Aqueous solubility speciation of Cr(VI) in ferrochrome bag filter dust

WPJ van Dalen

20321767

Dissertation submitted in partial fulfilment of the requirements for the degree *Magister Scientiae* in Chemistry at the Potchefstroom Campus of the North-West University

Supervisor: Dr JP Beukes

Co-supervisor: Dr PG van Zyl

May 2015

It all starts here ™

NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT
®

Acknowledgements

- I am all too grateful for everyone that supported me during my studies. I thank the Lord that he carried me through this Masters Degree, and gave me the strength to finish the project. And to all of my friends and family that motivated me with kind words of encouragement.

- I would like to thank both my parents, Willem and Suzette van Dalen for providing me with an education. Giving me the tools that are needed to tackle some of the everyday problems that life tends to throw at you. Also, my sister Marilize van Dalen, for being a loving sister that I can always count on. I am truly blessed to have the family that I do.

- Thanks to my study supervisors, Dr. Paul Beukes and Dr. Pieter van Zyl for all of the guidance that you provided to me. Thank you for not losing hope in me after I left Potchefstroom to continue with my M.Sc. as a part-time student, and for still supporting me as much as the other full-time students.

- Thanks to Monique Loock-Hattingh for teaching me how to use the Thermo Scientific Dionex ICS 300 ion chromatographic instrument. Without her help I would not have been able to complete this study.

- Most of all I would like to thank Chanell Herfurth for her support. For always being there for me, even when times got hard. All of the motivation that you gave me was crucial, since I would have lost sight of the end goal without it. Thank you for the special role that you play in my life.

Willem van Dalen

Preface

Introduction

This dissertation was submitted in article format, as allowed by the North-West University (NWU). This entails that the article is added into the dissertation in the format that it was submitted to a scientific journal, i.e. Water SA. This implies that the traditional results and discussions chapter, as well as experimental chapter are not included in this dissertation, since this information is presented in the article (Chapter 3). However, the background, motivation and objectives (Chapter 1), literature survey (Chapter 2) and project evaluation (Chapter 4) chapters are still included, containing some of the information that was already included or mentioned in the article. Therefore there will be some repetition. It also has to be noted that the article (Chapter 3) has different numbering than the rest of this document, because it was included exactly as it was submitted to the journal. The tables and figures that were used in the article appear at the end of the text, as is required by the journal to which it was submitted.

Rationale in submitting dissertation in article format

The NWU requires M.Sc. candidates to prepare a draft article. However, these draft articles rarely get submitted to peer reviewed ISI international accredited journals. By submitting this dissertation in article format that includes an article that was submitted, the candidate exceeds the requirements of the NWU. The co-authors of the above-mentioned article (Chapter 3) were:

W.P.J. van Dalen[a], J.P. Beukes[a]*, P.G. van Zyl[a], M.M. Loock-Hattingh[a], and J. Hendriks[b]

[a] *Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa*

[b] *Unit for Environmental Sciences and Management, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa*

Contributions to article

The co-authors made the following contributions to this work: The laboratory work for this study and the writing of the article and dissertation was conducted by the candidate, Willem van Dalen. Dr. Beukes (supervisor) and Dr. van Zyl (co-supervisor) both assisted by making conceptual contributions and recommendations that were key to the study, the laboratory work,

and also to the article. Monique Loock-Hattingh assisted with Cr(VI) analyses, while Johan Hendriks assisted with trace element analyses.

Formatting and current status of article

The article has been submitted to Water SA. The article was written in the format and style required by this journal. The guide to authors that was used to write the article was found at http://www.wrc.org.za/SiteCollectionDocuments/Water%20SA%20documents/Water%20SA%20Guide%20to%20Authors.pdf (Date of access: 2014/11/14).

Consent by the co-authors

The co-authors, i.e. J.P. Beukes, P.G. van Zyl, M.M. Loock, and J. Hendriks have been notified that the M.Sc. will be submitted in article format and have given their permission.

Index

Acknowledgements I

Preface II

Index IV

Abstract VI

Opsomming (Abstract in Afrikaans) VIII

Chapter 1 Background, motivation and objectives

1.1 Background and motivation 1

1.2 Objectives 3

Chapter 2 Literature survey

2.1 General information on Chromium 4

2.1.1 Historical perspective on Cr 4

2.1.2 Uses of Cr 5

2.2 Importance of South African Cr industry 6

2.2.1 Chromite ore reserves 6

2.2.2 Mining and beneficiation of chromite 7

2.2.3 Processes utilised by SA FeCr smelters 8

2.2.4 Historic and economic aspects of FeCr production in South Africa 11

2.3 Solid wastes of the FeCr industry 13

2.3.1 Slag 14

2.3.2 Bag filter dust 14

2.3.3 Sludge 15

2.4 Cr(VI) present in off-gas and Bag Filter Dust 15

2.5 Health impacts associated with Cr(VI) 17

2.6 Conclusions from literature and gaps therein 18

Chapter 3 Article

Abstract 19

Introduction 21

Experimental 22

Materials 22

Methods 23

SEM analyses 23

Particle size analysis 24

Trace metal analysis 24

Cr(VI) extraction and analysis 24

Results and discussions 26

Characterisation of the BFD samples 26

Leachability of trace metals, excluding Cr(VI) 27

Cr(VI) leachability 27

Conclusion 29

Acknowledgements 30

Chapter 4 Project evaluation and future perspectives

4.1 Project evaluation in relation to objectives 47

4.2 Future perspective 50

4.3 Overall project evaluation 50

Bibliography 51

Abstract

The production of ferrochrome (FeCr) from chromite ore is a reducing process, whereby the Cr(III) and Fe(II) in the ore are reduced to metallic chromium (Cr) and iron (Fe) in the final product. FeCr is mostly used for the production of stainless steel, which is a vital alloy in modern society. It is, however, impossible to exclude oxygen completely from all the high temperature steps during the production process and very small amounts of Cr(VI) are therefore formed, although not intended. The formed Cr(VI) is mostly associated with the off-gas of the high temperature processes, which are cleaned before it is released into the atmosphere by means of venturi scrubbers or bag filter systems. Certain Cr(VI) species are regarded as carcinogenic, with specifically airborne exposure to these Cr(VI) species being associated with cancer of the respiratory system.

FeCr smelter facilities generate three main types of waste materials, i.e. slag, venturi sludge and bag filter dust (BFD). Most of the Cr in the waste materials consists mostly of Cr(III). However, BFD generated during the cleaning of the off-gas of open/semi-closed furnaces, could contain more significant levels of Cr(VI) than the slag and sludge.

The aim of this study was to determine the solubility of different Cr(VI) species present in BFDs. This would allow that the Cr(VI) in BFD is categorised as water soluble Cr(VI), sparingly soluble and insoluble Cr(VI). These solubility categories can then be related to groups of Cr(VI) compounds, therefore taking the first step in better characterisation of Cr(VI) present in BFD.

Four different BFD samples from FeCr producers in South Africa were characterised in detail. Analytical methods such as scanning electron microscope (SEM), SEM with energy-dispersive X-ray spectroscopy (SEM-EDS), particle size analysis, trace metal analysis with inductively coupled plasma with a mass spectrometer detector (ICP-MS) and Cr(VI) analysis with ion chromatography (IC) were utilised in order to characterise and categorise the samples.

The results indicated that more Cr(VI) leached with an increase in pH. This was in contrast with the trend for most heavy metals. This was also an indication that not only soluble, but also sparingly- and insoluble Cr(VI) compounds occur in the BFD samples evaluated. Further analysis showed that approximately one third of the Cr(VI) species was insoluble and the remainder consisted of sparingly insoluble and soluble Cr(VI) compounds. The most significant finding was that the current leaching procedures applied by FeCr producers, prior to the chemical reduction of Cr(VI), do not effectively extract the sparingly water insoluble compounds. This results in Cr(VI) leaching from waste facilities at later stages, even if seemingly effective Cr(VI) treatment was applied. Therefore, it should be considered as an extremely important future perspective to develop economically feasible Cr(VI) extraction procedures that will ensure complete extraction of

sparing water soluble Cr(VI) compounds together with the water soluble fraction, prior to chemical reduction of Cr(VI) and subsequent storage of the residue on a waste facility.

Keywords: hexavalent chromium, Cr(VI), ferrochromium or ferrochrome (FeCr), bag filter dust (BFD)

Opsomming (Abstract in Afrikaans)

Die produksie van ferrochroom (FeCr) vanaf chromieterts is 'n reduksieproses, waartydens die Cr(III) en Fe(II) in die erts gereduseer word tot chroom en yster metaal in die finale produk. FeCr word hoofsaaklik gebruik vir die produksie van vlekvrye staal, wat 'n belangrike allooi is in die moderne samelewing. Dit is egter onmoontlik om suurstof heeltemal uit te hou tydens al die hoë temperatuur stappe van die produksie-proses en daarom word ‘n klein hoeveelheid Cr(VI) gevorm, alhoewel dit nie die bedoeling was nie. Die gevormde Cr(VI) word meestal geassosieer met die afgasse van die hoë temperatuur prosesse, wat skoon gemaak word voor vrylating in die atmosfeer deur middel van venturi skrobbers of sakfilterstelsels. Sekere Cr(VI) spesies word beskou as kankerwekkend, met veral atmosferiese blootstelling aan hierdie Cr(VI) spesies wat verband hou met kanker van die respiratoriese stelsel.

FeCr smelter fasiliteite genereer drie hooftipes afvalmateriaal, d.i. slak, venturi slik en sak filter stof (SFS). Die meeste van die Cr in die afvalmateriaal bestaan hoofsaaklik uit Cr(III). SFS wat tydens die skoonmaak van die proses-gasse van 'n oop/semi-toe oonde gegenereer word, bevat beduidende hoër vlakke Cr(VI) as slak en venturi slik.

Die doel van hierdie studie was om die oplosbaarheid van die Cr(VI) teenwoordig in SFS is eksperimenteel bepaal. Die resultate sal dit moontlik maak om Cr(VI) in die SFS te klassifiseer as water oplosbare Cr(VI), gedeeltelike oplosbare en onoplosbare Cr(VI) verbindings. Hierdie oplosbaarheid kategorieë kan in verband gebring word met groepe van Cr(VI) verbindings, dus is hierdie die eerste stap in 'n beter spesiasie van die Cr(VI) teenwoordig in SFS.

Vier verskillende SFS monsters van FeCr produsente in Suid-Afrika is gekarakteriseer. Analitiese metodes soos Skandeer elektronmikroskoop (SEM), SEM-dispersiewe X-straal-spektroskopie (SEM-EDS), deeltjiegrootte analise, spoormetaal- analise met induktiefgekoppelde plasma massaspektrometrie (IGP-MS) en Cr(VI) analise met ioon chromatografie (IC) is gedoen om die monsters te karakteriseer en katagoriseer.

Die resultate het aangedui dat meer Cr(VI) uitgeloog het by ‘n hoër aanvanklike pH. Dit was in teenstelling met die tendens vir die meeste swaar metale. Die resultate was ook 'n aanduiding dat dit nie net oplosbare, maar ook gedeeltelik- en onoplosbare Cr(VI) verbindings voorkom in die BFD monsters wat geëvalueer was. Verdere analise het getoon dat ongeveer een derde van die Cr(VI) was onoplosbare Cr(VI) en die res bestaan uit gedeeltelik oplosbare en oplosbare Cr(VI) verbindings.

Die huidige loging prosedures wat toegepas word deur FeCr produsente, voor die chemiese reduksie van Cr(VI), ekstraeer nie effektief die gedeeltelik water onoplosbare verbindings nie. Dit veroorsaak dat Cr(VI) uitloog vanaf afval fasiliteite op latere stadiums, selfs as

daar skynbaar doeltreffende Cr(VI) behandeling toegepas was. Die belangrikste bevinding was dat die huidige metode wat deur FeCr produsente toegepas word, voordat Cr(VI) chemies gereduseer word, nie die gedeeltelik oplosbare Cr(VI) fraksie loog nie. Dit veroorsaak dat Cr(VI) steeds vanaf slikdamme loog, al was die slik behandel. Dit is dus van uiterse belang dat toekomstige navorsings daarna sal streef om ekonomies haalbare Cr(VI) ekstraksie prosedures te ontwikkel wat volledige ekstraksie van die gedeeltelik water oplosbare Cr(VI) verbindings saam met die water oplosbare fraksie sal verseker, voor chemiese reduksie van Cr(VI) plaasvind en die daaropvolgende stoor van die slik op 'n afval fasiliteit.

Sleutelwoorde: heksavalente chroom, Cr(VI), ferrochroom (FeCr), sakfilterstof (SFS)

Chapter 1 Background, motivation and objectives

1.1 Background and motivation

Ferrochrome (FeCr) is an alloy produced by pyrometallurgical carbo-thermic reduction of chromite ore (Riekkoal-Vanhanen, 1999). FeCr is mostly used for the production of stainless steel, which is a vital alloy in modern society. Since its discovery in 1798, chromite has remained the only commercially viable source of new chromium (Cr) units (Nriagu, 1988a; Riekkoal-Vanhanen, 1999). It is generally accepted that South Africa holds approximately 75% of the world's viable chromite ore reserves (Mintek, 1990; Cramer *et al.*, 2004). The South African chromite reserves are situated within the Bushveld Complex. This geological phenomenon consists of an enormous saucer-like intrusive igneous mass. It extends for about 400km from east to west and roughly the same distance from north to south. It is located in the central and slightly western portion of the South African Highveld (Howat, 1994). According to the 2012 production statistics, South Africa produces nearly 41% of the world's chromite ore and 36% of the world's high-carbon FeCr, i.e. the most common grade of FeCr (ICDA, 2013). In the FeCr production process, Cr is present as Cr(III) in the chromite ore, while Cr(0) is present in the FeCr that is produced. Albeit completely unintended, small amounts of Cr(VI) are formed during FeCr production and can be present in waste materials (Beukes *et al.*, 2010; Beukes *et al.*, 2012). Certain Cr(VI) species are regarded as carcinogenic, with specifically airborne exposure to these Cr(VI) species being associated with cancer of the respiratory system (Yassi & Nieboer, 1988; Proctor *et al.*, 2002).

FeCr production results in the discard of relatively large quantities of slag as a waste material. Slag-to-FeCr generation ratios of 1.1:1 up to 1.9:1 are common in this industry, with ratios varying due to different production technologies employed at various production facilities (Beukes *et al.*, 2010). Although the volumes of slag generated are large, the Cr(VI) content of the slag is usually very low (Beukes *et al.*, 2010). Additional Cr(VI) treatment can also be applied, during the recovery of FeCr from the slag ((Coetzer *et al.*, 1997; Maine *et al.*, 2005)). In certain developed countries (e.g. Finland) FeCr slag is considered to be a marketable product (Riekkoal-Vanhanen, 1999). Zelić (2005) reported on the use of FeCr slag in concrete pavements, while Lind *et al.* (2001) reported on the use of FeCr slag in road construction. Relatively recently some South African FeCr slags have also been declassified, making commercial use applications possible (Gericke, 1998).

In addition to slag, mainly two other waste products are generated during FeCr production i.e. sludge and bag filter dust (BFD) (Van Staden *et al.*, 2014). Sludge is generated during the wet venturi scrubbing of closed furnace off-gas (Beukes *et al.*, 2010). This sludge does not usually contain significant Cr(VI) concentrations (Gericke, 1998). In contrast, BFD generated during the

cleaning of the off-gas of open/semi-closed furnaces, could contain more significant levels of Cr(VI) (Gericke, 1998; Maine *et al.*, 2005; Beukes *et al.*, 2012). This BFD cannot be disposed without proper Cr(VI) treatment (Beukes *et al.*, 2012). After the afore-mentioned treatment, the treated BFD is disposed of in fit-for-purpose waste facilities.

Cr(III) and Cr(0) are not classified as carcinogenic (IARC, 1997). Cr(III) is in fact used a dietary supplement for certain human health abnormalities (Hininger *et al.*, 2007). Due to these fundamental health impact differences most studies generally only refer to the differentiation between Cr(III) and Cr(VI), when Cr speciation is discussed (Cox *et al.*, 1985; Kotaś & Stasicka, 2000; Sreeram & Ramasami, 2001). However, the International Agency for Research on Cancer, which is part of the World Health Organization, makes a distinction between some Cr(VI) compounds (IARC, 1997). It is stated that:

- There is sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromates, strontium chromate and lead chromates.
- There is limited evidence in experimental animals for the carcinogenicity of chromium trioxide (chromic acid) and sodium dichromate.
- There is inadequate evidence in experimental animals for the carcinogenicity of barium chromate.

From the above-mentioned it is evident that the risk associated with FeCr BFDs cannot only be considered within the context of Cr(III)-Cr(VI) speciation. In addition, certain Cr(VI) cations have different aqueous solubility properties, which range from soluble Cr(VI) complexes to sparingly soluble and insoluble Cr(VI) complexes. This makes these results of general importance to the aqueous (surface- and ground water) pollution potential of FeCr BFD, since the differences in solubility of the various Cr(VI) compounds is closely linked to Cr(VI) leaching from FeCr BFD waste deposits into groundwater and nearby streams. The South African FeCr industry has a dominant role in global FeCr production and the risk associated with Cr(VI) containing wastes is present at all of the local FeCr smelters. In this study it will be attempted to improve the speciation of Cr(VI) in BFD, with regard to water soluble, partially soluble and insoluble Cr(VI) compounds, thus contributing to enhancing the quantification of Cr(VI) risks associated with these species.

1.2 Objectives

The objectives of this study were to:

a) conduct a literature survey to assess current state of knowledge with regard to Cr(VI) in FeCr BFD;

b) obtain different BFD samples, which are representative of processes utilised in South African FeCr industry;

c) characterisation of the BFD samples with analytical techniques, which will include scanning electron microscopy (SEM), SEM combined with energy dispersive spectroscopy (SEM EDS) and particle size analysis;

d) determine the solubility of Cr(VI) in BFD as a function of pH, as well as determine the water soluble, sparingly water soluble and water insoluble Cr(VI) contents of the BFD samples;

e) determine the leaching of other heavy metals during the pH-dependant leaching;

f) make recommendations relevant to the FeCr industry and give future perspectives that can guide research in this field of study.

Chapter 2 Literature survey

2.1 General information on Chromium

Chromium (Cr) metal has a grey colour, is hard and brittle, and since it is highly polishable, it can have a very lustrous shine to it. Cr tends to have a thin passive oxide layer form around it, which makes it very resistant to corrosion by conventional means. The oxide layer found on Cr has a very dense spinel structure. This makes Cr a great candidate for use in protective coatings and the production of stainless steel.

Cr can be found in many oxidation states, ranging from -4 to +6. The oxidation state of Cr determines in what compounds Cr are found. Elemental Cr metal, i.e. Cr(0), is not found in nature. In aqueous solutions Cr is found in the +2, +3 and +6 oxidation states. Cr(III) would typically be present due to it being the most stable oxidation state in solution, while Cr(VI) is known to be the most oxidising (Jacobs & Testa, 2005). Cr(III) can be oxidised to Cr(VI) in ambient air if the temperature is high enough and oxygen (O_2) is present. Oxidation of Cr(III) in aqueous solution is mostly achieved by addition of MnO_2 (Rai *et al.*, 1989), which acts as a catalist for dissolved O_2 oxydation of Cr(III). In aqueous solution Cr(VI) can also be reduced to Cr(III) by the addition of inorganic reducing agents such as Fe(II) (Beukes *et al.*, 2012) and sulphite (Beukes *et al.*, 1999), while it is also known that most organic coumpounds can reduce Cr(VI) (March, 1992). Cr does have interesting magnetic properties, since it has no attraction to magnetic fields at ambient temperatures, but above 38°C it is attracted to magnetic fields (Fawcett, 1988).

