

Liberation of chromium from ferrochrome waste materials utilising aqueous ozonation and the advanced oxidation process

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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 as it was submitted and accepted for publication. The conventional experimental as well as results and discussions chapters were excluded, since the relevant information is summarised in the article. Separate background and motivation (Chapter 1), literature (Chapter 2) and project evaluation chapters (Chapter 4) were included in the dissertation, even though some of this information was summarised in the article. This will result in some repetition of ideas/similar text in some of the chapters and in the article itself.

Rationale in submitting dissertation in article format

Currently it is a prerequisite for handing in an MSc dissertation at the NWU that a draft article be prepared. In practice, many of these draft papers are never submitted to peer-reviewed journals. However, in this study, the candidate decided to submit this MSc dissertation in article format, since it required that the candidate prepare a paper that was submitted to an ISI-accredited journal. Therefore, the prerequisite of the NWU was exceeded.

The co-authors of the above-mentioned article (Chapter 3) were:

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Contributions to article

Contributions of the various co-authors were as follows. The work was done by me, Yolindi van Staden, with conceptual ideas and recommendations by J.P. Beukes (supervisor) and P.G. van Zyl (co-supervisor) on the experimental work, as well as on the article. J.S. du Toit supplied the case study samples and provided conceptual recommendations/comments on the draft article, while N.F. Dawson was responsible for partial funding of the project and also gave conceptual recommendations/comments on the draft article.

Formatting and current status of article

The article has been published in *Minerals Engineering*, an Elsevier journal and was inserted into the dissertation in the format in which it was published. The author's guide that was followed in preparation of the article is available at <http://www.elsevier.com/journals/minerals-engineering/0892-6875/guide-for-authors> (Date of access: 29 October 13).

Consent by co-authors

All the co-authors, i.e. J.P. Beukes, P.G. van Zyl, J.S. du Toit and N.F. Dawson have been informed that the MSc will be submitted in article format and have given their consent.

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Abstract

During ferrochrome (FeCr) production, three types of generic chromium (Cr) containing wastes are generated, i.e. slag, bag filter dust (BFD) and venturi sludge. The loss of these Cr units contributes significantly to the loss in revenue for FeCr producers. In this study, the liberation of Cr units was investigated utilising two case study waste materials, i.e. BFD from a semi-closed submerged arc furnace (SAF) operating on acid slag and the ultra-fine fraction of slag (UFS) originating from a smelter operating with both open and closed SAFs on acid slag.

A detailed material characterisation was conducted for both case study materials, which included particle size distribution, chemical composition, chemical surface composition and crystalline content. Cr liberation was achieved utilising two methods, i.e. aqueous ozonation and the advanced oxidation method. Various advanced oxidation processes could be applied. However, the advanced oxidation processes considered in this study was the use of gaseous ozone (O_3) in combination with hydrogen peroxide (H_2O_2). Controlling parameters such as the influence of pH, ozonation contact time, waste material solid loading, gaseous O_3 concentration and temperature on Cr liberation were investigated for the aqueous ozonation process. The influence of pH, volume H_2O_2 added and the method of H_2O_2 addition were considered for the advanced oxidation process.

Results indicated that with aqueous ozonation, limited Cr liberation could be achieved. The maximum Cr liberation achieved was only 4.2% for BFD by varying the process controlling parameters. The Cr liberation for UFS was significantly lower than that of the BFD. The difference in the results for the two waste materials was attributed to the difference in characteristics of the materials. The Cr content in BFD was mostly related to

chromite and/or altered chromite particles, while the Cr content of the UFS was mostly related to FeCr particles. It is possible that the Cr(III) present in the chromite and/or partially altered chromite might be more susceptible to oxidation to Cr(VI) than the metallic Cr(0) present in the FeCr. During ozonation, aqueous O₃ spontaneously decomposes to form hydroxyl (OH[•]) radicals, which are very strong oxidants in water. The above-mentioned Cr liberation observed was related to the formation of the OH[•] radicals during the spontaneous decomposition of aqueous O₃. This was indicated especially by enhanced Cr liberation at higher pH values, which was attributed to the acceleration of the spontaneous decomposition to OH[•] radicals at higher pH levels.

The advanced oxidation method gave significantly higher Cr liberation results for both case study materials considered, achieving Cr liberations of more than 21%. The advanced oxidation processes improve normal oxidation methods. In this study, the H₂O₂ used in combination with O₃ enhanced the formation of the OH[•] radicals that are responsible for the oxidation of Cr. The Cr liberation levels achieved are possibly not high enough to be feasible for industrial purposes. However, a further investigation of the advanced oxidation process could optimise the process to yield even higher Cr liberation.

