniacal conditions [10]. The oxidation state of zinc remains Zn(II).

In the high zinc filter cake ZnS is found with XRD analysis. In order for the zinc from ZnS to dissolve the sulfur has to oxidize. Dissolution of ZnS in both alkaline and acidic solutions is a challenge and oxidation to ZnO is important. The oxidation state of sulfur in ZnS is S^{2-} .

In the conducted experiment, it is tried to oxidize or reduce sulfur under ambient oxidative environment with high ammonia concentration. Reaction 5-3 gives the dissolution of ZnS in an oxidative ammoniacal medium [11].

$$ZnS + 2O_2 + 4NH_3 \rightleftharpoons Zn(NH_3)_4SO_4 \tag{5-3}$$

5-2-1 Selection of oxidant

At the early stage of laboratory research the ammonia concentration is increased from 2 - 13 M (34,06 - 221.39 g/L). The preliminary experiments are conducted with air as the oxidant. Due to low leaching recoveries of zinc the oxidant was switched from air to hydrogen peroxide (H₂O₂). However, hydrogen peroxide can react with iron ions (Fe²⁺ and Fe³⁺) present in the feed, which is not in favour for the oxidation of ZnS and the recovery of zinc.

$$Fe^{2+} + H_2O_2 \rightleftharpoons Fe^{3+} + OH^- + OH \cdot \tag{5-4}$$

$$Fe^{2+} + OH \cdot \rightleftharpoons Fe^{3+} + OH^{-} \tag{5-5}$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe^{2+} + HO_2 + H^+ \tag{5-6}$$

$$Fe^{3+} + OH_2 \rightleftharpoons Fe^{2+} + O_2 + H^+ \tag{5-7}$$

When H_2O_2 reacts with Fe^{2+} or Fe^{3+} ions radical species are formed. The radical species are HO_2 and OH. Fe^{2+} or Fe^{3+} can come from the compounds FeO, Fe_2O_3 or $MgFe_2O_4$. Equations 5-4 to 5-7 summerize the main chemical reactions [35]. The described reactions are the Fenton's reaction and Fenton-like reaction. The Rapid decomposition of H_2O_2 was observed in a pH 9.0 system [36]. After the addition of hydrogen peroxide, it did not increase the reocvery of zinc as expected since the oxidant is finally changed to pure O_2 (g).



Figure 5-3: 3D zinc tetra ammine complex $Zn(NH_3)_4$

The concentration of ammonia in the experiments conducted with hydrogen peroxide is raised up to 221.39 g/L. In the experiments following with O_2 to oxidize the sulfur in ZnS a high ammonia concentration of 204.36 g/L is maintained. For several reasons a high concentration of ammonia ensures enough ammonia ions in solution to surround zinc, in order to form the co-orditanion sphere of the zinc ammine complex (Figure 5-3). Precipitation of hydroxides is less likely to occur at this ammonia concentration both due to the abundance of ammonia molecules and the pH range is secured in which zinc ammine complexes are stable. Furthermore the ammonia concentration contributes to the leaching kinetics [37]. With this high concentration the best possible kinetics are provided in the studied ammonia system. And as this is a feasibility study a high concentration is chosen, lower concentrations and other not-studied parameters in this research are part of the next step in understanding this zinc leaching process.

Constant parameters	Varying parameters
Stirring speed 600 rpm	Temperature 20 - 60° C
Ammonia concentration 221.39 g/L	Ammonium salt concentration $0.5 - 2$ M
Oxygen 20 L/h	Liquid-Solid ratio 2.5 - 7.5 $\mathrm{mL/g}$
-	With or without oxygen

Table 5-6: Parameters studied in experiments

The following sections contain results and discussion about the effect of different parameters such as three ammonium salts, temperature, ammonium salt concentration, liquid-solid ratio and the use of oxidant. The zinc removal is indicated in recovery curves, the zinc is removed from the solid phase and recovered in the liquid phase (leach solution). The recovery curves are plotted with the program Origin Pro 9 and the curves are fitted with a the B-Spline. It should be noted that the curves are a representation of the recovery based on sampling.

Figures in each section show the XRD patterns of the residues under different conditions from the changed parameters. In the graph zinc species ZnS, ZnO and Zn(OH)₂ are indicated above the plotted spectra. In order to compare the spectra they are plotted in the same graph.

5-2-2 Effect of ammonium salt type and temperature

Three different salts were chosen for the leaching experiments. For any chosen salt, the effect on the leaching rate under different temperatures was studied. Ammonium carbonate NH_3 - $(NH_4)_2CO_3$, ammonium chloride NH_3 - NH_4Cl and ammonium sulfate NH_3 - $(NH_4)_2SO_4$ are used during the laboratory experiments. NH_3 - $(NH_4)_2CO_3$ salt system is studied at 20, 30 and 40°C. NH_3 - NH_4Cl and NH_3 - $(NH_4)_2SO_4$ salt systems are used at 20, 30, 40 and 60°C. Ammonium carbonate is not used in leaching experiments over 40°C, due to the decomosition of this salt at above 35°C as shown in reaction 5-8.

$$(NH_4)_2 CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2 \tag{5-8}$$

The recovery of zinc from the conducted experiments is given in graphs for different ammonium salt and temperatures. First will be described what can be seen from the trendlines and then an explaination is discussed.