Cr can be dissolved in non-oxidising mineral acids, such as sulphuric and hydrochloric acid. It does not, however, dissolve as easily in nitric acid (Cotten & Wilkinson, 1988). The standard electrode potentials for some of the most important Cr oxidation states are:

$$Cr^{2+}(aq) + 2e^- = Cr(s)\ E^0 = -0.91\ V \quad \text{(Eq. 1)}$$

$$Cr^{3+}(aq) + 3e^- = Cr(s)\ E^0 = -0.74\ V \quad \text{(Eq. 2)}$$

$$Cr_2O_7^{2-}(aq) + 14H^+ + 6e^- = 2Cr^{3+}(aq) + 7H_2O\ E^0 = 1.33\ V\ pH = 0 \quad \text{(Eq. 3)}$$

$$CrO_4^{2-}(aq) + 4H_2O + 3e^- = Cr(OH)_3(s) + 5OH^-\ E^0 = -0.13\ V\ pH = 14 \quad \text{(Eq. 4)}$$

2.1.1 Historical perspective on Cr

The first discovery of a Cr containing compound was made by Johann Gottlob Lehmann, who found crocoite (lead chromate) deposits in the Ural Mountains between Russia and Kazakhstan in 1761 (Roza, 2008). The French chemist Nicolas-Louis Vauquelin managed to

produce Cr oxide (Cr_2O_3) by mixing crocoites with hydrochloric acid in 1797. He isolated metallic Cr one year later, in 1798 (Roza, 2008). Vauquelin named the new mineral chrome, after the Greek word chroma, meaning colour (Emsley, 2003). He also detected traces of Cr in precious gemstones, such as rubies and emeralds (Roza, 2008). In 1798 both Klaproth and Tobias Lowitz successfully isolated the Cr metal from chromite ore samples that came from the Ural Mountains, and one year later Tassaert isolated Cr in in a sample from the chrome iron ore deposits at Gassin in France (Nriagu, 1988a). Since then chromite ($FeCr_2O_4$), which is of the "spinel" crystal type, has remained the only viable commercial source of Cr (Riekkoal-Vanhanen, 1999).

Due to the lack of adequate technology, Cr could not be produced on a large scale for many decades after it was first discovered. In 1821 Pierre Berthier was able to produce metallic Cr by reducing the metal oxides with carbon (C). He was able to create corrosion resistant metal by mixing iron (Fe) and Cr into an alloy, but this new metal was very brittle and of little use (Roza, 2008). Over the course of the next five decades, many people made attempts at producing a useful metal alloy by combining Cr, Fe, and other metals in varying ratios. The combination of Fe with 30% to 35% of Cr and 2% of tungsten (W) by Woods and Clark in 1872 was the basis for the discovery of stainless steel (Roza, 2008). In 1893 the French chemist Henri Moissan found that he could produce a stronger metal alloy by adding C (in the form of coke) to Cr and Fe ore, and heating it in an electric furnace. The strength of the metal came from the presence of the C in the alloy. Moissant termed this new alloy ferrochromium (FeCr). Since Moissan's success, many scientists have attempted to improve this alloy, by varying the amount of Cr, Fe and C, until stainless steel as we know it today was developed (Roza, 2008).

2.1.2 Uses of Cr

The main uses for Cr include chemical production, refractory bricks, foundry sands and metallurgy (Nriagu, 1988b). In 2011, nearly 25 million tons of chromite was mined globally (ICDA, 2013), of which nearly 91% was smelted into FeCr, as indicated by Figure 1 (ICDA, 2012). FeCr is used for the production of stainless steel, alloyed steel and other metal alloys. Only about 5% of the chromite ore that was mined in 2011 was used for Cr chemical production (ICDA, 2012). Sodium dichromate ($Na_2Cr_2O_7$) and potassium dichromate ($K_2Cr_2O_7$) are the most well-known chrome containing chemicals, and they have some important applications. Other chemical products can be produced by using $Na_2Cr_2O_7$. Cr(III) salts and chromic sulphate ($Cr_2(SO_4)_3$) are used in the leather tanning industry. Cr containing compounds are often used as catalysts. Bright and colourful pigments in paints often contain Cr or some form of Cr compound. Even since the early 20th century Cr has been used as a preservative for wood. Items can be given a Cr plating in order to improve its resistance to corrosion, or simply to give it a brilliant lustrous Cr shine (Nriagu, 1988b). In 2011 the percentage of chromite that was used for foundry sands was nearly 3%, while chromite that was used for refractory purposes was less than 1%. The uses for chromite as

refractory bricks include ferrous and non-ferrous metallurgy, cement kilns and the glass industry (ICDA, 2012).

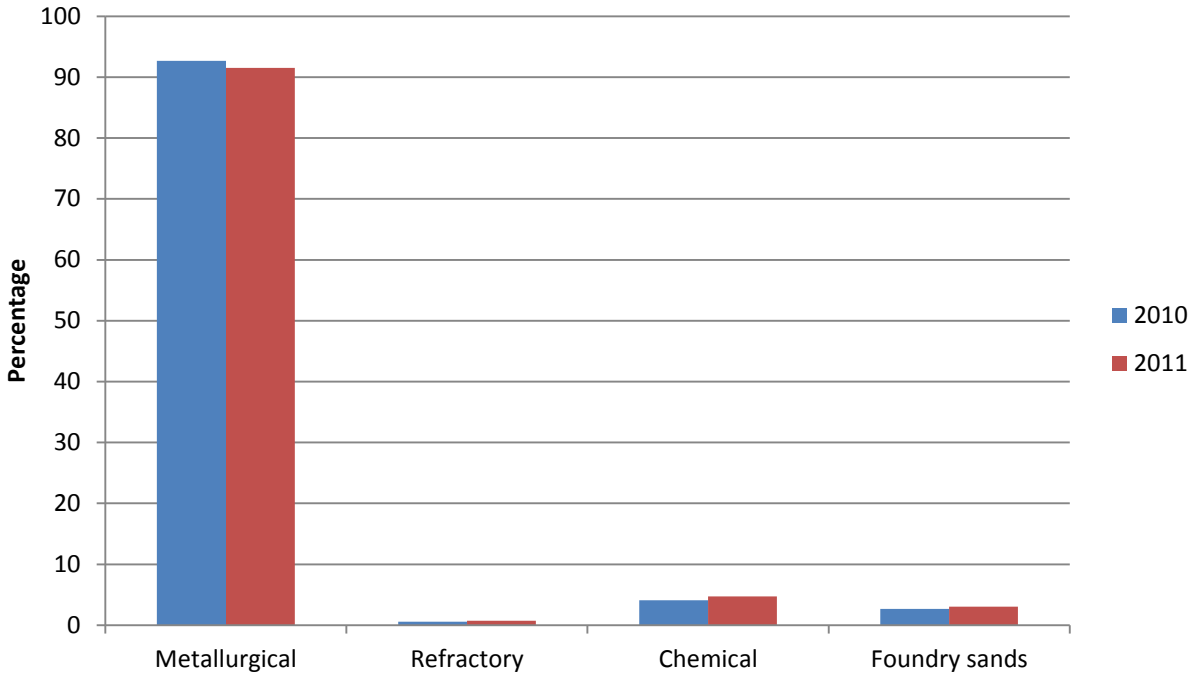


Figure 1: Chromite ore end uses for 2010 to 2011 (ICDA, 2012).

2.2 Importance of South African Cr industry

Since the FeCr industry is of importance in this study, only aspects related to it will be considered in this section.

2.2.1 Chromite ore reserves

As mentioned previously, the only commercially viable source of new Cr is chromite ore. Cr is present in chromite as a Cr spinel, which can be found in ultramafic igneous rock formations (Nriagu, 1988a). A typical Cr spinel consists of magnesium (Mg), Fe, aluminium (Al) and Cr. The ratios in which these elements are present can differ greatly (Murthy *et al.*, 2011).

It is generally accepted that South Africa holds approximately 75% of the world's viable chromite ore reserves (Cramer *et al.*, 2004; Mintek, 1990). According to the 2012 production statistics South Africa produced nearly 41% of the world's chromite ore and 36% of the world's high-carbon FeCr, i.e. the most common grade of FeCr (ICDA, 2013). This amounted to 10.4 million tons of FeCr for 2011 (ICDA, 2013). Other FeCr producing countries with chromite ores include Kazakhstan, India, Turkey, Zimbabwe, Finland and Brazil (Riekkoal-Vanhanen, 1999; ICDA, 2013). Substantial chromite ore deposits have recently been discovered in Canada, but currently these are still unmined.

The South African chromite reserves are situated within the Bushveld Complex (BC). This geological phenomenon consists of an enormous saucer-like intrusive igneous mass. As is indicated in Figure 2, the BC extends for approximately 400km from east to west and roughly the same distance from north to south. It is located in the central and slightly western part of the South African Highveld (Howat, 1994). Within the BC, four distinct regions exist, which include the eastern and western chromite belts, the Zeerust district and the areas south of Potgietersrus (Howat, 1994). The chromite deposits near Potgietersrus and Zeerust have the highest Cr_2O_3 content and Cr:Fe ratios of 2 to 2.9 (Howat, 1994). However, these chromite deposits are also the smallest. The largest chromite deposits are found in the eastern and western chromite belts of the BC. These deposits are of a lower quality, have less Cr_2O_3 content and have Cr:Fe ratios of 1.5 to 1.6 (Howat, 1994).

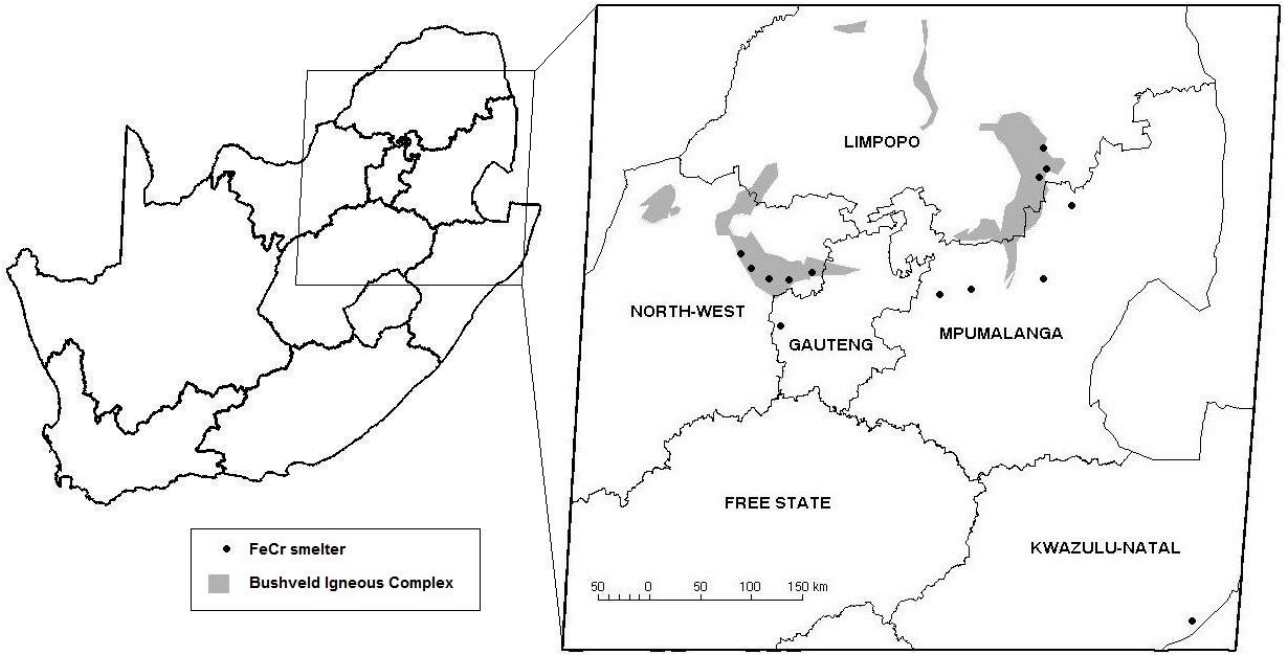


Figure 2: FeCr smelters located in the Bushveld Complex of South Africa

FeCr production facilities in South Africa also make use of upper group 2 (UG2) ore as feed material. This UG2 ore is primarily mined as a source of platinum group metals (PGMs) in South Africa (Cramer *et al.*, 2004). After the PGMs have been extracted, the remaining ore residue is sold to the FeCr industry. These UG2 ores tend to have Cr:Fe ratios of 1.3 to 1.4 (Cramer *et al.*, 2004).

2.2.2 Mining and beneficiation of chromite

Underground mining operations and open-pit mining are sources of chromite ore (Cramer *et al.*, 2004). Gu & Wills (1988) stated that the chromite that is available for commercial mining can be found in mafic and ultramafic rocks. The ore in these rocks can either be of the podiform

variety, which have unevenly shaped deposits with erratic and unreliable Cr content (e.g. found in Kazakhstan and Turkey), or they can be of the stratiform variety, which are conveniently situated in layers that run parallel to each other (e.g. the BC in South Africa). Stratiform chromite deposits can also be found in Finland and Zimbabwe (Cramer *et al.*, 2004).

Three distinct layers or zones can be identified within the South African BC. These are the upper group (UG), the middle group (MG) and the lower group (LG). Up to 5 layers can be present in the upper group, 10 layers in the middle group and 17 layers in the lower group. The seams that have the most economical importance are the lower group 6 (LG6), the middle group 1 and 2 (MG1 and MG2), and the upper group 2 (UG2) layers. PGMs are predominantly present in the UG2 seams (Cramer *et al.*, 2004; Soykan *et al.*, 1991), with approximately 80% of the world's PGMs production takes place in South Africa (Xiao & Laplante, 2004; Cawthorn, 1999).

It is best practice to use lumpy (particle size 6 – 150 mm) or chip/pebble ore (particle size 6 – 25 mm) ore as feedstock for FeCr smelters, if agglomerated material is not available (Gu & Wills, 1988). This is because fine ore can cause dangerous bed turn-overs in the furnace (Riekkoal-Vanhanen, 1999). South African chromite ore is regarded as friable, and tends to disintegrate or crumple into small crystals (Gu & Wills, 1988). Beneficiation must be applied to the ore before they can be fed into the smelters. This is can be performed by simple screening of the ore, heavy-medium separation, flotation, high-intensity magnetic separation and gravity concentration methods. Heavy-medium separation is the most cost effective method to use. Gravity separation methods include making use of shaking tables, jigs and spirals.

Only about 10 to 15% of the lumpy ore and 8 to 12% of chip/pebble ore (particle size 6 – 25 mm) is usually recovered after mining and beneficiation has been performed (Glastonbury *et al.*, 2010). The remaining 73% to 82% has a particle size less than 6 mm, and would usually be crushed or milled to a size less than 1 mm and then upgraded to have a Cr_2O_3 content of more than 45%. This fine ore is known as metallurgical grade ore (Glastonbury *et al.*, 2010). In order to prevent the bed turn-overs previously mentioned, these fine ores go through an agglomeration step before they can be used as feed in the furnace (Gu & Wills, 1988).

2.2.3 Processes utilised by SA FeCr smelters

Large amounts of energy are required to produce FeCr. The pyrometallurgical production of FeCr entails the carbo-thermic reduction of chromite ore (Riekkoal-Vanhanen, 1999). Carbonaceous reductants utilised include coke, char, anthracite and coal, while quartzite, bauxite, olivine, dolomite, limestone and calcite are generally used as additives to the slag (Riekkoal-Vanhanen, 1999). The main reactions for the FeCr production process are:

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3\,CO \qquad \text{(Eq. 5)}$$

$$FeO + C \rightarrow Fe + CO$$ (Eq. 6)

Figure 3 shows a flow diagram, giving the general processes that are utilized in FeCr production by the South African industry (adapted by Beukes *et al.*, 2010 from Riekkoal-Vanhanen, 1999).

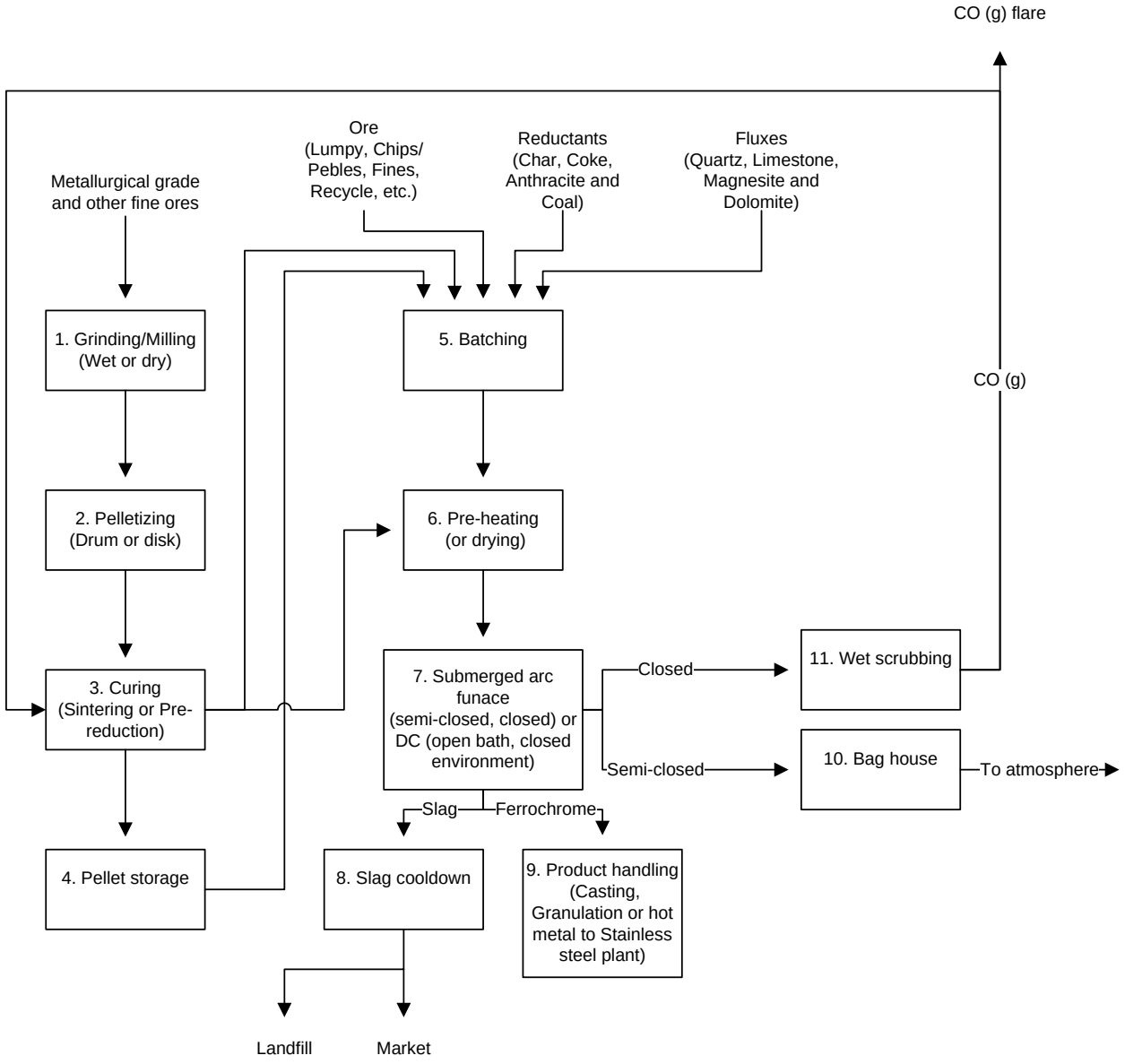


Figure 3: A flow diagram depicting the possible process steps and common combinations that are used by South African FeCr production facilities (Beukes et al., 2010 adapted from Riekkoal-Vanhanen, 1999)