Keywords: Ferrochrome waste; Chrome liberation; Aqueous ozonation; Ozone; Advanced oxidation process

Chapter 1

Background, motivation and objectives

1.1 Background and motivation

Chromium (Cr) is a hard, brittle, shiny metal with a crystalline structure and a high melting point (Kotz et al., 2006). The only commercially recoverable source of new Cr units is chromite (Murthy et al., 2011; Riekkola-Vanhanen, 1999), which occurs as a Cr spinel in layered ultramafic intrusive rocks (Niagru, 1988). Cr metal has the unique property of being corrosion resistant due to the formation of a strong, dense, nonporous chromium(III) oxide (Cr_2O_3) surface layer that forms when Cr metal comes in contact with atmospheric oxygen (Jacobs and Testa, 2005). The hardness of Cr and its resistance to corrosion make it an ideal metal to use in the production of alloys. The most significant application of Cr is in the production of stainless steel (ISSF, 2011), which is predominantly manufactured from stainless steel scrap and ferrochrome (FeCr).

Approximately 90% of all mined chromite is used in the manufacturing of FeCr (Rao, 2010). FeCr is mostly produced by the carbothermic reduction of chromite and consists of 50-70% Cr, 0.02-9% carbon (C) and 0.6-6% silicon (Si) (Riekkola-Vanhanen, 1999). South Africa holds approximately three quarters of the world's viable chromite reserves (Cramer et al., 2004) and produced approximately 36% of the global annual high carbon FeCr in 2011 (ICDA, 2013).

Various processes are utilised by South African FeCr producers. Beukes et al. (2010) presented an overview of these processes. There are essentially four main processes used by local FeCr producers, viz. i) conventional semi-closed submerged arc furnace (SAF)

operation, with bag filter off-gas treatment; ii) closed SAF operation that usually utilises oxidative sintered pelletised feed; iii) closed SAF operation with a pre-reduced pelletised feed, with venturi scrubbing of the off-gas; and iv) closed direct current (DC) arc furnace operation, with venturi scrubbing of the off-gas.

Three types of generic wastes are generated in the above-mentioned FeCr production processes, i.e. slag generated during the smelting process, bag filter dust (BFD) generated during the cleaning of off-gas originating from semi-closed SAFs, and sludge generated during the scrubbing of the off-gas from closed furnaces (both SAFs and DC).

Although slag is by volume the largest waste produced by FeCr producers (Beukes et al., 2010), BFD is by far the most environmentally important waste, since it contains significant amounts of Cr(VI). Cr(VI) is generally regarded as carcinogenic, although not all forms of Cr(VI) have been proven to be carcinogenic (IARC,1997). Compared to BFD, similar volumes of venturi sludge are generated, but it contains significantly smaller amounts of Cr(VI) than BFD.

Typical Cr recovery during FeCr smelting is 70-93%, depending on the specific smelting technology applied (Naiker and Riley, 2006; Cramer et al., 2004). All FeCr producers strive towards reduced waste generation with associated lower Cr unit losses due to increased cost, efficiency and environmental pressures. The loss of Cr units in FeCr production wastes, i.e. slag, BFD and venturi sludge, is a significant contributor to loss of revenue.

Methods for the recovery of Cr-units from FeCr wastes have mainly been associated with physical separation methods such as jigging, magnetic separation, dense media separation (DMS), flotation, shaking tables and spiralling (e.g. Sripriya and Murty, 2004; Shen and Forssberg, 2002; Coetzer et al., 1997; Visser and Barret, 1992). These processes have also predominantly been limited to the recovery of >75 µm particles, with waste streams consisting of smaller particles being somewhat neglected. Van der Merwe et al. (2012)

indicated that aqueous ozonation could be used to convert water-insoluble Cr(III) to soluble Cr(VI). However, these authors only focused on the possible health and environmental impacts associated with such conversion during water treatment. Additionally, Rodman et al. (2006) indicated that the conversion of Cr(III) propionate to Cr(VI) with the advanced oxidation process could be used as a means of pre-treatment for an analytical technique to detect Cr. From the afore-mentioned studies, it seems possible that the conversion of insoluble Cr(III) to soluble Cr(VI) could be considered as an alternative hydrometallurgical method for Cr recovery from wastes.

