

Sulfur stream identification and  
selective removal of heavy metals  
from ironmaking blast furnace dust

*Improved leaching of metal sulfides using oxidants  
and microwave treatment*

*Master thesis*

*by*

*A.T. Kempke*



# Sulfur stream identification and selective removal of heavy metals from ironmaking blast furnace dust

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Master Thesis

By

A.T. Kempke

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## Abstract

The main waste products of ironmaking at Tata Steel IJmuiden are  $\text{CO}_{2(g)}$  and a solid waste stream consisting of mainly carbon and iron-bearing compounds. This solid waste is generally called Zn rich filter cake which contains too much Zn to be reintroduced into the iron making process. Besides Zn, Pb and Cd are also present. These filter cakes originate from the flue dusts that are expelled from the top of the blast furnace. Currently the solid waste is separated based on size distribution which allows the recycling of most of the materials and concentrates the heavy metals into the Zn rich filter cake. Previous research has shown that these cakes are resistant to regular leaching methods for selectively dissolving the contained heavy metals. This is due to their sulfide form. The methods that do work (such as acid leaching) also dissolve additional material such as iron, which is the main component of the waste stream. Therefore Tata Steel Europe is investigating whether alternative options are available to selectively extract these heavy metals and reintroduce the remaining material as secondary ore back to ironmaking.

In this research the option of adding oxidants with and without additional microwave treatment is investigated. Based on what is applicable in reality, literature and thermodynamic evaluations several oxidants were selected to oxidize the metal-sulfides to metal-oxides which can be readily leached in ammonia based media. Furthermore the material was characterized and an investigation was done on where the sulfur originates and whether this stream can be reduced or avoided. The quality of the results was verified by comparing the heavy metals dissolved into the leaching solution by ICP analysis and by determining the heavy metal content in the solid material before and after leaching with XRF. It was found that 98% of the sulfur originates from the blast furnace and only 2% from the addition of sodium sulfide at the water cleaning department.

Leaching experiments were done with a 40 °C leaching solution, a 5:1 liquid to solid ratio. Leaching solutions were all ammonia based due to its selectivity to heavy metals. Leaching the sample material without microwaving or addition of oxidants the highest Zn, Pb and Cd recovery was 54%, 0.5% and 24% respectively. Potassium permanganate as the oxidant resulted in the highest extraction of Zn at 67% in a 2M ammoniumsulfate, 9M ammonia leaching solution. Ferric chloride in a 2M ammoniumsulfate, 9M ammonia leach solution reached extractions of Zn and Cd at 64% and 45% respectively for the IJmuiden filter cake. For Pb the best extraction was 5% in a 2M ammoniumcarbonate, 9M ammonia leach solution with the same oxidants. Microwaving the sample during leaching resulted in a higher extraction for both Pb and Cd, whilst matching the non-microwave oxidant leaching extraction for Zn. The highest extractions were 61%, 42%, 83% for Zn, Pb and Cd respectively. Aging has also been proven to have a detrimental effect on the extraction of heavy metals, however the aging effect is negated when using microwave treatment or oxidants. Extractions for lab reactor leaching of fresh samples without added oxidants or microwaving with an ammonia sulfate solution, resulted in extractions of 62%, 0%, 40% for Zn, Pb and Cd respectively.

It has been verified that most of the sulfur comes from the blast furnace. Further it has been reaffirmed that the metal sulfides this sulfur forms are difficult to leach out. One study states that metal sulfides can and will form in the blast furnace. The current study supports that, even though no direct study of the blast furnace itself was done. Oxidants and microwave assisted leaching seem to work well for Pb and Cd, but are less effective on extracting a higher percentage of Zn. It is recommended to use this method in combination with another process, a different ironmaking process such as HIsarna would be preferable due to the reduction of ZnS to ZnO which is readily leached with an ammonia leaching solution.



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## List of Abbreviations

BF	Blast Furnace
BAT	Best Available Technology
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CP	Cupola Process
EAF	Electric Arc Furnace
EU	European Union
EZINEX	Engitec Zn Extraction
FY	Financial Year
ICP	Inductive Coupled Plasma
MZP	Modified Zincex Process
PSD	Particle Size Distribution
RHF	Rotary hearth furnace
L/S	Liquid/Solid
Stoich.	Stoichiometric
Wt%	Weight percentage
XRD	X-ray Diffraction
XRF	X-ray Fluorescence



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# 1. Introduction

In 2013 the Dutch government made an agreement regarding renewable energy with companies, unions and environmental agencies. This agreement had targets set for 2023. Then in 2015 a much more extensive agreement was reached in Paris. The Paris agreement [12] did not only mention increasing renewable energy but also reducing existing CO<sub>2</sub> - production.

In 2030 which is the near future, greenhouse gases will have to be reduced by at least 40 % and in 2050 already with 80%. Apart from CO<sub>2</sub> other pollutants are also being targeted. Solid waste has to be repurposed, re-used, recycled or recovered in some other fashion. According to the third Dutch national waste plan (LAP3) [13] solid waste can be prohibited from being landfilled if certain criteria are met. For example the processing technique should have less of an impact on the environment than landfilling. However an arguably more important condition is that the technique should be cheaper than €175 per ton of processed material. So if someone were to show that a certain technique would cost less than this boundary the government could force the manufacturer of this waste to install this processing step, or otherwise deny them the right to landfill the material. Instead of this a fine could be given which would probably be at least that boundary amount until they agree to process it. In any case the taxes on landfilling will go up, as stated in the revision of the tax system by the state secretary of finance in 2018. [14]

Due to the awareness of climate change and the good PR effect of being 'green' reducing waste and aiming for a circular process is rapidly becoming the standard. Not just by (future) legislation or economic benefit, but also by way of a growing understanding of the impact a non-circular economy has on the planet and its diverse inhabitants. With this in mind Tata Steel Europe has already been moving toward a greener more efficient process.

The focus for any industry in general has always been to increase quality and/or quantity to increase profitability. These things also go hand in hand with the reduction of any superfluous costs, either by increasing efficiency or by creating synergy through mergers and take overs. This capitalist mind-set is the basis for the way the government (and the EU) hopes to reduce CO<sub>2</sub>, solid waste and other waste streams/emissions as can be read in the tax revision statement released by the Dutch state secretary of finance. [14]

For CO<sub>2</sub> it is a simple case of raising the CO<sub>2</sub> certificate prices to a high enough level. Which will incentivise companies to look for more cost effective ways to get rid of CO<sub>2</sub>, for example by using a CCS , or CCU.

Even though greenhouse gases such as CO<sub>2</sub> are the main focus right now, smaller by-laws have also been implemented to reduce solid waste material. This is most explicitly stated in the Dutch governments communications for bottom ash and waste incinerators in general and the national waste plan. [14, 15] However I would argue that it is a safe assumption, that higher taxes or costs will be implemented for all non-renewable waste generation. Such as Zn rich filter cakes, which is the focus of this study. After all the governments slogan is "The polluter pays the bill".

## 1.1. Project background

To reduce Tata Steel Europe's waste streams the focus for this study is on its solid blast furnace zinc rich waste, which is currently landfilled. The interesting thing about this landfilled material is that it is basically iron and carbon, but it has a too high heavy metal content. The landfilled material is a mix of medium and high zinc waste. The high zinc waste contains roughly 4-8% Zn, 0.5%-1.5% Pb and 0.02% Cd. After mixing this is reduced substantially to 1 – 2 % Zn. However the mix still contains too much Zn to be used in the blast furnace where Zn has a detrimental effect on production stability. When it is possible to economically separate these heavy metals from the waste, the resulting materials will be secondary resources for ironmaking. The current cost of landfilling is roughly €30 per ton[16]. However as explained in the introduction this might go up to about €175 per ton. With a total landfilled waste of about 50 thousand tonnes the cost comes to between € 1.500.000 and €8.750.000 annually. That might seem like enough incentive to stop landfilling. However if separating the heavy metal is possible then two new resources are generated. Both of these streams also have economic value. At the current Zn price of 2250 Eur/tonne the landfilled Zn is worth about €1.735.000,- annually. The carbon and iron together are the largest mass contributor to the waste stream. These two total at about 49 thousand tonnes, a tonne of hot rolled coil is currently priced at about €530. So if about half is iron oxide then about 18.7 thousand tonnes of hot rolled coils can be produced which total at about € 10.13 million. This very crude calculation then leads to an additional annual gross revenue of between €13.37 million at current prices and €20.62 million with the higher landfilling cost.

This thesis work builds on the foundation that has been laid down by Rosa Verburg[17] and Erik Feenstra[18]. Verburg identified and analysed the material extensively and tried leaching with different solutions. She also focussed on optimizing the parameters used such as time, liquid to solid ratio (L/S), temperature and a few others. Feenstra then continued her work by adding an additional roasting step to improve leaching extractions. These were reasonably successful but not economically viable.

### Redacted: Confidential company information

Zn mid and historical material amounts have dropped tremendously. This is also clear from Figure 1-2, where before it was difficult to maintain the upper limit of Zn addition now there is a shortage of Zn bearing material. This is because most of the historical materials have been reprocessed already and the Zn mid fraction has a too high concentration of Pb and Cd to be used, which instead is therefore landfilled. There is also an imbalance in the input and output of Zn in the system. More Zn is leaving than is coming in. The reason for this is not yet fully understood.[16]

One of the main issues with the material is its high metal sulfide content. Verburg found that off the total zinc amount a minimum of 68% and maximum 88% was present as zinc sulfide. [17]. In literature and other sources these types of dusts are treated and are mainly demonstrated to be made from zinc oxides. Therefore the lack of public information regarding treating high sulfur BF dusts would indicate that this is a unique situation. Which makes the focus for this thesis, the origin of the sulfur and how to convert metal sulfides into metal oxides for more readily leaching.

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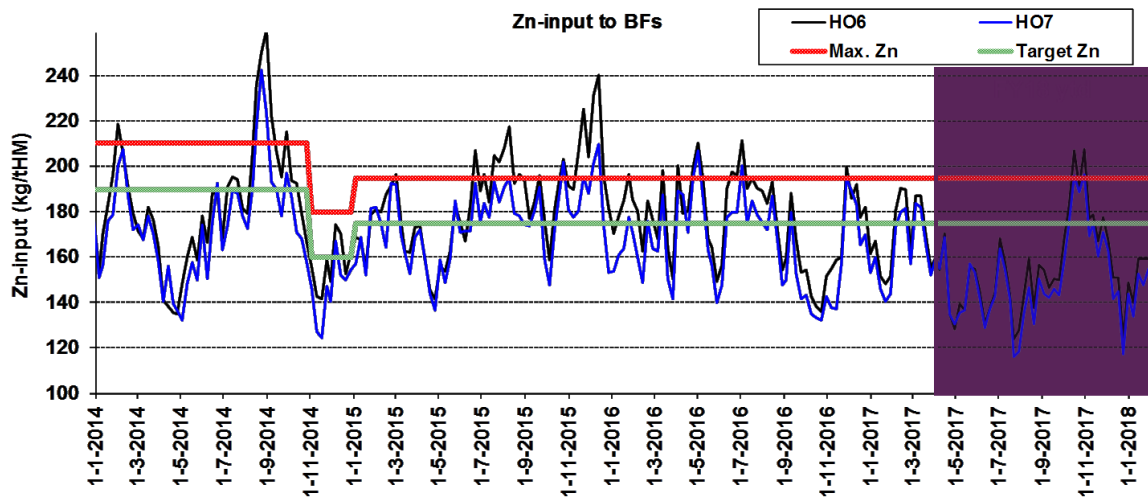
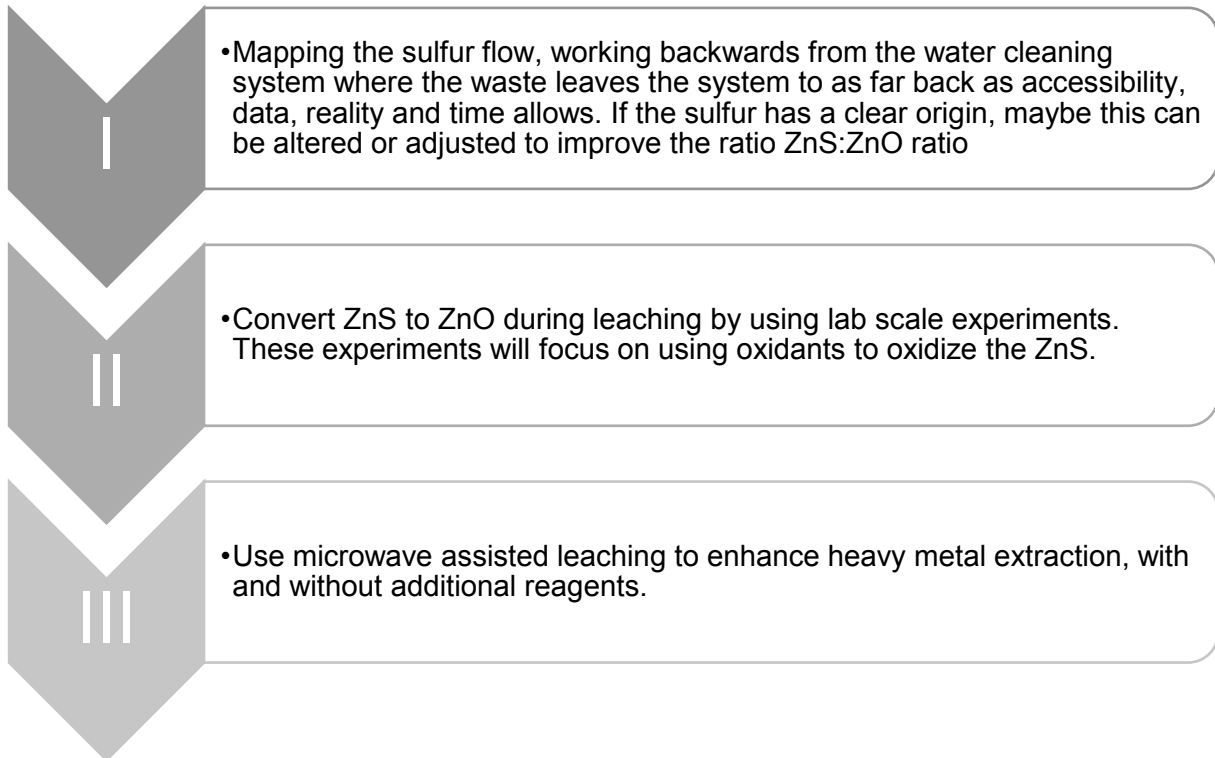


Figure 1-2: Zn input blast furnaces 2014 - 2018

## 1.2. Goal of study

This thesis will use a three pronged problem solving system. The problem that is targeted to be solved is the removal of high heavy metal content through alkaline leaching, of which Zn is the main target. The secondary problem is that the Zn is present as Zn sulfide which is resistant to leaching.



## 2. Literature study

In this literature study material will be gathered compared and analysed for the purpose of creating a solid basis of available theory and best practice for the removal of heavy metals from BF operations. The study will focus on hydrometallurgical methods to extract Zn, Pb and Cd from BF slurries. Success of the current study will be measured in total Zn removed, therefore the focus in this literature study will be on Zn removal. First an overview will be given of current methods for Zn removal. The material characteristics of the Zn rich filter cake found at Tata Steel Europe in IJmuiden and Port Talbot will be discussed and relevant methods will be addressed for them.

### 2.1. Industrial methods for Zn removal

#### 2.1.1. Pyrometallurgical technologies

##### Rotary Hearth Furnace (RHF)

The RHF technology has been in development for a long time. The first operational RHF was constructed in 1976 in by Canadian company INMETCO. The plant was used for processing metallurgical waste. In general a RHF is used for processing waste streams, low grade iron, steel plant dust and other materials unsuited for more typical iron production methods such as blast furnaces. [19, 20] In Table 2-1 an overview is given of production scale factories using RHF technology. Since RHF is mainly used for waste stream treatment the production capacity varies with the local supply of material. For example Lomon only has a tenth of the production capacity of Rong Steel.

Table 2-1: Summary of production scale factories summary from: [19]

Factories	Production capacity kt/y	start production
INMETCO	-	1978
Nippon Steel (Hirota)	140	1988
Amer-Steel MR&E	200	1997
Iron Dynamics	520	1998
Nippon Steel (Dry Iron)	-	2001
Kobe (Kakogawa)	850	2001
Nippon Steel(Kimitsu 2)	700	2002
Nippon Steel (Kimitsu 1)	800	2004
Lomon	100	2007
Ma Steel	200	2009
POSCO & Nippon steel (Pohang Works)	200	2009
Rong Steel	1000	2010
Rizhao Steel	400	2011
Lai Steel	200	2011
Sha Steel	300	2012

In general a RHF works as is shown in Figure 2-1, which is by feeding pellets at one end and moving the floor they are fed on. This moves the pellets to the heating zone where they are heated to about 1000°C, then moving on to the reduction zone even higher temperatures are reached upwards of 1100°C. At these temperatures the reduction of zinc and iron oxides takes place with carbon. Zinc is evaporated and follows the gas stream in the opposite direction of the pellet stream. The pellets containing reduced iron are then expelled from the furnace. Depending on the further composition these pellets can then be inserted into a blast furnace or other iron producing plant. [2]

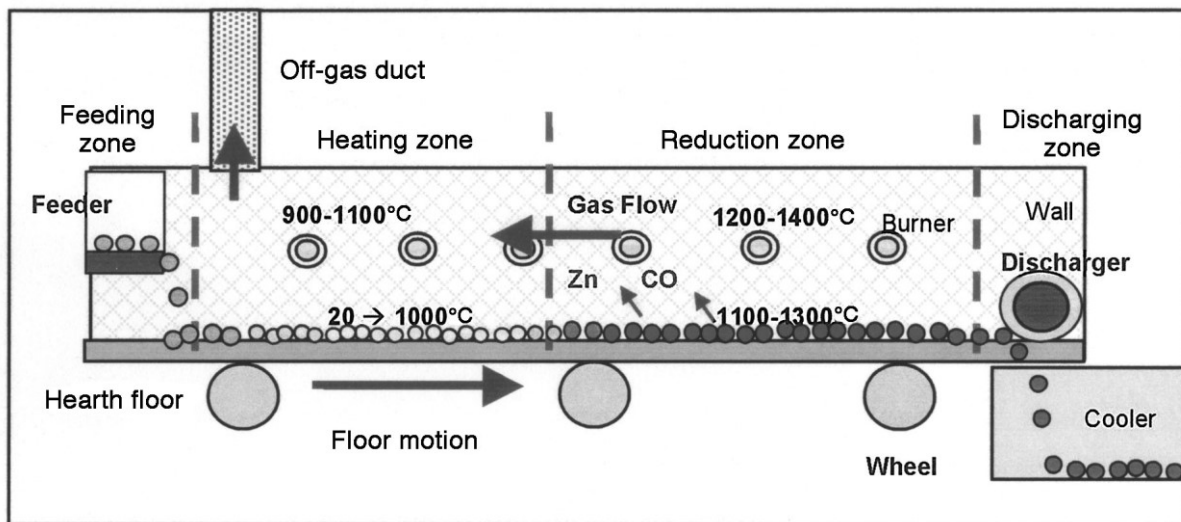


Figure 2-1: Overview of the general RHF process from [2]

### Waelz Kiln

The Waelz Kiln process was invented stepwise in the period 1888 to 1923, where different companies and people improved upon previous rotary kiln concepts until in 1923 two German companies worked together to create the first version of a modern Waelz kiln. [4] Over the past 95 years improvements have been made and currently this process is included in the European Union's BREF documents as a BAT for the extracting of Zn and other metals from EAF dusts. A typical Waelz kiln process is shown in Figure 2-2 and starts with pelletizing the pre-treated dust. This is then led through the Waelz kiln where reduction of the metal oxides occurs. The Zn is evaporated and oxidizes with air to Zn oxide. Over 90% of worldwide EAF dust treatment is done with this process. [21, 22]

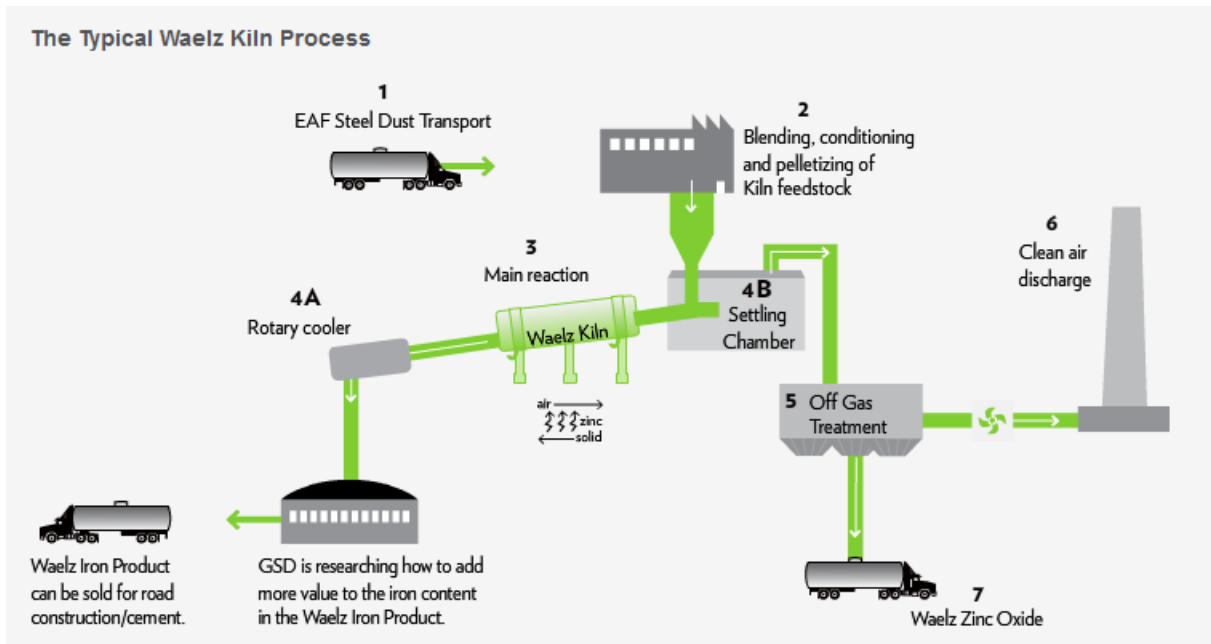


Figure 2-2: Overview of typical Waelz kiln process from [4]