In South Africa, FeCr producers tend to utilize one of the following process combinations (Beukes *et al.*, 2010):

a) Conventional open/semi-closed submerged arc furnace (SAF) operation with bag filter off-gas treatment. Even though this is the oldest technology utilised, it still contributes significantly to the total FeCr production in South Africa (Gediga & Russ, 2007). Coarse (lumpy chunks and chip/pebble type ore) and also some fine ore can be used as feed to these SAFs, without having to agglomerate the ores. Even though it has been mentioned by (Riekkoal-Vanhanen, 1999) that fine ores cannot be safely used as feed in a SAF without causing dangerous gas blow-outs or bed turn-overs, a small amount of fine ores are consumed by some open/semi-closed SAFs in South Africa. The process steps for this type of operation, as indicated in Fig 3 are 5, 7, 8, 9, and 10. If pellets are used, as with some open/semi-closed SAFs, then steps 1 to 4 would also be included. In South Africa, most of the open/semi-closed SAFs are operated under acidic slag conditions, with a basicity factor (BF) < 1. The BF is calculated with Eq. 7.

$$BF = \frac{\%\, CaO + \%\, MgO}{\%\, SiO_2} \qquad \text{(Eq. 7)}$$

Occasionally some open/semi-closed SAFs operate on BF > 1. However, this is not very common and might only be a temporary arrangement to compensate for refractory linings that are in a poor condition (basic slag have a higher liquidous temperature), or if enhanced sulphur removing capacity by the slag is required (higher calcium concentrations result in more calcium, CaS, formation). South African FeCr producers that make use of open/semi-closed furnaces, include the facilities at Lydenburg, Machadodorp, ASA, Tubatse, Wonderkop and Rustenburg (Table 1).

b) Closed SAF operations make use of oxidative sintered pelletised feed material (Outotec, 2008). This is the most commonly used technology in South Africa, with most of the green and brown field expansions during the last decade making use of this process. The process steps as indicated in Fig 3 for this operation include steps 1, 2, 3, 4, 5, 7, 8, 9, and 11. Step 6 may also be included. In all green field FeCr developments the pelletising (step 2) and sintering (step 3) sections were combined with closed furnaces. Pelletising and sintering sections have also been constructed at plants where the pelletised feed is utilized by conventional open/semi-closed furnaces. These furnaces are run under acidic slag (BF < 1). South African facilities that make use of this technology can be found at Machadodorp, Tubatse, ASA, Hernic, International Ferro-Metals, Ferrometals Witbank, Middelburg Ferrochrome, Wonderkop and SA Chrome (Boshoek) (Table 1).

c) Closed SAF operation with pre-reduced pelletised feed material (Botha, 2003; Naiker, 2007; Kleynhans *et al.*, 2012.; Neizel *et al.*, 2013). The process steps as indicated in Fig 3 for this type of operation are 1, 2, 3, 4, 5, 7, 8, 9, and 11. The pelletised feed material is first pre-reduced in rotary kilns, and then fed into the furnace while still hot. The SAF are closed and run under basic slag conditions (BF > 1). The only facilities in South Africa that use this process are Lion Ferrochrome and Lydenburg (Table 1).

d) Direct current (DC) arc furnaces exclusively utilise fine feed material (Curr, 2009; Denton *et al.*, 2004). The furnaces are operated under basic slag conditions. The process steps as indicated in Fig 3 for this type of operation are 5, 7 (with a DC, instead of a SAF), 8, 9, and 11. The South African FeCr producers that make use of this technology are the Middelburg Ferrochrome and Mogale (Table 1).

2.2.4 Historic and economic aspects of FeCr production in South Africa

Due to the relatively low Cr-to-Fe ratios of most South African chromite ore, these ores were not historically utilised for FeCr production. Two FeCr production plants were commissioned in the 1950s because of the sheer amount of chromite that was available in South Africa. However, only in the 1970s did FeCr production in South Africa start to drastically increase up to the high levels of production at which it operates today (ICDA, 2013; Howat, 1994). The FeCr industry in South Africa has grown over the years, and there are now over 14 FeCr production facilities operating in the country (Beukes et al., 2010). These FeCr smelters are mostly situated in or in close proximity of the BC with their locations indicated in Fig. 2. The production capacities for each of these facilities are listed in Table 1. The combined production capacity of these facilities amounts to over 5.1 million tons per year.

Table 1: FeCr production facility capacities for the South African FeCr smelters (updated from Beukes et al., 2012)

Production facility	Location	Production capacity in kilo tons per year
ASA Metals Dilokong	Dilokong (Burgersfort)	360
Assmang Chrome	Machadodorp	300
Hernic Ferrochrome	Brits	420
International Ferro-Metals	Rustenburg-Brits	267
Middelburg Ferrochrome	Middelburg	285
Mogale Alloys	Krugersdorp	130
Samancor Ferrometals	Emalahleni (Witbank)	550
Tata (Steel) Ferrochrome	Richards Bay	135
Tubatse Ferrochrome	Steelpoort	360
Xstrata Lydenburg	Lydenburg	400
Xstrata Merafe Boshoek	Rustenburg – Sun City	240
Xstrata Merafe Lion	Steelpoort	728
Xstrata Rustenburg	Rustenburg	430
Xstrata Wonderkop	Rustenburg-Brits	545
Total		5150

South Africa used to be the market leaders in the supply of FeCr due to South Africa's abundance of chromite ore reserves and historically relatively low-cost electricity. However, as indicated in Fig. 4, in recent years, China has increased its production of FeCr to levels beyond that of South Africa. This is mainly due to electricity shortages, significant price increases of electricity and labour unrest (Kleynhans *et al.*, 2012.) in South Africa. From Fig. 4 and 5, it is evident that the production of FeCr in China relies heavily on imported chromite ore, since it does not produce enough to sustain the current levels of FeCr production. Significant volumes of South African chromite ore is exported to China.

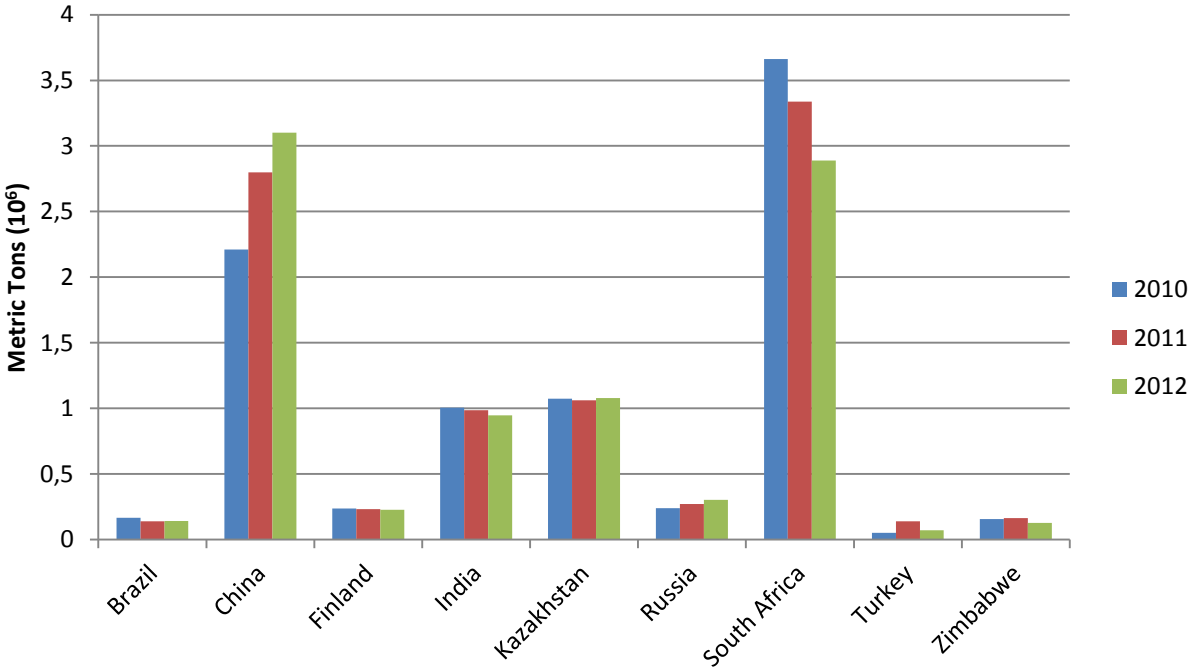


Figure 4: Global high carbon charge grade FeCr production for 2010 to 2012 (ICDA, 2013).

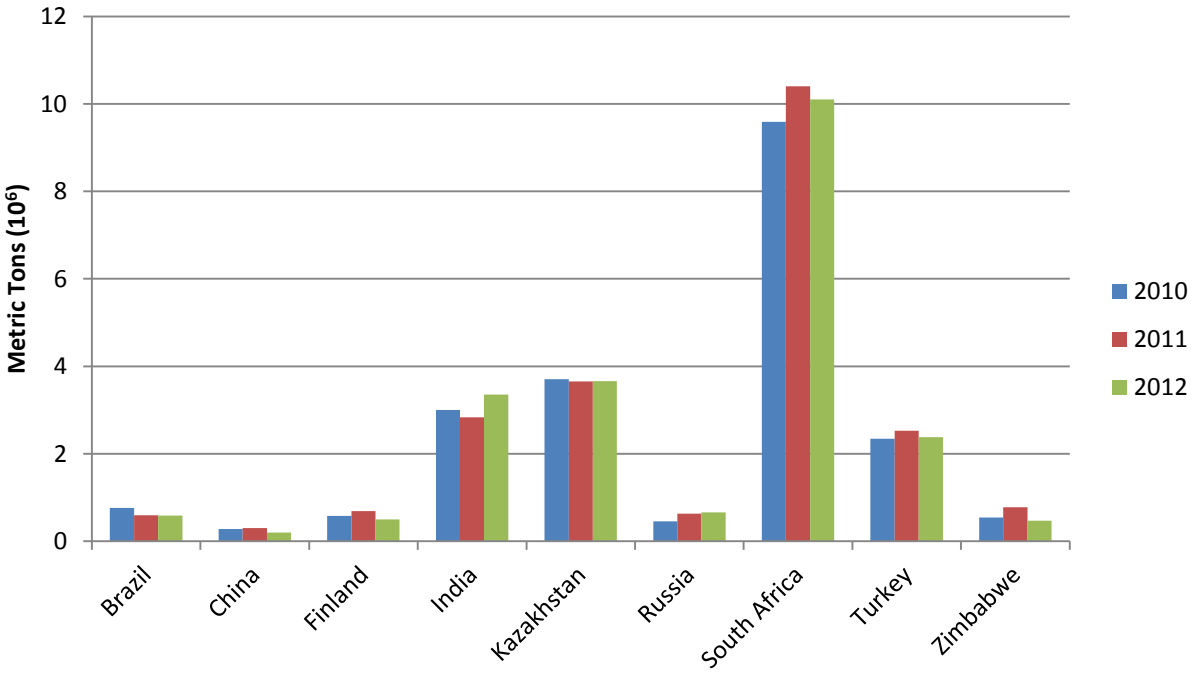


Figure 5: Global chromite production for 2010 to 2012 (ICDA, 2013).

2.3 Solid wastes of the FeCr industry

FeCr smelter facilities generate three main types of waste materials, i.e. slag, sludge and bag filter dust (BFD). Most of the Cr in the waste materials consists mainly of Cr(III). Cr(VI) is also present in some of the wastes, especially in BFD. Beukes *et al.* (2012) gave an overview of the

techniques and strategies employed by FeCr producers in South Africa to treat Cr(VI) containing waste materials.

2.3.1 Slag

Slag is the stony waste material (after solidification) that gets separated from FeCr metal during the smelting in the furnace. Slag is generated in relatively large quantities. For every ton of FeCr produced, between 1.1 and 1.9 tons of slag can be generated (Beukes *et al.*, 2010). Beukes *et al.* (2010) stated that in South Africa, nearly 5.3 million tons of slag was generated in 2007 alone. The amount of slag that is produced is dependent on the furnace technology that is used and on the quality of the feed material (Beukes *et al.*, 2010). Some South African FeCr slag waste materials have recently been declassified by the government, allowing these slags to be used in building materials and in concrete (Beukes *et al.*, 2012).

2.3.2 Bag filter dust

BFD is formed and collected from open/semi-closed SAF facilities. Figure 6 indicates typical BFD particles originating from such furnaces. As is evident from this micrograph, the BFD particles are mostly small rounded particles, indicating that they have undergone melting or have been exposed to high temperatures. The spherical particles in BFD may also be fume condensate.

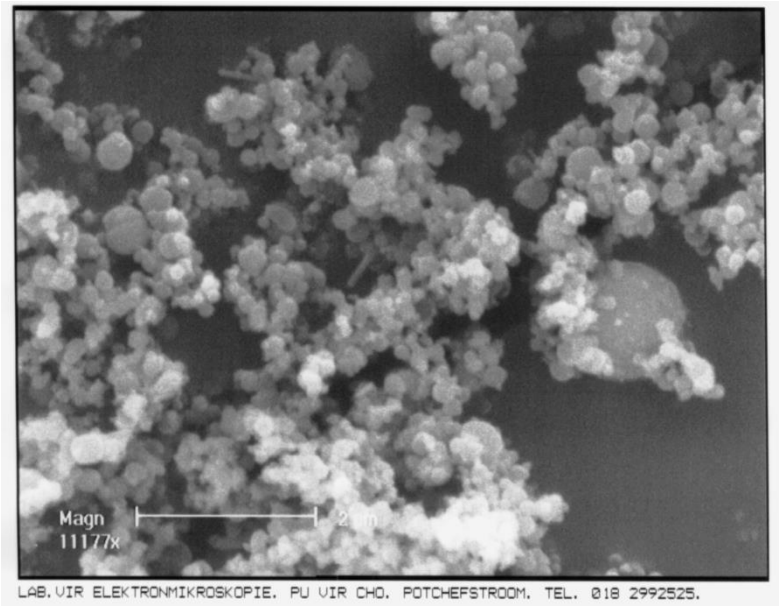


Figure 6: Scanning electron microscopy (SEM) micrograph of baghouse dust particles originating from a semi-closed FeCr smelter at 11 177 time magnification (with permission from Beukes *et al*., 1999)

Since BFD contains small amounts of Cr(VI), it is considered to be an environmentally hazardous waste (Beukes *et al.*, 2010). Even though not all Cr(VI) containing compounds are proven to be carcinogenic, the carcinogenic effects of some Cr(VI) compounds are very well known (IARC, 1997). BFD is fine and dry, and can easily be carried by the wind or inhaled by workers at FeCr production facilities if appropriate precautionary steps are not taken. Since the health risk associated with exposure to airborne Cr(VI) is much higher than that of aqueous Cr(VI) (Proctor *et al.*, 2002), it is very important to remove airborne BFD by bringing the BFD into contact with water as soon as possible (Beukes *et al.*, 2012). Cr(VI) is especially well known as a carcinogen in the respiratory system (IARC, 1997). Beukes *et al.* (2012) gave essential recommendations for the treatment of Cr(VI) containing BFD.

2.3.3 Sludge

Venturi scrubbers are a form of wet scrubbers. These devices bring the off-gas from a furnace into contact with water, where the dust and small particles from the smelting process are captured by the water spray or mist. Venturi scrubbers are usually installed on closed SAFs. The resulting waste from these scrubbers, are known as sludge. Sludge from venturi scrubbers is generated in roughly the same amounts as BFD, but it contains far less Cr(VI) (Beukes *et al.*, 2012; Gericke, 1995).

2.4 Cr(VI) present in off-gas and Bag Filter Dust

Cr is present as Cr(III) in the chromite ore, while Cr(0) is present in the FeCr that is produced. Albeit completely unintended, small amounts of Cr(VI) are formed during FeCr production and can be present in waste materials (Beukes *et al.*, 2010), as already indicated. In contrast to slag and sludge that contain relatively low concentrations of Cr(VI), BFD tends to contain Cr(VI) in far more significant concentrations (Beukes *et al.*, 2012; Gericke, 1998; Maine *et al.*, 2005). Therefore BFD cannot simply be stockpiled or placed in landfill storage (Gericke, 1995). BFD must undergo treatment to reduce Cr(VI) concentrations before disposal, which is usually achieved by the aqueous reduction of Cr(VI) by ferrous Fe (Beukes *et al.*, 2012).

Cr(III) can be oxidised to Cr(VI) in the presence of O_2, and therefore the availability of O_2 in the furnace during smelting will have a large effect on the formation of Cr(VI) (Beukes *et al.*, 2010). Consequently, in theory, a closed furnace should generate less Cr(VI) than an open/semi-closed furnace, since it does not have air entering the furnace to provide a semi-oxidising environment (Beukes *et al.*, 2010). However, many other factors can also influence the formation of Cr(VI), such as the presence of alkaline compounds. A furnace with a basic slag would typically generate more Cr(VI) than a furnace with an acidic slag (Beukes *et al.*, 2010). By introducing fine feed

material into the furnace, more small particulate chromite ore can be sucked into the off-gas extraction system that can be partially oxidised to Cr(VI) (Beukes *et al.*, 2010). Fine chromite feed carry the added threat of causing dangerous bed turnovers, because these fine feeds compacts the material inside the furnace, which then tend to cause a build-up of trapped process gasses (Beukes *et al.*, 2010). The temperature on top of the feed material inside the furnace is also of great importance, since the oxidation of Cr(III) to Cr(VI) is also dependant on the temperature (Antony *et al.*, 2001). The distribution of heat inside the furnace can be controlled by adjusting the length of the electrodes, with short electrodes providing a hotter surface layer, and longer electrodes providing a cooler surface layer (Beukes *et al.*, 2010). Gericke (1995) gave an indication of the concentrations of Cr(VI) that are present in the wastes generated by semi-closed and closed ferrochromium furnaces in South Africa, as indicated in Table 2 below.

Table 2: Typical water soluble Cr(VI) content of SA FeCr BFD as presented by Gericke (1995).

Process description	Cr(VI) / ppm
Closed furnace, with acid slag operation	5
Closed furnace, with basic slag operation	100
Semi-closed furnace, with acid slag operation	1000
Semi-closed furnace, with basic slag operation	7000

By bringing the BFD from the extraction system into contact with water, as currently conducted with wet venturi scrubbers, the risk to humans is significantly reduced, since airborne Cr(VI) dust is more likely to affect on-site workers than dissolved Cr(VI) (Proctor *et al.*, 2002). After the BFD made contacted with water, reduction of the Cr(VI) can be performed. The most common treatment process for Cr(VI) containing wastes in the South African FeCr industry at the moment is the aqueous chemical reduction of Cr(VI) by ferrous iron (Fe^{2+}), followed by the precipitation of Cr(III) hydroxides and then land filling in specially designed waste facilities (Beukes *et al.*, 2012). Fe^{2+} is preferred over many organic compounds that can also reduce Cr(VI), because many of the other compounds form water-soluble Cr(III) complexes that could be transported by ground or surface water only that can make contact with manganese oxides, which is a naturally occurring oxidant for Cr(III) (Bartlett, 1991; Eary & Rai, 1987). This might cause Cr(VI) to be formed far from the original waste source (Beukes *et al.*, 2012).

2.5 Health impacts associated with Cr(VI)

Cr(VI) in drinking water was brought to the attention of the general public in 1993, when Erin Brockovich highlighted Cr(VI) concentrations found in the groundwater near Hinkley, California (Mclean *et al.*, 2012). The carcinogenicity of inhaled Cr(VI) has been assessed and summarised in the Integrated Risk Information System for Cr (U.S. Environmental Protection Agency (USEPA); Kimbrough *et al.*, 1999; IARC, 1990)

Millions of workers are exposed to fumes, mists and dust particles that contain Cr or Cr compounds in the global chromate production, welding, chrome pigment manufacture, chrome plating, spray painting, mining, FeCr and stainless steel production industries (IARC, 1997). Exposures for workers to Cr(VI) concentrations as high as 1 mg/m^3 were found to be present in some of these industries in the past (IARC, 1997). The drinking water limit for Cr(VI) has been set to 0.05 mg/ℓ by the US Environmental Protection Agency (EPA), because of the toxicity and carcinogenicity of Cr(VI) (Calder, 1988).