Although the above-mentioned method for Cr recovery seems counterintuitive, since Cr(VI) is generally considered to be carcinogenic, the risks associated with aqueous Cr(VI) are certainly much fewer than the risks associated with airborne Cr(VI). Furthermore, the risks associated with aqueous Cr(VI) can be mitigated (Beukes et al., 2010). Therefore, the possible recovery of Cr units from BFD and the ultra-fine slag fraction (UFS) with aqueous ozonation and the advanced oxidation process was considered in this study.

1.2 Objectives

The specific objectives of this study were to:

- i) obtain case study waste materials (BFD and UFS) from a large South African FeCr producer and perform a detailed characterisation of both these materials;
- ii) determine the liberation of Cr units from BFD and UFS through the use of aqueous ozonation;
- iii) investigate the above-mentioned reaction system as a function of pH, ozonation contact time, waste material solid loading, gaseous ozone (O_3) concentration and temperature;

- iv) determine the liberation of Cr units from BFD and UFS through the use of the advanced oxidation process. The advanced oxidation process can be applied in many different manners. In this study, O₃ was used in combination with hydrogen peroxide (H₂O₂);
- v) investigate the above-mentioned reaction system as a function of pH, volume H₂O₂ added and the method of H₂O₂ addition;
- vi) make recommendations with regard to the industrial relevance of this process and possible future research.

Chapter 2

Literature survey

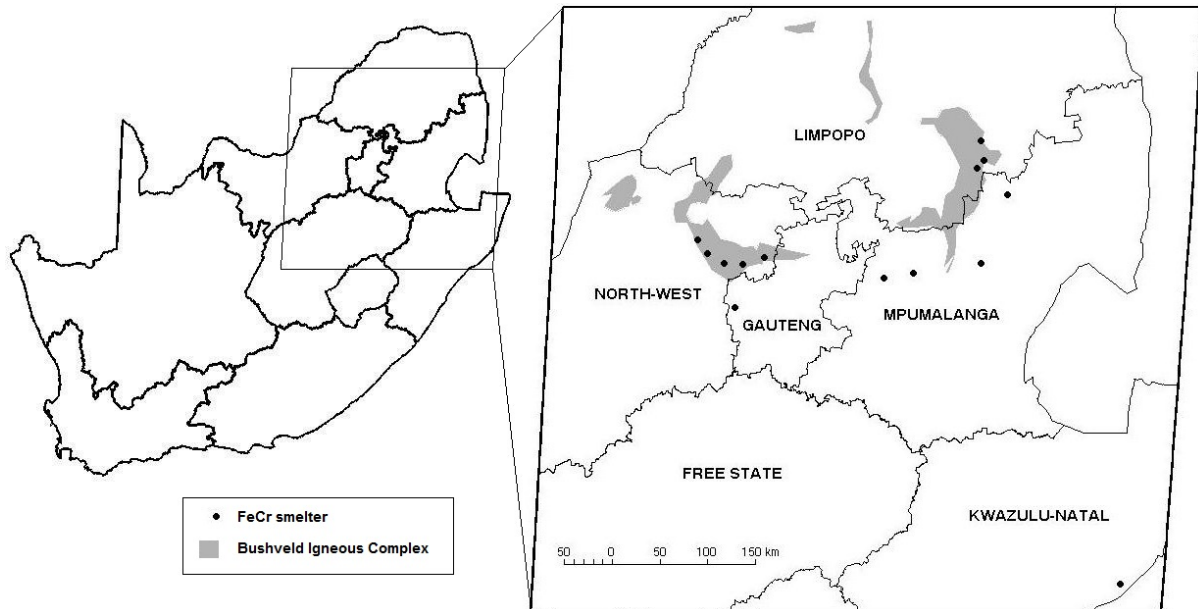
2.1 Importance of Cr industry in South Africa

2.1.1 Chromite ore reserves in South Africa

South Africa holds approximately 75% of the world's viable Cr ore (chromite) reserves (Cramer et al., 2004). Other major Cr ore producers include Kazakhstan, India, Turkey, Zimbabwe, Finland and Brazil (Riekkola-Vanhanen, 1999). Chromite is the only economically viable form of new Cr units and occurs as a Cr spinel in ultramafic igneous rocks (Niagru, 1988). A Cr spinel is a complex mineral containing magnesium (Mg), iron (Fe), aluminium (Al) and Cr in which the ratios of these elements in the spinel differ depending on the deposit (Beukes et al., 2010, Murthy et al., 2011).