### DK cupola and OXYCUP process

Tata Steel IJmuiden's BF dust used to be transported to DK Recycling und Roheisen in Germany to be processed using the cupola process (CP). This is a process which can take high amounts of zinc which regular BF's are unable to handle. The DK process uses 100% sinter, they have their own sinter plant to produce the sinter from different (waste) sources. It uses a feed consisting mainly of BOF dust at 53%, others include mill scale 12,8%, iron ore 7,6%, BF sludge 5,4%, sand 4.3% and several others. The feed has a high zinc load of 38 kg/tHM which is collected in the wet gas cleaning as a BF sludge concentrate. This concentrate contains 65 – 68% zinc and very few impurities.[23]

The OXYCUP process as shown in Figure 2-3 is a variation of the traditional CP. It uses the function of melting from the cupola furnace and combines it with the reducing function of a BF. Self-reducing briquettes called C-brick are made from sludge and other waste materials by adding a cement binder. These are melted in an oxygen cupola where oxygen enriched air is blasted in. The briquettes also contain scrap and fluxes. The process results in pig-iron and top dust, the top dust is re-used in new briquettes. This recycling increases the zinc content in the top dust which is taken out and sold once it has reached sufficiently high levels of zinc.[6]

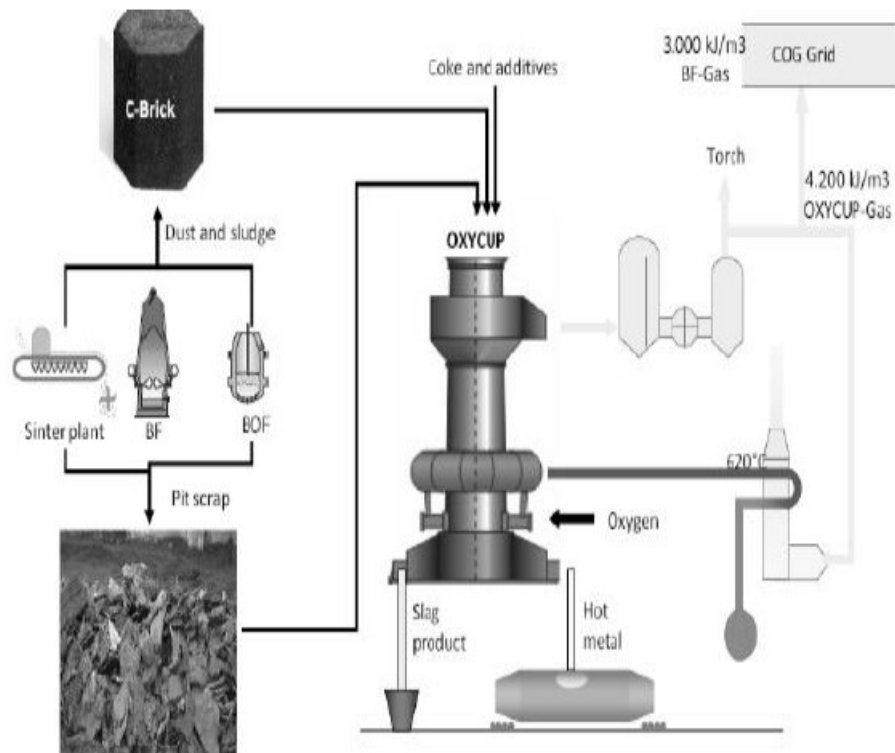


Figure 2-3: Overview of the general oxycup process from [6]

### 2.1.2. Hydrometallurgical technologies

Compared to Hydrometallurgy, pyro-metallurgy is capital and energy intensive therefore methods have been devised and research has been done into hydrometallurgical methods to extract resources from ore and waste streams. However due to the dominant position and proven effectiveness of the pyrometallurgical processes only few commercial hydrometallurgy processes are used in treating steel making dust. Below two industrial methods are discussed.

#### Modified Zincex Process

The MZP is a modified and simplified version of the original Zincex process. It used two of the primary stages of the original process, which are the electro wining and cationic solvent extraction cycle. It works by mildly leaching the Zn material at atmospheric pressure with dilute sulfuric acid at about 40°C. The fluid is thickened, filtered and if necessary lime is added to remove impurities. The pregnant leach solution is then sent to the solvent extraction circuit. The Zn is extracted into the organic phase. The loaded organic solution is washed and prepared for the electro winning, where a pure metal Zn is produced. The process is developed for the treatment of Zn oxides, ash and EAF dust. However efficiency is also linked to the Zn ferrite content, as the Zn ferrite is not extracted. [24]

#### Engitec Zn Extraction Process + Indutec

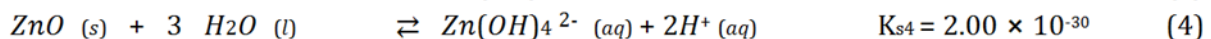
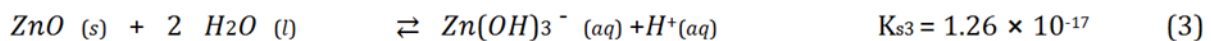
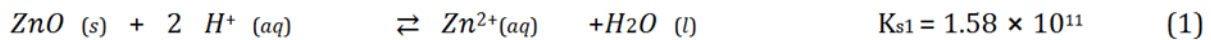
The ENZINEX is an alkaline leaching process. It is currently only applied in the Ferriere Nord facility in Italy. Engitec has been running trials there to create a process to compete with the Waelz Kiln process. In 2016 they released an article introducing the Indutec process which in combination with ENZINEX has the ability to treat EAF and other Zn bearing dusts. In Figure 2-4 the process is schematically shown with the in and out flow for each step. The process works by leaching the dust with ammonium chloride to selectively target the heavy metal oxides. This is done at atmospheric conditions at 70-80°C for one hour.[7, 21, 25]



## 2.2. Leaching

The main interest for leaching of iron and steel making dust has been with acidic leaching, many papers are available on that topic. However acidic leaching has low selectivity, which means that it easily dissolves a wide variety of materials. In this case it's relevant because it also dissolves iron, which is undesirable. [26] Several papers indicate values of iron extracted between 10 and 60%. [27-31] Only a handful of papers reportedly were able to keep iron extraction low in an acidic leaching environment. In one of those papers microwave assisted leaching was used, which drastically shortened the time it took to leach out the Zn. The shorter duration in an acidic environment could then explain the lower iron extracted. [32, 33] Alkaline leaching has been shown to have higher selectivity towards Zn and other heavy metals, leaving the iron in the solid material. [17, 34]

The reaction mechanism for Zn Oxide leaching in acidic and alkaline conditions are given by reaction 1 – 4. These are from Stumm et.al. and also include the solubility products at 25°C. [18, 35] Based on reactions 1 – 5 the solubility of Zn oxide can be derived as was done by Feenstra in his thesis work. He also displayed iron solubility's in the same graph to demonstrate the selectivity of alkaline leaching towards Zn. The graph is shown in Figure 2-5



$$[\text{Zn}_{\text{total}}] = K_{s1}[\text{H}^+]^2 + K_{s2}[\text{H}^+] + K_{s3}[\text{H}^+]^{-1} + K_{s4}[\text{H}^+]^{-2} \quad (5)$$

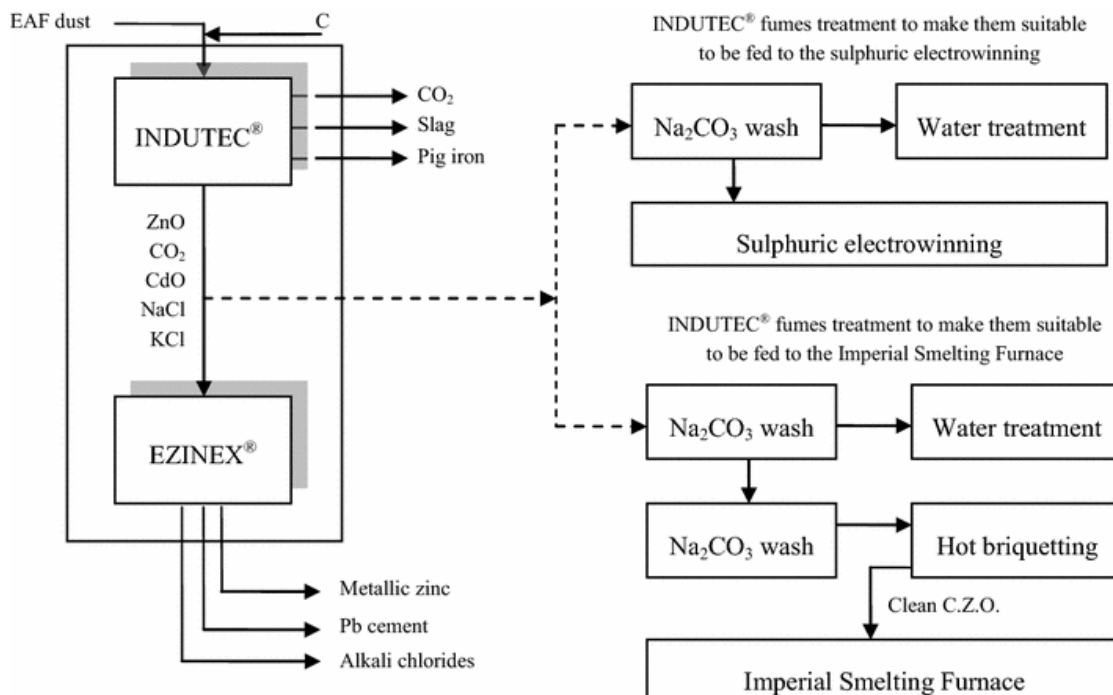


Figure 2-4: Flowsheet between INDUTECH and EZINEX [7]

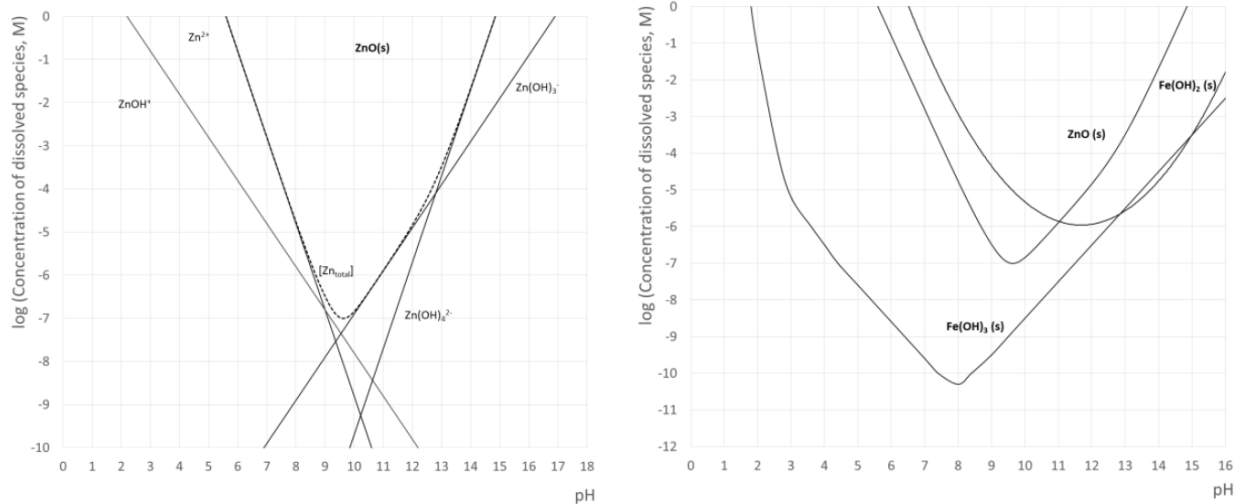
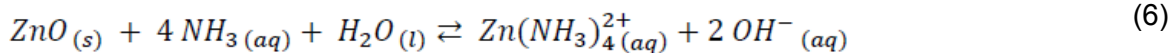
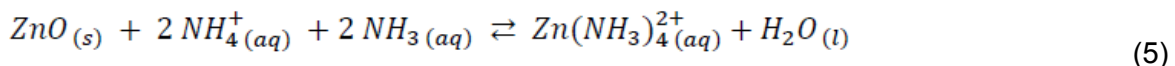


Figure 2-5: Left Solubility of ZnO in water Right Solubility of ZnO, Fe(II), and Fe(III) hydroxides in relation to pH at 25°C [18]

### 2.2.1. Ammoniacal leaching

A form of Alkaline leaching is Ammoniacal leaching where the formation of ammonia metal complexes is the basis of the reaction. The reaction mechanism for this is given in reactions 5 and 6. [36]. Under alkaline conditions Zn normally precipitates as varying types of Zn hydroxides depending on specific pH. However due to the creation of Zn ammonia complexes, Zn remains in the solution and is actually also leached from the solid feed. Verburg and Feenstra [17, 18] are the only ones so far to have used ammoniacal leaching on this type of BF sludge. They both concluded that ammoniacal leaching works very well for the ZnO part of the feed, but requires additional work to also leach out the other species of Zn such as Zn ferrite and Zn sulfide.



### Oxidation order of sulfide metals

In an ammonia leaching system ZnS is oxidized almost as last. This was determined experimentally in 1969 by Majima and Peters. They found the following oxidation order : Cu<sub>2</sub>S > CuS > CuFeS<sub>2</sub> > Sb<sub>2</sub>S<sub>3</sub> > PbS > FeS = FeS<sub>2</sub> = ZnS. Since the BF dust contains many elements in low percentages it is not unlikely that a few if not all of these compounds are present. [37]

### 2.2.2. Oxidant assisted leaching

Previous research has shown that Zn oxide is leached very well by ammoniacal leaching. The case is not the same for Zn sulfides and Zn ferrite. [17] Therefore oxidants will be introduced into the ammoniacal leaching system to improve Zn sulfide extraction.

Different oxidants exist which could be used to extract Zn and other heavy metals from the filter dust. However it is important not to introduce new waste streams or too many additional steps to remove the newly introduced by-products. Therefore materials such as sodium based oxidants are not considered at all.

To minimize unwanted reactions and by-products the following oxidants are considered, either because they or their by-products are not harmful to the process or because harmful (by-)products are expected to be manageable:

-FeCl <sub>3</sub>	Ferric Chloride
-Fe(OH) <sub>3</sub>	Ferric Hydroxide
-KMnO <sub>4</sub>	Potassium Permanganate

### Ferric Chloride

Herck et al. [31] investigated the use of Ferric Chloride on BF sludge as an hydrolysing agent and to increase the redox potential. Hydrolysing has the effect, depending on pH, of precipitating Iron out of the solution as Fe(OH)<sub>3</sub>. Lowering the iron content in the solution reduces iron loss to the solution. Herck et al. remark that the precipitating iron might be a sorption point for Zn and Pb, which is unwanted and therefore something to keep in mind.

Patoczka et al. [38] used FeCl<sub>3</sub> to remove trace amounts of Pb, Cd, nickel, chromium and Zn from waste water streams. They used 30 mg/L which effectively reduced Cr and Ni concentrations from .10 and 0.08 respectively to 0.01 mg/l for both Ni and Cr. This is the exact opposite of what we need for the experiments in this thesis. Therefore pH and solubility will have to be closely monitored.

From Boon and Heijnen [39] the metals sulfide reaction mechanism is given in 7 and from Da Silva [40] reaction 8. Da Silva states that in solution the oxidation reaction as given in 8 is brought about by the reduction of ferric ions to ferrous ions i.e. from Fe<sup>3+</sup> to Fe<sup>2+</sup>.



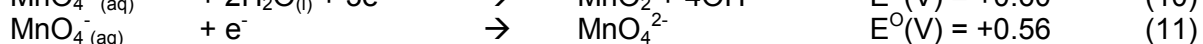
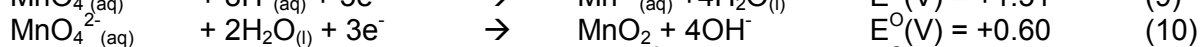
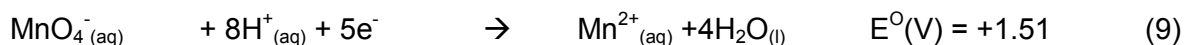
Leclerc et al. [41] used FeCl<sub>3</sub> to break up the ferrite structure in steelmaking dust. They used an oxygen/chloride anion exchange mechanism to extract the Zn as Zn chloride and the iron as hematite. They started with synthetic Zn ferrite and after proof of concept they used different samples of EAF dust. The synthetic Zn ferrite was completely transformed into the desired products ZnCl and αFe<sub>2</sub>O<sub>3</sub>. The extraction of Zn from the EAF dust samples ranged from 98 to 99.8 %.

### Ferric Hydroxide

Published literature on heavy metal removal from steelmaking dust with ferric hydroxide has not been uncovered during this literature study. However since this material is abundantly available at BF operations and the oxidizing effect of other ferric compounds is known, this material will be considered in the experiments

### Potassium permanganate

In acid media potassium permanganate or KMnO<sub>4</sub> is a strong oxidiser. Where it reacts like reaction 9 under atmospheric conditions at room temperature. In neutral media the oxidising effect becomes less strong and the reaction goes like (10). In basic media the reaction is even less oxidative and goes like 11. However even though it is less oxidizing than in acid media it is still a strong oxidizer.



### **2.2.3. Microwave assisted leaching**

Since the previous thesis work by Verburg and Feenstra, several articles have been published regarding microwave assisted leaching.

Al-Harashsheh & Kingman [42] summed up the potential of microwave leaching in their 2004 review as follows: “ Unique microwave heating characteristics are the main driver for potential implementation in metal extraction. These include: low processing time, direct, selective and volumetric heating, and a more controllable heating process.”

These characteristics clarify why this technique is currently being researched for viability in general and in this thesis work. The volumes of material processed in IJmuiden make it important that they are treated with a low processing time and for efficiency it is important to be as direct, selective and controllable as possible.

Microwave leaching has shown a great selectivity between Zn and Fe, where only very low amounts of Fe are leached due to the fast Zn extraction rates, independence of temperature for Zn extraction and the dependence on temperature for Fe. [42, 43] One of the Fe minerals found in BF sludge is ferrite which is known to be particularly refractory against leaching.[44] Alkaline leaching seems to be advantageous for leaching out Zn from ferrite although it would require a concentrated leaching medium. [45] Also leaching kinetics of Zn and Pb have been shown to have improved significantly in caustic solutions with microwave energy. Where the efficiency depended on power, concentration and L/S ratio.

In more recent years Al-Harashsheh et.al [46, 47] continued experiments with microwave assisted leaching with differing results for EAF dusts. In their 2014 paper they recovered 97% of Zn, using microwave treatment, hot water washing and polyvinyl chloride (PVC). The PVC works by releasing hydrogen chloride, which reacts with the metal oxides to break the Zn ferrite bonds. Interesting is that they separated the microwave and leaching steps. So they first made a sample containing EAF dust and PVC, which they treated with microwave radiation. Then the samples were crushed and leached. A similar approach was done in their 2017 paper, but instead of using PVC they used Tetrabromobisphenol A or TBBPA.

Wang et al. [48] used microwave heating to investigate the kinetics behind the decomposition of Zn ferrite. They found that the temperature and microwave power have a positive effect on Zn ferrite decomposition and extraction of Zn. A higher temperature resulted in more Zn extraction, whereas the higher microwave power only resulted in a faster extraction of Zn, with only slight differences in total extraction of Zn.

Yang et al. [49] used microwave leaching on an oxide-sulfide Zn ore with an ammonia-ammonium chloride leaching solution. First they roasted the samples with microwave radiation and then leached it with a 7.5 M/l ammonium chloride leach. They obtained a 82,06% Zn extraction rate, whereas they only reached 30,62% without the microwave roasting step.

Kim et al. [50] used microwave leaching as a minor part of their research into the selective leaching of Pb, Cu, Ni and Zn from Pb smelter residues. They found that the FeS was completely converted to iron oxides and reported an increase in heavy metal leaching efficiency.