Certain Cr(VI) species are regarded as toxic, mutagenic and carcinogenic, with specifically airborne exposure to these Cr(VI) species being associated with cancer of the respiratory system (Yassi & Nieboer, 1988; Proctor *et al.*, 2002; Hininger *et al.*, 2007). Trace concentrations of Cr(III) on the other hand are required in the human body to metabolise lipids and carbohydrates. Dietary supplements assist in any Cr(III) deficiencies and also serve as antioxidants (Hininger *et al.*, 2007). In the studies that were performed by the World Health Organisation (WHO) and the International Agency for Research on Cancer (IARC), it was found that Cr(0) as a powder had no carcinogenic properties, while Cr(III) also had no adverse carcinogenic effects on the laboratory mice that were used in their study (IARC, 1997). Calcium chromate, Cr trioxide (chromic acid), sodium dichromate, lead chromate, zinc chromate and strontium chromate, which are all Cr(VI) compounds have been tested on laboratory mice, and all of these compounds led to some form of cancer developing in the test subjects, with lung tumours being observed in many of the laboratory mice (IARC, 1997). Barium chromate was also studied for its carcinogenic effects on mice, but their studies were inadequate to allow for a proper evaluation of the carcinogenicity of barium chromate (IARC, 1997).

Epidemiological studies that were performed on workers in the chromate production industry and workers in the production of chromate pigments have all consistently shown a great degree of risk for developing lung cancer (IARC, 1997). Workers in the chromate pigments industry are often exposed to Cr(VI) not only directly by the pigments that is produced, but also from soluble Cr(VI) compounds that are present in the raw materials that they use to produce the pigments. Workers that perform chrome plating have also been diagnosed with lung cancer after spending years in their profession (IARC, 1997). For workers in the FeCr production industry the biggest risk comes from BFD, which contains small amounts of Cr(VI) that can be easily inhaled. Stainless steel welders often inhale Cr(VI) in the welding fumes, which have also been found to be

a cause of lung cancer, but since welders are often exposed to many other compounds as well, Cr(VI) exposure cannot be seen as the only contributing factor (IARC, 1997). Cr(VI) compounds are known to effect the skin, the respiratory system, and even kidneys in humans (IARC, 1997).

The IARC, which is part of the WHO, makes distinction between some Cr(VI) compounds (IARC, 1997). It is stated that:

- There is sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromates, strontium chromate and lead chromates.
- There is limited evidence in experimental animals for the carcinogenicity of Cr trioxide (chromic acid) and sodium dichromate.
- There is inadequate evidence in experimental animals for the carcinogenicity of barium chromate.

2.6 Conclusions from literature and gaps therein

South Africa has a very large FeCr industry. Risks associated with Cr(VI) therefore have to be quantified. The IARC make a distinction with regard to the carcinogenicity of some Cr(VI) compounds. Ideally, the presence of individual Cr(VI) compounds present in FeCr BFD needs to be quantified to determine the possible health impact of BFD better. In this study the first step in such quantification was taken, by determining the water soluble and sparingly water soluble, as well as water insoluble Cr(VI) contents present in BFD samples. These solubility classes can at least partially be related to the Cr(VI) compounds being present. Additionally, afore-mentioned solubility categorisation and determination of Cr(VI) leachability as a function of pH, will enable the candidate to determine whether the currently applied Cr(VI) leaching and chemical treatment procedures applied by FeCr producers are adequate.

Chapter 3 Article

Aqueous solubility of Cr(VI) in ferrochrome bag filter dust and the implications thereof

WPJ van Dalen[a], JP Beukes[a]*, PG van Zyl[a], MM Loock-Hattingh[a] and J Hendriks[b]

[a] *Chemical Resource Beneficiation, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa*

[b] *Unit for Environmental Sciences and Management, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa*

Abstract

The production of ferrochrome (FeCr) is a reducing process, whereby Cr(III) and Fe(II) in the ore are reduced to metallic chromium (Cr) and iron (Fe) in the final product. It is, however, not possible to exclude oxygen completely from all the high temperature steps during the production process, which leads to the formation of small amounts of Cr(VI) through the oxidation of Cr(III). The formed Cr(VI) is mostly associated in the off-gas of these high temperature processes, which are cleaned by means of venturi scrubbers or bag filter systems before released into the atmosphere. Certain Cr(VI) species are regarded as carcinogenic, while specifically airborne exposure to these Cr(VI) species is associated with cancer of the respiratory system. In this study the solubility of Cr(VI) present in BFD were determined experimentally. The Cr(VI) in BFD were categorised as water soluble Cr(VI), sparingly soluble and insoluble Cr(VI) compounds. These solubility categories could then be related to groups of Cr(VI) compounds, which therefore took the first step in better speciation of Cr(VI) present in BFD. Four different BFD samples from FeCr producers in South Africa were considered. The results indicated that more Cr(VI) leached with an increase in pH. This was in contrast with the trend for most heavy metals, i.e. lower pH is associated with an increase of solubility for these metals. A 0.05M $(NH_4)_2SO_4$ - 0.05M NH_4OH extraction buffer that is capable of leaching all soluble and sparingly soluble Cr(VI) compounds and a 3% Na_2CO_3 – 2% NaOH extraction buffer that can quantitatively extract all Cr(VI) in the BFD samples, including the water insoluble fraction was used to indicate that not only soluble, but also sparingly- and insoluble Cr(VI) compounds occur in the BFD samples evaluated. Further analysis showed that approximately one third of Cr(VI) was insoluble , while the rest of the Cr(VI) in the BFD were sparingly soluble and insoluble Cr(VI) compounds. The main finding from the study was that the current leaching procedures applied by FeCr producers to BFD, prior to the chemical reduction of Cr(VI), do not effectively extract the sparingly water insoluble compounds. This results

in Cr(VI) leaching from waste facilities at later stages, even if seemingly effective Cr(VI) treatment was applied.

Keywords: hexavalent chromium, Cr(VI), ferrochromium or ferrochrome (FeCr) bag filter dust (BFD)

* Corresponding author:
Tel.: +27 (0) 18 299 2337; fax: +27 18 (0) 299 2350; e-mail: paul.beukes@nwu.ac.za

Introduction

Ferrochrome (FeCr) is produced by pyrometallurgical carbo-thermic reduction of chromite ore (Riekkoal-Vanhanen, 1999). FeCr is mostly used in the production of stainless steel, which is a vital alloy in modern society. Since its discovery in 1798, chromite has remained the only commercially viable source of new chromium (Cr) units (Nriagu, 1988; Riekkoal-Vanhanen, 1999). It is generally accepted that South Africa holds approximately 75% of the world's viable chromite ore reserves (Mintek, 1990; Cramer *et al.*, 2004). The South African chromite reserves are deposited within the Bushveld Complex. This geological phenomenon consists of an enormous saucer-like intrusive igneous mass. It extends for about 400km from east to west and approximately the same distance from north to south. It is located in the central and slightly western portion of the South African Highveld (Howat, 1994), as indicated in Figure 1. According to the 2012 production statistics South Africa produces nearly 41% of the world's chromite ore, and 36% of the world's high-carbon FeCr, i.e. the most common grade of FeCr (ICDA, 2013). In the FeCr production process, Cr is present as Cr(III) in the chromite ore, while Cr(0) is present in the FeCr that is produced. Although completely unintended, small amounts of Cr(VI) are formed during ferrochrome production and can be present in waste materials (Beukes *et al.*, 2010; Beukes *et al.*, 2012). The main types of waste generated are slag, sludge and bag filter dust (BFD) (Van Staden *et al.*, 2014). Certain Cr(VI) species are regarded as carcinogenic, with specifically airborne exposure to these Cr(VI) species being associated with cancer of the respiratory system (Yassi & Nieboer, 1988; Proctor *et al.*, 2002).

Insert Figure 1

Ferrochrome production results in relatively large quantities of slag. Slag-to-FeCr generation ratios of 1.1:1 up to 1.9:1 are common in this industry, with ratios varying according to different production technologies employed at various production facilities (Beukes *et al.*, 2010). Although the volumes of slag generated are large, the Cr(VI) content of the slag is usually very low (Beukes *et al.*, 2010). Additional Cr(VI) treatment can also be applied during the recovery of FeCr from the slag (Coetzer *et al.*, 1997; Maine *et al.*, 2005). In certain developed countries (e.g. Finland) FeCr slag is considered to be a marketable product (Riekkoal-Vanhanen, 1999). Zelić (2005) reported on the use of ferrochrome slag in concrete pavements, while Lind *et al* (2001) reported on the use of FeCr slag in road construction. Relatively recently some South African FeCr slags have also been declassified, making commercial use thereof possible. Sludge is generated during the wet venturi scrubbing of closed furnace off-gas (Beukes *et al*., 2010). This sludge does not usually contain significant Cr(VI) concentrations (Gericke, 1998). In contrast to slag and sludge, BFD generated during the cleaning of off-gas from open/semi-closed FeCr furnaces contain more significant levels of Cr(VI) (Gericke, 1998; Maine *et al.*, 2005; Beukes *et al.*,

2012), which cannot be disposed without proper Cr(VI) treatment (Beukes *et al.*, 2012). After the BFD is treated to remove Cr(VI) it is disposed in fit-for-purpose waste facilities.

In contrast to Cr(VI), Cr(III) and Cr(0) are not classified as carcinogenic (IARC, 1997). Cr(III) is in fact used a dietary supplement for certain human health abnormalities (Hininger *et al.*, 2007). Due to these fundamental health impact differences most studies generally only refer to the differentiation between Cr(III) and Cr(VI) containing species when Cr speciation is discussed (e.g. Cox and Linton, 1985; Kotas *et al*, 2000; Sreeram *et al*, 2001). However, the International Agency for Research on Cancer, which forms part of the World Health Organization, makes a distinction between specific Cr(VI) compounds (IARC, 1997). It is stated that:

- There is sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromates, strontium chromate and lead chromates.
- There is limited evidence in experimental animals for the carcinogenicity of Cr trioxide (chromic acid) and sodium dichromate.
- There is inadequate evidence in experimental animals for the carcinogenicity of barium chromate.

From the above-mentioned it is evident that the risk associated with FeCr BFD should not only be considered within the context of Cr(III)-Cr(VI) speciation. Ideally the cation associations with the chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) anions, which are the main form of Cr(VI) in compounds should be determined, since it will give greater insight into the possible health impacts of BFD. However, determining these associations is challenging. Therefore, as a first step towards better categorisation of Cr(VI) in BFD based on the specific anion-cation associations of these species, the solubility of Cr(VI) present in BFDs were determined in this study. This allowed that Cr(VI) species could be categorised as being water soluble Cr(VI), sparingly soluble and insoluble Cr(VI) compounds. These solubility categories can then be related to groups of Cr(VI) compounds, therefore taking the first step in better speciation of Cr(VI) present in BFD. These results are also of general importance to natural aqueous systems (surface- and ground water), since the above mentioned differences in solubility of the various Cr(VI) compounds are closely linked to Cr(VI) leaching from FeCr wastes into these systems.

Experimental

Materials

Four different BFD samples were obtained from FeCr producers in South Africa, i.e. two samples from producers in the Mpumalanga Province and two samples from producers in the North West Province. These samples will subsequently be referred to as Mpu A and Mpu B (Mpumalanga) and NW A and NW B (North West). Numerous factors can influence the compositions of BFD. These include production technology employed (e.g. open or partially closed

furnace technology, type of filters used in the bag filter plant), physical separation in the bag filter plant itself (e.g. some compartments containing finer material than other), metallurgical operating conditions (e.g. basic or acid slag operating conditions) and composition of feed material (e.g. chemical and physical differences of ores). The above-mentioned samples were therefore selected to be representative of a wide variety of parameters that could influence its composition.

All chemicals used were analytical grade (AR) reagents obtained from the different suppliers and used without any further purification. Standard Cr(VI) solutions were prepared from a 1009 ± 5 mg/mℓ aqueous chromate CrO_4^{-2} analytical solution (Spectrascan, distributed by Teknolab AB, Sweden), which were used for calibration and verification of the analytical technique employed. The post-column reagent that was used during Cr(VI) analysis was prepared using 1,5-diphenylcarbazide (DPC) (FLUKA), 98% sulphuric acid (Rochelle Chemicals) and HPLC grade methanol (Ace). Solutions of sodium hydroxide (Merck) and perchloric acid (Merck) were used to adjust the pH of aqueous solutions/mixtures. 99% ammonium sulphate (Merck SA) and 25% ammonia solution (Associated chemical enterprises) were used to prepare a 0.05M $(NH_4)_2SO_4$ - 0.05M NH_4OH extraction buffer that is capable of leaching all soluble and sparingly soluble Cr(VI) compounds (Ashley *et al.*, 2003). Sodium hydroxide (Promark chemicals) and anhydrous sodium carbonate (Merck SA) were used to prepare a 3% Na_2CO_3 – 2% NaOH extraction buffer, to quantitatively extract all Cr(VI) in the BFD samples, including the water insoluble fraction (Ashley *et al.*, 2003). Ultra-pure water (resistivity, 18.2 $M\Omega \cdot cm^{-1}$), produced by a Milli-Q water purification system, was used for all dilutions and aqueous extractions. 99.999% pure nitrogen gas (N_2) (AFROX) was used to provide an inert environment during leaching. Hydrophilic PVDF 0.45 μm filters (Millipore Millex, USA) were used for the filtration of solutions.

Methods

SEM analyses

Scanning electron microscopy with energy dispersive x-ray detectors (SEM-EDS) was used to perform surface characterisation of the BFD particles. A Zeiss MA 15 SEM incorporating a Bruker AXS XFlash®5010 Detector X-ray EDS system operating with a 20 kV electron beam at a working distance of 17.4 mm was utilised. BFD samples were prepared with two different procedures for SEM analysis. Firstly, samples were mounted onto a specimen stub with carbon coated tape and subsequently gold coated in order to determine the general BFD particle characteristics with micrographs, e.g. size and shapes. In order to analyse the surface chemical composition of the samples by SEM-EDS, the samples were set in resin and polished in water before the cross sectional SEM and SEM-EDS analyses were conducted. The polishing step was performed at Mintek, and they took measures to prevent Cr(VI) from leaching out during sample

preparation. The SEM-EDS analysis was performed by scanning over a wide rectangular area of the sample surface in a raster like pattern for 60 seconds. Spot analyses were also performed to determine the composition of certain individual particles present in the BFD.

Particle size analysis

A Malvern mastersizer 2000 was used to determine the particle size distribution of the BFD samples. A diluted suspension of material was ultra-sonicated for 1 min prior to the particle size measurement, in order to disperse the individual particles and to prevent the use of a chemical dispersant. Laser obscuration was kept at 10 to 15%, while mechanical stirring was set to 2000 rpm. Ten measurements were repeated for each sample and the average taken.

Trace metal analysis

Similar to Van Zyl *et al*. (2013) inductively coupled plasma mass spectroscopy (ICP-MS) was used to determine the concentrations of all the heavy metals present in aqueous solution, with an Agilent 7500CE ICP-MS with Octopole Reaction System.

Cr(VI) extraction and analysis

0.50 g of each BFD sample were weighed off accurately and transferred into a 100 mℓ glass beaker, which contained 50 mℓ of milli-Q water. The initial pH of the milli-Q water had been adjusted to a predetermined value and the water had been de-air rated by bubbling N_2 through the water for 10 min. Each beaker and its contents were placed on a magnetic stirrer and stirred for a period of 2 hours. A steady stream of N_2 was continually bubbled through the suspension, to ensure an inert environment during leaching to prevent oxidation of Cr(III) to Cr(VI) (Ashley *et al.*, 2003). Magnesium hydroxide could also be used to suppress the oxidation of Cr(III) (Zatka, 1985), but it was not used in this study, since N_2 was more readily available. After applying this leaching process, the solutions were filtered through Hydrophilic Millipore PVDF 0.45μm filters to remove particulate matter from the filtrate. The pH was measured again to ensure that no pH drift occurred. Thereafter the filtrates were transferred to 100 mℓ A-grade volumetric flasks and diluted to a final volume of 100 mℓ with pH adjusted milli-Q water. 50 mℓ of each solution was used for aqueous trace metal analyses, while the remaining 50 mℓ was used for Cr(VI) analysis. All pH measurements were conducted with a HANNA - HI 991001 pH meter with a temperature probe. Additional to the extraction of Cr(VI) at specific pH values, Cr(VI) extractions were also carried out using hot plate digestion utilising either 0.05M $(NH_4)_2SO_4$ - 0.05M NH_4OH or 3% (m/v) Na_2CO_3 - 2% (m/v) NaOH, as described by (Ashley *et al.*, 2003; NIOSH 7605, 2003), which leached the

water soluble and water insoluble Cr(VI) fractions present in the BFD samples, respectively (Ashley *et al.*, 2003).

The Cr(VI) concentrations of aliquots were determined with a Thermo Scientific Dionex ICS 3000 ion chromatograph (IC) according to the procedure described by Loock *et al.* (2014) and Du Preez *et al.* (2014), which was derived from Dionex Application Update 144 (2003), Dionex Application Update 179 (2011) and Thomas *et al.* (2002). The IC system was equipped with a Dionex IonPac AG7 4 x 50 mm guard column and a Dionex IonPac AS7 4 x 250 mm analytical separation column. A 1000 µℓ injection coil and a 2 x 750 µℓ knitted reaction coil (for better peak response) coupled to a uv-visible absorbance detector set at a wavelength of 530 nm were used. 250 mM ammonium sulphate was used as an eluent and an isocratic pump carried the eluent and the injected sample through the flow lines and columns of the IC. 2 mM DPC solution was used for post column colouration, which was delivered into the system by an AXP pump. The flow rates of the eluent and colourant were 1.0 mℓ.min^{-1} and 0.5 mℓ.min^{-1}, respectively. In order to minimize the baseline noise generated by the pulses of the AXP pump on chromatograms, additional polyetherketone tubing was fitted in-between the AXP pump and the back pressure tubing. A six-point calibration was performed for Cr(VI), ranging from 5 to 75 µg/ℓ. The correlation coefficient of this linear calibration line was more than 99.96%. With this technique, a detection limit of 0.06 µg/ℓ could be achieved (Thomas *et al.*, 2002; Dionex Application Update 144, 2003) and false positive results for Cr(VI) concentrations, which are typical for the direct DPC uv-visible method, were avoided (Ashley *et al.*, 2003).

For the IC eluent 66 g ammonium sulfate and 15.08 g ammonium hydroxide was dissolved in deionized water and diluted in a 2 ℓ volumetric flask. The DPC post-column colourant was prepared by adding 28 mℓ of 98% sulfuric acid to 100 mℓ deionized water in a 1 ℓ volumetric flask. The warm solution was cooled down to room temperature before proceeding. 0.5 g DPC was added to a 100 mℓ volumetric flask with ~ 80 mℓ methanol. The DPC solution was ultra-sonicated in order to dissolve it and the solution was then made up to 100 mℓ with methanol. Once the acidic solution had cooled down sufficiently the DPC methanol solution was slowly added to it, which was then left to cool down to room temperature. Before the DPC solution was used on the IC instrument, it was filtered with a 0.45 µm milli-pore filter to ensure that no solid particles were present that could block the fine tubing of the instrument.

Extracted Cr(VI) results were expressed in mg Cr(VI) / kg of BFD by considering the aqueous Cr(VI) concentrations, weight of BFD leached and the dilutions applied. The mean Cr(VI) content extracted at each pH, as well as with the buffer solutions, is presented with the standard deviations derived from the three repetitions that were performed.