Ammonium salt

The role of ammonium salt in the ammoniacal lixiviant is to provide an anion and balance with the zinc-ammonine complex, and it is said to act like a pH buffer. Addition of an adequate amount of ammonium salt can prevent the build-up of an oxidized phase, the conditions are based on the equilibrium given in 5-9 [38]. Two of the ammonia molecules of the zinc ammine complex originate from ammonia and the other two from the added salt.

$$Zn(NH_3)_4^{2+} + 2OH^- \rightleftharpoons ZnO \cdot H_2O + 4NH_3 \tag{5-9}$$

The selection of salt has an influence on further process design. Cl^- ion from NH_4Cl is not desirable in the blast furnace charge. If the residue contains chloride ions than the residue's recyclability decreases. SO_4^{2+} and CO_3^{2+} ions from $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ can have an influence on the impurities in solution, they can form precipitates with Sn, Pb and Mn [37].

All experiments are conducted with the same molar concentration of ammonium salt. For $NH_3-(NH_4)_2CO_3$, NH_3-NH_4Cl and $NH_3-(NH_4)_2SO_4$ this is respectively 96.06 g/L,53.49 g/L and 132.14 g/L. Recovery of zinc with each ammonium salt is shown in Figure 5-4 at different temperatures. The recovery is plotted depending on temperature and time. The constant parameters in these experiments are oxygen flow rate of 20 L/h, aggitation at 600 rpm, solid-liquid ratio of 5 and ammonia concentration of 221.39 g/L.

Laboratory experiments are conducted with the three salt types at a variety of temperatures. In order to understand which of the salt is suitable for the following laboratory experiments by comparing the zinc recovery. During sampling the pH is measured, and Figures 5-4 (a), (c) and (e) show the recovery and pH curves. In Figures 5-4 (b), (d) and (f) each curve represents the recovered zinc at a defined retention time.

What differs in the role of anions on dissolution of zinc or zinc-ammine complex formation is a point of discussion. In literature it is found that chloride ions can cooridinate with most metal ions to form metal complexes. This can cause the introduction of unwanted metal complexes in the solution. Lixiviants with the $NH_3 - (NH_4)_2SO_4 - H_2O$ system do not suffer from the formation and dissolution of unwanted metallic complexes [39]. However how anions SO_4^{2-} , CO_3^{2-} and Cl^- influence the recovery of zinc from high zinc filter cake is unclear.

In presence of Cl^- and CO_3^{2-} anions dissolution of zinc is lower than in the presence of SO_4^{2-} , this is based on the recovery of zinc in Figure 5-4.

Oxidation of sulfur to SO_4^{2-} in reaction 5-12 can occur, however oxidation to elemental sulfur (S^{o}) or other oxidation states of sulfur are not excluded.

$$ZnS + 2O_2 \rightleftharpoons Zn^{2+} + SO_4^{2-} \tag{5-10}$$

$$ZnS + 2O_2 \rightleftharpoons Zn^{2+} + SO_4^{2-}$$
 (5-10)
 $(NH_4)_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$ (5-11)

$$Zn^{2+} + 2NH_3 + 2NH_4^+ + 2OH^- \rightleftharpoons Zn(NH_3)_4^{2+} + H_2O$$
(5-12)



Figure 5-4: For three salts recovery is plotted along temperature and time, at 20, 30, 40 and 60° C

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Effect of Temperature

Temperature is an important parameter for the leaching rate. With increasing temperature the recovery is often increased [40], [39], [6], [32]. In Figure 5-5 the leaching trends are plotted for each studied temperature. One plot shows the trends of $NH_3-(NH_4)_2CO_3$, NH_3-NH_4Cl and $NH_3-(NH_4)_2SO_4$.



Figure 5-5: Recovery of zinc for three ammonium salts at 20, 30, 40 and 60°C

Influence of temperature on the zinc recovery depends on the type of salt in the lixiviant. Recovery of zinc does not exceed 50% for both $NH_3-(NH_4)_2CO_3$ and NH_3-NH_4Cl . The $NH_3-(NH_4)_2SO_4$ system reached the highest zinc recovery with 69%.

With increasing temperatures the recovery increases slightly for ammonium carbonate, at 40° C zinc dissolution stalls after 30 minutes and then increases again after 50 minutes. The shape of trendlines in NH₃-(NH₄)₂CO₃ leaching are similar for 30 and 40° C while leaching at 20° C gives a slightly different trend. From temperature measurements it was found that at 180 min it was 22° C instead of $20\pm0.5^{\circ}$ C. The recovery trendlines of leaching experiments

with ammonium chloride are fluctuating. The recovery increased until 30 minutes then it decreased after this it increased ending with a decreasing trend. At 60°C with the NH₃-NH₄Cl and NH₃-(NH₄)₂SO₄ lixiviants the leaching is stopped after 30 minutes. The pH in the reactor was around 8 and stability of the ammine complex lies between 8 - 11 (Figure 5-2). For experiments conducted with ammonium sulfate the recovery trendlines of all (except for 60°C) have the same pattern. pH decreases faster at higher temperatures than 30°C. A thick froth formed that kept increasing when ammonia was added to the reactor with NH₃-(NH₄)₂SO₄ at 60°C. Thus it was descided to turn off the oxygen and stirring until it subsided this took up to 5 mintes of the experiment. At 30°C with NH₃-(NH₄)₂SO₄ (132.14 g/L) the highest recovery is 69% zinc. When it is assumed that ZnO presents for 32% of zinc and ZnS for 68% (based on 5-4), then if the recovery is over 32% at least a part of dissolved zinc should originate from ZnS.