The compiled results of this subchapters literature on microwave leaching experiments and its parameters are shown in Table 2-2

Feed	Material		Leaching parameters			Microwave parameters				Results		
	Zn	Fe	Lixiviant	M	L:S	t	Power	Leach step	Additives	Zn extr.	Fe extr.	Ref
	%	%	ml/g			minutes	Watt			%	%	
Metallurgical residue	12.8	21	H <sub>2</sub> SO <sub>4</sub>	4		120	1200	Before	-	97.9	-	[41]
Blast furnace sludge	1.98	41.4	H <sub>2</sub> SO <sub>4</sub>	1	15	3	90	During	-	92.0	9.23	[25]
Electric arc furnace	26.7	16.9	H <sub>2</sub> O	-	-	3	160	Before	PVC	99.0	55.0	[39]
Oxide sulfide Zn ore	35.2	-	NH <sub>3</sub> -NH <sub>4</sub> -Cl	8	10	5	800	Before	Na <sub>2</sub> O <sub>2</sub>	82.1	-	[42]
Electric arc furnace	25.9	18	H <sub>2</sub> O	-	-	1-3	-	Before	TBBPA	52.0	-	[40]
Pb smelting matte	0.48	50	HNO <sub>3</sub>	1	-	15	-	During	-	-	-	[43]

Table 2-2: Summary of research found in literature



### 3. Implications from literature on the present research and detailed research questions

#### 3.1. Implications of literature study for experiments

Before the literature study was done a basic framework and general scope was there. However, a thesis has to be backed by theory and literature. Therefore in this sub chapter the implications of the found literature will be elucidated.

The source material is very fine, which might be good for the extraction of Zn. According to Wang et al. a smaller particle size increase the rate and speed at which Zn is recovered. [48] It is known that Zn is not normally (very) soluble in the pH range which is used for the experiments proposed in this thesis work. [3] In Figure 2-5 and Figure 3-1 the theoretical solubility's of Zn and Zn hydroxide are shown vs pH. Even though Zn and its differing species are not soluble at pH levels between 8 and 11, the Zn ammonia complex is. As can be seen in According to Wang et al. [48] the microwave power is not very relevant for total extracted Zn. However, it is shown that increased microwave power reduces the time it takes to reach the maximum extracted Zn. A faster process is desirable. . It is therefore also very important to monitor and adjust the pH to remain within the soluble range of 8 and 11.

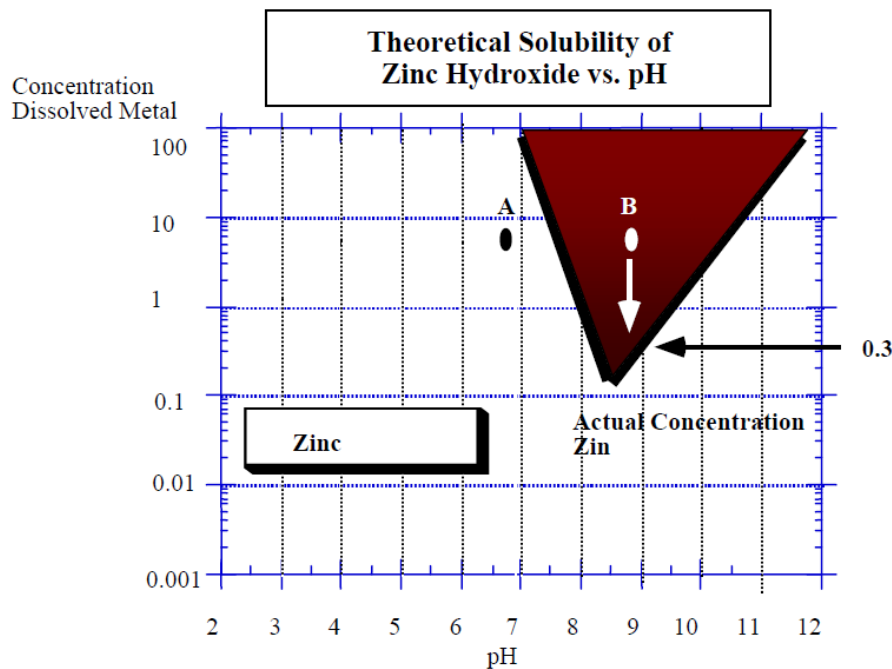


Figure 3-1: Theoretical solubility in water, y axis in mg/L from [3]

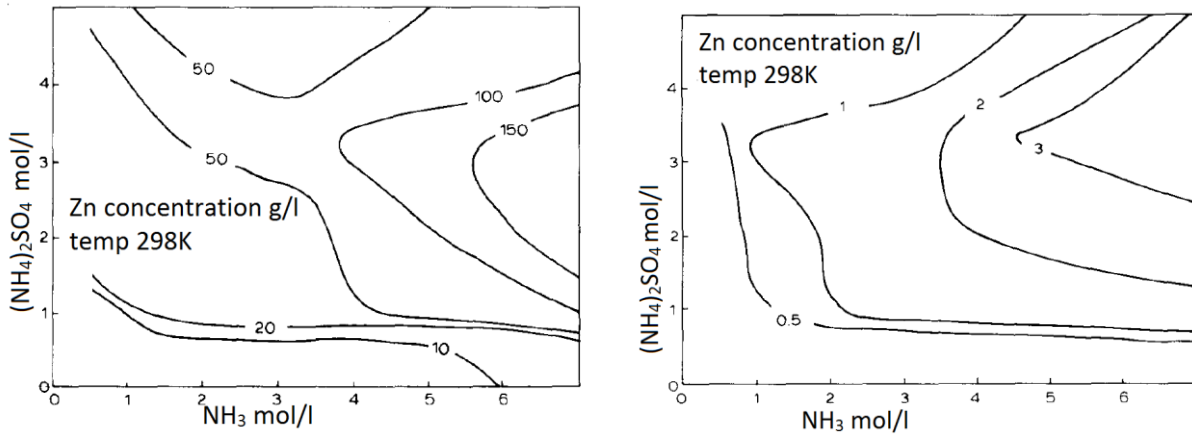


Figure 3-2: Solubility's of Zn in ammonium sulfate. Left: Zn Oxide right: Zn Sulfide, from[5]

In order to control the pH and balance the amount of ammonia ions, a combined ammonia-ammonium salt leaching solution will be used. Two ammonium salts will be used which are, ammonium carbonate and – sulfate. By keeping the pH in the right range with ammonia addition, different ammonia concentrations can be achieved. Guy et al. [5] investigated the solubility of several compounds including Zn sulfide, Zn oxide and Pb sulfide at different ammonia and ammonium sulfate concentrations, see Figure 3- and Figure 3-. From these figures it can be derived that the highest solubility levels are obtained at high ammonia concentrations and an ammonium sulfate concentration between 2 and 3 M. One can also conclude that Zn sulfide is much less soluble than Zn oxide. From Figure 3- it would seem that Pb sulfide is easier to dissolve than Zn sulfide, however this solubility was only attained after 105 hours of agitated leaching. Therefore it would seem unlikely that these solubility levels will be reached during the experiments. Zn sulfide and Zn ferrite are known to be

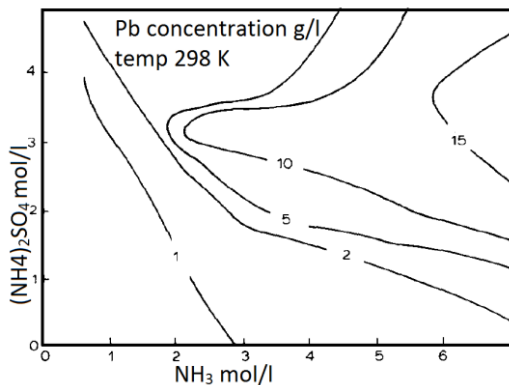


Figure 3-3: Solubility of Pb in ammonium ammonia sulfate, from[5]

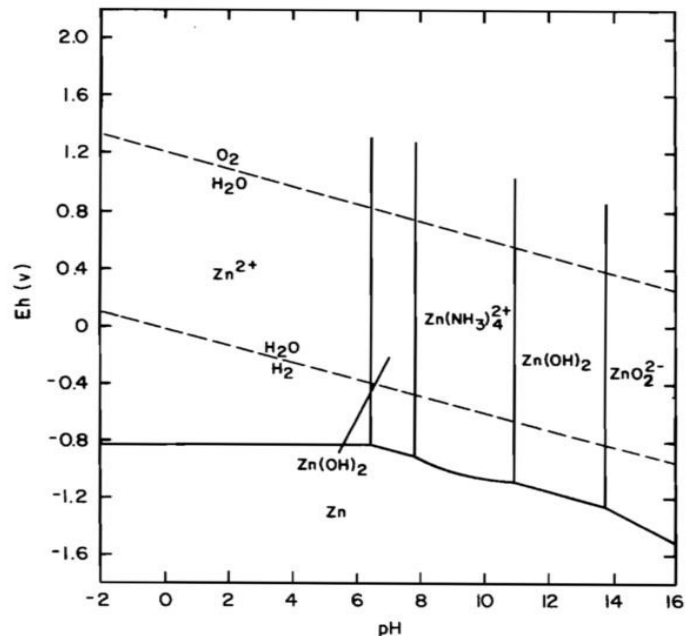


Figure 3-4: Eh-pH diagram of Zn-NH<sub>3</sub>-H<sub>2</sub>O system at 25°C and 101.3 kPa. Ammonia concentration = 1.0 M from Meng et al. [10]



difficult to leach with an ammonia-ammonium complex. However the complex is good for Zn oxide and has a very good selectivity to the heavy metals that are the main goal to extract. Since the feed material contains much iron, an acidic approach is unwanted.

Three valent iron has been selected as a candidate of which two types are used. These are  $\text{FeCl}_3$  and  $\text{Fe}(\text{OH})_3$ . For  $\text{FeCl}_3$  several papers have been found which state that ferric chloride enhances oxidation. As is shown in equation 7 the ferric iron reduces to ferrous iron, which also starts equation 8. The downside of ferric chloride is that it acidifies the solution greatly by producing Hydrochloric acid (HCl). This is also why  $\text{Fe}(\text{OH})_3$  or ferric hydroxide is chosen as an alternative. It has the reducing property of three valent iron and also releases hydroxide which keeps the pH high. Since these two substances have not yet been used in the way that is suggested with this research, very little is known about the concentrations that are required. Since using oxidants will likely increase reaction kinetics, sampling intervals will be in close succession in the first 30 minutes.

From literature it is clear that microwave assisted leaching increases the reaction kinetics, or reduces the time it takes for Zn to be leached out of the solid feed. Therefore instead of a sample interval of 15 or even 30 minutes, a much lower interval should be selected. Every minute or two a sample should be taken.

According to Wang et al. [48] the microwave power is not very relevant for total extracted Zn. However, it is shown that increased microwave power reduces the time it takes to reach the maximum extracted Zn. A faster process is desirable. Harahsheh et al. [46] and others as shown in table 1 have separated the steps between microwaving and leaching. This is an undesired approach for the current study, since it would add additional steps to the industrial application process.

From literature several promising mechanisms are found that indicate oxidation of metal sulfides will be possible for the BF sludge. Empirical data demonstrates that extraction of metal from metal sulfides by using microwave or oxidizing agents is possible. However results vary greatly between different studies. Furthermore it is believed that based on the previous work and results from literature that a viable processing route will be possible. The research carried out for this thesis will have to indicate whether this believe can be substantiated by empirical data.

### **3.2. Research questions**

The main research question for this thesis is:

Based on literature review, sampling on site and lab scale tests what is the effectiveness of enhanced leaching techniques on heavy metal extraction and oxidation of metal sulfides in BF filter cakes?

In order to address the multifaceted main research question, supporting sub questions are created:

- In what way and quantity are Pb and Cd present in the BF sludge and how do they react to leaching?
- How effective are oxidants and microwave assisted leaching at promoting ZnS oxidation?
- Where, when and how is sulfur introduced into the system?



#### 4. Material characteristics of IJmuiden Blast Furnace Cake

To be able to do useful experiments it is important to know the material that is produced at the IJmuiden BFs. In previous thesis work on IJmuiden BF sludge by Verburg [17] a study on the material was done using XRF, XRD and SEM-EDS. She found that the IJmuiden furnace sludge contained mostly sulfidic Zn species. Which is contrary to what most other BF operators report. In most BFs this sludge would be a mixture of oxides. [25, 31] In the succeeding thesis work by Feenstra[18] it was explained that finding accurate data on the exact composition or speciation of the material is difficult due to several factors. These factors include, point of sampling, size separation and difficulties with XRD. The size of the filtered material has a high impact on which materials are found in the analysis. Also specific Zn phase or species identification with XRD is quite difficult because Zn is usually present as very small particles and the XRD peaks coincide with magnetite. [18]

Despite the before mentioned difficulties it is possible to identify the basic elements and some compounds by XRF and C/S analysis. This was done at ANA laboratory at Tata Steel in IJmuiden and results are shown in Table 4-1. The results vary between the times the different thesis works were undertaken. Recently the zinc and sulphur levels have increased by a factor 2. The zinc input in the BF has steadily gone down since 2015 so that does not explain why the zinc in the filter cake has increased so much. Most likely the increase has to do with increased efficiency of the hydrocyclones at the water cleaning facility. And since zinc bonds with sulphur 1:1 it makes sense that if one doubles the other does as well. Further proof of a high ZnS presence.

Also analysed at the ANA laboratory was the PSD for Verburg's thesis work. She found a D50 of 13  $\mu\text{m}$  and D80 of 81  $\mu\text{m}$ . These numbers seem to be accurate as in theory the hydro cyclones separate the solid particles by size. The high Zn fraction is mainly found in the very small particles. After the hydrocyclones over 94% of Zn is below 60  $\mu\text{m}$ . [51]

Table 4-1 XRF<sup>(1)</sup> and C/S<sup>(2)</sup> analyses on the BF Zn rich filter cake

	Verburg[17]	Feenstra [18]	Kempke
	July-2015	Feb-2016	Jan-2018
Element or compound	Wt. %	Wt. %	Wt. %
Al <sub>2</sub> O <sub>3</sub> <sup>(1)</sup>	2.87	2.88	3.07
C <sup>(2)</sup>	35.60	36.1	38.20
CaO <sup>(1)</sup>	4.87	5.03	3.17
Cd		0.02	0.02
Fe <sub>2</sub> O <sub>3</sub> <sup>(1)</sup>	35.10	34.0	29.20
K <sub>2</sub> O <sup>(1)</sup>	1.44		1.48
MgO <sup>(1)</sup>	1.42	1.47	1.06
MnO <sup>(1)</sup>	0.13		0.12
P <sub>2</sub> O <sub>5</sub> <sup>(1)</sup>	0.15	0.15	0.23
PbO <sup>(1)</sup>	0.62	0.54	1.51
S <sup>(2)</sup>	1.70	1.14	2.89
SiO <sub>2</sub> <sup>(1)</sup>	5.70	5.72	6.14
TiO <sub>2</sub> <sup>(1)</sup>	0.17		0.13
ZnO <sup>(1)</sup>	4.91	4.01	9.05

#### 4.1. Material Characterization

Tata Steel IJmuiden produces Zn rich filter cake. Three samples were taken from three different points in the process. Sample one taken directly from the filter press is called “Fresh”. Sample two taken from the storage bunker is called “Bunker” and the third is taken from the final hydrocyclone step and is called “Hydrocyclone”. For the bulk of the experiments the bunker material was used. Another sample came from Port Talbot, also a BF dust.

##### 4.1.1. SEM-EDS characterization of sample material

To see how the target metals are present in the sample material SEM-EDS analysis was done. In Figure 4-1 a SEM image is shown taken from a fresh polished non-leached sample. Larger grains are visible differing from white to black shades in a fine material matrix. When comparing these larger grains to the EDS map that is shown in Figure 4-2 it is clear that these large grains are mainly ore and carbon. In that figure the Zn and S distributions are also shown. These resemble more white noise television screens than any definable large grains. Studying the picture closely does show two grains which might be Zn sulfide, therefore point samples were also taken. The results of the point samples are shown in Table 4-2. These confirm that the large grains are iron oxides and carbon. As the point sample indicates a high percentage of Fe for the ore particles and C for the carbon particles. Off the two areas that might be ZnS the one with a clear grain was sampled. This grain is sampled by points 6 and 7. In Table 4-2 it can be seen that it has Zn and Pb inside and a layer of C, Fe, S, Pb and Zn around it. To find a ZnS particle is quite difficult and then to find it encapsulated inside other material is very interesting. If this build-up of particles is common in the BF dusts then it will be extremely difficult to leach without pre-processing steps such as milling and grinding.

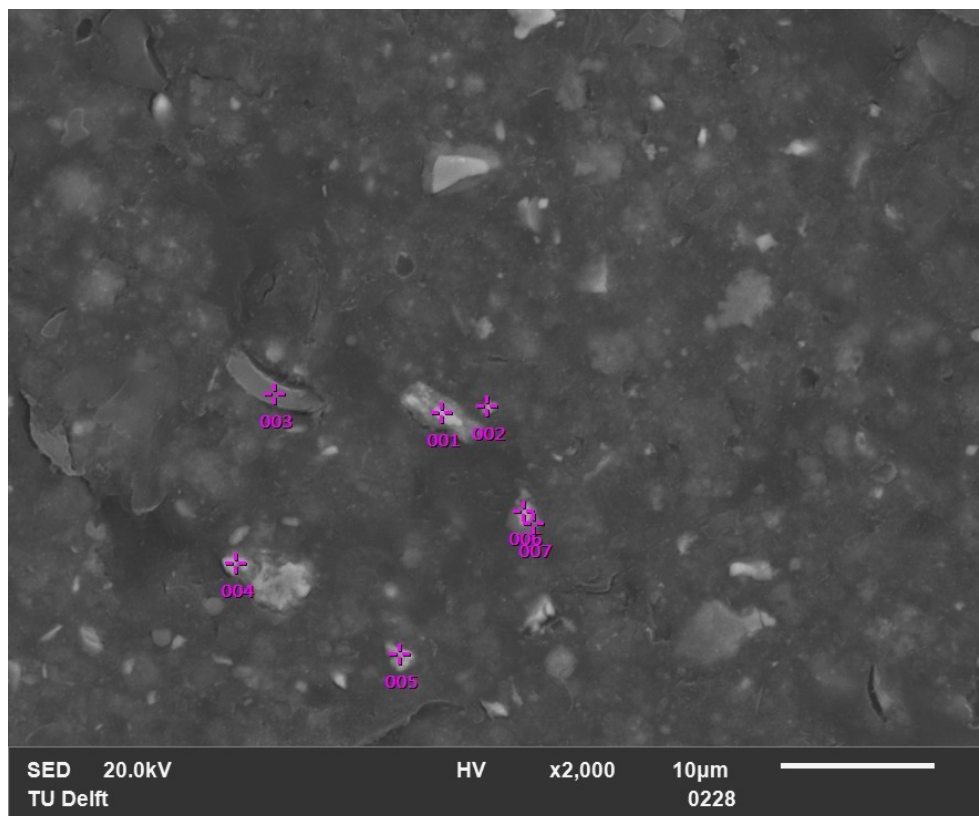


Figure 4-1: SEM image of BF “Fresh” sample, also showing sample points for EDS

Table 4-2: Composition according to EDS of the 7 points in Figure 4-1

Point #	Fe%	K%	O%	Pb%	C%	Na%	Mg%	Al%	Si%	S%	Ca%	Zn%
1	41.98		40.93		17.08							
2	25.71		36		35.32	1.62			1.35			
3			14.69		85.31							
4	41.76		36.01		22.23							
5	23.76		40.41		31.54	1.19		0.83	1.42		0.85	
6	5.43		25.98	25.39	33.63	0.43	0.25	0.47			4.92	3.49
7	13.35	0.23	22.32	5.05	47.4		0.33	0.94	1.3	1.3	1.87	5.91

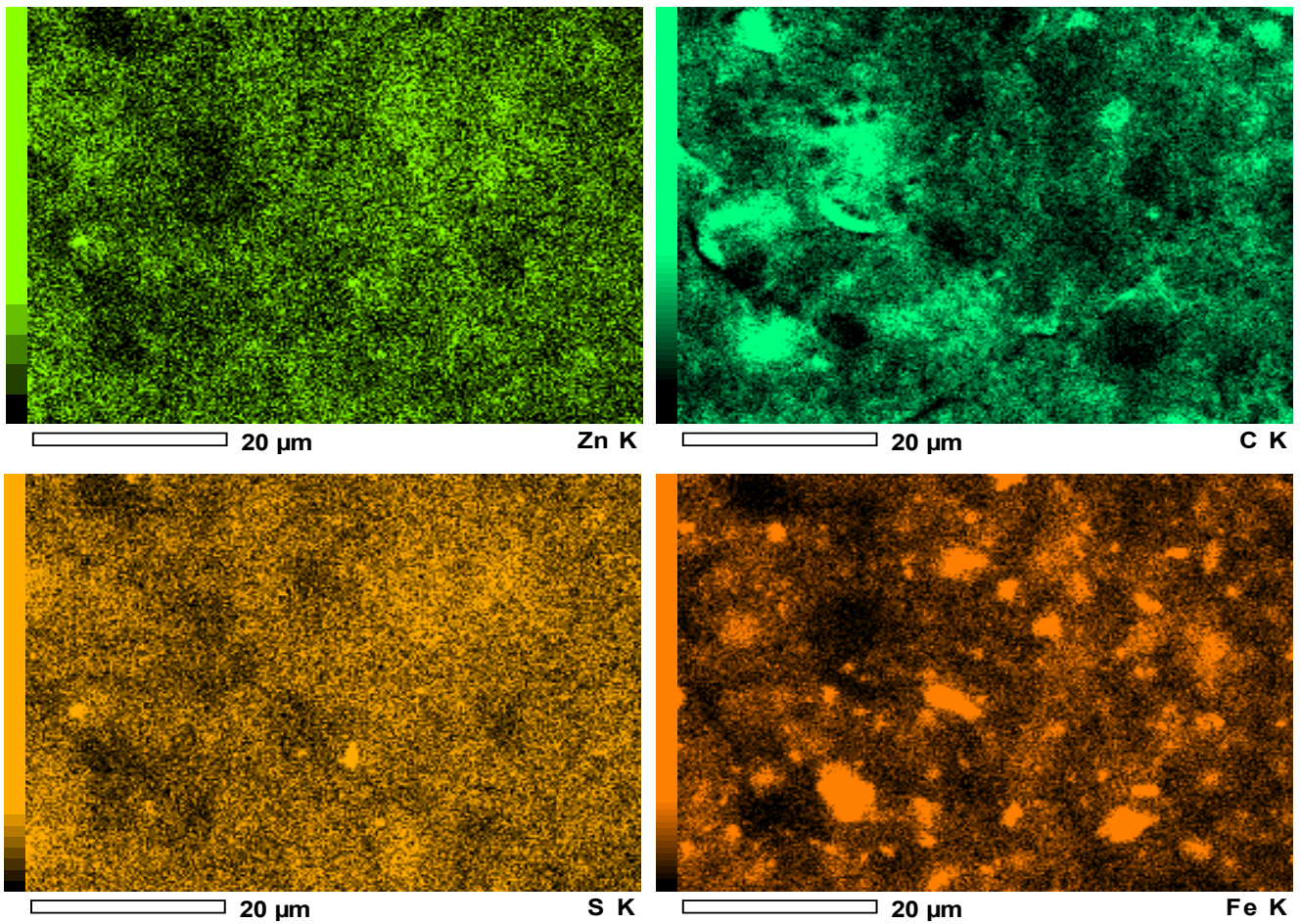


Figure 4-2: SEM-EDS map of same area as Figure 4-1, showing Zn, Carbon, Sulfur and Iron

#### 4.1.2. Chemical Analysis

From a first glance at Table 4-3 the composition of the bunker and fresh samples are fairly similar. Any changes can likely be attributed to the time at which the samples were taken. The fresh sample was taken to check if aging of the bunker material had any influence on the leaching and therefore effectiveness of the experiments. As previous research[17, 18] has indicated it is hard to determine the exact phases and their quantities of the material. Therefore the fresh material was also subjected to several of the same experiments as the bunker material to check for significant deviations. These results can be found in 6.2.3. The Port Talbot sample was requested to see if the same experiments would be beneficial for this material. The composition is similar to the ones from Tata steel, heavy on carbon and iron and also containing similar other elements. The main difference is in the wt. % uptake, it has much more iron and much less heavy metals. The hydrocyclone material was sampled and has a higher heavy metal concentrations than the other two samples. This is especially significant for Pb and Cd, where the amount has doubled. After the hydrocyclone the material goes to a slurry tank where it mixes with the slurry from settler 13 as can be seen in Figure 6-3. Residence time and mixing is likely responsible for the lower concentrations of heavy metals in the filter cake.