Results and discussions

Characterisation of the BFD samples

The d_{10}, d_{50} and d_{90} of the particle size distribution of the different BFD samples are presented in Table 1. The d_{90} is defined as the equivalent particle size for which 90% of the particles are smaller, with definitions of d_{50} and d_{10} derived similarly. The particle size analyses indicated that the d_{90} of all four BFD samples ranged between 32.8 and 152.2 µm, with the Mpu A and B samples being coarser than the NW A and B samples.

Insert Table 1

Figures 2 – 5 indicate SEM micrographs obtained for Mpu A, Mpu B, NW A and NW B, respectively. Each of these figures present combined images, with the larger images indicating a cross sectional polished micrograph, while the smaller image in the bottom right hand corner is a micrograph of the BFD pressed onto a stub with carbon tape. It is evident from these micrographs that the BFD samples consisted mainly of very small particulate matter, with larger particles up to approximately 75µm also being present. Since it was previously proven that the larger uneven shaped particles observed in BFD are unreacted, or partially reacted raw materials such as chromite, fluxes or reductants, while the very small spherical shaped particles are actual off-gas particulates (Beukes *et al.*, 1999; Beukes *et al.*, 2010; Van Staden *et al*., 2014), this phenomena was not reinvestigated in the study. However, to confrim that unreacted/partialy-reacted chromite particles were present in the samples, the unevenly shaped grey particle marked with a red box in Figure 2 (Mpu A) was analysed with SEM-EDS, which revealed 30.7 and 20.8 wt% Cr and iron (Fe) content, respectively. This Cr/Fe ratio correlates very well with typical South African chromite ore used for FeCr production (Kleynhans *et al.*, 2012; Cramer *et al*., 2004). The Mpu A and Mpu B BFD samples also clearly contained more unreacted/partially reacted larger raw material particles (Figures 2 and 3) compared to NW A and B (Figures 4 and 5). This visual inspection confirms the particle size analyses results presented, which indicated that the Mpu A and Mpu B sample were coarser. As previously indicated the presence of a larger number of larger raw material particles in the BFD could be ascribed to various differences in the technology applied or the feed material used at the different production facilities. For instance certain FeCr smelters use a proper cyclone to remove larger particles before the off-gas is cleaned in the bag filter plant, while others merely use a drop out box. SEM-EDS chemical analyses of cross sectional polished surfaces of the four BFD samples are presented in Table 2. Carbon (C) was not analysed for, since it also occurred in the resin used to set the BFD samples prior to polishing. Cr content of the samples varied between 3.28% (sample NW A) and 7.62% (sample Mpu B). As expected, the elements with lower elemental mass that are typically associated with actual off-gas particles, such as magnesium (Mg), aluminium (Al), silicon (Si) and zinc (Zn) were present in significant concentrations in all the

BFD samples. Also of particular interest was that no significant amount of sodium was detected in some BFD samples. It is well known that alkali roasting of chromite is an industrial process for the production of the Cr(VI) compound sodium chromate, of which the formation efficiency depends on the amount of O_2 and alkali present, as well as the temperature during the production process (Antony *et al.*, 2001). The EDS detection limit for Na is higher than for K which might indicate why no significant amount of sodium was detected. It is unlikely that any Cr(VI) phases would be detected by EDS. Maine *et al.* (2005) proposed that Cr(VI) could mainly be associated with alkali metals in South African FeCr BFD, but did not present any evidence to support this statement. However, SEM-EDS results presented in this paper indicate that it is unlikely that Cr(VI) in the BFD would be associated only with alkali metals. Alkaline metal compounds of Cr(VI) are water soluble, while some other Cr(VI) salts are not (Ashley *et al.*, 2003).

Insert Figures 2 - 5

Insert Table 2

Leachability of trace metals, excluding Cr(VI)

It is generally accepted that higher concentrations of most heavy and transitional metals will leach out of a solid sample (e.g. waste and soil) at lower pH values (Pyeong-Koo *et al.*, 2012; Ding *et al.*, 2014). This was also determined experimentally as indicated in **Figures 6 – 9**, which present the concentration (mg/kg) of leachable metals as a function of pH.

Insert Figures 6 - 9

Cr(VI) leachability

Figure 10 presents the leachable Cr(VI) concentrations (mg Cr(VI) / kg BFD) as a function of pH of the solution from which Cr(VI) was leached. From these results it is clear that the leachable Cr(VI) increased with an increase in initial pH of the leached solution for all the samples evaluated. This is in contrast to the results obtained for all the other trace metals (**Figures 6 - 9**) for which the leachability increased at lower initial pH.

Insert figure 10

Literature (Ashley *et al.*, 2003) indicates that water soluble Cr(VI) compounds (e.g. Na_2CrO_4, K_2CrO_4) dissolve at any pH, while the solubility of sparingly soluble Cr(VI) compounds (e.g. $SrCrO_4$) and insoluble Cr(VI) compounds (e.g. $BaCrO_4$ and $PbCrO_4$) are enhanced by increasing

alkalinity of the aqueous solution. Ashley *et al.* (2003) indicated by which means the dissolution of insoluble Cr(VI) compounds are enhanced at higher pH levels by the addition of carbonate (CO_3^{2-}):

$$MCrO_4 + CO_3^{2-} \leftrightarrow MCO_3 + CrO_4^{2-}, \text{ M = cation associated with chromate} \quad \text{(Eq. 1)}$$

In the presence of a large excess of CO_3^{2-} the equilibrium shifts quantitatively to the right of Eq. 1 and insoluble Cr(VI) becomes soluble. The observed increase of Cr(VI) leached with an increase in pH of the aqueous solution is therefore an indication that not only soluble, but also sparingly- and insoluble Cr(VI) compounds occur in the BFD samples evaluated.

Partial quantification of the Cr(VI) compounds into solubility groups can be obtained by using two separate extractions techniques. A buffered $(NH_4)_2SO_2$ - NH_4OH hot plate extraction is known to quantitatively extract soluble- and sparingly soluble Cr(VI) compounds, while a buffered Na_2CO_3 - NaOH hot plate extraction is known to extract all Cr(VI) compounds, including insoluble species (Ashley *et al.*, 2003). **Figure 10** indicates the leached Cr(VI) concentrations obtained as a function of pH, as well as with the afore-mentioned extraction buffers, for all four of the samples. In **Figure 11** all of the concentrations are expressed as the percentage of Cr(VI) that could be leached, with 100% Cr(VI) extraction represented by the Cr(VI) extracted by the Na_2CO_3 - NaOH buffer. From these results it is clear that the buffered $(NH_4)_2SO_2$ - NH_4OH hot plate extraction, which is known to quantitatively extract soluble- and sparingly soluble Cr(VI) compounds, extracted on average approximately 66.7% of the total Cr(VI) present. All extractions performed at pH levels ≤ 9, extracted only approximately 30% of the total Cr(VI) present in the BFD samples. Only when the pH was increased to 13, was complete extraction of the water soluble and sparingly water soluble Cr(VI) compounds achieved. This data therefore also indicates that approximately a third of all Cr(VI) present in the BFDs are insoluble Cr(VI) compounds.

Insert figure 11

In addition to categorising the Cr(VI) present in the BFD samples into two groups, i.e. soluble combined with sparingly soluble and insoluble Cr(VI), the above-mentioned data has numerous other implications:

- This data contradicts the general perception that total Cr(VI) extraction from ferrochrome BFD can be achieved by neutral or acidic aqueous solutions. Maine *et al.* (2005) indicated that >100 hours of extraction is required with neutral water to completely extract Cr(VI) from South African ferrochrome BFD. Gericke (1995) maintained that 24 hour leaching with aqueous solutions of pH 2 – 6 is adequate for Cr(VI) extraction from South African BFD. Bulut *et al.* (2009) stated that only 30 minutes was required to dissolve all Cr(VI) present in Turkish BFD and that the pH of the solution did not play a significant role. None of these authors utilised

basic hot plate extraction, as recommended by Ashley *et al.* (2003) to ensure extraction of insoluble Cr(VI) compounds.

- The data has practical implications for FeCr producers. BFD produced by FeCr producers is contacted between 5 minutes and 2 hours, depending on the configuration and plant layout, before Cr(VI) reduction (usually with the addition of ferrous ion) takes place (Beukes *et al*., 2012). This implies that not all Cr(VI) is extracted prior to Cr(VI) treatment taking place according to the results obtained in this study. This explains why Cr(VI) keeps on leaching from waste facilities such as slimes dames, even after Cr(VI) treatment of the incoming waste stream was applied. Previously, Maine *et al.* (2005) explained the slow release of Cr(VI). It was postulated that most of the Cr(VI) is condensated onto the surface of the rounded fly ash type particles, which can dissolve very rapidly into water. However, a small fraction of Cr(VI) might be trapped by the glassy surface of these fly ash type particles that resulted in the slow release of the remaining Cr(VI). The results presented in this paper prove that the slow release of Cr(VI), after the initial quick dissolution of a substantial fraction of the Cr(VI), can rather be attributed to the presence of sparingly- and insoluble Cr(VI) compounds. The authors propose that alternative Cr(VI) treatment procedures are investigated in future, that improves the methods currently applied by FeCr producers (Beukes *et al.*, 2012). Such treatment procedures should ensure the extraction of all water soluble and water sparingly soluble Cr(VI) compounds, before chemical reduction of the Cr(VI) are perfomed. This will ensure that sparingly water soluble Cr(VI) compound do not leach out over time from the waste storage facilities, which is currently the case.
- These results clearly show that the past South African legislative practice of classifying possible Cr(VI) containing waste by the use of low pH extracting solutions (e.g. acid rain or TCLP test) might not extract all the Cr(VI). As an example, most South African FeCr slags were historically classified as hazardous waste, based on the extraction of heavy metals such as Mn and Fe. However, low pH extractions will solubilize these metals (as indicated in **Figures 6 - 9**), but might not extract all Cr(VI) (as indicated in **Figures 10 and 11**). If wastes are classified based on the extraction of Fe or Mn, a possible precautionary measure would be the addition of lime to the waste dump, since this would reduce/eliminate Fe and Mn leaching. However, such a precautionary measure could effectively increase Cr(VI) leaching, since Cr(VI) is more soluble at higher pH values.

Conclusion

During the unbuffered aqueous extraction of Cr(VI) it was found that more Cr(VI) leached with increased pH, indicating that not only soluble, but also sparingly- and insoluble Cr(VI) compounds occur in the BFD samples. Since human health impacts are associated with the cation association of the Cr(VI) containing anion species CrO_4^{2-} or $Cr_2O_7^{2-}$, these cation-anion

associations should be quantified in future research. In this study the first step toward such quantification was taken, by at least categorising the Cr(VI) present in FeCr BFD into solubility classes by using buffered extractions. From the results it could be concluded that approximately one third of Cr(VI) present in the BFD samples was insoluble Cr(VI) and the remainder consisted of sparingly insoluble and soluble Cr(VI) compounds.

The most important deduction that can be made from the results presented is that the current leaching procedures applied by FeCr producers, prior to the chemical reduction of Cr(VI), do not effectively extract the compounds that are sparingly soluble in water. This results in Cr(VI) leaching from waste facilities, even if seemingly effective Cr(VI) treatment was applied. It should be considered as an extremely important future perspective to develop economically feasible Cr(VI) extraction procedures that will ensure complete extraction of all the sparing water soluble Cr(VI) compounds together with the water soluble fraction, prior to chemical reduction of Cr(VI) and subsequent storage of the residue on a waste facility. From the results presented, it seems that a highly alkaline leach (pH approximately 13) would be an option. However, investigations must confirm that complete chemical Cr(VI) reduction can be achieved at such high pH levels in practise. Ferrous (Fe^{2+}) reduction of Cr(VI) is currently the most commonly applied technique by FeCr producers to reduce aqueous Cr(VI) chemically. However, dissolved O_2 oxidises dissolved Fe^{2+} to Fe3+ quicker at higher pH values. Therefore the effectiveness of this and other potential reductants at elevated pH levels need to be investigated.

Acknowledgements

The authors of this paper wish to thank the four FeCr production facilities that provided the BFD case study samples that were used in this study.

References

ANTONY, M.P., TATHAVADKAR, V.D., CALVERT, C.C. & JHA, A. 2001. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium. Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, 32(6):987-995. December.

ASHLEY, K., HOWE, A.M., DEMANGE, M. & NYGREN, O. 2003. Sampling and analysis considerations for determination of hexavalent chromium in workplace air. *Journal of Environmental Monitoring*, 5:707-716. 8 August.

BEUKES, J.P., DAWSON, N.F. & VAN ZYL, P.G. 2010. Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry. *The Journal of The Southern African Institute of Mining and Metallurgy*, volume 110:743-750. December.

403 BEUKES, J.P., PIENAAR, J.J., LACHMANN, G. & GIESEKKE, E.W. 1999. The reduction of
404 hexavalent chromium by sulphite in wastewater. *Water SA*, 25(3):363-369. July.

405 BEUKES, J.P., VAN ZYL, P.G. & RAS, M. 2012. Treatment of Cr(VI) containing wastes in the
406 South African ferrochrome industry - A review of currently applied methods. *The Journal of The*
407 *Southern African Institute of Mining and Metallurgy*, 112(5):347-352.

408 BORAI, E.H., EL-SOFANY, E.A. & ABDEL-HALIM, A.S. 2002. Speciation of hexavalent chromium
409 in atmospheric particulate samples by selective extraction and ion chromatographic
410 determination. *Trends in analytical chemistry*, 21(11):741-745.

411 BULUT, U., OZVERDI, A. & ERDEM, M. 2009. Leaching behavior of pollutants in ferrochrome arc
412 furnace dust and its stabilization/solidification using ferrous sulphate and Portland cement. *Journal*
413 *of Hazardous Materials*, 162(2-3):893-898. 15 March.

414 COETZER, G., GIESEKKE, E.W. & GUEST, R.N. 1997. Hexavalent chromium in the recovery of
415 ferrochromium slag. *Canadian Metallurgical Quarterly*, 36(4):261-268.

416 COX, X.B., LINTON, R.W. & BUTLER, F.E. 1985. Determination of chromium speciation in
417 environmental particles. Multitechnique study of ferrochrome smelter dust. *Environmental Science*
418 *and Technology*, 19(4):345-352.

419 CRAMER, L.A., BASSON, J. & NELSON, L.R. 2004. The impact of platinum production from UG2
420 ore on ferrochrome production in South Africa. *Journal of The South African Institute of Mining and*
421 *Metallurgy*, 104(9):517-527. October.

422 DING, Y., SONG, Z., FENG, R., GUO, J. 2014. Interactions of organic acids and pH on multi-
423 heavy metal extraction from alkaline and acid mine soils. International Journal of Environmental
424 Science & Technology, 11(1):33-42. February

425 DIONEX APPLICATION UPDATE 144. 2003. Determination of Hexavalent Chromium in Drinking
426 Water Using Ion Chromatography. *Application Update 144*

427 DIONEX APPLICATION UPDATE 179. 2011. Sensitive Determination of Hexavalent Chromium in
428 Drinking Water. *Application Update 179*

429 DU PREEZ, S.P., BEUKES, J.P. & VAN ZYL, P.G. 2014. Cr(VI) generation during flaring of CO-
430 rich off-gas from closed ferrochromium submerged arc furnaces. *Metallurgical and Materials*
431 *Transactions B*

432 GERICKE, W.A. 1995. Environmental aspects of ferrochrome production. (*In* Proceedings
433 Ferroalloys 7th international congress (INFACON XII). Trondheim, Norway. p. 131-140.)

434 GERICKE, W.A. 1998. Environmental solutions to waste products from ferrochrome
435 production. (*In* The proceedings of the eight International ferroalloys congress (INFACON
436 8). Beijing China. p. 51-58.)

GLASTONBURY, R.I., VAN DER MERWE, W., BEUKES, J.P., VAN ZYL, P.G., LACHMANN, G., STEENKAMP, C.J.H., DAWSON, N.F. & STEWART, H.M. 2010. Cr(VI) generation during sample preparation of solid samples - a chromite ore case study. *Water SA*, 36(1):105-110. January.

HININGER, I., BENARABA, R., OSMAN, M., FAURE, H., ROUSSEL, A.M. & ANDERSON, R.A. 2007. Safety of trivalent chromium complexes: No evidence for DNA damage in human HaCaT keratinocytes. *Free Radical Biology & Medicine*, 42:1759 - 1765. 24 March.

HOWAT, D.D. 1994. Chromium in South Africa. *Journal of the South African Institute of Mining and Metallurgy*, 86(2):37-50. March.

IARC. 1997. vol. 49 vols. World Health Organisation. IARC monographs on the evaluation of carcinogenic risks to humans. *In*: *Chromium, Nickel and Welding*, International Agency for Research on Cancer. 17-33 p.

ICDA. 2013. *Statistical Bulletin*. Paris, France.

KLEYNHANS, E.L.J., BEUKES, J.P., KESTENS, P.H.I. & LANGA, J.M. 2012. Unique challenges of clay binders in a pelletised chromite pre-reduction process. *Minerals Engineering*, 34:55-62.

KOTAś, J. & STASICKA, Z. 2000. Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, 107(3):263-283.

LIDE, D.R., *ed*. 2006. Chromium. *In*: *Handbook of Chemistry and Physics*, 87th ed. Boca Raton, Florida: CRC Press / Taylor and Francis Group. 10 p.

LIND, B.B., FALLMAN, A.M. & LARSSON, L.B. 2001. Environmental impact of ferrochrome slag in road construction. *Waste Management*, 21:255-264.

LOOCK, M.M., BEUKES, J.P. & VAN ZYL, P.G. 2014. A survey of Cr(VI) contamination of surface water in the proximity of ferrochromium smelters in South Africa. *Water SA*, 40(4):709-716.

MAINE, C.F., SMIT, J.P. & GIESEKKE, E.W. 2005. *The solid stabilization of soluble wastes generated in the South African ferrochrome industry*.

MINTEK. 1990. *Mintek Bulletin No 31*.

NIOSH 7600. 1994. CHROMIUM, HEXAVALENT Method 7600. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(2) 15 August.

NIOSH 7604. 1994. CHROMIUM, HEXAVALENT Method 7604. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(2) 15 August.

NIOSH 7605. 2003. CHROMIUM, HEXAVALENT by Ion Chromatography Method 7605. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(1) 15 March.

NRIAGU, J.O. 1988. 20 vols. Historical perspectives. *In*: NRIAGU, J.O., Nieboer, E., ed. *Chromium in the natural and human environment*, New York: Wiley. 1-19 p.

PROCTOR, D.M., OTANI, J.M., FINLEY, B.L., PAUSTENBACH, D.J., BLAND, J.A., SPEIZER, N. & SARGENT, E.V. 2002. Is hexavalent chromium carcinogenic via ingestion? A weight-of-evidence review. *Journal of Toxicology and Environmental Health*, 65(Part A):701-746.

PYEONG-KOO, L., MIN-JU, K., HO, J., SANG-HOON, C. 2012. Sequential extraction and leaching characteristics of heavy metals in abandoned tungsten mine tailings sediments. Environmental Earth Sciences. 66(7):1909-1923. August.

RIEKKOAL-VANHANEN, M. 1999. Finnish expert report on best availible techniques in ferrochromium production. Helsinki: The Finnish Environment Institute.

SREERAM, K.J. & RAMASAMI, T. 2001. Speciation and recovery of chromium from chromite ore processing residues. *Journal of Environmental Monitoring*, 3(5):526-530.

THOMAS, D.H., ROHRER, J.S., JACKSON, P.E., PAK, T. & SCOTT, J.N. 2002. Determination of hexavalent chromium at the level of the California Public Health Goal by ion chromatography. *Journal of Chromatography A*, 956:255-259.