All trendlines start off steep which indicates a high recovery rate at the beginning for all three studied ammonia-ammonium salt systems. pH is monitored during the experiments. The pH in an ammonia solution depends on the ratio of NH_3 and NH_4^+ concentrations (equation 5-13), when $NH_3 < NH_4^+$ then the pH decreases.

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$
(5-13)

The recovery trend can indicate what type of mechanism is behind the dissolution of a metal ion. Leaching trends are commonly known to have a certain smooth shape, however all trendlines from these conducted experiments show a different leaching trend. Waving trendlines refer to partial precipitation of zinc for example as $Zn(OH)_2$. Zinc dissolution in ammoniacal solutions, despite the stability of $Zn(NH_3)_4^{2+}$ complexes, can reverse as dissolved zinc undergoes partial precipitation after 30 - 60 minutes depending on the ammonium salt and temperature. G. Senanayake et al., [13] find in their research to leaching of zinc that the dissolved zinc(II) undergoes partial precipitation after 5-40 minutes depending upon the ammonia concentration and temperature.

Formation of zinc ammine complexes depends on the formation constant K_i . Metal ions in solution are solvated, they are bound to a definite number of solvent molecules (2, 4 or 6). Metal solubility (ZnO, Zn(OH)₂, ZnS, ..) increases by complex formation. With excess base zinc can form soluble complexes with OH⁻. The high ammonia concentration that is used for this study doesnot only introduce a large concentration of ammonia or ammonium, it also introduces a high concentration of hydroxides ions (see equation 5-14). The formation reactions of soluble zinc hydroxides in the presence of excess OH⁻ is given in Equations 5-15 and 5-16.

$$NH_3 \rightleftharpoons NH_4^+ + OH^- \tag{5-14}$$

$$Zn^{2+} + OH^- \leftrightarrow ZnOH^+$$
 (5-15)

$$ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2(aq)$$
 (5-16)

Formation of zinc hydroxides or oxides can cause the partial precipitation of zinc from the leaching solution, visible in the recovery trend by the wave shape. Zinc hydroxides can form



Figure 5-6: Partial precipitation of zinc in ammoniacal leaching with addition of SO₂ [13]

by reaction 5-17, assuming zinc is dissolved as Zn^{2+} . Or when zinc is dissolved as an ammine complex then the hydroxide formation can be as in Equation 5-18. The pH range where the leaching of zinc in ammine complexes occurs is the same range where zinc hydroxides are insoluble.

$$Zn^{2+} + 2OH^{-} \rightleftharpoons Zn(OH)_2(s) \tag{5-17}$$

$$Zn(NH_3)_4^{2+} + OH^- \rightleftharpoons Zn(OH)^+ + 4NH_3 \tag{5-18}$$

Solubility of zinc hydroxides is studied at pH 6.75 to 13.8 at 4 different temperatures, the solubility is listed in Figure 5-7. The data shown in the Figure can explain the partial precipitation of zinc that results in the waving trendlines [16]. Dissolution of zinc hydroxide is minimum in the pH range 11.5 - 8.5 at 25°C. From the trendlines it can be concluded that when the pH in the reactor 'hits' the pH range of insolubility of zinc hydroxides then the recovery drops and as the pH becomes lower than the boundary of zinc insolubility the extraction of zinc recovers.

Figures 5-7 - 5-9 give XRD plots of the experiments discussed in this section. Above each plot \bigcirc indicates the location of ZnS, \square ZnO and \triangle Zn(OH)₂. The indicated peaks of zinc species compared to the intensity of surrounding peaks gives an indication which species are present in the leach residues. Presence of ZnS in residues compared to high zinc filter cake can give a better insight how effective the studied treatment is for tackling ZnS. Locations of Zn(OH)₂, ZnO and ZnS peaks are given in Table 5-9. With the program Origin Pro 9 the raw XRD data is plotted, which makes it possible to compare the XRD patterns.