Table 4-3: XRF<sup>1</sup> and C/S<sup>(2)</sup> analyses of samples, XRF at ANA laboratory Tata Steel C/S at TU Delft

Element or compound	Bunker	Fresh	Hydrocyclone	Port Talbot
	22-02-2018	17-07-2018	01-06-2018	07-2018
	Wt. %			
Al <sub>2</sub> O <sub>3</sub>	3.07	3.10	4.19	2.20
C	38.20	37.28	34.20	29.60
CaO	3.17	2.84	3.03	3.02
<i>Cd</i>	<i>0.02</i>		<i>0.05</i>	<i>0.006</i>
Fe <sub>2</sub> O <sub>3</sub>	29.20	23.76	25.90	45.00
K <sub>2</sub> O	1.48	1.23		
MgO	1.06	1.08	1.01	0.98
MnO	0.12	0.14	0.23	0.20
Na <sub>2</sub> O	0.50	0.36		
P <sub>2</sub> O <sub>5</sub>	0.23		0.22	0.14
<i>Pb</i>	<i>1.40</i>	<i>1.67</i>	<i>2.95</i>	<i>0.084</i>
S	2.89	2.62	3.36	0.52
SiO <sub>2</sub>	6.14	5.85	6.37	5.93
TiO <sub>2</sub>	0.13	0.14	0.13	0.13
<i>Zn</i>	<i>7.27</i>	<i>7.29</i>	<i>8.84</i>	<i>1.04</i>

## 5. Experiments

In this chapter the procedures for the experiments will be explained in a step by step way to provide clarity and reproducibility. The material characteristic determination methods will also be elucidated.

### 5.1. Experimental Method

Based on the literature review a process of ammoniacal leaching in combination with oxidants and/or microwaving is proposed. The viability of this method is confirmed in literature. The main parameters are shown in Table 5-1. These are temperature, O<sub>2</sub> addition, pH, ammonia and ammonium concentrations, time, temperature, solids loading, particle size and oxidant addition. The effectiveness of treating BF Zn rich dust had to be tested experimentally. The following section describes the design of the experimental set-up and procedures. In Table 5-2 the reagents used for the experiments are shown. Their brand and CAS number has been added as well to help identify the specific substance used.

Table 5-1: Parameters used in experiments

Constant parameters	Variable parameters
Stirring speed 600 RPM	Oxidants (FeCl <sub>3</sub> /Fe(OH) <sub>3</sub> /KMnO <sub>4</sub> )
Ammonia concentration 9 M	Ammonium salt ( carbonate or sulfate )
Oxygen 20 L/h	With or without oxygen
Liquid/Solid ratio 5 mL/g	With or without microwaving
Temperature 40°C	
Ammonium salt concentration 2 M	
Sample amount lab reactor 40 g	
Sample amount Anton Paar microwave 3 g	
Microwave power 5 Watt	

Table 5-2: overview of reagents used in experiments

Reagents	Brand	Cas number
Ammonia Hydroxide 25%	Sigma-Aldrich Puriss	1336-21-6
Ammonium Sulfate	Merck Suprapur	7783-20-2
Ammonium Carbonate	Merck Emsure	10361-29-2
Ferric Chloride	C.I.F.	7705-08-0
Ferric Hydroxide	Alfa Aesar α-phase 99%	20344-49-4
Potassium permanganate	Merck Emsure	7722-64-7

### 5.1.1. Lab reactor leaching

#### General leach Equipment and Setup

The oxygen purging leach setup is displayed in Figure 5-1. The main components are numbered and described in the legend next to it.

In this general setup the design has been optimized in comparison to the previous thesis work by Feenstra and Verburg. The current leaching reactor has one inlet and one outlet. Oxygen is inserted on the left of Figure 5-1. through the tube via a Brooks airflow control machine. The oxygen, ammonia and other gasses can only leave through the Dimroth condenser which is slightly over dimensioned to ensure as much of the ammonia gas can condense and re-enter the fluid as possible. During sampling the gas flow and stirrer are turned off and a plug is removed to insert a pipet to extract a sample. Sample size varied between 5 to 10 mL.

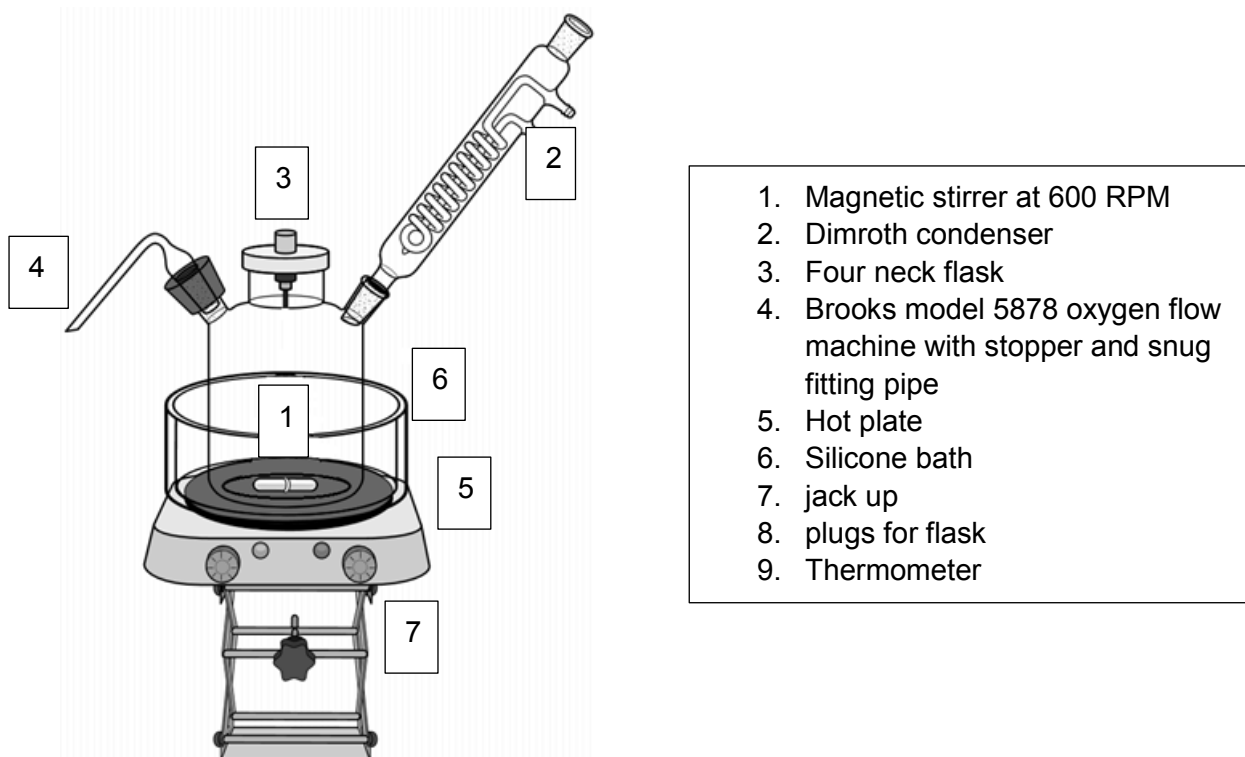


Figure 5-1: main leaching test setup



## Kinetics leach Equipment and Setup

The lab reactor setup is displayed in Figure 5-2. The main components are numbered and described in the legend next to it.

This setup has a top stirrer which was fine for the kinetics experiments since no additional oxygen or air was supplied to the system. However when adding air or oxygen the resulting flow of gasses does not fully pass through the condenser. The top stirrer is not airtight and therefore gasses will flow from both the top and through the condenser.

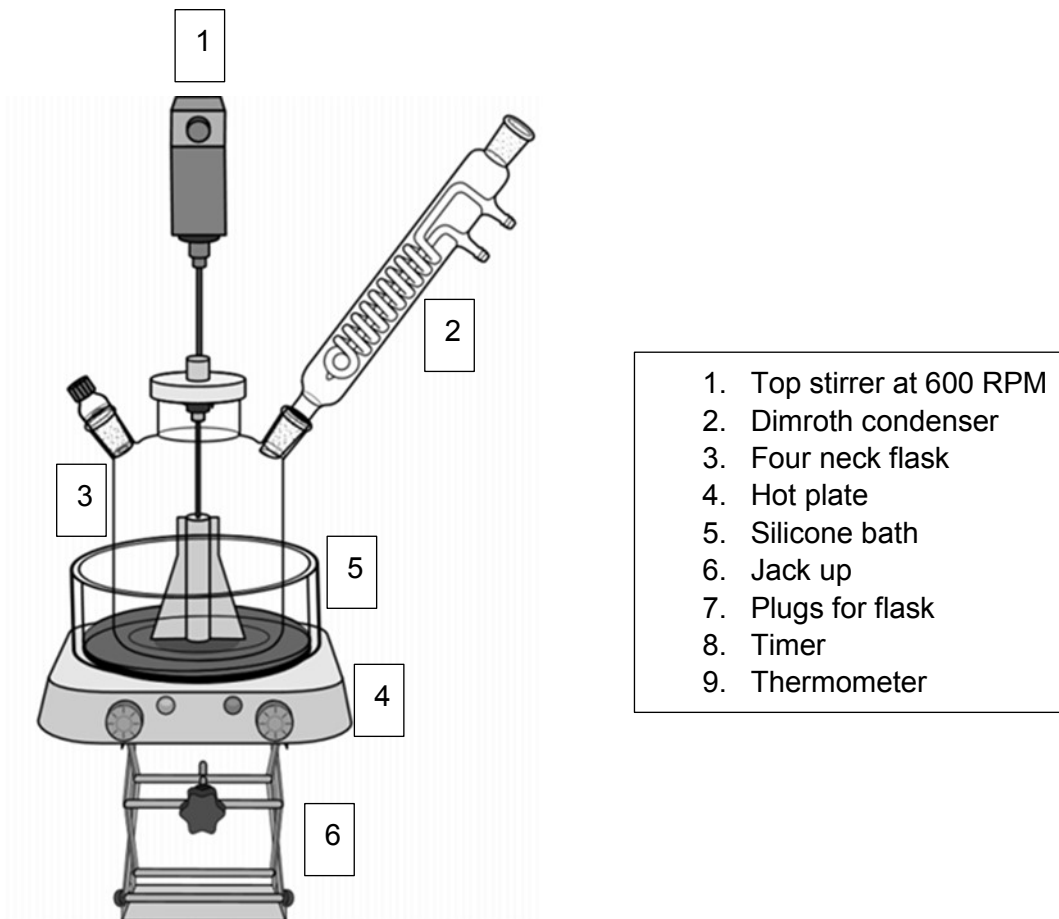


Figure 5-2: Kinetics leaching setup

### 5.1.2. Microwave-assisted leaching

The laboratory grade microwave used is an Anton Paar Monowave 400. This microwave is shown in Figure 5-3. The largest possible vials were used, these are 30 ml. To ensure safe working conditions a maximum of two thirds of the volume is used. The vials were filled externally, then shaken and inserted into the machine. This ensured that the material is mixed and the machine stays clean. The machine displays the working conditions on the touchscreen, which helps to keep control over the process and fine-tune the settings. In Figure 5-3 an example is given of the shown parameters. Since the focus of these experiments is on using microwave energy to enhance leaching of metal sulfates it is important to have a continuous application of this energy to the system. However since the vials are small the liquid heats up fast and the experiment should be done at low temperatures to preserve the ammonia in the solution. Therefore it was decided to use a low power continuous application instead of short high power. In this case low power is 5 Watt.

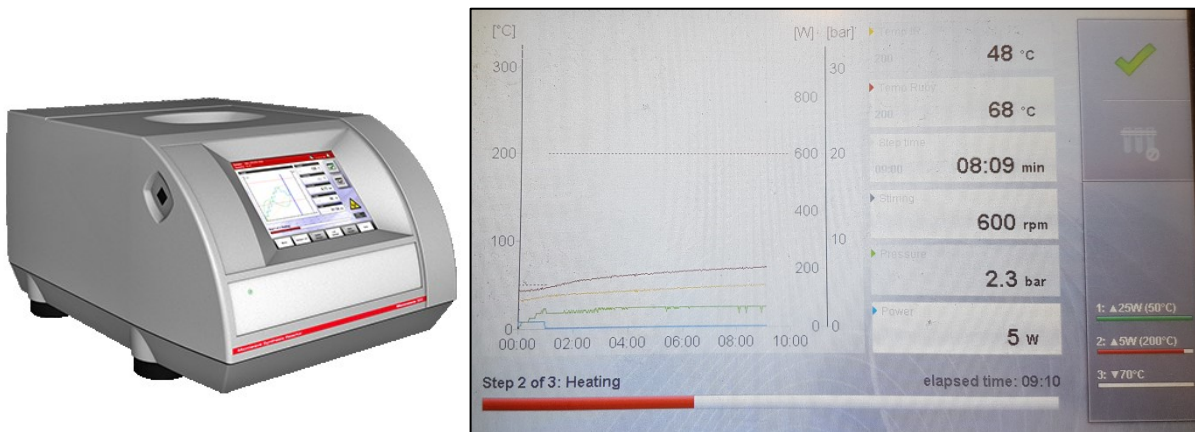


Figure 5-3: On the left: Anton Paar monowave 400, On the right: an indication of what a running experiment looks like.

### **5.1.3. General procedures**

The Zn rich filter cake is collected at Tata Steel, due to the desired quantity for the main series of experiments it has to come from the storage bunker instead of directly from the filter press. Additional small samples are taken from the hydrocyclone and fresh from the filter press. The material is air dried and homogenized at the sampling department. The material is then taken to the lab in Delft where it is fully dried in an oven at 105°C for 24 hours. After which, the material is ground into fines with a mortar and pestle and used for a series of experiments. A virgin sample is also sent to the analytical lab at Tata Steel in IJmuiden for XRF analysis.

#### **Sampling procedure**

1. Stop stirrer 30 seconds before required sampling time
2. Remove plug
3. Insert pipet and take sample from just under the surface of the liquid
4. Put sample into small beaker
5. Re-insert plug and start stirrer
6. Fill syringe with sample from beaker and screw on filter
7. Empty syringe through the filter into a vial
8. Close and label vial, then store for analysis
9. Clean glassware, dispose of used filters and syringes

#### **Experiment procedure reactor leaching**

1. Measure required sample material and add to flask
2. Measure required leaching liquid and put in fume cupboard
3. Put flask in setup inside the fume cupboard and insert stirrer/magnet
4. Insert condenser and turn on the water flow
5. Jack silicone bath up so that silicone envelops the flask and the bottom of the flask is nearly touching the bottom of the bath
6. Add leaching liquid and close the open holes with plugs
7. Start stirrer and timer
8. Take samples at designated times as described in the sampling procedure
9. After completion of the experiment the residue is filtered, dried and stored for analysis

#### **Experiment procedure microwave leaching**

1. Prepare experiment settings on microwave
2. Measure sample material and leaching liquid, add both to vial
3. Close vial and shake vigorously
4. Insert vial into microwave and click start experiment
5. Insert thermometer
6. After experiment is done extract thermometer
7. Take vial and use pipet to take fluid from sample
8. Follow sampling procedures steps 4,6 – 8
9. After completion of the experiment the residue is filtered, dried and stored for analysis

## 5.2. Characterization methods

### XRF

X-Ray Fluorescence: To get an overview of all the main elements that are present in solid samples an XRF analysis is used. This analysis is done at Tata Steel, the sample is added and weighed into a platinum cup with a known flux. The sample is then pre-oxidized at 1000°C in a Linn furnace. The carbon is hereby mostly converted to CO<sub>2(g)</sub>. The remaining sample is dissolved in a flux that is a mixture of Li-tetraborate and Li-metaborate. The mixture is then poured into a platinum dish which results in a pearl. This pearl is analysed on the X-ray spectrometer (An Axios or PANanalytical).

### ICP

Induction Coupled Plasma: This analysis is done on the liquid samples at the analytical department at Tata Steel, they are familiar with the type of material which results in more comparable and accurate findings. The measured contents are focused on Zn, Pb and Cd. The sample is diluted and acidized with aqua regia, after which it is sprayed into a plasma as a fine mist. The resulting emissions of wavelengths are analysed and attributed to specific elements.

### Leco CS744

Carbon and sulfur: At the laboratory of the Material Science Engineering department of Delft University of Technology the carbon and sulfur content were analysed using a Leco CS744 device. Ignition oxidants are added to the sample in a ceramic crucible, which is then placed in the device. The sample is burned in a 18 MHz high frequency induction furnace with an integrated oxygen lance to complete combustion and improve extraction. Carbon is converted to CO<sub>2(g)</sub> and S to SO<sub>2(g)</sub> the concentrations are measured by infrared detection.

### Eltra Carbon Sulfur

Carbon and sulfur: At the analytical laboratory of Tata Steel the carbon and sulfur content were analysed in an Eltra analyser. A sample is placed in an oxygen flow and burned in a High Frequency induction furnace/oven. Carbon is converted to CO<sub>2(g)</sub> and S to SO<sub>2(g)</sub> the concentrations are measured by infrared detection.

### SEM-EDS

Scatter Electron Microscopy-Energy Dispersive Spectroscopy: This analysis is done at the material science engineering department of Delft University of Technology. Solid samples were polished and inserted into a Jeol JSM-IT100 device. SEM provides detailed high resolution images of the sample by rastering a focussed electron beam across the surface and detecting secondary or backscattered electron signals. After localizing an interesting area with SEM the area can be mapped with Energy Dispersive X-ray Spectroscopy (EDS) to determine the elements present. This however takes some time, so another option is to do spot checks which reduces the time required for analysis.