VAN STADEN, Y., BEUKES, J.P., VAN ZYL, P.G., DU TOIT, J.S. & DAWSON, N.F. 2014. Characterisation and liberation of chromium from fine ferrochrome waste materials. *Minerals Engineering*, 56:112-120. February.

VAN ZYL, P.G., BEUKES, J.P., DU TOIT, G., HENDRIKS, J., PIENAAR, J.J., LAAKSO, L., MABASO, D., VAKKARI, V., TIITTA, P. & KULMALA, M. 2014. Assessment of atmospheric trace metals in the western Bushveld Igneous Complex, South Africa : research article. *South African Journal of Science*, 110(3 & 4):1-11. March / April.

YASSI, A. & NIEBOER, E. 1988. 20 vols. Carcinogenicity of chromium compounds. *In*: NIAGRU, O.J., Nieboer, E., ed. *Chromium in the natural and human environment*, New York: Wiley. 443-495 p.

ZATKA, Vladimir J. 1985. Speciation of Hexavalent Chromium in Welding Fumes Interference by Air Oxidation of Chromium. *American Industrial Hygiene Association Journal*, 46(6):327-331.

ZELIć, J. 2005. Properties of concrete pavements prepared with ferrochromium slag as concrete aggregate. *Cement and Concrete Research*, 35(12):2340-2349. December.

Table 1: **The d_{10}, d_{50} and d_{90} of the particle size distribution of the BFD samples. d_{90} is defined as the equivalent particle size for which 90% of the particles are finer, with d_{50} and d_{10} derived similarly. The values are given in μm.**

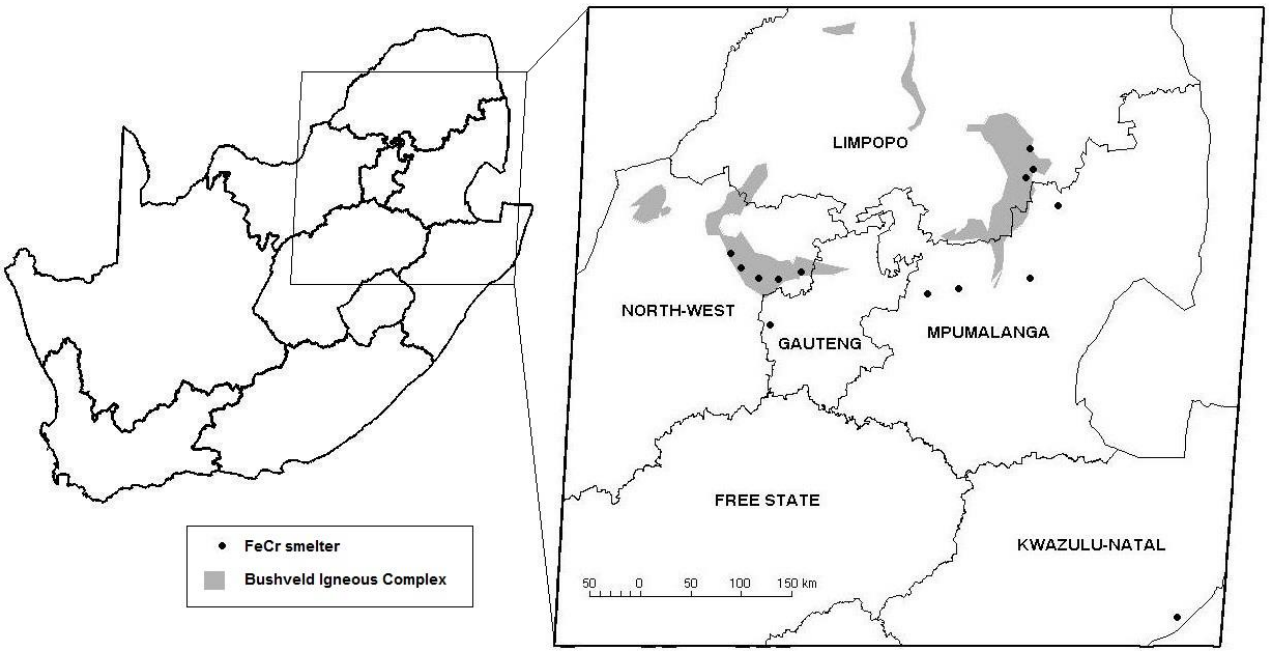
Sample Name	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
BFD Mpu A - Average	4.3	39.4	140.6
BFD Mpu B - Average	4.2	37.6	152.2
BFD NW A - Average	1.7	10.3	32.8
BFD NW B - Average	1.7	9.7	33.3

504 **Table 2: SEM-EDS analyses of cross sectional polished BFD samples.**

Sample	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Zn	O	Total
Sample Mpu A	6.24	3.38	11.71	1.55	5.38	3.11	1.29	6.81	7.97	18.66	33.91	100
Sample Mpu B	6.66	2.98	11.75	1.63	4.67	3.01	1.06	7.62	8.47	18	34.2	100
Sample NW A	12.3	2.26	21.77	1.18	1.6	2.66	0.59	3.28	2.85	9.4	42.09	100
Sample NW B	13.23	2.58	20.12	1.33	1.57	2.36	0.92	3.84	3.76	8.57	41.71	100

505

506



507
508 **Figure 1: FeCr smelters located in the Bushveld Complex of South Africa**

509

510

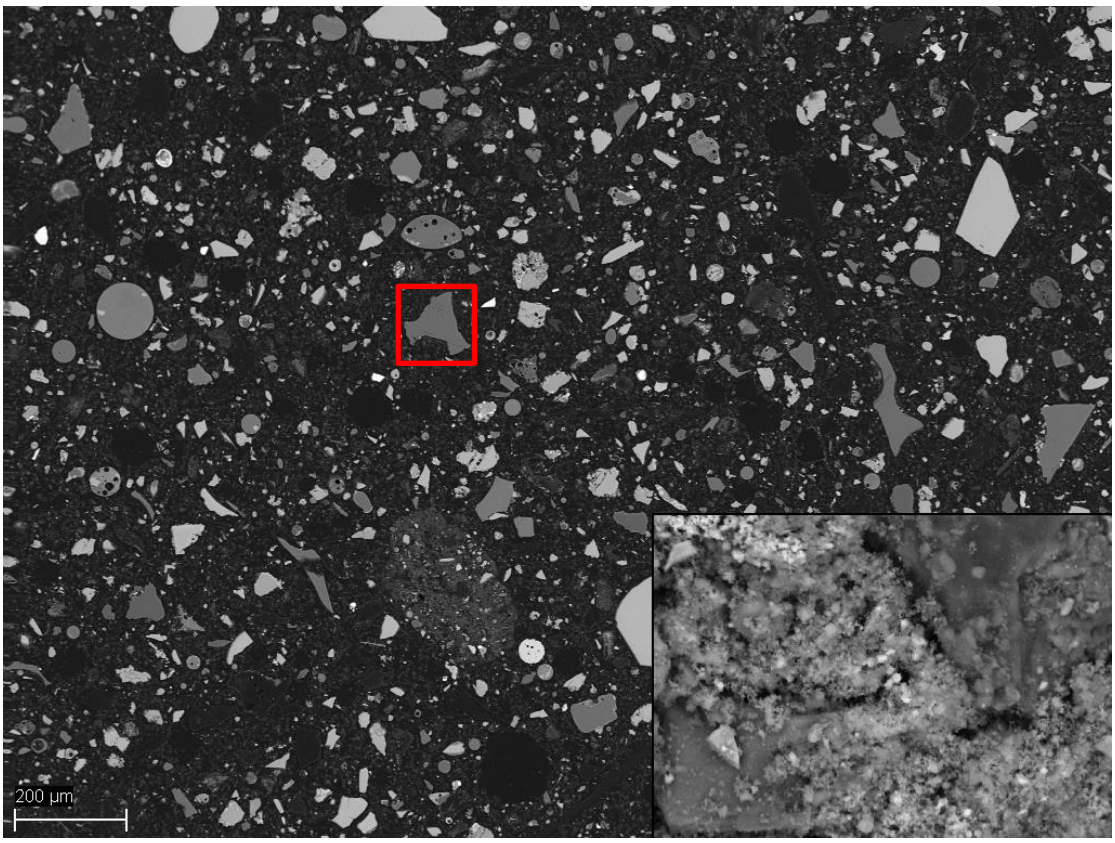
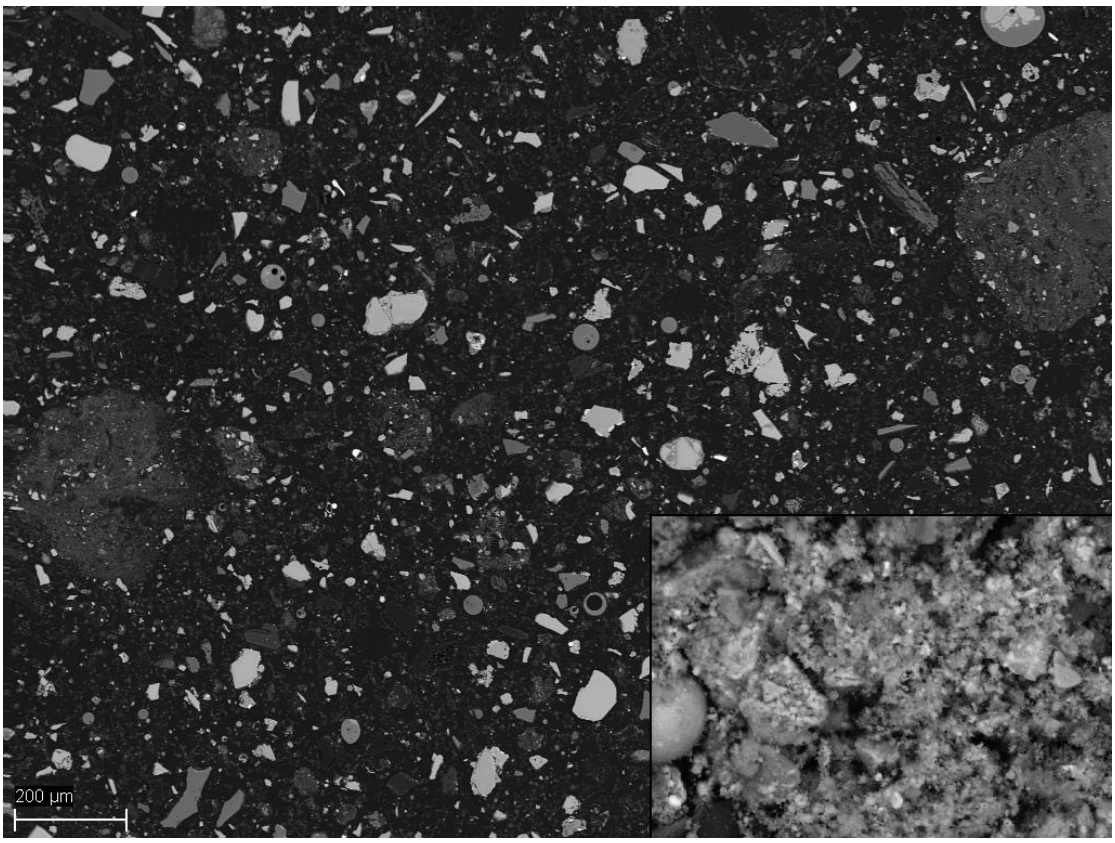


Figure 2: SEM characterisation for Mpu A: 100 and 2000 X zoom. Large unevenly shaped particle marked with red box is an example of an un-reacted chromite particle