12.5 °C		25.0 °C		50.0 °C		75.0 °C	
pН	$S (x 10^5)$	pН	$S (x 10^5)$	pН	$S (x 10^5)$	pH	$S (x 10^5)$
13.80	327	13.19	178	12.50	261	12.22	1029
13.71	261	12.97	67.3	12.24	88.7	11.95	319
13.51	91.8	12.77	28.3	11.99	33.7	11.68	104
13.34	45.1	12.52	11.2	11.76	14.8	11.35	29.1
13.18	25.2	12.29	5.74	11.55	8.03	11.14	12.6
12.85	6.12	11.05	0.54	11.25	2.92	10.85	5.27
12.21	1.68	10.84	0.46	10.99	2.14	10.54	3.06
11.51	0.50	10.14	0.31	10.75	1.38	10.22	2.14
11.50	0.31	9.43	0.38	10.25	0.92	10.01	2.06
11.10	0.24	9.18	0.54	10.02	0.84	9.71	1.84
9.83	0.23	8.97	0.61	9.55	0.76	9.54	1.76
9.49	0.23	8.91	0.92	9.08	0.87	8.93	1.68
9.27	0.23	8.72	0.84	8.77	0.99	8.55	1.84
9.14	0.31	8.67	1.22	8.52	1.15	8.38	2.06
8.99	0.46	8.41	1.30	8.27	1.45	8.08	2.06
8.55	1.33	7.90	4.74	8.04	1.84	7.89	1.99
7.96	13.2	7.63	17.2	7.82	2.43	7.65	2.37
7.70	48.3	7.44	32.1	7.54	4.97	7.18	7.22
7.32	265	7.31	49.7	7.26	10.7	6.94	13.1
7.22	415	7.00	204	7.05	19.6		
7.06	844			6.75	53.4		

Table 5-7: Solubility (S) of zinc hydroxides as a function of pH at 12.5, 25.0, 50.0 and 75.0 o C [16]. Solubility is expressed in mol of zinc per kg of water

The peak intensities of the three indicated zinc species change for the different temperatures. In Figure 5-7 the XRD patterns of the experiments with ammonium carbonate are shown. Zinc hydroxide is not found in any of the XRD analyses (Table 5-8) and this is confirmed by the XRD patterns. ZnS and ZnO peaks at 20, 30 and 40 o C do not differ a lot in size or shape.



Figure 5-7: XRD plot of $(\mathsf{NH}_4)_2\mathsf{CO}_3$ at 20, 30 and 40 $^o\mathsf{C}$



Figure 5-8: XRD plot of NH₄Cl at 20, 30, 40 and 60 $^o\mathrm{C}$

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Figure 5-9: XRD plot of $(\mathsf{NH}_4)_2\mathsf{SO}_4$ at 20, 30, 40 and 60 $^o\mathsf{C}$

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Experiments with NH₄Cl are conducted at 20, 30, 40 and 60 °C. The two Zn(OH)₂ peaks around 20 2θ do not occur in any of the XRD patterns and neither do the other two around 27 and 33 2θ . This observation from the XRD patterns is coherent with the zinc species in Table 5-8. The ZnS peaks around 28 and 31 2θ decreases in height as the temperature of increases. Around 36 2θ the ZnO peak disappears more in the a bigger peak as the temperature increases, until it is no longer a separate peak. This peak possible increased and is murched with the bigger peak. At 42 2θ the ZnO peak is found in all XRD patterns.

The XRD patterns at 20, 30 and 40 °C for experiments conducted with $(NH_4)_2SO_4$ have the Zn(OH)₂ peaks around 20 2θ . These are not found in the patterns of experiments with $(NH_4)_2CO_3$ and NH₄Cl. At 60 °C these Zn(OH)₂ peaks are no longer found, this is confirmed by Table 5-8. ZnS peaks around 27 and 47 2θ are visible at throughout all XRD patterns. The $(NH_4)_2SO_4$ XRD patterns differ from $(NH_4)_2CO_3$ and NH₄Cl at the ZnO peak around 36 2θ . This peak does not murge with the big peak on the left.

 $Zn(OH)_2$ peaks at 20, 27.5 and 32.5 2θ are not very clear in the XRD patterns and the peak at 20 2θ seems visible in the untreated sample while no $Zn(OH)_2$ is present. The peaks at 27.5 and 32.5 are not clearly visible in the XRD patterns. For the identification of any compound at least 3 peaks should be identified and with less identified peaks a compound is indicated in the XRD pattern. This means that for all XRD patterns that $Zn(OH)_2$ is an indicated compound in the leaching residues instead of identified. The indication of $Zn(OH)_2$ is often based on the presence of 21 2θ .

Table 5-8: Zinc compounds in the residues - detected by XRD

Experiment	20 °C	30 °C	40 °C	60 °C
$NH_3-(NH_4)_2CO_3$	ZnO, ZnS	ZnO, ZnS	ZnO, ZnS	-
NH_3-NH_4Cl	ZnO, ZnS	ZnO, ZnS	ZnO, ZnS	ZnO, ZnS
$\rm NH_3$ -($\rm NH_4$) $_2\rm SO_4$	$Zn(OH)_2, ZnS$	$Zn(OH)_2$, ZnO , ZnS	$Zn(OH)_2$, ZnO , ZnS	ZnO, ZnS

Table 5-9: Locations of $Zn(OH)_2$, ZnO, ZnS and the main compounds without zinc in XRD analysis

$\operatorname{Zn}(\operatorname{OH})_2$	ZnO	ZnS	$\rm Fe_2O_3$	$CaCO_3$	С	Fe
20	36	27	24	29.5	26.5	40.5
21	42	28.5	33	39.5		
27.5	61	30.5	35.5			
32.5		47.5	40.5			
		52	49.5			
		56.5	54			
			62.5			
			64			

5-2-3 Effect of salt concentration

In this section the NH_3 - $(NH_4)_2SO_4$ system is studied at different concentrations of $(NH_4)_2SO_4$ (66.07, 132.14 and 264.28 g/L). Figure 5-10 shows the recovery curves of experiments conducted with varying ammonium sulfate concentrations. From [38] the prevention of zinc oxides formation is said to correlate to the right ammonium salt concentration. This concentration can be calculated.