In South Africa, the chromite resources are found within the Bushveld Complex. The Bushveld Complex is a large saucer-like, layered igneous intrusion located in the northern part of South Africa (Howat, 1994). The Bushveld complex has a surface area of approximately 65 000 km² with a diameter larger than 350 km, excluding the far western limb with a surface area of 100 km² (Perritt and Roberts, 2007). The extent of the Bushveld Complex is graphically presented in Fig. 2.1.

Figure 2.1: A graphical representation of the extent of the Bushveld Complex and the positioning of FeCr smelters in South Africa. Google Earth was used to locate the various FeCr smelters and the map was compiled with Matlab.



According to Howat (1994), chromite ore in South Africa is mined in four major regions, which include the eastern chromite belt, the western chromite belt, the Zeerust district and the areas south of Potgietersrus. The Zeerust and Potgietersrus deposits have limited resources, although these deposits have the highest Cr_2O_3 content, i.e. 50-57% Cr_2O_3 , as well as the highest Cr:Fe ratios, ranging between 2-2.9. The major deposits are in the eastern and western chromite belts in the Bushveld Complex situated in the Burgersfort/Steelpoort and Brits/Rustenburg/Sun City areas, respectively. The Cr resources in these areas are of lower grade, with approximately 45% Cr_2O_3 content and Cr:Fe ratios ranging between 1.5-1.6 after beneficiation.

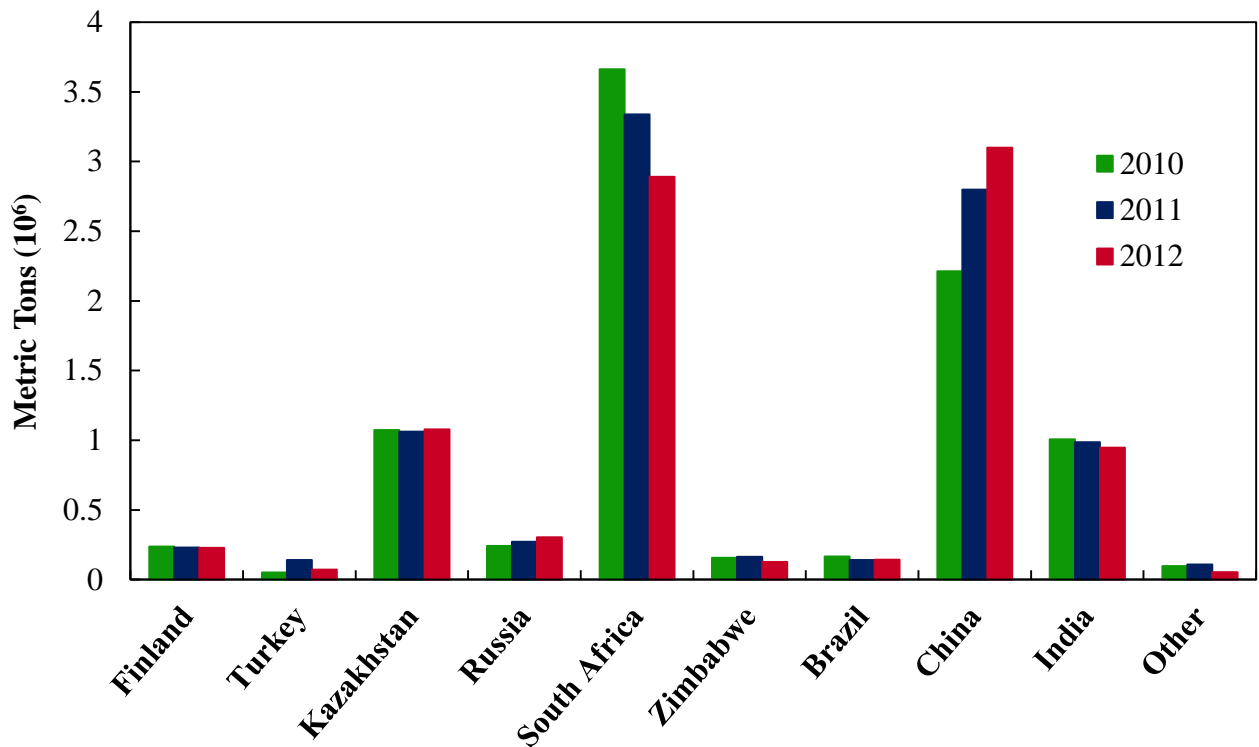
Platinum group metals (PGMs) are also found within the Bushveld Complex, with UG2 ore (UG2 is an underground chromitite layer that is explained in Par 2.2.1) being the predominant source of PGMs. The residue UG2 ore remaining after PGM extraction also

contains significant Cr units. Beneficiated UG2 process residue can also be used as feed material by FeCr producers.