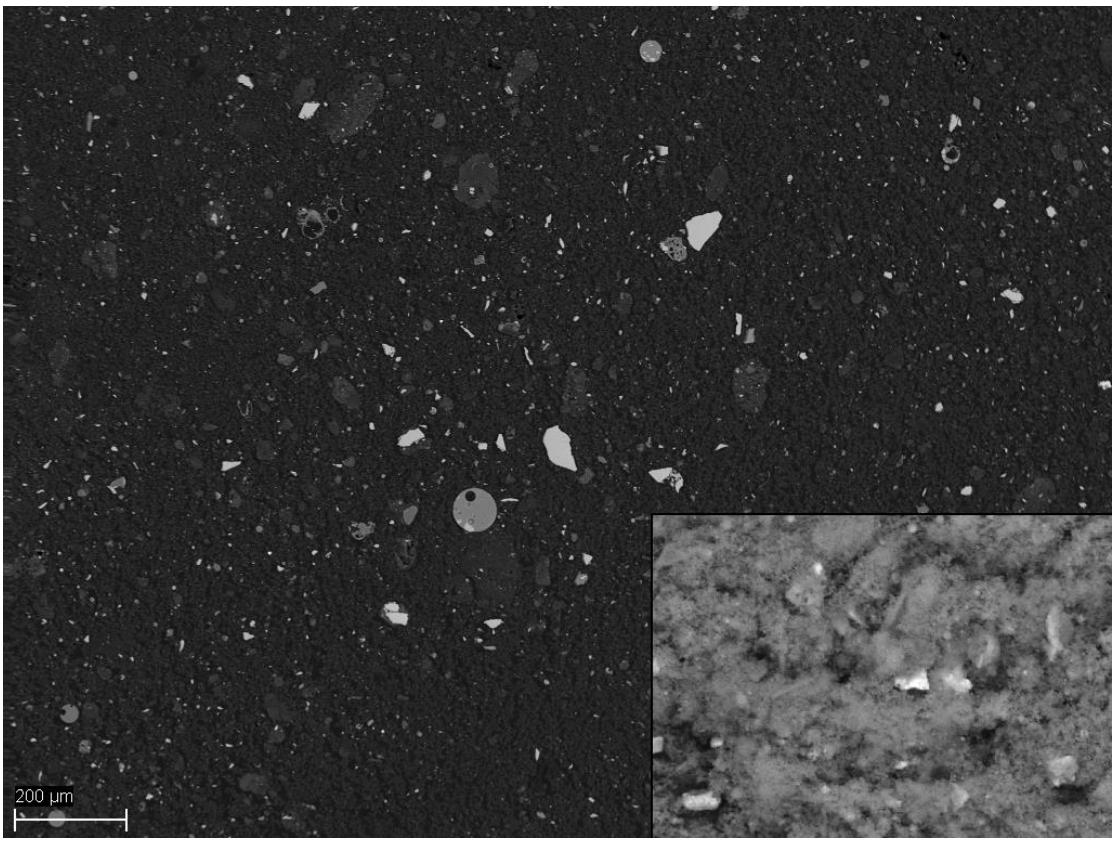


516

517 **Figure 3: SEM characterisation for Mpu B: 100 and 2000 X zoom**

518

519



520

521 **Figure 4: SEM characterisation for NW A: 100 and 2000 X zoom**

522

523

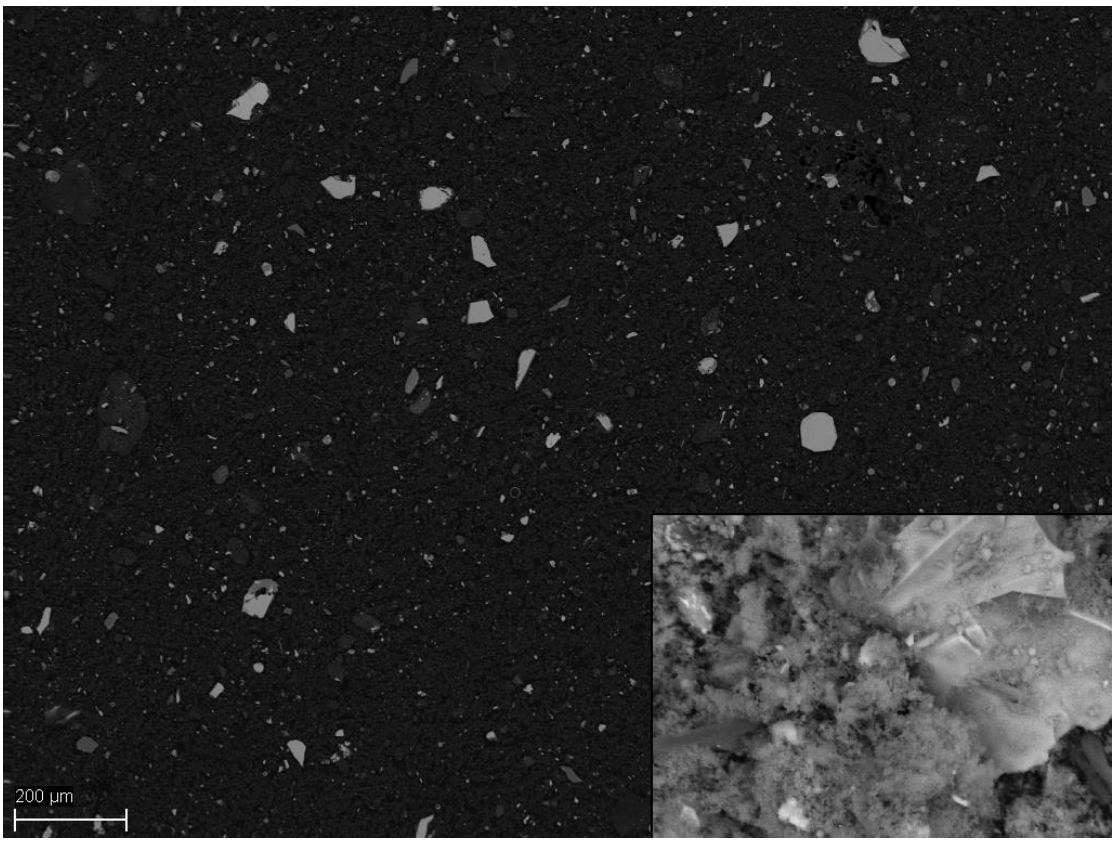


Figure 5: SEM characterisation for NW B: 100 and 2000 X zoom

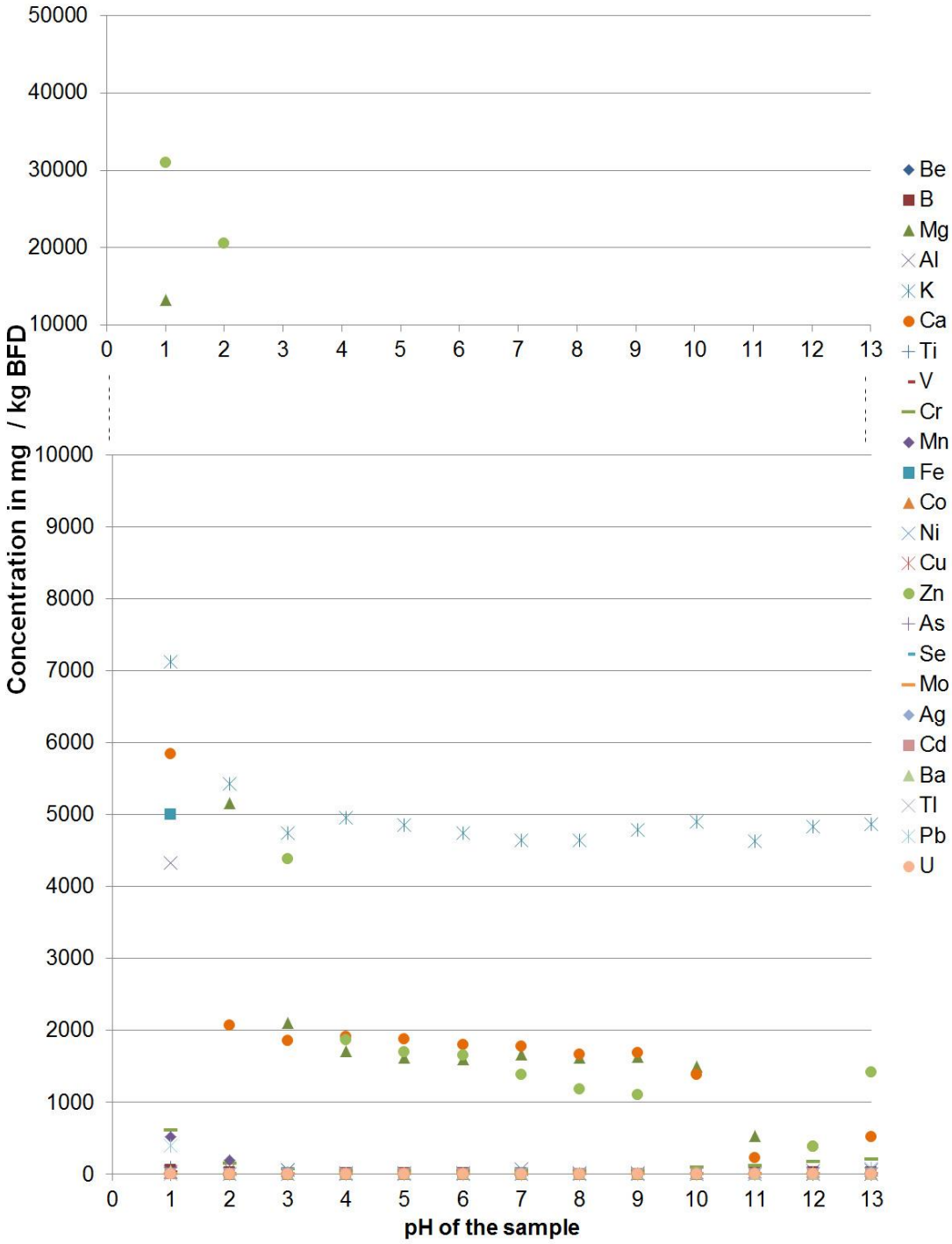
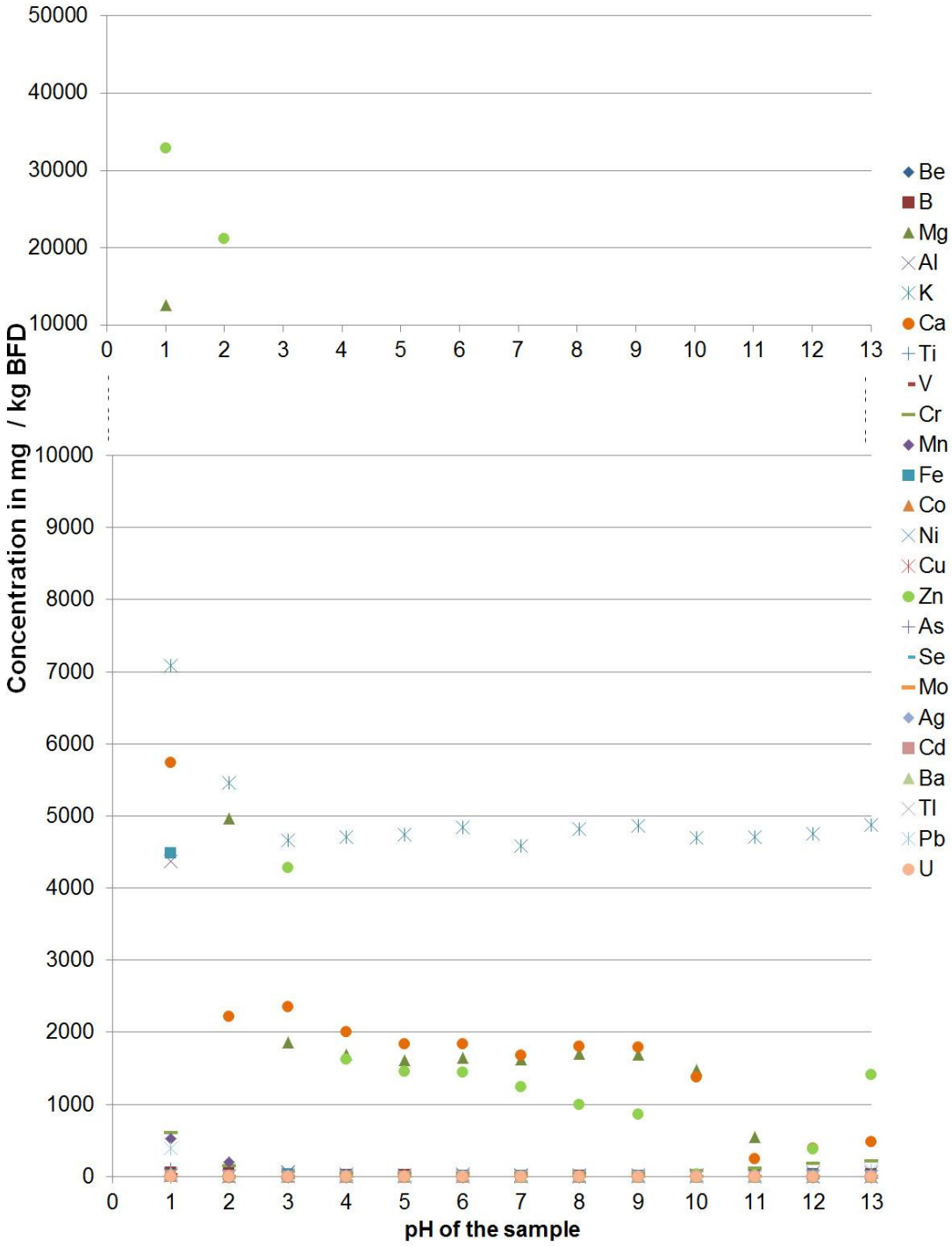


Figure 6: ICP-MS - Heavy metal analysis as a function of pH for Mpu A



532

533 **Figure 7: ICP-MS - Heavy metal analysis as a function of pH for Mpu B**

534

535

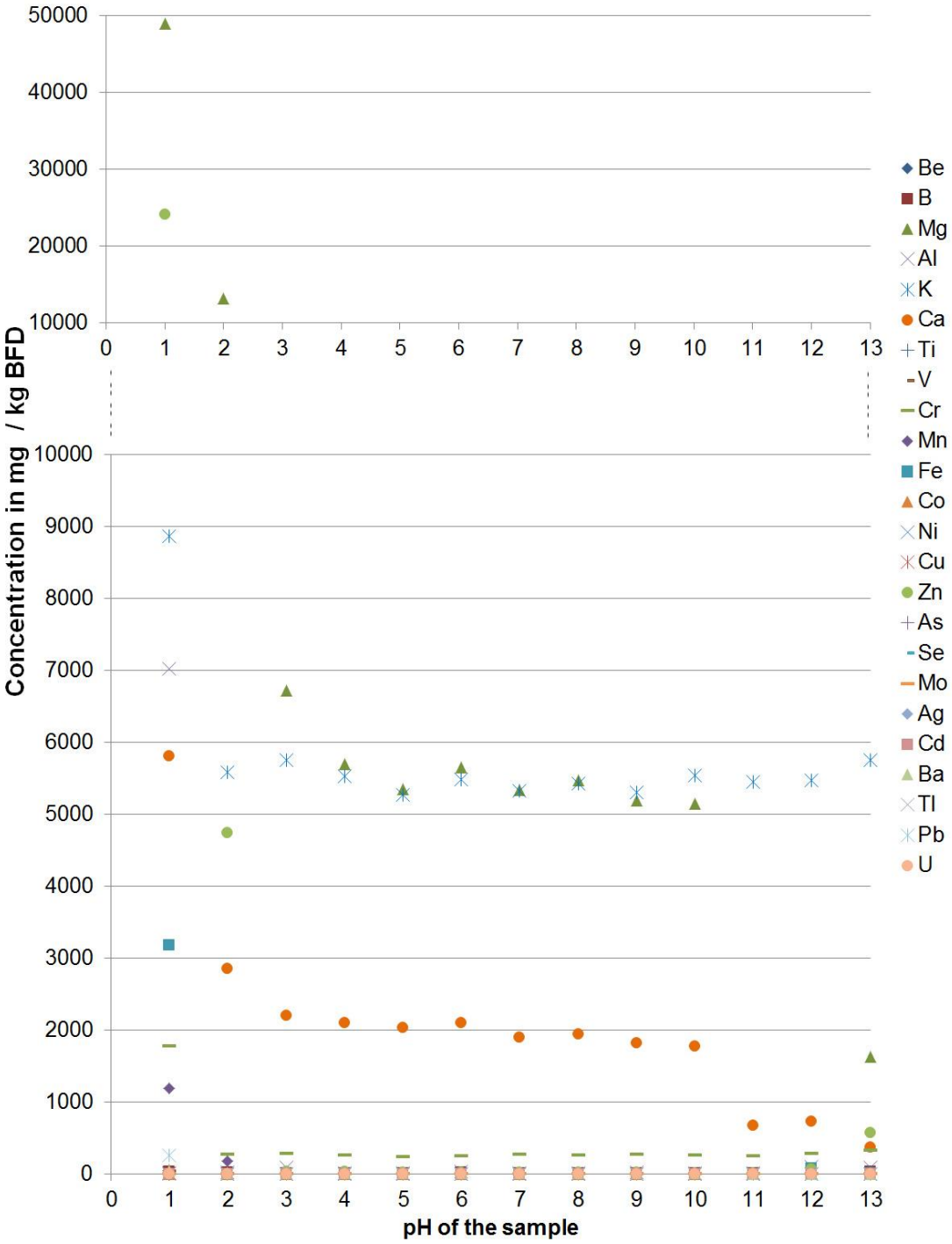


Figure 8: ICP-MS - Heavy metal analysis as a function of pH for NW A

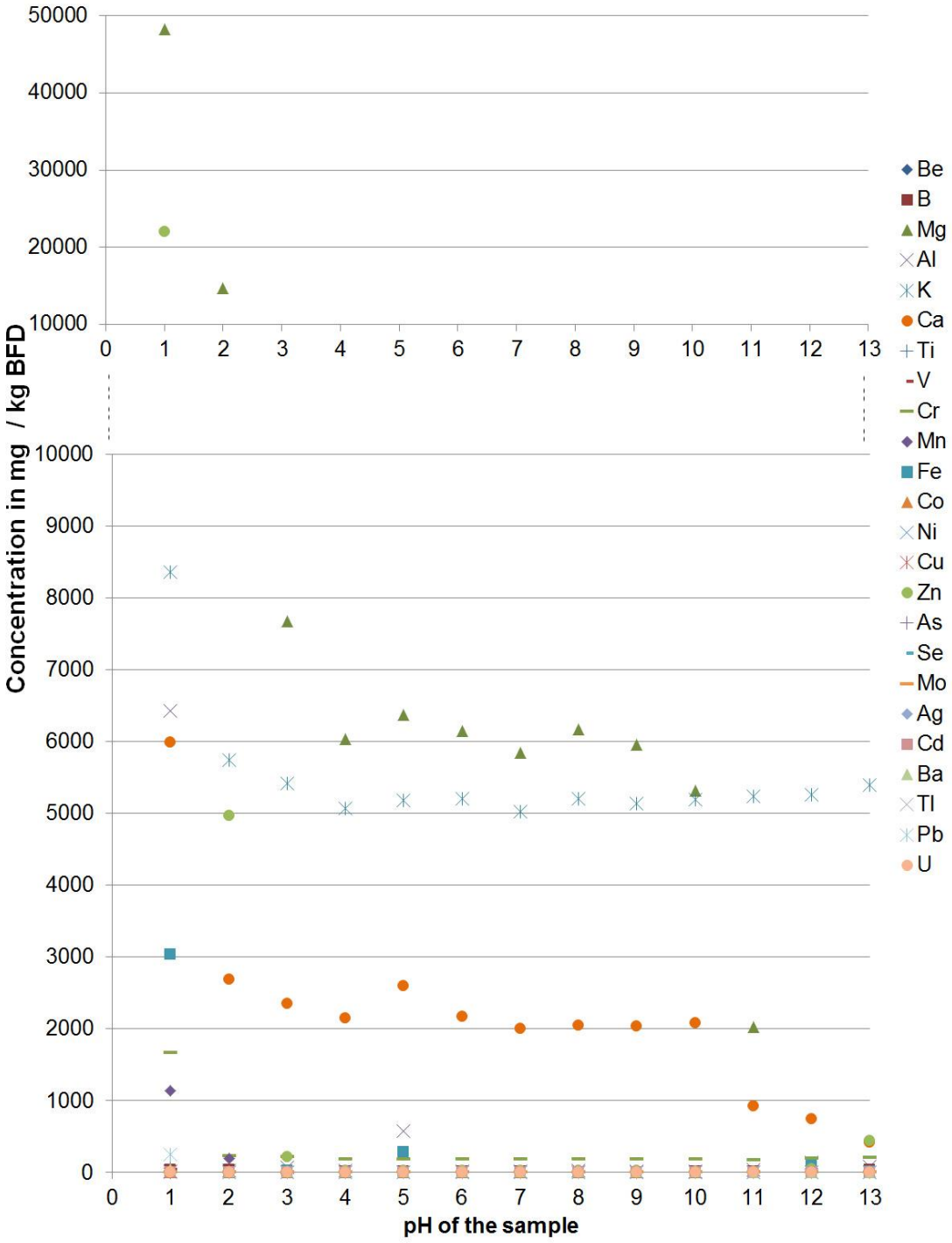
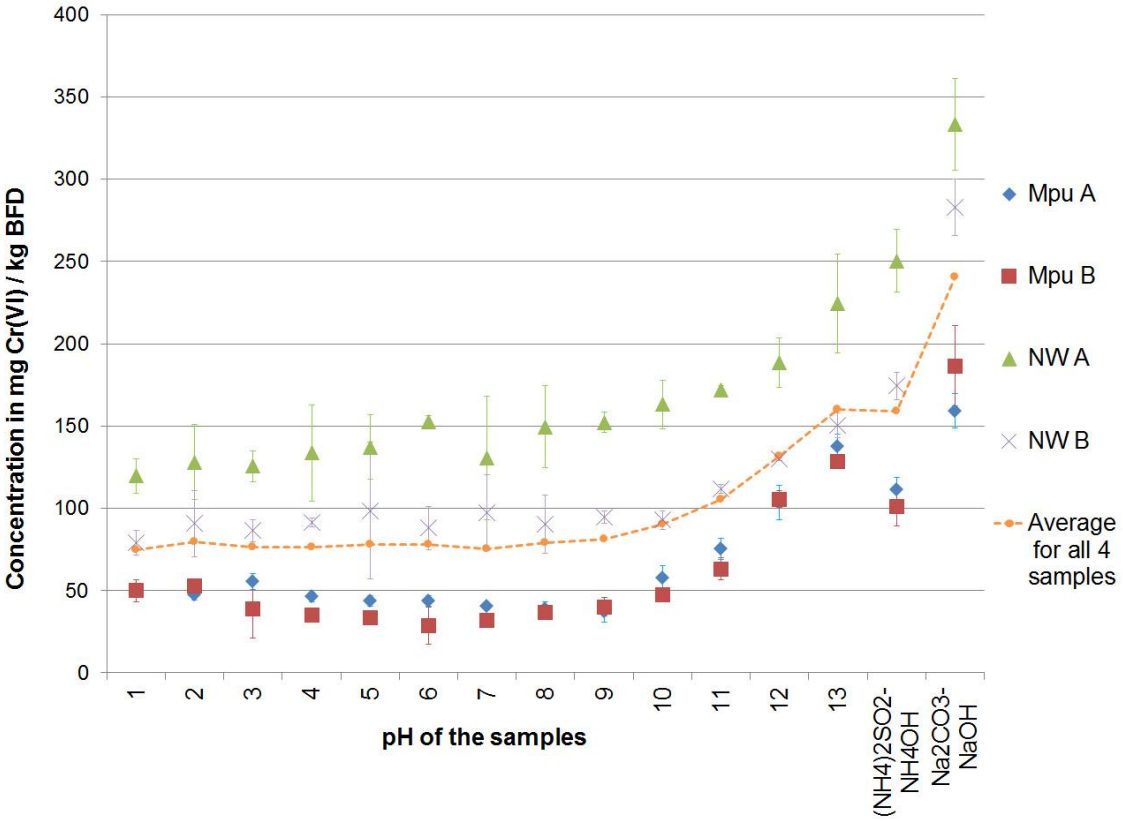


Figure 9: ICP-MS - Heavy metal analysis as a function of pH for NW B

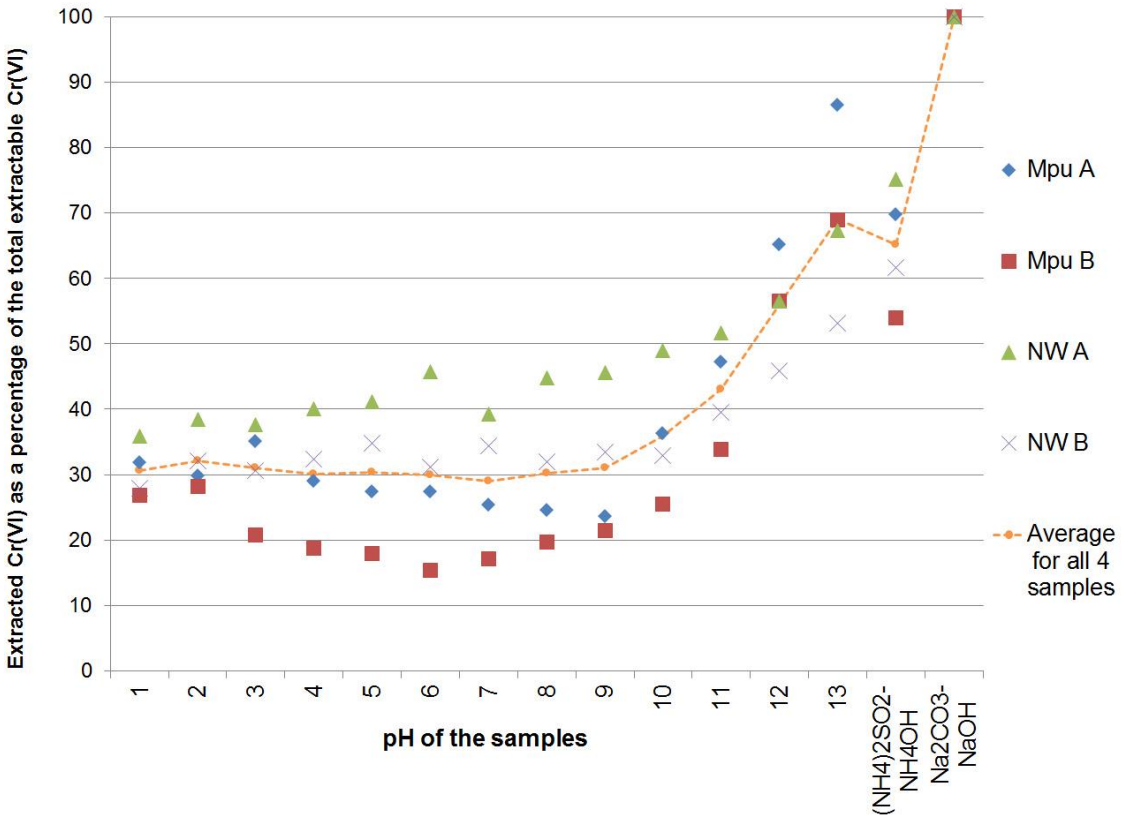


544

545 **Figure 10: Leachable Cr(VI) as a function of the pH of the solution**

546

547



548

549 **Figure 11:** **Leachable Cr(VI) as a function of the pH of the solution, expressed as a**
550 **percentage of the total Cr(VI) content**

551

552

Chapter 4 Project evaluation and future perspectives

4.1 Project evaluation in relation to objectives

The objectives that were set out for this project were listed in Chapter 1. The project evaluation is discussed in accordance with the objectives set in Par. 1.2. Some future prospects are also mentioned and the overall success of the project is gauged.