Figure 5-10: Influence of ammonium sulfate concentration on the recovery of zinc

One leaching experiment is conducted to see if zinc can dissolve from this type of material without the addition of ammonium salt. In this experiment after a retention time of 4 hours, 20.98 mg/L (0.30% recovery) of zinc is dissolved, which proves that ammoniacal leaching without salt is inefficient and addition of ammonium salt increases the dissolution of zinc.

Zinc species found in the residues differ for all three concentrations as is shown in Table 5-10. Zinc hydroxide is found in the residue with 132.14 g/L salt concentration. This can be explained by the pH value at the end of leaching (~ 9.7). This pH value lies both in the range of stable ammine complexes and insoluble hydroxides. The pH range of insoluble zinc hydroxides shown in Figure 5-7 is between 11 and 8.5. pH values of the other two experiments are close to the region where zinc hydroxides solubility is possible. The ammine complex is stable between pH 8 - 11 at 25° C.

Table 5-10: Zinc compounds in the residues - detected by XRD

Experiment	Compounds detected
$0.5 \text{ M of NH}_3\text{-}(\text{NH}_4)_2\text{SO}_4$	ZnO, ZnS
$1.0 \text{ M} \text{ of } \text{NH}_3\text{-}(\text{NH}_4)_2 \text{SO}_4$	$ZnO, Zn(OH)_2$ and ZnS
$2.0 \text{ M} \text{ of } \text{NH}_3\text{-}(\text{NH}_4)_2\text{SO}_4$	ZnO

Recovery of zinc with 264.28 g/L salt initially is higher than with 66.07 g/L and has no ZnS in the residue. The amount of sulfate ions introduced with 264.28 g/L salt resulted in 1) oxidation of sulfur and/or 2) promoted an exchange reaction. With 0.5 M (66.07 g/L) of salt the leaching rate is lowest.

In ammoniacal leaching addition of an adequate quantity of an ammonium salt can prevent the build up of an oxidized phase. The amount of ammonium salt needed for total dissolution of a metal sulfide (that can form stable ammine complexes) can be calculated as explained by C. Ek et al. [38]. The influence of ammonium salt on formation, dissolution and precipitation of zinc hydroxides is not discussed by C. Ek et al., The question remains if the right amount of ammonium salt can prevent hydroxides from forming. And if the pH plays a more important role.



Figure 5-11: XRD patterns of experiment with NH_3 - $(NH_4)_2SO_4$ at 30° with 2.5, 5 and 7.5 liquid solid ratio

In the XRD plot 5-11 $\text{Zn}(\text{OH})_2$ is not found in the spectra of 0.5 and 2 M of salt (red and pink). The fact that $\text{Zn}(\text{OH})_2$ is only present in the 1 M salt experiment can be explained by the different way these residue samples are dried. Both the 0.5 and 2 M samples are air dried and the 1 M sample is dried in an oven at 105 °C. The experiment with 2 M salt only shows the compound ZnO in the XRD pattern and no ZnS is visible.

5-2-4 Effect of solid-liquid ratio

Three liquid-solid ratios (mL/g) are studied in the NH₃- $(NH_4)_2SO_4$ system at 30°C.



Figure 5-12: Influence of liquid solid ratio on the recovery of zinc

Changing the solid liquid ratio results in a change of the leaching kinetics. In the final stage of the experiment, zinc dissolution increased for 7.5 L/S ratio. While the L/S ratio of 2.5 has a decreasing recovery trendline after a maximum around 30 minutes. This can be influenced by the low salt concentration, compared to the amount of ZnS and ZnO fed to the system. Low ammonium salt concentrations can cause the formation of insoluble zinc oxides [38]. Presence of zinc hydroxide in the 2.5 and 5 L/S residues can be related to the pH. In the L/S of 7.5 no hydroxides are found by XRD analysis. The pH drop during this experiment was fast what can have an influence on the change of $Zn(OH)_2$ formation. In the XRD spectrum (Figure 5-13) of 5 L/S the $Zn(OH)_2$ peaks are most clear followed by L/S 2.5.

Table 5-11: Zinc compounds in the residues - detected by XRD

Experiment	Compounds detected
$NH_3-(NH_4)_2SO_4 2.5 mL/g$	$ZnO, Zn(OH)_2$ and ZnS
NH_3 - $(NH_4)_2SO_4 5 mL/g$	$ZnO, Zn(OH)_2$ and ZnS
NH_{3} - $(NH_{4})_{2}SO_{4}$ 7.5 mL/g	ZnO, ZnS

Overall the XRD pattern of 7.5 ml/g is the smoothest, it has the least peaks. From the three zinc compounds only ZnS has a clear peak around 47 2θ in all three XRD patterns. For 7.5 ml/g the ZnS peaks around 27 and 47 2θ are visible in the pattern. The ZnO peak around 42 2θ is present in all the patterns.