### Determination of percentage metal extracted from sample

The samples are leached and the resulting leaching liquid is then analysed using ICP analysis. This gives a concentration of elements present in the leaching liquid in mg or grams per litre. Then also the leached solid sample material is analysed using XRF resulting in a wt% of compounds present. The leaching solution can leach out about ten times more material than it is provided with. Therefore in theory all leachable material should be able to

be leached out. After analysis the concentration of elements is known in the liquid. The analysed concentration is divided over the amount of element that should be present based on analysis of the non-leached sample. This is done as shown in formula 1

$$\mathbf{Extraction\ \%_{liquid} = \frac{Leached\ out\ material\ in\ grams/litre}{virgin\ sample\ concentration\ in\ grams/litre} * 100\% \quad (1)}$$

In Table 4-3 it is shown that 7.27wt% of Zn was detected in the Bunker sample by XRF analysis. So a representative sample of 40 grams should then contain 2.908 grams of Zn. The sample of 40 grams is put in a 250 mL leaching liquid. Therefore the maximum concentration will then be 11.63 grams/litre. Then if lab analysis reports a concentration of 9.1 grams/Litre of Zn the extraction percentage will be  $9.1/11.63 = 78.2\%$ . A similar method is applied for the solid material. After leaching the solid material is dried and send to the analysis department for XRF. The remaining wt% is determined and divided over the original amount giving the percentage as follows from formula 2

$$\mathbf{Extraction\ \%_{solid} = \frac{virgin\ sample\ wt\% - leached\ sample\ wt\%}{virgin\ sample\ wt\%} * 100\% \quad (2)}$$



## 6. Results & Discussion

### 6.1. Sulfur in the water cleaning system

The way sulfur gets into the system and how it is spread is essential to know to develop a good processing route. In this chapter it will be looked at from a general flow first before focussing on the water cleaning department where the sludge is divided into three streams of which two are recirculated into the BF system and the third fraction is collected and prepared for landfilling.

#### 6.1.1. The general sulfur route

In 2017 Schrama et.al. [8] published an article about sulfur removal at Tata Steel IJmuiden. This article focusses on the main flows which is good to get a general understanding of the sulfur flow and distribution. Schrama made a Sankey diagram which is shown below in Figure 6-1. The off-gas and dust, indicated by the green circle in Figure 6-1 are the known sources for BF sludge. From the figure it is clear that this is only a small part of the total sulfur in IJmuiden. Per tonne of produced steel this part represents about 0,121 kg or 4.3% of the total sulfur that is introduced into the BF. At a production of 6,5 Mtonnes per year this leads to an average of roughly 2150 kg of sulfur every day. As Schrama made a general mass balance based on a particular steel grade this value should be taken as a rough indication.

The critical eye is drawn to the balance fraction, this is a much larger portion than what is attributed to the off-gas and dust combined. What it means is that the system described by Schrama is not perfectly closed, so the amount of sulfur in the 'balance' is lost somewhere. If the amount of sulfur from the balance is added to the off-gas and dust it would mean an enormous increase in total sulfur in the sludge. However the amount of sulfur in the water cleaning system is quite well monitored and therefore it is unlikely that the balance can be added in any substantial way to the off-gas and dust.

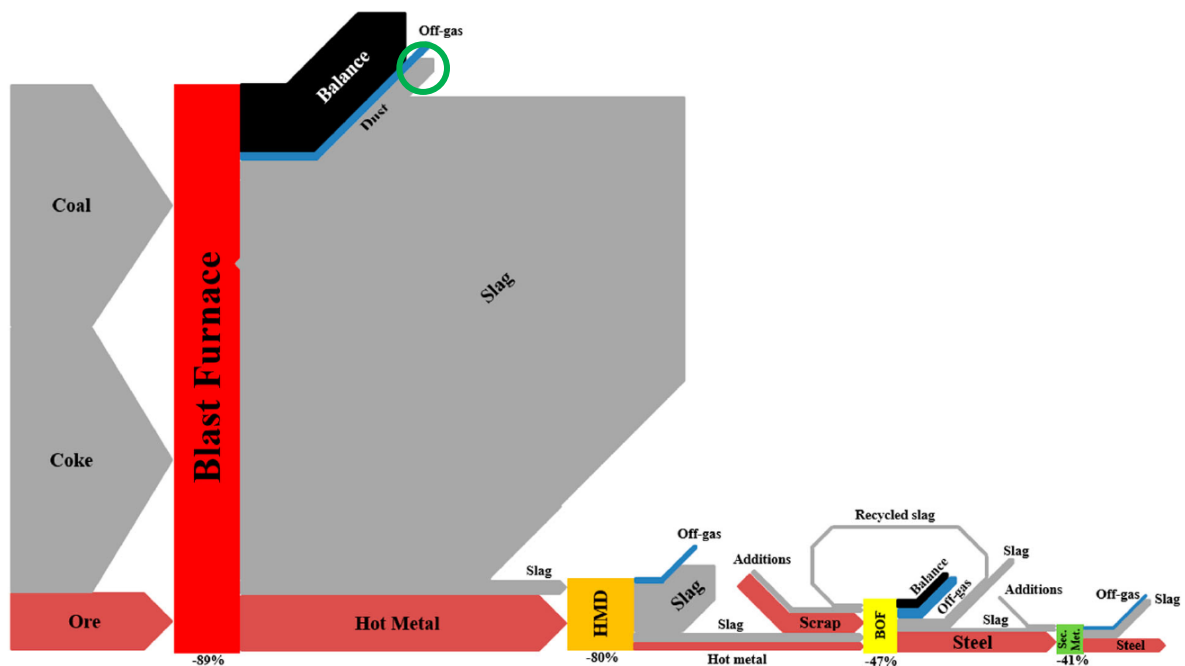


Figure 6-1: Sankey diagram of sulfur route IJmuiden, from [8]

### 6.1.2. Sulfur in the water cleaning department

Dust is generated in the BF which is then expelled from the top of the furnace. Here it is collected and separated into fine and coarse material. The average total daily expelled material for 2017 contains about 2040 kg of sulfur of which 20% leaves with the coarse fraction and 80% with the fines. This ratio was based on averaging production numbers of coarse dust from January 2017 until December 2017, the average sulfur content during that time and on the work by Schrama et al.[8]. The coarse is recycled to the sinter plant and the fines are sent to be washed from the gasses by the Bisschoff wasser as shown in Figure 6-2. The Bisschoff wasser uses water from the water cleaning department to capture particles from the gas stream. It does this by spraying a fine mist of water in the path of the gas stream. When the water hits a solid particle in the gas stream it will attach to the water droplet and fall down to be collected and sent off to the water cleaning department. The solid material that is washed from the BF gasses is then sent to the water cleaning department as a slurry. There are two BFs and both streams are mixed just before entering the water cleaning system. Having two BFs mix complicates the analysis of the effect of the operating conditions on sulfur content.

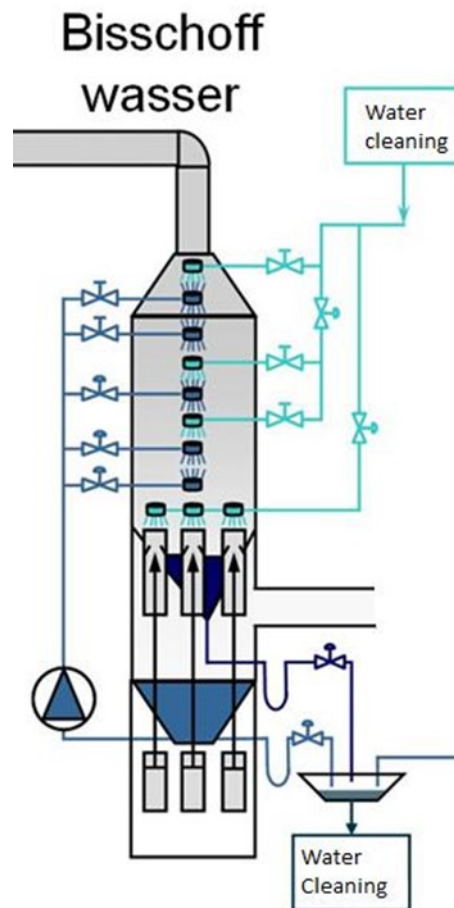
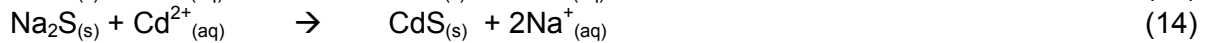
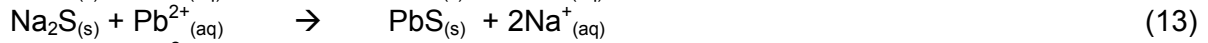
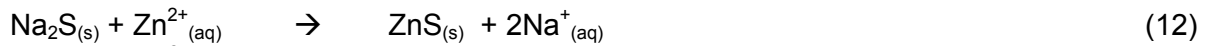


Figure 6-2: Schematic view of the Bisschoff wasser as used in IJmuiden



Redacted: Confidential company information



### 6.1.3. Origin of sulfur

Where the exact amount of metal sulfides come from is difficult to determine. However, we can trace sulfur flows and certain is that most of it comes from the BF which in 2017 was about 1632 kg/day and another amount of 27 kg/day is being added at the water cleaning department. The exact amount of sulfide ( $\text{S}^{2-}$ ) that is added at the water cleaning department varies depending on what is required, but the target value is 660 mg/litre. In Figure 6-4 an overview is given of the sulfide concentration in the settling tank 13 for the past year. In theory this sulfur should react with the metal ions to precipitate as metal sulfides. In practice it seems likely that this actually works since about 10% of the water from settling tank 13 goes to the Bio 2000+ facility where a high Zn content will kill off the biological agents cleaning the water. Therefore the incoming water is closely monitored. It is then safe to assume that the remaining 90% also has a similar Zn and sulfur content. This can be assumed because it is the same well mixed water and 10% of the total flow is randomly siphoned off and send to the Bio 2000+ facility.

The amount of sulfur added is enough to remove/precipitate on average 70 % of the Zn that goes into settling tank 13. The amount of Zn goes down significantly and barely any sulfur is going with the overflow to be reintroduced into the clean water system. This can also be seen in Figure 6-5. Sporadic sulfur tests indicate that only about 0.5 mg/l  $\text{S}^{2-}$  is going with the overflow, which means that basically all sulfur is used for precipitating as metal sulfides.

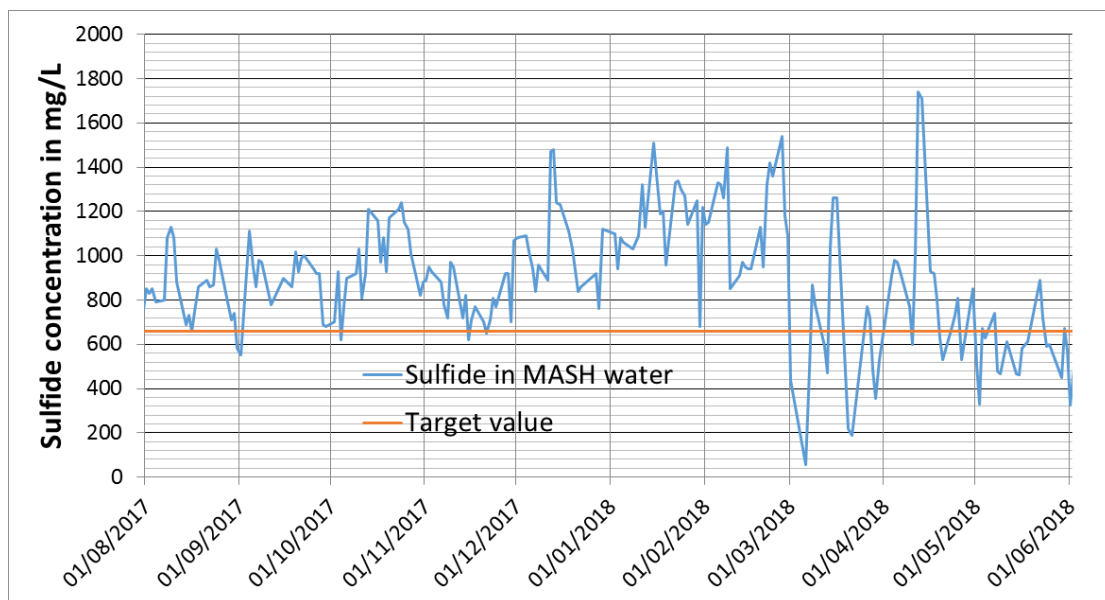


Figure 6-4: concentration of sulfide in settling tank 13 water

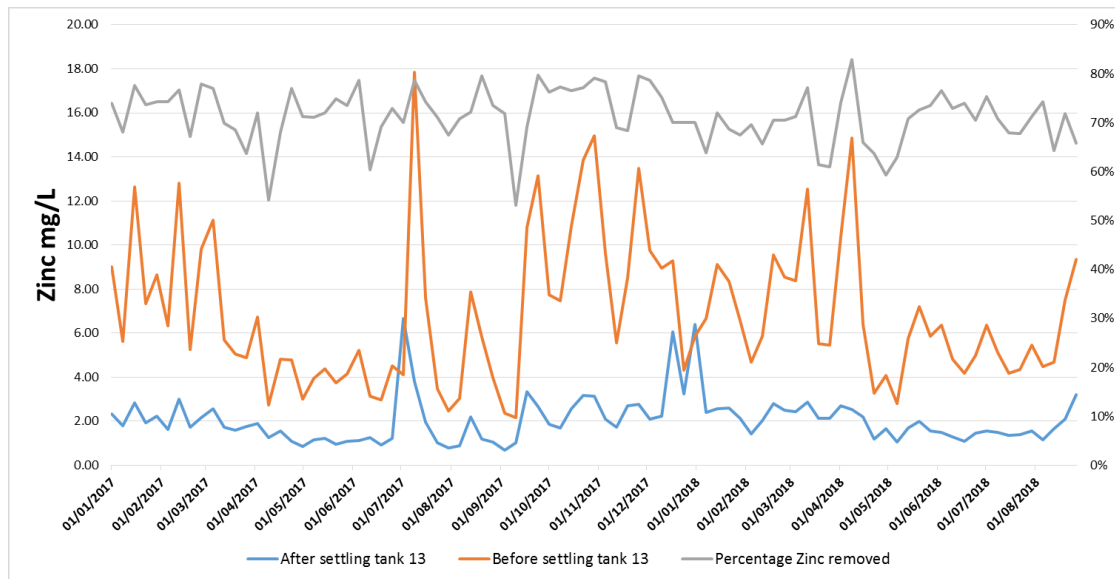
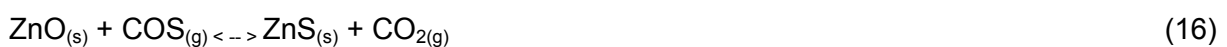


Figure 6-5: Left axis; Zn concentration before and after settling 13 Right axis: percentage Zn precipitated after settling tank 13

#### 6.1.4. Reaction analysis of metal sulfides

Due to the problems zinc gives in the blast furnace this metal has been studied a great deal. However those studies mainly focus on zinc as an oxide and on the problems within the blast furnace itself. The zinc accumulating process is shown in Figure 6-6. This figure is from a paper by Esezobor and Balogun from 2006 [9]. In it ZnS is only mentioned once and the focus is entirely on oxides. From analysis of the Zn rich BF filter cakes it is clear that not all Zn can come out of the BF as an oxide. Or if it does then somewhere about two thirds of it reacts from ZnO to ZnS. At the final processing stage metal sulfides appear due to the addition of Na<sub>2</sub>S at the water cleaning system. However as explained in this chapter the amount is so low that it cannot account for all the metal sulfides in the filter cake.

To be able to understand why there is such a large fraction of ZnS present in the BF dust it will have to be looked into more fundamentally. In 1999 as a part of his Ph.D. studies M. Van der Velde[52] did some fundamental research on zinc in the blast furnaces of Tata Steel IJmuiden. He also found the general assumption in other research and literature to be that ZnO is more likely to form. This is assumed because it is more thermodynamically stable than ZnS. However he also found that in reality the dust actually mainly contained very fine wurtzite which is a phase of ZnS which is stable at above 1020 degrees Celsius as is clear from Figure 6-7. He explains this by showing that thermodynamically ZnO is more stable than ZnS, but that ZnO<sub>(s)</sub> and Zn<sub>(g)</sub> then further react with COS<sub>(g)</sub> or H<sub>2</sub>S<sub>(g)</sub> to form ZnS by reaction 15 and 16. The formed ZnS is then either expelled from the furnace or reduced again to Zn and S in the lower part of the blast furnace.



Van der Velde also mentioned the particle size, which was analysed in previous studies. The wurtzite is very fine which is an indicator for it being formed from a gaseous phase. The fact that it is still wurtzite is also an indicator of rapid cooling since it is only stable above 1020 degrees Celsius. Analysis shows that the wurtzite is smaller than 1 micrometre and even a large part is present as below 0,1 micrometre.[53] The SEM-EDS pictures from 4.1.1 also indicate a very fine material.

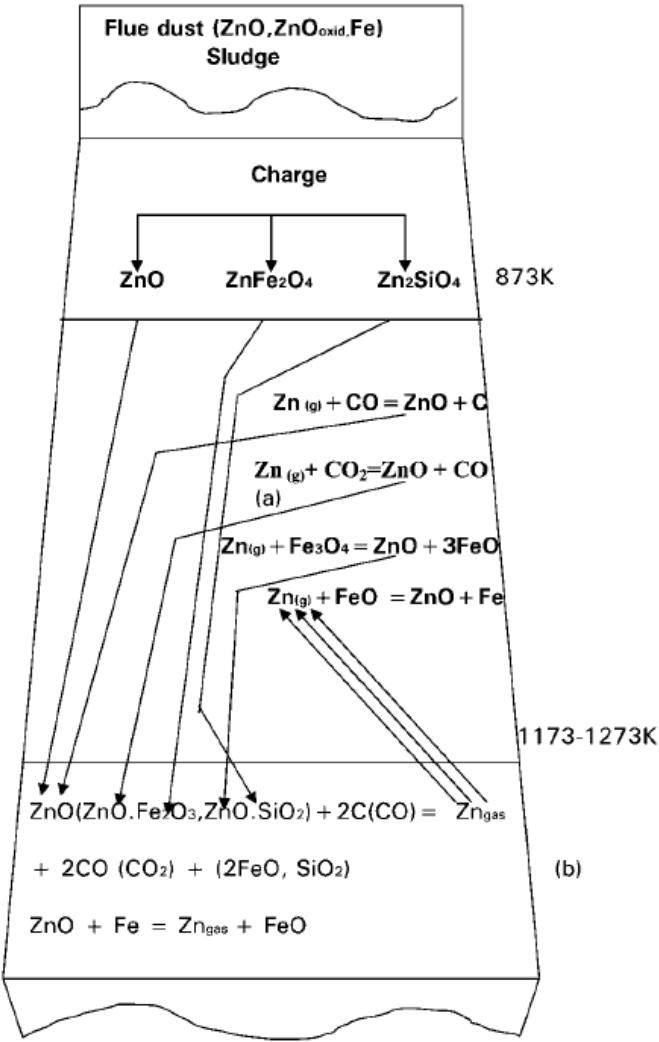


Figure 6-6: Mechanism of zinc oxidation, reduction and circulation in blast furnace from: [9]

# FeS-ZnS

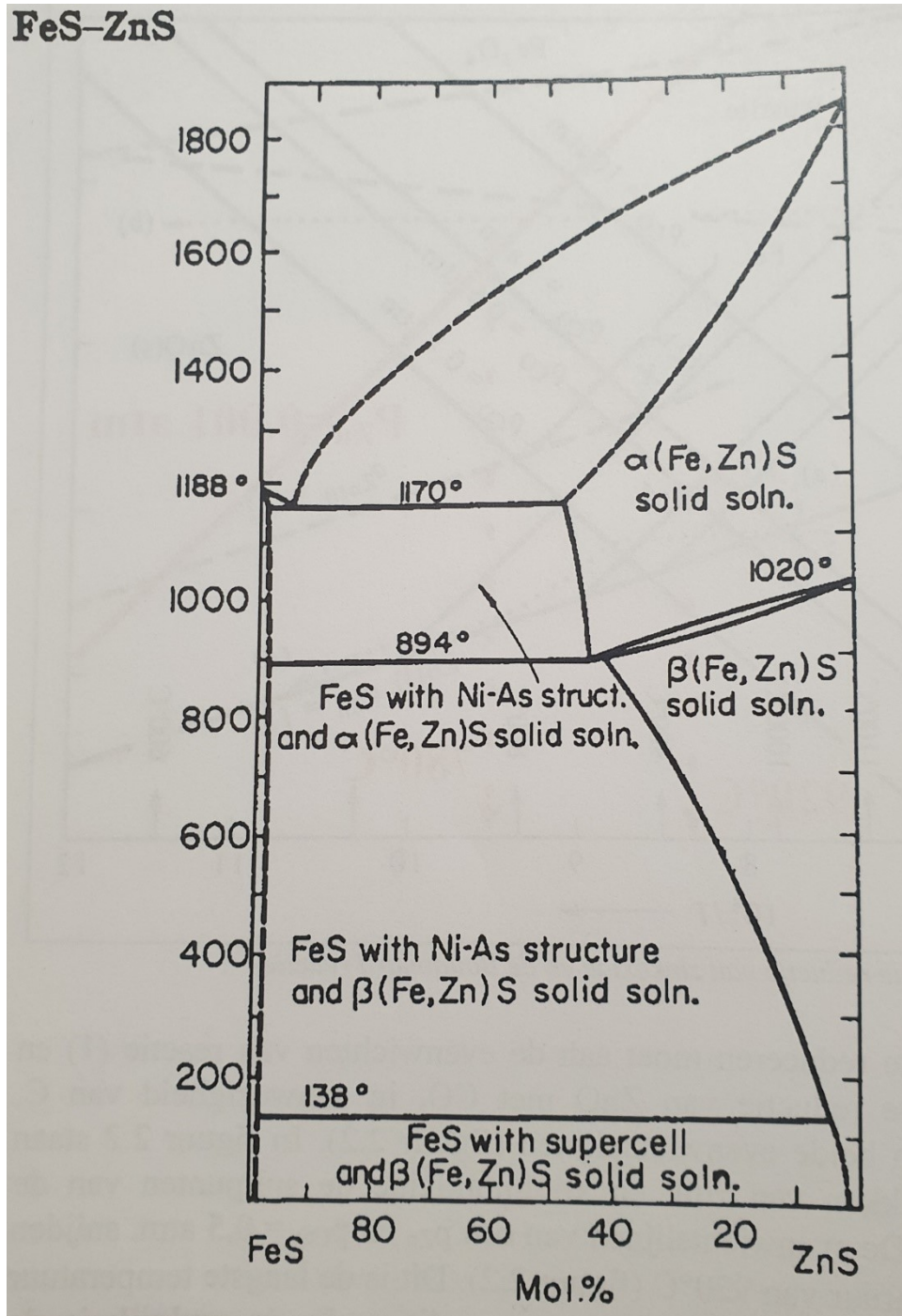


Figure 6-7: Phase diagram of FeS and ZnS from [1]