a) *Conduct a literature survey to assess current state of knowledge with regard to Cr(VI) in FeCr BFD.*

A thorough literature survey was performed and presented in Chapter 2. It clearly indicated the importance of the FeCr industry in South Africa (Par. 2.2). The most common processes that are in use at these types of industries were described in Par. 2.2.3. The relatively large quantities of Cr-containing waste materials that are being produced, along with the desired FeCr products, was discussed in Par. 2.3. Some details were given with regard to each of the three different types of waste, i.e. slag, venturi sludge and bag filter dust (BFD). Because the focus of this study was on BFD, more details regarding Cr(VI) in BFD was presented in Par. 2.4. The dangers that Cr(VI)-containing wastes can pose to the environment, if the Cr(VI) contents were to leach out of the BFD and into the ground- or surface water were described. The current Cr(VI) treatment methods for such wastes were also considered. The health impacts associated with Cr(VI) exposure was discussed (Par. 2.5), along with the beneficial properties of Cr(III). The literature survey indicated that no papers, quantifying the solubility properties of Cr(VI) in FeCr BFD of open or partially closed FeCr furnaces, have been published in the peer reviewed public domain.

b) *Obtain different BFD samples, which are representative of processes utilised in South African FeCr industry.*

Four different BFD samples were obtained from FeCr producers in South Africa, i.e. two from producers in Mpumalanga and two from producers in the North West Province. Numerous factors can influence the composition of BFD. These include the production technology employed (e.g. open or partially closed furnace technology, type of filters used in the bag filter plant), physical separation in the bag filter plant itself (e.g. some compartments containing finer material than others), metallurgical operating conditions (e.g. basic or acid slag operating conditions) and composition of feed material (e.g. chemical and physical differences in ores). The above-mentioned samples were therefore selected to be

as representative as possible of a wide variety of parameters that could influence its composition. None of the BFD samples obtained can be considered as representative of closed FeCr furnace off-gas particulate matter, since wet venturi scrubbers are used to clean such off-gas.

c) *Characterisation of the BFD samples with analytical techniques, which will include scanning electron microscopy (SEM), SEM combined with energy dispersive spectroscopy (SEM EDS) and particle size analysis.*

Material characterisation was performed on all four of the BFD samples obtained. From the SEM images it was deduced that the NW A and NW B samples had finer particles than the Mpu A and Mpu B samples. The SEM analysis showed that the samples consisted mainly of very small particulate matter (real off-gas particles), with larger particles (unreacted feed materials particles) also being present. SEM-EDS surface chemical analyses of the four BFD samples gave an indication of the differences in the composition of these samples. The particle size analysis confirmed that the Mpu A and Mpu B samples were coarser than the NW A and NW B, which confirmed the earlier observations derived from SEM visual analysis that the Mpu A and B samples contained more unreacted/partially reacted raw material particles.

d) *Determine the solubility of Cr(VI) in BFD as a function of pH as well as the water soluble, sparingly water soluble and water insoluble Cr(VI) contents of the BFD samples.*

This solubility investigation was carried out over a wide range of pH 1 - 13. The results presented in the research article (Chapter 3) clearly showed that pH has a strong effect on the extraction of Cr(VI) from the BFD samples. Extractions were also carried out using hot plate digestion utilising a 0.05 M ammonium sulfate - 0.05 M ammonium hydroxide buffer for the dissolution of sparingly soluble and soluble Cr(VI) compounds, while a solution of 3% sodium carbonate - 2% sodium hydroxide was used for the dissolution of insoluble Cr(VI) compounds. This facilitated the differentiation between the water soluble, sparingly soluble, and water insoluble Cr(VI) fractions present in the BFD samples. During the unbuffered extraction of Cr(VI) more Cr(VI) leached with increased initial pH, indicating that not only soluble, but also sparingly- and insoluble Cr(VI) compounds occur in the BFD samples evaluated. The buffered Na_2CO_3 – NaOH hot plate extraction, which is able to quantitatively extract all Cr(VI) in the BFD samples, including the water insoluble fraction provided the total Cr(VI) concentrations that could serve as a reference value of 100%, when all other results were normalised to it. The $(NH_4)_2SO_2$ - NH_4OH hot plate extraction, which is known to quantitatively extract all soluble- and sparingly soluble Cr(VI)

compounds, extracted approximately 66.7% of the total Cr(VI) present. All pH extractions, with pH ≤ 9, extracted about 30% of the total Cr(VI) present in the BFD samples. Only at pH ≥ 13 were all the sparingly water soluble Cr(VI) compounds extracted. This data, indicated that a third of all Cr(VI) in FeCr BFD might be insoluble Cr(VI) compounds.

e) *Determine the leaching of other heavy metals during the pH-dependant leaching.*

The data from the ICP-MS analysis that was performed on the leachate of the pH-dependant leaching of all of the BFD samples indicated that higher concentrations of most heavy metals tend to leach out of the FeCr BFD samples at lower pH values. This is in contrast to the trend that was found for Cr(VI), where an increase in the pH led to more Cr(VI) leaching out of the samples. Most South African FeCr slags were historically classified as hazardous waste, based on the extraction of heavy metals such as Mn and Fe by acid leach tests. However, low pH extractions will solubilize these metals, but might not extract all Cr(VI) as was indicated in this study. If the wastes are classified due to the extraction of Fe or Mn, a possible precautionary measure would be the addition of lime to the waste dump, since this would reduce/eliminate Fe and Mn leaching. However, such a precautionary measure could effectively increase Cr(VI) leaching, since more Cr(VI) compounds are soluble at higher pH values.

f) *Make recommendations relevant to the FeCr industry and give future perspectives that can guide research in this field of study.*

The results from this study facilitated the differentiation of the water soluble, sparingly soluble, and water insoluble Cr(VI) fractions present in the BFD samples, but did not provide any clarity on the exact fractional occurrence of different Cr(VI) compounds present in the BFD. Future research is needed to resolve the cation association of Cr(VI) compounds, which also determines the health impact thereof.

Probably the most significant finding relevant to the FeCr industry, is that only approximately 30% of Cr(VI) is leached from BFD at pH ≤ 9 and that the sparingly water soluble Cr(VI) fraction does not dissolve at this pH level. Only at pH ≥ 13 the sparingly water soluble Cr(VI) fraction is also solubilised. This implies that the current leaching procedures applied prior to Cr(VI) chemical reduction, are ineffective in leaching the important Cr(VI) fractions from the BFD. These results also resolve the long standing issue of the origin of Cr(VI) leaching from slimes dams that have been treated seemingly properly for Cr(VI) reduction, prior to the slimes being deposited onto the dam. From the results presented in this paper, the origins of continued Cr(VI) leaching from such slimes dams are the sparingly water soluble Cr(VI) fraction that was not extracted properly.

4.2 Future perspective

Two relatively well defined future research perspectives can be proposed, i.e.:

- For effective Cr(VI) treatment, extraction of both the water soluble and sparingly water soluble Cr(VI) fraction needs to be achieved. One possible solution would be to extract Cr(VI) at pH ≥ 13, but a suitable chemical reductant must be established and the costs implications thereof established.
- In this study the Cr(VI) water soluble, sparingly water soluble and insoluble fractions were determined. To quantify the health impact of Cr(VI) in BFD better, the exact Cr(VI) compounds present in FeCr BFD needs to be established in future.

4.3 Overall project evaluation

The objectives that were set out for this study in Par. 4.1 have been successfully met. The paper, containing all the results that were obtained in this study was submitted for publication in an ISI-accredited peer-reviewed journal. This goes beyond what is expected of a M.Sc. study, as per the minimum requirements of the North-West University. In general the project can therefore be regarded as successful. However, there were some shortcomings in this investigation, but most of these have been mentioned as future perspectives. A meaningful scientific contribution was made in improving the understanding of the solubility dependencies of FeCr BFD.

Bibliography

ANTONY, M.P., TATHAVADKAR, V.D., CALVERT, C.C. & JHA, A. 2001. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 32(6):987-995. December.

ASHLEY, K., HOWE, A.M., DEMANGE, M. & NYGREN, O. 2003. Sampling and analysis considerations for determination of hexavalent chromium in workplace air. *Journal of Environmental Monitoring*, 5:707-716. 8 August.

BARTLETT, R.J. 1991. Chromium cycling in soils and water: links, gaps and methods. *Environmental health perspectives*, 92:17-24.

BEUKES, J.P., DAWSON, N.F. & VAN ZYL, P.G. 2010. Theoretical and practical aspects of Cr(VI) in the South African ferrochrome industry. *The Journal of The Southern African Institute of Mining and Metallurgy*, volume 110:743-750. December.

BEUKES, J.P., PIENAAR, J.J., LACHMANN, G. & GIESEKKE, E.W. 1999. The reduction of hexavalent chromium by sulphite in wastewater. *Water SA*, 25(3):363-369. July.

BEUKES, J.P., VAN ZYL, P.G. & RAS, M. 2012. Treatment of Cr(VI) containing wastes in the South African ferrochrome industry - A review of currently applied methods. *The Journal of The Southern African Institute of Mining and Metallurgy*, 112(5):347-352.

BORAI, E.H., EL-SOFANY, E.A. & ABDEL-HALIM, A.S. 2002. Speciation of hexavalent chromium in atmospheric particulate samples by selective extraction and ion chromatographic determination. *Trends in analytical chemistry*, 21(11):741-745.

BOTHA, W. 2003. Ferrochrome production through the SRC process at Xstrata, Lydenburg Works. *Journal of the South African Institute of Mining and Metallurgy (SAIMM)*, 103(6):373-389.

BULUT, U., OZVERDI, A. & ERDEM, M. 2009. Leaching behavior of pollutants in ferrochrome arc furnace dust and its stabilization/solidification using ferrous sulphate and Portland cement. *Journal of Hazardous Materials*, 162(2-3):893-898. 15 March.

CALDER, L.M. 1988. 20 vols. Chromium contamination of groundwater. *In*: NRIAGU, J.O., Nieboer, E., ed. *Chromium in the natural and human environments*, New York: Wiley. 215-229 p.

CAWTHORN, R.G. 1999. The platinum and palladium resources of the Bushveld Complex. *South African journal of science*, 95:481-489.

COTTEN, F.A. & WILKINSON, G. 1988. The elements of the first transition series. *In*: *Advanced inorganic chemistry*, 5th ed. New York: Wiley. 649-775 p.

COX, X.B., LINTON, R.W. & BUTLER, F.E. 1985. Determination of chromium speciation in environmental particles. Multitechnique study of ferrochrome smelter dust. *Environmental Science and Technology*, 19(4):345-352.

CRAMER, L.A., BASSON, J. & NELSON, L.R. 2004. The impact of platinum production from UG2 ore on ferrochrome production in South Africa. *Journal of The South African Institute of Mining and Metallurgy*, 104(9):517-527. October.

CURR, T. 2009. *History of DC arc furnace process development*. Date of access: 22 July 2009. http://www.mintek.co.za/Mintek75/Proceedings

DENTON, G.M., BENNIE, J.P.W. & DE JONG, A. 2004. An improved DC-arc process for chromite smelting. (*In* Proc. Ferroalloys 10th international congress (INFACON X). Cape Town, South Africa. p. 60-67.)

DIONEX CORP., SUNNYVALE, CALIF. 2003. Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography. *Application Update 144*

DIONEX CORP., SUNNYVALE, CALIF. 2011. Sensitive Determination of Hexavalent Chromium in Drinking Water. *Application Update 179*

DU PREEZ, F., BEUKES, J.P. & VAN ZYL, P.G. 2014. M.Sc. thesis.

EARY, L.E. & RAI, D. 1987. Kinetics of chromium(III) oxidation to chromium(VI) by reaction with manganese dioxide. *Environmental science and technology*, 21:1187-1193.

EMSLEY, J. 2003. Nature's building blocks : an A-Z guide to the elements. London, Oxford: Oxford University Press.

FAWCETT, E. 1988. Spin-density-wave antiferromagnetism in chromium. *Reviews of Modern Physics*, 60(1):209-283.

GEDIGA, J. & RUSS, M. 2007. *Life cycle inventory (LCI) update of primary ferrochrome production*.

GERICKE, W.A. 1995. Environmental aspects of ferrochrome production. (*In* Proceedings Ferroalloys 7th international congress (INFACON XII). Trondheim, Norway. p. 131-140.)

GERICKE, W.A. 1998. Environmental solutions to waste products from ferrochrome production. (*In* The proceedings of the eight International ferroalloys congress (INFACON 8). Beijing China. p. 51-58.)

GLASTONBURY, R.I., VAN DER MERWE, W., BEUKES, J.P., VAN ZYL, P.G., LACHMANN, G., STEENKAMP, C.J.H., DAWSON, N.F. & STEWART, H.M. 2010. Cr(VI) generation during sample preparation of solid samples - a chromite ore case study. *Water SA*, 36(1):105-110. January.

GU, F. & WILLS, B.A. 1988. Chromite- mineralogy and processing. *Minerals Engineering*, 1(3):235-240.

HININGER, I., BENARABA, R., OSMAN, M., FAURE, H., ROUSSEL, A.M. & ANDERSON, R.A. 2007. Safety of trivalent chromium complexes: No evidence for DNA damage in human HaCaT keratinocytes. *Free Radical Biology & Medicine*, 42:1759 - 1765. 24 March.

HOWAT, D.D. 1994. Chromium in South Africa. *Journal of the South African Institute of Mining and Metallurgy*, 86(2):37-50. March.

IARC. 1990. vol. 49 vols. World Health Organisation. IARC monographs on the evaluation of carcinogenic risks to humans. *In*: *Chromium, Nickel and Welding*, International Agency for Research on Cancer.

IARC. 1997. vol. 49 vols. World Health Organisation. IARC monographs on the evaluation of carcinogenic risks to humans. *In*: *Chromium, Nickel and Welding*, International Agency for Research on Cancer. 17-33 p.

ICDA. 2012. *Statistical Bulletin*. Paris, France.

ICDA. 2013. *Statistical Bulletin*. Paris, France.

JACOBS, J.A. & TESTA, S.M. 2005. Overview of chromium(VI) in the environment: background and history. CRC Press.

KIMBROUGH, D.E., COHEN, Y., WINER, A.M., CREELMAN, L. & MABUNI, C. 1999. A Critical Assessment of Chromium in the Environment. *Critical Reviews in Environmental Science and Technology*, 29(1):1-46.

KLEYNHANS, E.L.J., BEUKES, J.P., KESTENS, P.H.I. & LANGA, J.M. 2012. Unique challenges of clay binders in a pelletised chromite pre-reduction process. *Minerals Engineering*, 34:55-62.

KOTAś, J. & STASICKA, Z. 2000. Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, 107(3):263-283.

LIDE, D.R., *ed*. 2006. Chromium. *In*: *Handbook of Chemistry and Physics*, 87th ed. Boca Raton, Florida: CRC Press / Taylor and Francis Group. 10 p.

LIND, B.B., FALLMAN, A.M. & LARSSON, L.B. 2001. Environmental impact of ferrochrome slag in road construction. *Waste Management*, 21:255-264.

LOOCK, M.M., BEUKES, J.P. & VAN ZYL, P.G. 2014. Ph.D thesis. North West University of Potchefstroom, North West, South Africa.

MAINE, C.F., SMIT, J.P. & GIESEKKE, E.W. 2005. *The solid stabilization of soluble wastes generated in the South African ferrochrome industry*.

MARCH, J. Advanced Organic Chemistry, 4th ed. John Wiley and Sons,

USA.,1992.

MCLEAN, J.E., MCNEILL, L.S., EDWARDS, M.A. & PARKS, J.L. 2012. Hexavalent chromium review, part 1: Health effects, regulations, and analysis. *Journal - American Water Works Association*:348-357.

MINTEK. 1990. *Mintek Bulletin No 31*.

MURTHY, Y.R., TRIPATHY, S.K. & KUMAR, C.R. 2011. Chrome ore beneficiation challenges & opportunities - A review. *Minerals Engineering*, 24(5):375-380. April.

NAIKER, O. 2007. The development and advantages of Xstrata's Premus Process. (*In* Proceedings Ferroalloys 11th international congress (INFACON XI). New Delhi, India. p. 112-119.)

NEIZEL, B., BEUKES, J.P., VAN ZYL, P.G & DAWSON, N.F. 2013. Why is CaCO3 not used as an additive in the pelletised chromite pre-reduction process? *Minerals Engineering*, 45:115-120.

NIOSH 7600. 1994. CHROMIUM, HEXAVALENT Method 7600. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(2) 15 August.

NIOSH 7604. 1994. CHROMIUM, HEXAVALENT Method 7604. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(2) 15 August.

NIOSH 7605. 2003. CHROMIUM, HEXAVALENT by Ion Chromatography Method 7605. *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition(1) 15 March.

NRIAGU, J.O. 1988a. 20 vols. Historical perspectives. *In*: NRIAGU, J.O., Nieboer, E., ed. *Chromium in the natural and human environments*, New York: Wiley. 1-19 p.

NRIAGU, J.O. 1988b. 20 vols. Production and uses of chromium. *In*: NRIAGU, J.O., Nieboer, E., ed. *Chromium in the natural and human environments*, New York: Wiley. 81-103 p.

OUTOTEC. Outotec homepage. http://www.outotec.com/default_6764.aspx?epslanguage=EN Date of access: 21 October 2008.

PROCTOR, D.M., OTANI, J.M., FINLEY, B.L., PAUSTENBACH, D.J., BLAND, J.A., SPEIZER, N. & SARGENT, E.V. 2002. Is hexavalent chromium carcinogenic via ingestion? A weight-of-evidence review. *Journal of Toxicology and Environmental Health*, 65(Part A):701-746.

RAI, D., EARY, L.E. & ZACHARA, J.M. 1989. Environmental chemistry of chromium. *Science of the Total Environment*, 86(1-2):15-23.

RIEKKOAL-VANHANEN, M. 1999. Finnish expert report on best availible techniques in ferrochromium production. Helsinki: The Finnish Environment Institute.

ROZA, G. 2008. Chromium. *In*: *Understanding the elements of the periodic table*, New York: Rosen Central.

SOYKAN, O., ERIC, R.H. & KING, R.P. 1991. Kinetics of the reduction of bushveld complex chromite ore at 1416 °C. *Metallurgical and materials transactions B*, 22(6):801-810.

SREERAM, K.J. & RAMASAMI, T. 2001. Speciation and recovery of chromium from chromite ore processing residues. *Journal of Environmental Monitoring*, 3(5):526-530.

THOMAS, D.H., ROHRER, J.S., JACKSON, P.E., PAK, T. & SCOTT, J.N. 2002. Determination of hexavalent chromium at the level of the California Public Health Goal by ion chromatography. *Journal of Chromatography A*, 956:255-259.

U.S. ENVIRONMENTAL PROTECTION AGENCY (USEPA). IRIS Chromium. http://www.epa.gov/ncea/iris/subst/0144.htm Date of access: 9 November 2014.

VAN STADEN, Y., BEUKES, J.P., VAN ZYL, P.G., DU TOIT, J.S. & DAWSON, N.F. 2014. Characterisation and liberation of chromium from fine ferrochrome waste materials. *Minerals Engineering*, 56:112-120. February.

XIAO, Z. & LAPLANTE, A.R. 2004. Characterizing and recovering the platinum group minerals - a review. *Minerals engineering*, 17(9-10):961-979.

YASSI, A. & NIEBOER, E. 1988. 20 vols. Carcinogenicity of chromium compounds. *In*: NIAGRU, O.J., Nieboer, E., ed. *Chromium in the natural and human environment*, New York: Wiley. 443-495 p.

ZELIć, J. 2005. Properties of concrete pavements prepared with ferrochromium slag as concrete aggregate. *Cement and Concrete Research*, 35(12):2340-2349. December.