Figure 5-13: XRD patterns of experiment with NH_3 - $(NH_4)_2SO_4$ at 30° with 2.5, 5 and 7.5 liquid solid ratio

5-2-5 Effect of oxidant

Experiments are conducted at 30° C with NH₃-(NH₄)₂CO₃, NH₃-NH₄Cl and NH₃-(NH₄)₂SO₄ lixiviants, liquid solid ratio 5 and with/without oxygen purged at 20 L/h. The recoveries are given with the measured pH in Figure 5-14. In Table 5-12 the zinc species detected in XRD characterization are given.

Oxygen is purged during leaching for the oxidation of sulfur from ZnS in order for zinc to dissolve and form an ammine complex.



Figure 5-14: For three salts recovery and pH is plotted over time, all experiments are conducted at 30° C with lixiviant NH₃ - (NH₄)₂SO₄

Before conducting experiments without the addition of an oxidant the recovery was expected

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to be significantly lower than with oxygen. Decreasing zinc dissolution of carbonate and cholide based lixiviants seemed to occur at an earlier stage than with ogygen purging. The recovery trend changes over time and when the pH is below 10 in the ammonium chloride system the recovery increases again (Figure 5-14b). Overall for all salts zinc the recovery did not decrease, in line with the assumption that with oxygen purging zinc recovery is higher because of oxidation of sulfur from ZnS (dissolving the zinc).



Figure 5-15: Zinc extraction inlfuenced by the presence of metal ions [14]

Experiments with and without oxygen reached a comparible zinc recovery. And the same zinc species are found in XRD analysis for both with and without oxygen. The dissolution of zinc seems less dependent on oxidation of sulfur than expected. An explanation of dissolution of zinc despite the lack of oxygen purging is related to the interaction with other elements present in the raw material. From literature [14] it is found that dissolution of zinc in ammoniacal solutions from zinc sulfide depends on the presence of other metal ions. The study behind this paper compared zinc extraction from just zinc sulphide and in the presence of Cu(I), Ag(I), Pb(II), Ni(II) and Co(II) ions. Their influence on zinc extraction is illustrated by Figures 5-15. In Figure 5-15a extraction of zinc from ZnS is shown without other ions present and 5-15b shows how the zinc extraction changes with the presence of other ions. Only 4 - 8% zinc dissolution is achieved from ZnS, while addition of Cu(I), Ag(I) and Pb(II) increased dissolution of zinc to 20 - 50%.

In the high zinc filter cake no copper or silver is present, however lead is. With Pb(II) ions zinc extraction from ZnS is increased from $\sim 4\%$ to $\sim 20\%$ as shown in Figure 5-15b. Instead of purging O₂ the presence of Pb(II) can promote the extraction of zinc. Pb is identified as PbO in the filter cake PbO turns into PbOH⁻ with OH⁻ as is shown in Equations 5-19 and 5-20. PbOH⁻ undergoes an exchange reaction with ZnS to form PbS 5-21. If lead is present

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or converted into $PbO \cdot PbSO_4$ it can no longer be leached to form the intermediate $PbOH^+$ product.

$$PbO + H_2O \rightleftharpoons Pb^{2+} + 2OH^- \tag{5-19}$$

$$Pb^{2+} + OH^{-} \rightleftharpoons PbOH^{+} \tag{5-20}$$

$$PbOH^+ + ZnS + 4NH_3 \rightleftharpoons PbS + Zn(NH_3)_4^{2+}$$
(5-21)

With up to 20% zinc extraction promoted by the presence of Pb(II) ions and exaction of all zinc from ZnO by the reaction 5-12 the recovery of zinc without O_2 purging is above the assumed Zn coming from ZnO due to the presence of Pb(II) that promotes zinc dissolution of ZnS. The small difference in recovery with and without oxygen shows that introducing oxygen during leaching is less effective than expected.



Figure 5-16: NH_3 -(NH_4)₂CO₃ residues with and without O₂



Figure 5-17: NH $_3$ -NH $_4$ Cl residues with and without O $_2$



Figure 5-18: NH_3 -(NH_4)₂SO₄ residues with and without O₂

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Zinc species found in XRD analysis are the same for experiments with and without oxygen purging.

Experiment	Compounds detected	
NH_3 - $(NH_4)_2CO_3$ with O_2	ZnO, ZnS	
$NH_3-(NH_4)_2CO_3$ without O_2	ZnO, ZnS	
NH_3 - NH_4Cl with O_2	ZnO, ZnS	
NH_3 - NH_4Cl without O_2	ZnO, ZnS	
NH_3 - $(NH_4)_2SO_4$ with O_2	$ZnO, Zn(OH)_2, ZnS$	
NH_3 - $(NH_4)_2SO_4$ without O_2	$ZnO, Zn(OH)_2, ZnS$	

Table 5-12: Zinc compounds in the residues - detected by XRD

The XRD patterns of $(NH_4)_2CO_3$ show that with oxygen the peaks are more prominent than without oxygen. For example the ZnS peaks around 27, 47 and 52 2θ . Overall all peaks that occur in the pattern with oxygen also occur in the pattern without it. For the XRD patterns of NH₄Cl the other way around applies for the peaks with and without oxygen. The ZnS peak around 47 2θ is more prominent in the pattern without oxygen than with. In the XRD plot of NH₃-(NH₄)₂SO₄ Zn(OH)₂ peaks at 20 and 21 2θ are smaller when no O₂ is purged, the left peak is almost gone.