## 6.2. Lab reactor leaching of IJmuiden blast furnace sludge

### 6.2.1. Kinetics of lab reactor leaching

A series of leaching experiments was done to test the reproducibility of the used method and to understand the leaching kinetics. This series was also done to test the equipment and also to get an idea of when sampling should be done to limit the amount of samples sent to the analysis laboratory. For these experiments the bunker sample was used. These experiments were done identically in triplicate with a 2 M ammonium salt and 9 M ammonia solution, with a L/S ratio of 5. All other experiments were also done under the same conditions, but not in triplicate. The system is fairly closed, although air can escape through the top at the stirrer, no oxygen or other gasses are purged into the system. The temperature is monitored and kept at 40°C. The results of these experiments expressed in extraction and concentration for Zn, Cd and Pb are presented separately and shown in Figure 6-8, Figure 6-9 and Figure 6-10. Zn and Cd show a nice curve, whereas lead seems to be fairly straight. Looking closely at the extraction of Pb it is almost zero. This could explain the lack of curvature, and it is immediately clear that neither a sulfate nor a carbonate leach is particularly effective for leaching out Pb. The error bars indicate the standard error that was found for the experiments. As can be seen these are quite low for the Zn results but quite high for the Pb and Cd results. Both Cd and Pb have very low concentrations in solution which makes the influence of instrumental and human errors more pronounced.. After 60 minutes the increase in extraction is only slight and at 10 minutes over two-thirds of the extraction has been reached. With the addition of oxidants the maximum extraction should be reached faster. Based on these results it was decided to use 10 and 60 minutes as sampling points

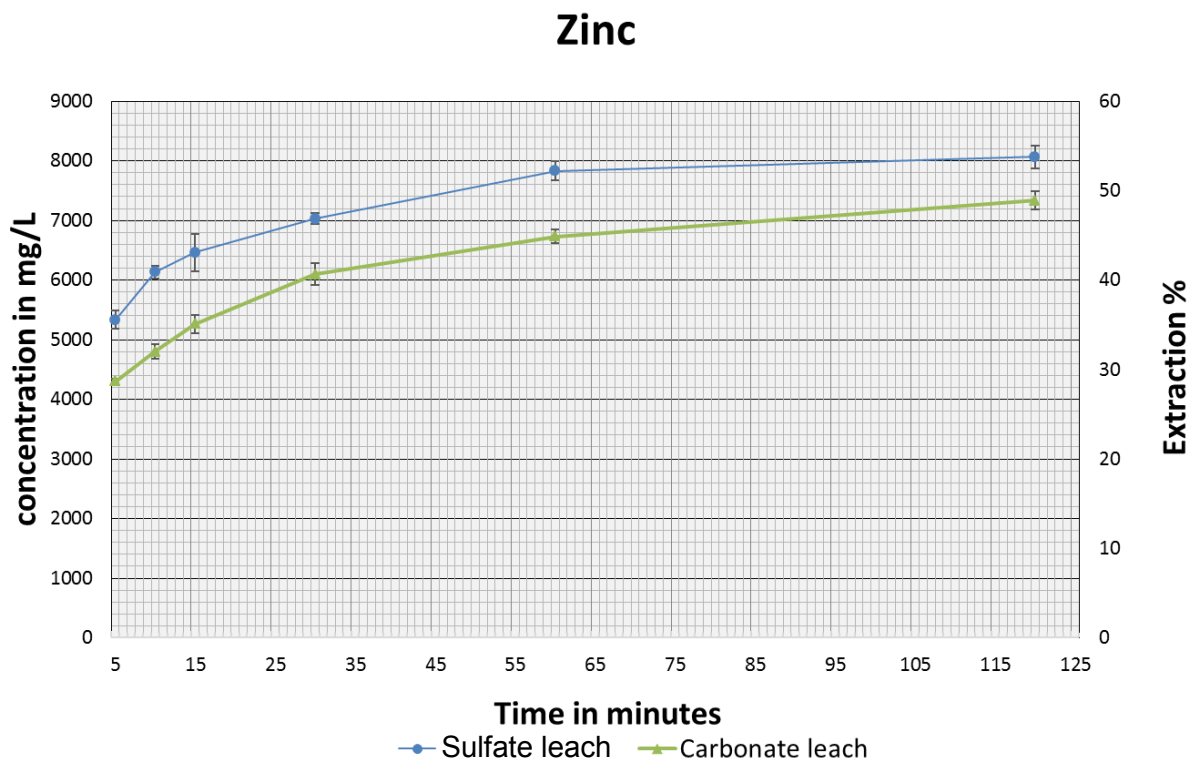


Figure 6-8: Left axis: Concentration of dissolved Zn. Right axis: Extraction of Zn

## Cadmium

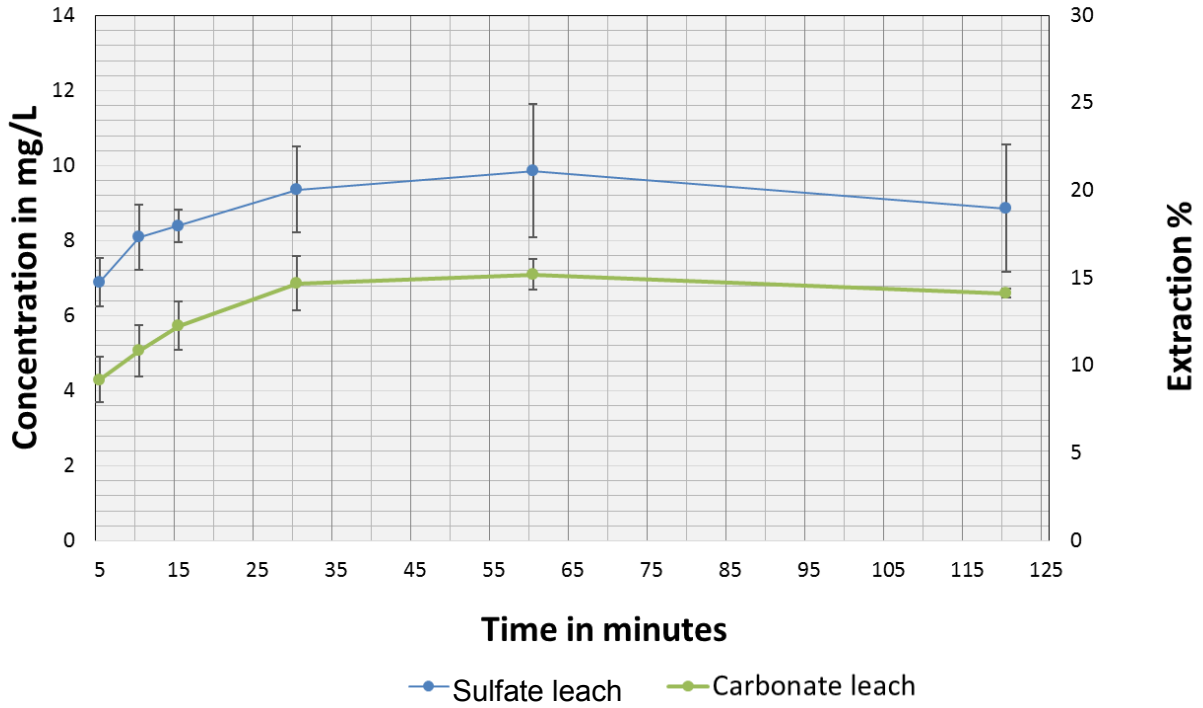


Figure 6-9: Left axis: Concentration of dissolved Cd. Right axis: Extraction of Cd

## Lead

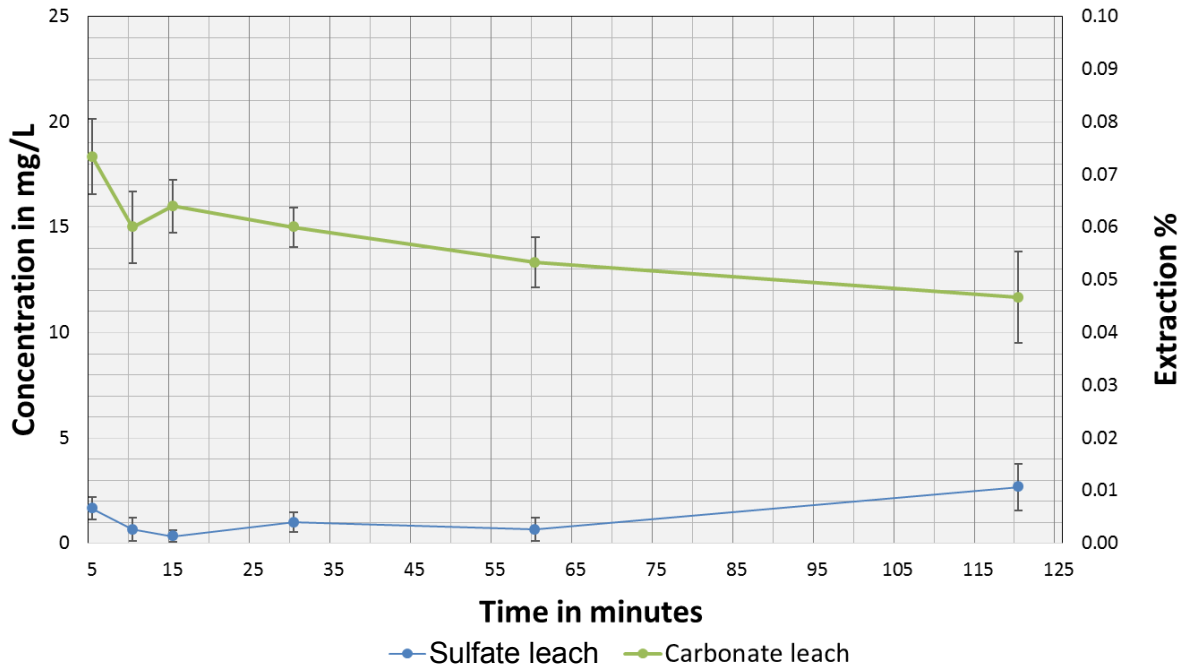


Figure 6-10: Left axis: Concentration of dissolved lead. Right axis: Extraction of lead

### **6.2.2. The effect of adding oxidants to lab reactor leaching**

For the oxidant addition experiments the main parameters were kept the same as given in 6.2.1 for the baseline experiment. Due to the addition of oxygen the experimental setup was re-evaluated and improved so there was only one inlet(oxygen) and one outlet (condenser), see Figure 5-1.

Before adding oxidants it should be known how much needs to be added. Based on the literature review this was decided to be lower than the stoichiometric amount required. This is in part due to the secondary oxidation mechanisms as described in 2.2.2. The stoichiometric amount is the amount of oxidant required to reduce ZnS to ZnO. Where S originally exists as  $S^{2-}$  and is reduced to  $S^{+6}$ . For reporting purposes the stoichiometric amount is used in percentages in the tables and figures. In Appendix C – Oxidant stoichiometric values the stoichiometric amount in grams per litre is shown for the percentages in which they are used in the experiments.

To evaluate the effect of oxidant addition a baseline experiment was done without oxidant addition. The results from this baseline experiment are given in Table A 2. All results of the lab reactor leaching experiments are shown in Table A 1 of the appendix. An arbitrary colour scheme is used to indicate differences between results, where green is the highest and red the lowest extraction.

In Figure 6-11 and Figure 6-12 the extraction percentages of Zn are shown. Figure 6-11 shows the results when using a sulfate leach, whereas Figure 6-12 shows the results for a carbonate leach, where all other parameters and lab conditions were identical. Except for  $KMnO_4$ , It is clear that Zn extraction benefits from a longer leaching time. For  $KMnO_4$  a shorter leaching time seems better. This also makes sense compared to the observations made during the experiments. Generally after a leaching experiment a strong ammonia smell is present in the fume cupboard. Specifically, after opening the lab reactor for final sampling and removal of material. However after the last sampling for  $KMnO_4$  there was just a faint whiff of ammonia left, which would indicate that all the ammonia has been removed from the solution. Without sufficient ammonia in the solution the pH will decrease and the complexes binding Zn into solution will reduce. This is likely due to the high reactivity  $KMnO_4$  is known for.

The baseline experiment results can be found in the appendix Table A 2. The baseline has its highest Zn extraction with a sulfate leach at 53,9% and 46,3% for the carbonate leach. This is lower than the extractions found with the addition of oxidants. The highest extraction is found to be about 67% with a sulfate leach, potassium permanganate oxidant and sampling time of 10 minutes. Whereas the other values were reached after 60 minutes. The higher extraction is logical since potassium permanganate is known for its strong reductive properties, even in basic liquids. The Zn extraction seems to work best for sulfate solutions but carbonate is not far behind. Pb is poorly leached with both leaching solutions with a highest extraction of 5%, however sulfate leach solutions barely extract anything whereas carbonate leaches out some. Comparing the values of Pb with the baseline there is a significant increase from well below 0.10% for a carbonate leach to about 5% for a carbonate leach with added ferric hydroxide. Pb extractions can be found in the appendix in Table A 1. For Cd the extractions vary greatly, but these are also enhanced by adding oxidants. In the baseline it ranges from 17 to 24% whereas the values in Figure 6-13 and Figure 6-14 range from 32% to 45%.



### Zn extraction - Sulfate leaching liquor

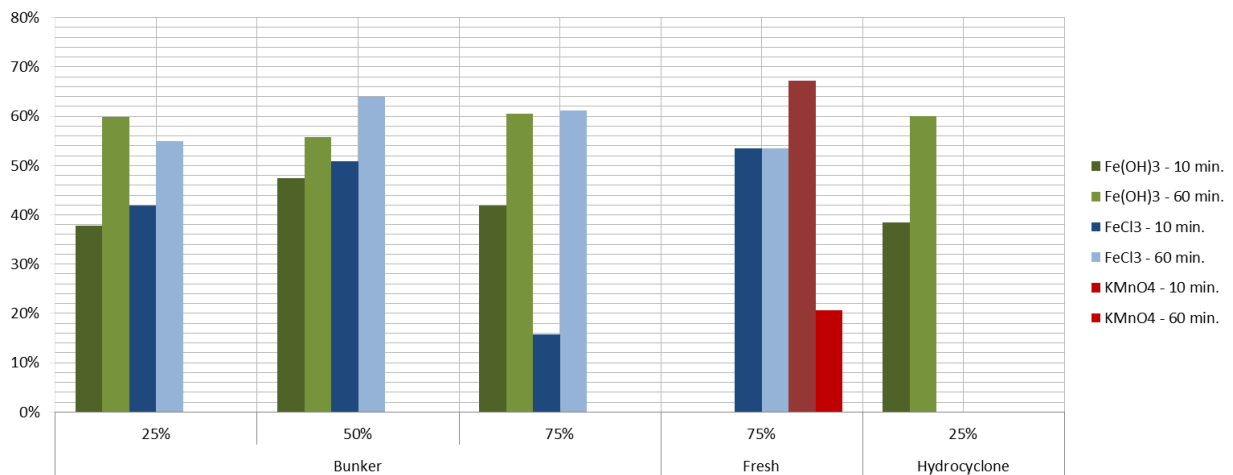


Figure 6-11: Zn extraction for samples from different sources and differing amounts and kinds of oxidant in a sulfate leaching solution.

### Zn extraction - Carbonate leaching liquor

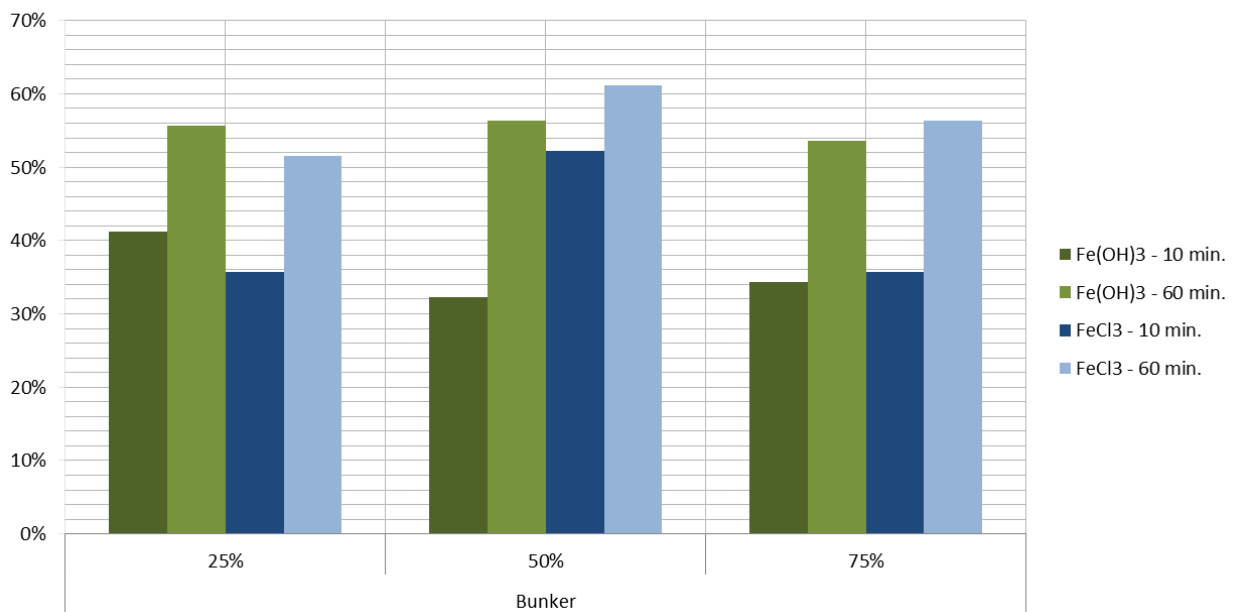


Figure 6-12: Zn extraction for samples from different sources and differing amounts and kinds of oxidant in a carbonate leaching solution.

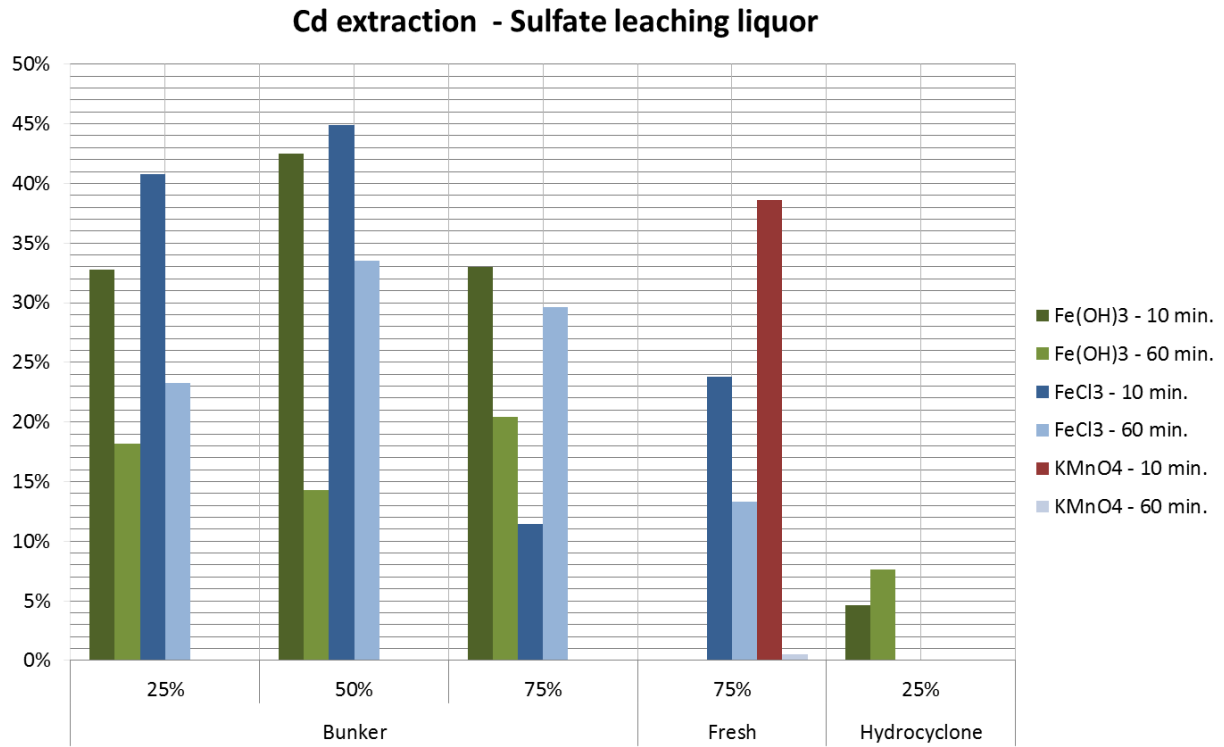


Figure 6-13: Cd extraction for samples from different sources and differing amounts and kinds of oxidant in a sulfate leaching solution.