5-3 Selectivity

Iron loss

Iron recycling to the blast furnace, next to removal of zinc, is an objective from this study. Selectivity of ammonia leaching experiments is confirmed with Figure 5-19, the maximum loss is 0.045% of iron in the ammonium sulfate lixiviant at 30° C with O₂ purging and without O₂ the iron loss decreased. This can be explained by oxidation of some iron by oxygen purging. Iron is present as FeO and Fe₂O₃ in the feed material, FeO can be oxidized. Equations 5-22, 5-23 and 5-24 give the oxidation reactions of FeO and the formation of soluble hydroxides.

The iron species are not altered in a way they could not be fed to the BF. From XRD analysis no iron hydroxides are characterized.

$$FeO + H_2O \rightleftharpoons Fe^{2+} + 2OH^- \tag{5-22}$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-} \tag{5-23}$$

$$Fe^{3+} + 2OH^- \rightleftharpoons Fe(OH)_2^+$$
 (5-24)



Figure 5-19: Loss of iron during the conducted experiments

Parallel to the ammonia - ammonium salt leaching experiments a acidic leaching experiment is conducted to compare the iron loss. The experiment was conducted with HCl leach liquor at 60° C for 60 minutes. After leaching a second step was needed for the removal of iron, the removal was achieved by addition of NaOH. The pH increase by the addition of NaOH caused the iron to precipitate as Fe(OH)₂. Iron loss from the leaching step was 12% and this cannot be recovered as Fe₂O₃. The recovered Fe(OH)₂ in the second treatment step is extremely fine and causes production issues when fed to the sinter plant. This parallel experiment confirms that acidic leaching is less selective and that a part of the iron is lost due to a change in species.

Dissolution of Ca

Calcium dissolution is found from ICP analysis, $CaCO_3$ is the source of calcium in high zinc filter cake. Formation of calcium sulfate is unlikely, maybe calcium hydroxides have formed. Hydroxide source can be from ammonia dissolution. Calcium dissolution is highest when the liquid solid ratio is 7.5 Figure 5-20. The calcium dissolution is between 5 and 8%. For the other experiments the Ca^{2+} dissolution is between 1 - 2%.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{5-25}$$

$$CaCO_3 \rightleftharpoons CaO + CO_2$$
 (5-26)

$$Ca^{2+} + 2OH^{-} \rightleftharpoons Ca(OH)_2(aq) \tag{5-27}$$



Figure 5-20: Dissolution of Ca during the conducted experiments with varying L/S ratios

5-4 Flow sheet

Zinc extraction from zinc filter cake, reached with the studied treatment, lies between 3 - 6 g/L. For zinc to be successfully recovered from the ammoniacal solution the zinc concentration of 3 - 6 g/L is not enough. A zinc concentration of 15 - 20 g/L is sufficient, which means the current leach liquor needs to be upgraded. A concept treatment plant of blast furnace sludge is designed and it is shown in Figure 5-21. The blast furnace sludge is treated directly as it comes from the off gas cleaning system. There would no longer be need for the current water treatment plant. This decreases the material streams from the off gas treatment from 4 (Dry dust, Zinc poor, Zinc middle and Zinc rich filter cake) to 1. The enrichment of zinc in the leaching solution is achieved by recycling the leach liquor before zinc is extracted from the filtrate. In the primary leaching tank fresh blast furnace sludge is leached. Then as the zinc concentration is sufficient, the leach solution is filtrated. After washing and filtration the solid phase can be recycled to the sintering plant. For the high zinc solution a costumer is needed who would be able to execute the zinc extraction treatment.

Solvent extraction of zinc from the filtrate depends on the concentration of total ammonia, aqueous pH and the concentration of the extractant [42]. The effect on anion species from different ammonium salts (Cl⁻, CO₃²⁻, SO₄²⁻) on the extraction of zinc depends on the used mixture. Recycling of ammonia liquor is described in a patent [43].



Figure 5-21: Concept of the implemented ammoniacal treatment

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Before recycling of the zinc poor residue to the sinter plant is feasible with this process, the behaviour of cadmium and lead need to be understood. Lead is not recovered and when this remains in the leaching residue it will partly separate from the sinter through fumes. This will decrease the lead content, however it is not a favourable situation. Cadmium is recovered for around 50%. The current parameter set should be reviewed more critically before this treatment is tested on a pilot plant scale. For example what extractant is effective to recover zinc from this solution and if recycling the lixiviant will give the desired zinc concentration of 15 - 20 g/L (or more).

Chapter 6

Conclusions and Recommendations

6-1 Conslusions

Zinc in the high zinc filter cake is characterized both as ZnS and ZnO by XRD analysis. One of the main objectives was to oxidize ZnS to ZnO. The oxidation of ZnS by adding an oxidant, in this case oxygen, is not found very effective. Leaching with oxygen increased the zinc removal by less than 10%. Without effective oxidation with oxygen the zinc recovery in the NH₃ - $(NH_4)_2SO_4$ lixiviant was >60%. This recovery is likely dependent on the presence of other ions like Pb(II).

Trendlines of the zinc recovery and the formation of zinc hydroxides are connected. The pH ranges of insolubility of $Zn(OH)_2$ and the stability of $Zn(NH_3)_4$ ²⁺ overlap. The pH change and the reaction rate are not directly related. When 2 M (264.28 g/L) ammonium sulfate is used then there is no ZnS found in the XRD pattern of the leaching residue, which can indicate that the oxidation of ZnS is dependent on the concentration of added ammonium salt.

Ammoniacal leaching is to a certain degree effective in removing zinc from blast furnace dust. The set goal (from the original business case) of 80% zinc recovery is not reached. The mechanisms that control the zinc recovery in the studied method are not yet revealed. More research is needed for example more detailed characterization of the material and more laboratory experiments. Complexity of the material creates to many optional mechanisms during the leaching process.

The studied ammoniacal leaching treatment of high zinc filter cake is proven to be selective. The highest iron loss was 0.045% in the NH₃ - (NH₄)₂SO₄ lixiviant.

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6-2 Recommendations

6-2-1 The studied treatment

The $2.38\%_w$ of un-identified zinc after XRD analysis should be identified. Only when the characterization is complete then the process can be understood better. Addition of PARC analysis (Phase Recognition and Characterization) to the current characterization conducted on the BF (zinc rich) dust/sludge can help understand the complete composition of the material. PARC is a microanalysis technique and is used at the CRC laboratory at Tata Steel IJmuiden. From PARC in combination with FEG-SEM-EDS a reliable stoichiometric analysis can be obtained on samples with crystals smaller than 500 nm, even trace elements and phases can be detected. The challenge in microanalysis is to get accurate qualitative and quatitative analysis on even the smallest phases [44].

From the beginning of this project the ZnS compound has been the focus. Better understanding of the limitations and the main influencing factors on dissolution of zinc from this type of material has to be gained. With laboratory experiments on pure ZnS and then ZnS and ZnO mixtures the controlling mechanism and influence of other elements can be better understood. From there one can build up the knowledge what the leading reactions are, what compounds/elements/ions are an influence on the extraction of zinc. When the mechanisms are known, then upscaling and pilot plant experiments can follow.

In a succeeding research to the ammoniacal leaching of blast furnace sludge the influence of evaporation of ammonia should be included, as should the other influences on the course of pH during leaching.

The effect of changing the ammonia concentration can be further studied, as well as the recycling of the lxiviant and possibilities to reach 15 - 20 g/L zinc in the leach solution.

6-2-2 Additions to the studied treatment

During this study a few flotation experiments were conducted, but these are not used in the discussion as it was a side track next to leaching experiments. Flotation can be a valuable addition in the treatment concept of blast furnace high zinc filter cake. Reusing carbon from this material is one of the main objectives. By separating carbon prior to the leaching step, mass and espescially the volume of material to treat is decreased. This can decrease the need of leaching lixiviant and creates a carbon recyclate [45], [46].

Stirring and air purging with the flotation machine that is used in the experiments were difficult to control. A machine with better control and other concentrations of reagents can improve the flotation separation. The carbon in blast furnace sludge can be oxidized and is extremely fine, which are characteristics that make a good separation challenging. The preliminairy results from the few conducted froth flotation experiments show incomplete separation of the carbon from the rest of the material.

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Appendices

SEM Images

In this appendix the SEM point measurements are given where zinc is found in Figures 6-1 (points 1.2 and 1.5), 6-2 (points 2.2, 2.3, 2.4 and 2.6) and 6-3 (point 5.4). It was assumed that the lightest particle (high compound specific weight) contain ZnS, however it often turned out to be iron oxide. Figure 6-4 shows an iron oxide particle.



Figure 6-1: Sample analysis at MSE TU Delft



Figure 6-2: Sample analysis at MSE TU Delft



Figure 6-3: Sample analysis at MSE TU Delft

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Figure 6-4: Sample analysis at MSE TU Delft

Zinc removal, additional graphs

For each lixiviant type $(NH_3-(NH_4)_2CO_3, NH_3-NH_4Cl \text{ and } NH_3-(NH_4)_2SO_4)$ the highest removal of zinc is indicated. The ammonia and ammonium salt concentrations were respectively 12 M and 1 M.



Figure 6-5: NH_3 - $(NH_4)_2CO_3$, NH_3 - NH_4CI and NH_3 - $(NH_4)_2SO_4$ at what pH is the highest recovery for each studied temperature



Figure 6-6 shows the accuracy of EDTA titration with Eriochrome Black T, compared to ICP analysis.

Figure 6-6: Zinc recovery found by EDTA titration and ICP analysis for NH_3 - $(NH_4)_2CO_3$ and NH_3 - $(NH_4)_2SO_4$