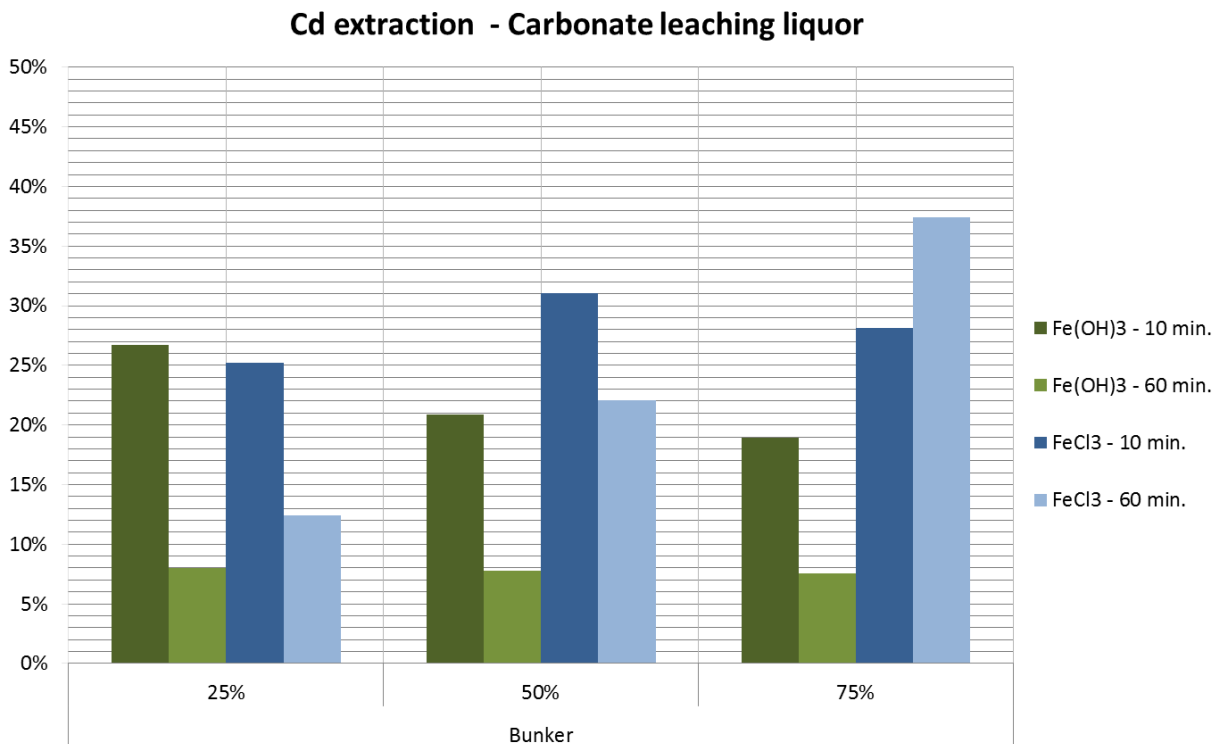


Figure 6-14: Cd extraction for samples from the bunker and differing amounts and kinds of oxidant in a carbonate leaching solution.

### **6.2.3. *The effect of aging***

Since samples were taken at different points it is important to check whether the time difference between the sampled material and the experiments has an effect. The bunker sample was at least several months old, whereas the hydrocyclone and fresh sample were taken directly from the water treatment plant and have therefore not been influenced by potential aging effects. In Figure 6-15 and Figure 6-16 the results of the experiments done on the four different samples are gathered. These experiments were done in the main leaching setup as shown in Figure 5-1 at a temperature of 40°C, a stirring speed of 600 RPM, a L/S ratio of 5, a sulfate leach solution with 2 M ammonium and 9M ammonia and purging of 20L of O<sub>2(g)</sub> per hour. The procedure for sampling and time of sampling was also identical. The results show that the extraction of Zn and Cd is much better for material taken directly from the hydrocyclone than aged samples from the bunker. And both fresh and hydrocyclone samples outperform the bunker sample in regards to Zn extraction.

### **6.2.4. *Leaching Port Talbot blast furnace sludge***

Only one sample was received from Port Talbot and its exact origin and method of sampling is not clear. However out of curiosity the sample was put through the same experiment routine as described in the previous paragraph. From Figure 6-15 and Figure 6-16 it is clear that the method is not very effective for this material, with only 38% Zn extracted after 60 minutes it has performed poorly compared to the other similar materials. What is interesting to see is that the Cd extraction is substantially higher than the other experiments. However this could also be because the amount of Cd is a factor 10 lower than the other samples. And since Cd is not an element often tested for in the lab it always comes with a warning that it is only an indicative value.

### Zn extraction

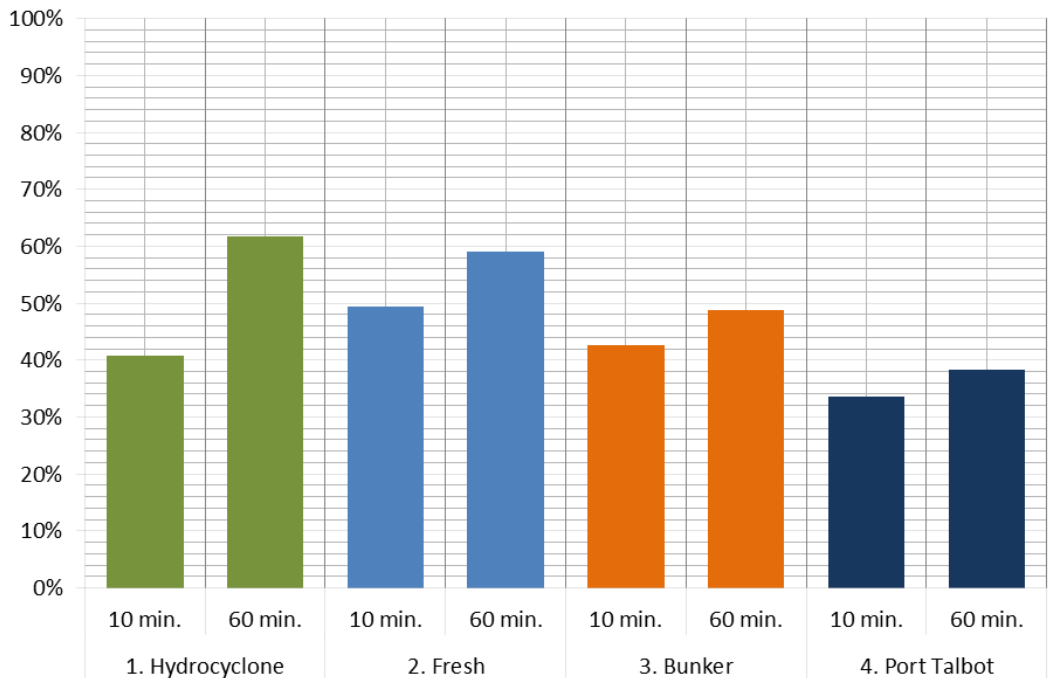


Figure 6-15: Zn extraction for different sample sources

### % Cd extraction

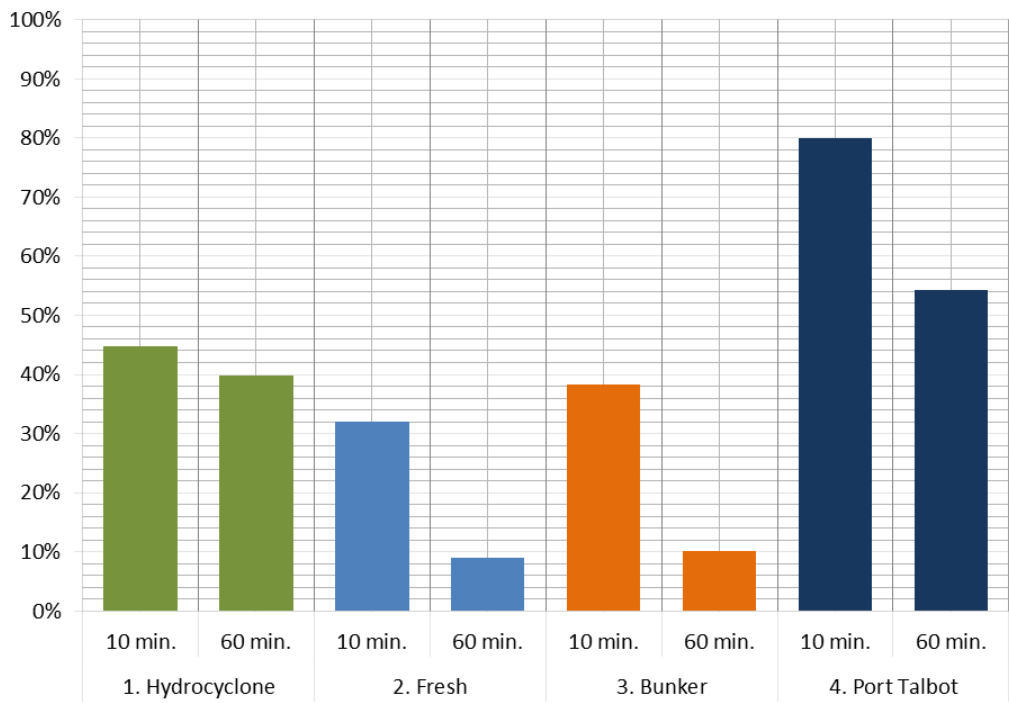


Figure 6-16: Cd extraction for different sample sources

### 6.3. Microwave leaching with oxidants

To investigate microwave leaching the Anton Paar machine was used as shown in Figure 5-3. During the preparation of experiments it became clear that this type of device is not wholly suited for this type of experiment. The vials are small, stirring is not possible and an unknown amount of pressure builds up. For these experiments only the bunker sample was used.

#### 6.3.1. Anton Paar microwave experiments

The extraction percentages of Zn, Cd and Pb from the Anton Paar microwave experiments are compiled in Figure 6-157 to figure 23.

The same experiments without added oxidants were also performed as a baseline their extractions are MLE1 and MLE2 as shown in Table B 1. The complete list of results can be found in the same table in appendix B. When comparing the baseline results with the oxidant addition experiments a large difference is seen. From these results it could be concluded that adding oxidants increases extraction with a huge factor. Coming from almost 20% for Zn without oxidants and going to well over 60% with the addition of oxidants. This conclusion would be a little hasty though. Due to the small amount of liquid that fits inside of the microwave machine it was only possible to sample once. Therefore for the baseline it was decided to leach for 2 hours. In hindsight this decision might not have been the best choice. Because extraction seems to decrease with time, as is evident from the figures. Whether this is due to the oxidant added or due to another effect was not investigated.

The optimum amount of time of microwave assisted leaching is 10 minutes for Pb and Cd extractions, in a carbonate leach solution but regardless of oxidant. The optimum for Zn extraction varies greatly. However from the figures it becomes clear that the best leaching conditions are in a sulfate leach with a  $\text{FeCl}_3$  oxidant and an optimum of 10 minutes. This could be because the  $\text{FeCl}_3$  dissolves readily into the leaching solution and warms the fluid while doing so. Therefore both the fact that it dissolves, which means it can react as it should, and the fact that the liquid is heated will lead to better extractions.  $\text{Fe(OH)}_3$  does not readily dissolve in the fluid greatly reducing the potential for reducing the present metal sulfides.

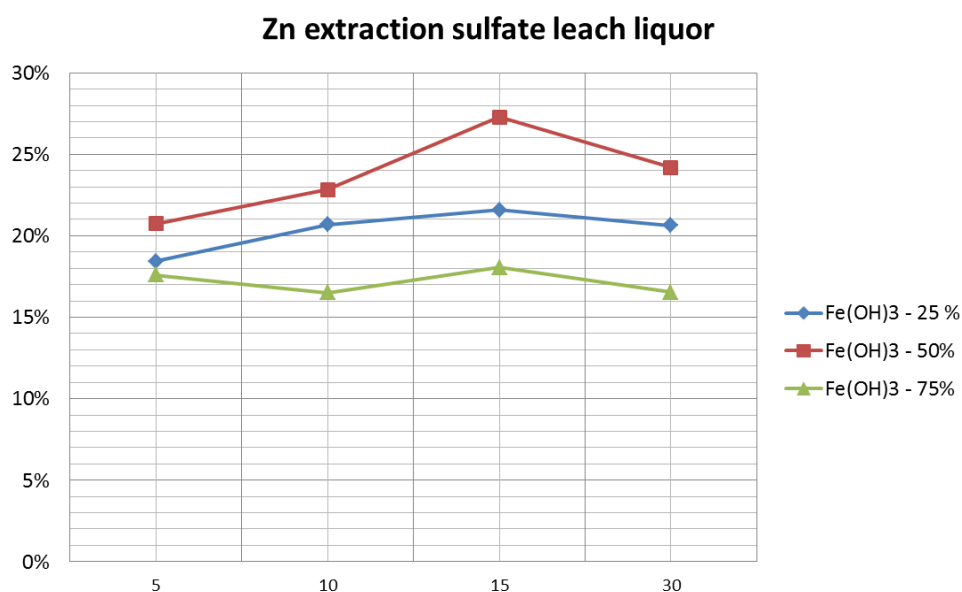


Figure 6-157: Zn extraction with  $\text{Fe(OH)}_3$  oxidant in sulfate leach solution

### Zn extraction carbonate leach liquor

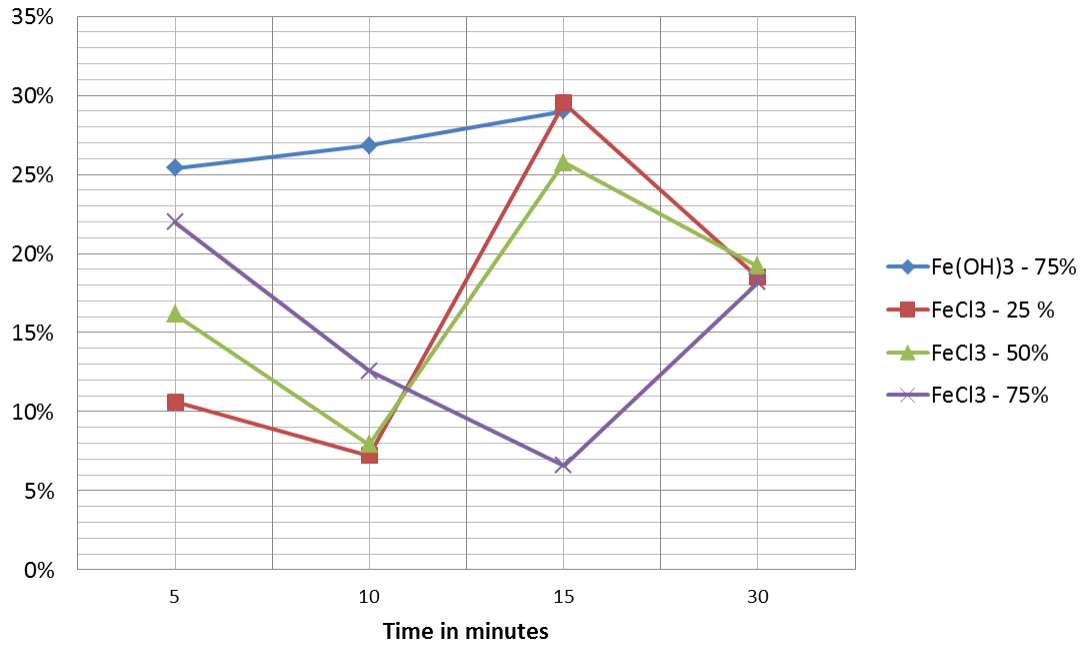


Figure 6-18: Zn extraction with Fe(OH)<sub>3</sub> and FeCl<sub>3</sub> for carbonate leach solution

### Zn extraction sulfate leach liquor

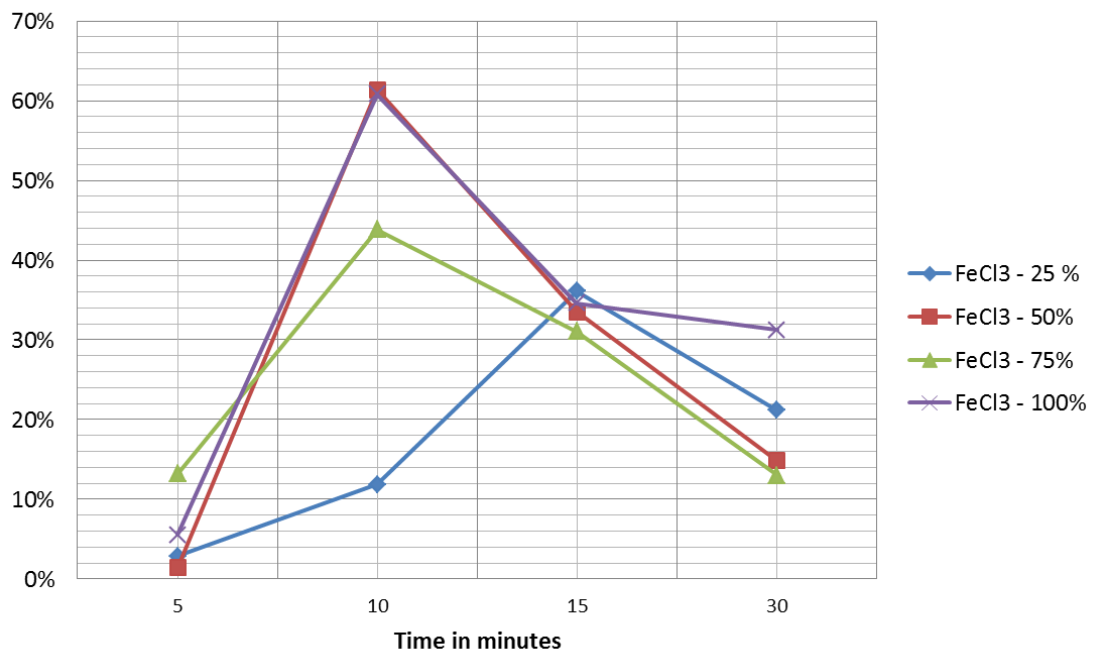


Figure 6-19: Zn extraction with FeCl<sub>3</sub> oxidant in sulfate leach solution

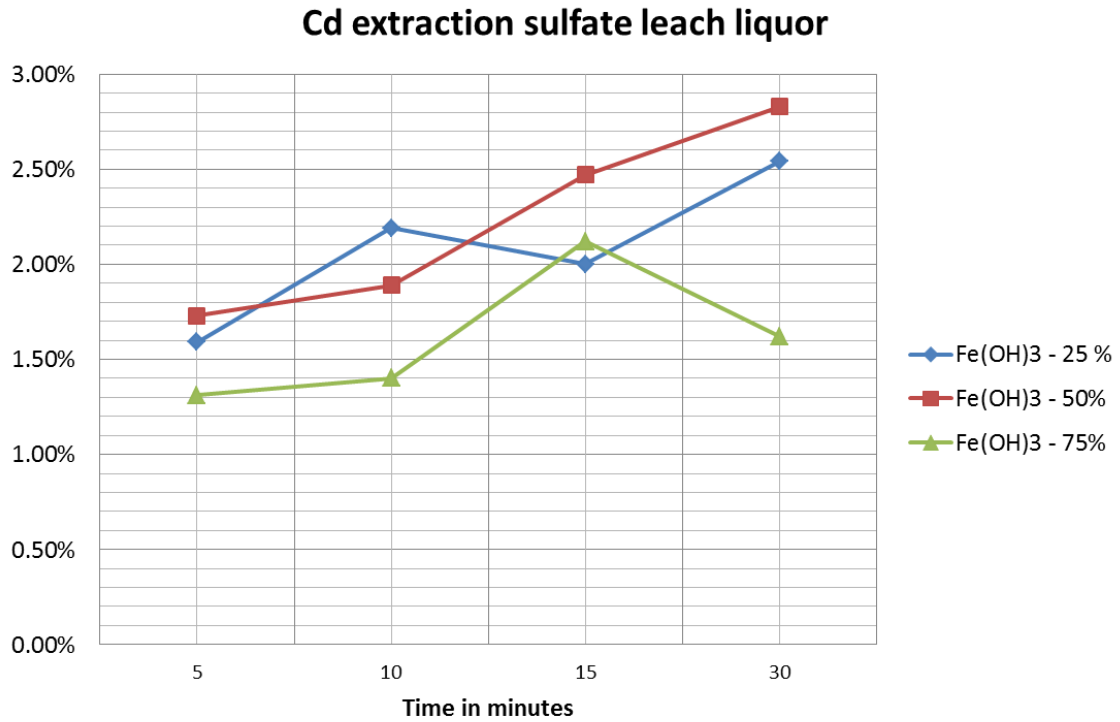


Figure 6-20: Cd extraction with Fe(OH)<sub>3</sub> oxidant in sulfate leach solution

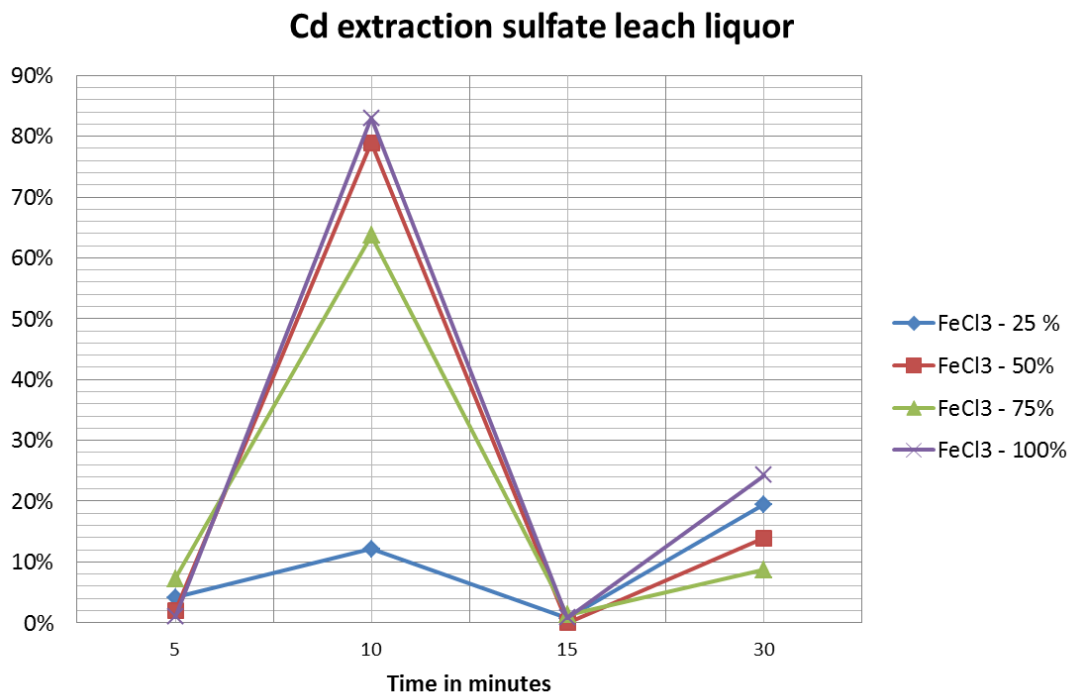


Figure 6-21: Cd extraction with FeCl<sub>3</sub> oxidant in sulfate leach solution

### Cd extraction carbonate leach liquor

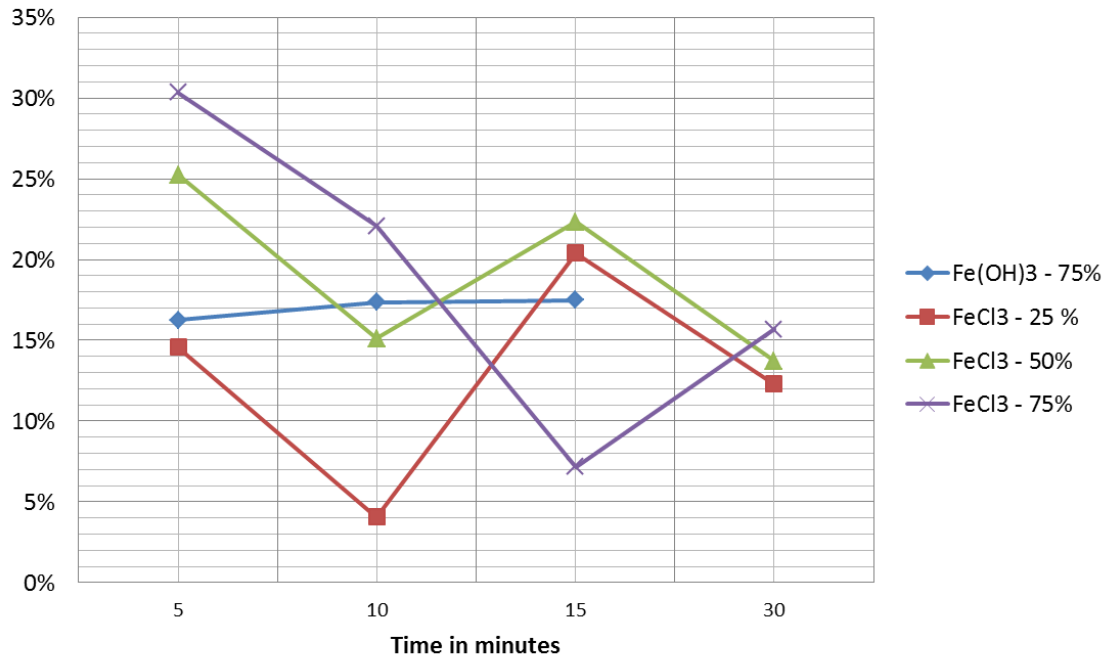


Figure 6-2216: Cd extraction with oxidants in carbonate solution

### Pb extraction sulfate leach liquor

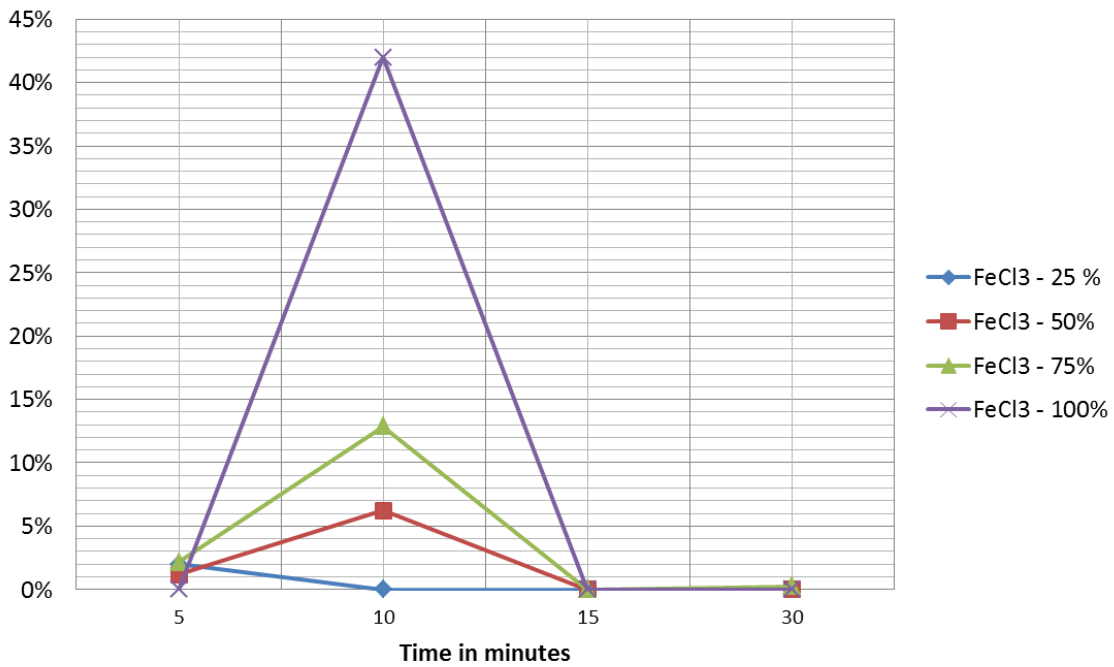


Figure 6-23: Pb extraction with FeCl<sub>3</sub> oxidant in sulfate leach solution



## 7. Conclusions & Recommendations

It has been shown that reducing heavy metal content from the blast furnace dust is possible. A reduction of up to 55% in zinc can be reached with regular alkaline leaching methods. Lead and cadmium have proven more resistant to the regular alkaline leaching method. Adding oxidants will increase the recovery, and adding microwave treatment helps to recover lead and cadmium but only has a minimal beneficial effect on zinc recovery.

The major difficulty with extracting the heavy metals is the way they are present in the waste. The metals exist as very fine particles in and on other small ore and coal grains. The reason for this can be traced back to the way they were created in the blast furnace. Due to the high temperature, the metals are in gas form and when going up with the gas flow in the blast furnace they will condensate on other particles leaving with the off-gas. Another issue is the fact that the particles leave the blast furnace as metal sulfides which are generally resistant to mild leaching techniques.

### 7.1. Answer to the research questions

*Based on literature review, sampling on site and lab scale tests what is the effectiveness of enhanced leaching techniques on heavy metal extraction and oxidation of metal sulfides in BF filter cakes?*

It has been shown that the extraction of heavy metals can be improved using enhanced leaching techniques. However the beforehand decided upon measure for effectiveness was a extraction target of at least 80%. In this case the used enhancement was not effective.

*In what way and quantity are Pb and Cd present in the BF sludge and how do they react to leaching?*

Pb was resistant to leaching in almost all experiments. Where most extractions hovered around 0% the highest lab reactor experiment was just 5%. The only improvement in extraction came when using the microwave with a  $\text{FeCl}_3$  oxidant. Then extraction reached a max of 40%. Cd was comparatively easier to leach out with an extraction of around 45 % being possible for IJmuiden BF cakes and max 80% for Port Talbot BF cake. From SEM analysis it is clear that Pb and Cd as well as Zn are present as very small particles that are deposited or condensed on larger particles of ore. This agrees with the known processes of the BF. Where Zn condenses already before leaving the top of the BF due to the lower temperature, here it then deposits on passing dust which ends up in the filter cakes.

*How effective are oxidants and microwave assisted leaching at promoting ZnS oxidation?*

The used microwave method does not indicate an improvement on regular leaching with or without oxidants for ZnS. However for Pb and Cd there does seem to be a significant improvement compared to the non-microwave experiments.  $\text{FeCl}_3$  is most effective as an oxidant overall. However  $\text{KMnO}_4$  is best when only Zn is targeted.

*Where, when and how is sulfur introduced into the system?*

On average for 2017, 2040 kg of sulfur ( $\text{S}^{2-}$ ) comes from the BF with the off-gasses per day. This is about 125 g/THM. The fines contain about 80% of the sulfur coming out of the BF, this goes to the water cleaning department. The remaining 20% is recirculated into the BF process. Therefore 1632 kg of sulfur comes from the BFs daily and an additional 27 kg of sulfur is added at the water treatment plant as  $\text{Na}_2\text{S}$  to precipitate heavy metals.

## 7.2. Recommendations

A recommendation would be to find out where the metal sulfides actually form. If the formation of metal sulfides is in a very narrow bandwidth as some literature suggest The bandwidth of conditions present should be analysed if possible. Then possibly changing process parameters might prevent the formation of ZnS. Instead a higher percentage of ZnO might be obtained which would improve post processing of the flue dust.

It seems that filter cakes and the metal sulfides therein are resistant to mild leaching techniques, with and without added oxidants. Only if in the future an extraction of max ~70% is economical then the mild ammonia ammonium system is a reliable and relatively cheap method to process the BF cakes. Therefore it would seem prudent to look further for alternative processing methods for the metal sulfides. This ammonia ammonium system would be a good way to post process the BF cakes in cooperation with for example Hlsarna. Hlsarna can take the high Zn content and reduces the ZnS to ZnO after which it does not condense inside the furnace like it does in the BF, instead it will be gathered downstream in a baghouse or filtering system.

The used concentration of ammonia and ammonium was quite high. In theory the used solution can dissolve 150 grams/litre of Zn. In reality the amount of zinc rich sample used was only enough to get to a maximum concentration of 15 grams per litre. Therefore when post processing the Hlsarna Zn and other metal oxides dust it could be done by a much lower concentration of ammonia and ammonium.

Microwave experiments with 100% stoichiometric  $\text{FeCl}_3$  as shown in figures 6-19,6-21 and 6-23 in a sulfate leach liquor show an extraction of 60% Zn, 44% Pb and 82% Cd removal. Even though the extraction of Zn is not higher than the lab reactor experiments the Cd and Pb extraction is much higher. You cannot put too much Zn back into the blast furnace but the amount of Cd is even more stringent. This in combination with declining Zn input over the last few years could result in full recycling of the bulk filter cake material.

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## Appendix A – Lab reactor leaching experiment results

Table A 1: Results from lab reactor experiments

Experiment	Sample source	Leach solution	Sampling time	Oxidant	Stoich %	Zn extr.	Pb extr.	Cd extr.
LE1	Bunker	Sulfate	10	FeCl <sub>3</sub>	75	16%	0%	11%
LE1	Bunker	Sulfate	60	FeCl <sub>3</sub>	75	61%	0%	30%
LE2	Bunker	Sulfate	10	FeCl <sub>3</sub>	50	51%	0%	45%
LE2	Bunker	Sulfate	60	FeCl <sub>3</sub>	50	64%	0%	34%
LE3	Bunker	Sulfate	10	FeCl <sub>3</sub>	25	42%	0%	41%
LE3	Bunker	Sulfate	60	FeCl <sub>3</sub>	25	55%	0%	23%
LE4	Bunker	Carbonate	10	FeCl <sub>3</sub>	75	36%	0%	28%
LE4	Bunker	Carbonate	60	FeCl <sub>3</sub>	75	56%	0%	37%
LE5	Bunker	Carbonate	10	FeCl <sub>3</sub>	50	52%	0%	31%
LE5	Bunker	Carbonate	60	FeCl <sub>3</sub>	50	61%	1%	22%
LE6	Bunker	Carbonate	10	FeCl <sub>3</sub>	25	36%	0%	25%
LE6	Bunker	Carbonate	60	FeCl <sub>3</sub>	25	52%	1%	12%
LE7	Bunker	Sulfate	10	Fe(OH) <sub>3</sub>	75	42%	0%	33%
LE7	Bunker	Sulfate	60	Fe(OH) <sub>3</sub>	75	61%	0%	20%
LE8	Bunker	Sulfate	10	Fe(OH) <sub>3</sub>	50	47%	0%	42%
LE8	Bunker	Sulfate	60	Fe(OH) <sub>3</sub>	50	56%	0%	14%
LE9	Bunker	Sulfate	10	Fe(OH) <sub>3</sub>	25	38%	0%	33%
LE9	Bunker	Sulfate	60	Fe(OH) <sub>3</sub>	25	60%	0%	18%
LE10	Bunker	Carbonate	10	Fe(OH) <sub>3</sub>	75	34%	1%	19%
LE10	Bunker	Carbonate	60	Fe(OH) <sub>3</sub>	75	54%	4%	8%
LE11	Bunker	Carbonate	10	Fe(OH) <sub>3</sub>	50	32%	1%	21%
LE11	Bunker	Carbonate	60	Fe(OH) <sub>3</sub>	50	56%	5%	8%
LE12	Bunker	Carbonate	10	Fe(OH) <sub>3</sub>	25	41%	1%	27%
LE12	Bunker	Carbonate	60	Fe(OH) <sub>3</sub>	25	56%	5%	8%
LE13	Hydrocyclone	Sulfate	10	Fe(OH) <sub>3</sub>	25	38%	0%	5%
LE13	Hydrocyclone	Sulfate	60	Fe(OH) <sub>3</sub>	25	60%	0%	8%
LE14	Hydrocyclone	Sulfate	10		0	41%	0%	45%
LE14	Hydrocyclone	Sulfate	60		0	62%	0%	40%
LE15	BOF	Sulfate	10		0	0%	0%	38%
LE15	BOF	Sulfate	60		0	1%	0%	48%
LE16	Fresh	Sulfate	10	FeCl <sub>3</sub>	75	54%	0%	24%
LE16	Fresh	Sulfate	60	FeCl <sub>3</sub>	75	54%	0%	13%
LE17	Fresh	Sulfate	10	KMnO <sub>4</sub>	75	67%	0%	39%
LE17	Fresh	Sulfate	60	KMnO <sub>4</sub>	75	21%	0%	0%
LE18	Fresh	Sulfate	10		0	49%	0%	32%
LE18	Fresh	Sulfate	60		0	59%	0%	9%
LE19	Port Talbot	Sulfate	10		0	34%	0%	80%
LE19	Port Talbot	Sulfate	60		0	38%	0%	54%
LE20	Bunker	Sulfate	10		0	43%	0%	38%
LE20	Bunker	Sulfate	60		0	49%	0%	10%

Table A 2: Oxidant baseline experiment

Experiment	Sample source	Leach solution	Sampling time	Zn extr.	Pb extr.	Cd extr.
Baseline	Bunker	Sulfate	10	42.2%	0.02%	19.7%
Baseline	Bunker	Sulfate	60	53.9%	0.02%	24.0%
Baseline	Bunker	Carbonate	10	33.0%	0.49%	12.3%
Baseline	Bunker	Carbonate	60	46.3%	0.43%	17.2%

## Appendix B – Microwave leaching experiment results

Table B 1: Results from Anton Paar microwave experiments

Experiment	Sampling time	Oxidant	Stoich. %	Leaching solution	Cd extr.	Pb extr.	Zn extr.
MLE1	120			Sulfate	12%	0%	17%
MLE2	120			Carbonate	14%	0%	19%
MLE3	5	FeCl <sub>3</sub>	100	Sulfate	1%	0%	6%
MLE3	10	FeCl <sub>3</sub>	100	Sulfate	83%	42%	61%
MLE3	15	FeCl <sub>3</sub>	100	Sulfate	1%	0%	35%
MLE3	30	FeCl <sub>3</sub>	100	Sulfate	24%	0%	31%
MLE4	5	FeCl <sub>3</sub>	75	Sulfate	7%	2%	13%
MLE4	10	FeCl <sub>3</sub>	75	Sulfate	64%	13%	44%
MLE4	15	FeCl <sub>3</sub>	75	Sulfate	1%	0%	31%
MLE4	30	FeCl <sub>3</sub>	75	Sulfate	9%	0%	13%
MLE5	5	FeCl <sub>3</sub>	50	Sulfate	2%	1%	1%
MLE5	10	FeCl <sub>3</sub>	50	Sulfate	79%	6%	61%
MLE5	15	FeCl <sub>3</sub>	50	Sulfate	0%	0%	34%
MLE5	30	FeCl <sub>3</sub>	50	Sulfate	14%	0%	15%
MLE6	5	FeCl <sub>3</sub>	25	Sulfate	4%	2%	3%
MLE6	10	FeCl <sub>3</sub>	25	Sulfate	12%	0%	12%
MLE6	15	FeCl <sub>3</sub>	25	Sulfate	1%	0%	36%
MLE6	30	FeCl <sub>3</sub>	25	Sulfate	19%	0%	21%
MLE7	5	FeCl <sub>3</sub>	75	Carbonate	30%	20%	22%
MLE7	10	FeCl <sub>3</sub>	75	Carbonate	22%	1%	13%
MLE7	15	FeCl <sub>3</sub>	75	Carbonate	7%	0%	7%
MLE7	30	FeCl <sub>3</sub>	75	Carbonate	16%	0%	18%
MLE8	5	FeCl <sub>3</sub>	50	Carbonate	25%	11%	16%
MLE8	10	FeCl <sub>3</sub>	50	Carbonate	15%	0%	8%
MLE8	15	FeCl <sub>3</sub>	50	Carbonate	22%	0%	26%
MLE8	30	FeCl <sub>3</sub>	50	Carbonate	14%	0%	19%
MLE9	5	FeCl <sub>3</sub>	25	Carbonate	15%	2%	11%
MLE9	10	FeCl <sub>3</sub>	25	Carbonate	4%	0%	7%
MLE9	15	FeCl <sub>3</sub>	25	Carbonate	20%	0%	30%
MLE9	30	FeCl <sub>3</sub>	25	Carbonate	12%	0%	18%
MLE10	5	Fe(OH) <sub>3</sub>	75	Sulfate	1%	0%	18%
MLE10	10	Fe(OH) <sub>3</sub>	75	Sulfate	1%	0%	17%
MLE10	15	Fe(OH) <sub>3</sub>	75	Sulfate	2%	0%	18%
MLE10	30	Fe(OH) <sub>3</sub>	75	Sulfate	2%	0%	17%
MLE11	5	Fe(OH) <sub>3</sub>	50	Sulfate	2%	0%	21%
MLE11	10	Fe(OH) <sub>3</sub>	50	Sulfate	2%	0%	23%
MLE11	15	Fe(OH) <sub>3</sub>	50	Sulfate	2%	0%	27%
MLE11	30	Fe(OH) <sub>3</sub>	50	Sulfate	3%	0%	24%
MLE12	5	Fe(OH) <sub>3</sub>	25	Sulfate	2%	0%	18%
MLE12	10	Fe(OH) <sub>3</sub>	25	Sulfate	2%	0%	21%
MLE12	15	Fe(OH) <sub>3</sub>	25	Sulfate	2%	0%	22%
MLE12	30	Fe(OH) <sub>3</sub>	25	Sulfate	3%	0%	21%
MLE13	5	Fe(OH) <sub>3</sub>	75	Carbonate	16%	0%	25%
MLE13	10	Fe(OH) <sub>3</sub>	75	Carbonate	17%	0%	27%
MLE13	15	Fe(OH) <sub>3</sub>	75	Carbonate	17%	0%	29%

## Appendix C – Oxidant stoichiometric values

Table C 1: Oxidant in grams per litre and their corresponding stoichiometric percentage

% stoichiometric	Concentration in grams/litre		
	FeCl <sub>3</sub>	Fe(OH) <sub>3</sub>	KMnO <sub>4</sub>
25	58.50	38.55	56.98
50	116.95	77.05	113.97
75	175.45	115.60	170.95
100	233.93	-	-