2.1.2 *Production of FeCr*

In Fig 2.2, the global high carbon charge grade FeCr production for 2010 to 2012 is presented. South Africa produced approximately 36% of the world's high carbon charge grade FeCr in 2011, which is the most common FeCr grade (ICDA, 2013). This made South Africa the largest producer of FeCr in the world during that year. The demand for FeCr is largely driven by its use in the production of stainless steel. Global stainless steel production is therefore largely dependent on FeCr supply from South Africa. However, recent FeCr production increases in especially China (as indicated in Fig. 2.2) and reduced production due to electricity shortages and price increases (Kleynhans et al., 2012) are threatening South Africa's dominant role as a global FeCr supplier. It is evident from Fig 2.2 that China has currently overtaken South Africa as the world's leading FeCr producer.

Figure 2.2: The global high carbon charge grade FeCr production for 2010 to 2012 (ICDA, 2013).



Chromite ores mined in South Africa were not considered for FeCr production until about the 1950s when the first two FeCr plants were commissioned. This was due to the low Cr:Fe ratios. However, it was only in the 1970s that FeCr production in South Africa actually started to escalate to the high production levels that it has today (ICDA, 2013; Howat, 1994). At present, South Africa has at least fourteen FeCr smelters (Beukes et al., 2010), of which the locations are indicated in Fig. 2.1. In Table 2.1, the production capacity figures of all the FeCr smelters in South Africa are listed. These plants can jointly produce approximately 4.3 million tons of FeCr per annum.

Table 2.1: Production capacities of the various FeCr smelters in South Africa (Beukes et al., 2012).

Plant	Locality	Production capacity (kilo ton 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	Steelport	360
Glencore Lydenburg	Lydenburg	400
Glencore Merafe Chrome	Boshoek	240
Glencore Merafe Lion	Steelport	364*
Glencore Rustenburg	Rustenburg	430
Glencore Wonderkop	Between Rustenburg and Brits	545
TOTAL		4 340

* An expansion project for this facility is currently under way and will double its current capacity

2.2 Processes utilised by the South African FeCr industry

2.2.1 Mining and beneficiation of chromite

Chromite is mainly mined through open-pit and underground mining (Cramer, 2004). According to Gu and Wills (1998), the world's chromite is mainly mined from rocks of mafic (which hosts the chromite and platinum) and ultramafic composition, which is subdivided into two types of ore, viz. stratiform and podiform deposits.

Podiform chromite deposits are irregular shaped deposits with an unpredictable distribution that makes it costly to explore and exploit. Podiform deposits are mainly found in Turkey, Albania and Kazakhstan. Stratiform deposits are found in parallel seams in large, layered igneous-rock complexes such as the Bushveld Complex in South Africa. Stratiform deposits are also found in Finland and Zimbabwe (Cramer, 2004). The Bushveld Complex is divided into three zones, i.e. the Upper and Lower Zone, Upper and Lower Critical Zone, and the Main Zone. Chromite and platinum group elements (PGEs) are found in the Critical Zone, which makes this zone of significant economic importance (Perrit and Robert, 2007; Barnes et al., 1983). The Critical Zone is also subdivided into two zones, i.e. the lower pyroxenitic and upper antorthostic zones. Chromite is mainly exploited from the pyroxenite zone due to the higher Cr:Fe ratio in this zone. The pyroxenite zone of the Critical Zone in the western sector of the Bushveld complex is between 915 and 1750 m and contains thirteen chromitite layers that are of potential economic value. In the eastern sector, the pyroxenite zone of the Critical Zone is between 1220 and 1370 m, containing between 5 and 28 chromitite layers (Edwards and Atkinson, 1986). The economically most important chromitite layer in the eastern belt is the lower group 6 (LG6) layer, while other important chromitite layers for chromite mining include middle group 1 and 2 (MG1/2) and upper group 2 (UG2) layers. As previously stated in Par 2.1.1, although the UG2 layer is primarily an important source of PGMs, it can be used as feedstock for the FeCr industry after extraction of PGMs from the ore and residue ore is beneficiated to a suitable Cr content and/or Cr:Fe ratio (Mondal and Mathez, 2007; Cramer, 2004).

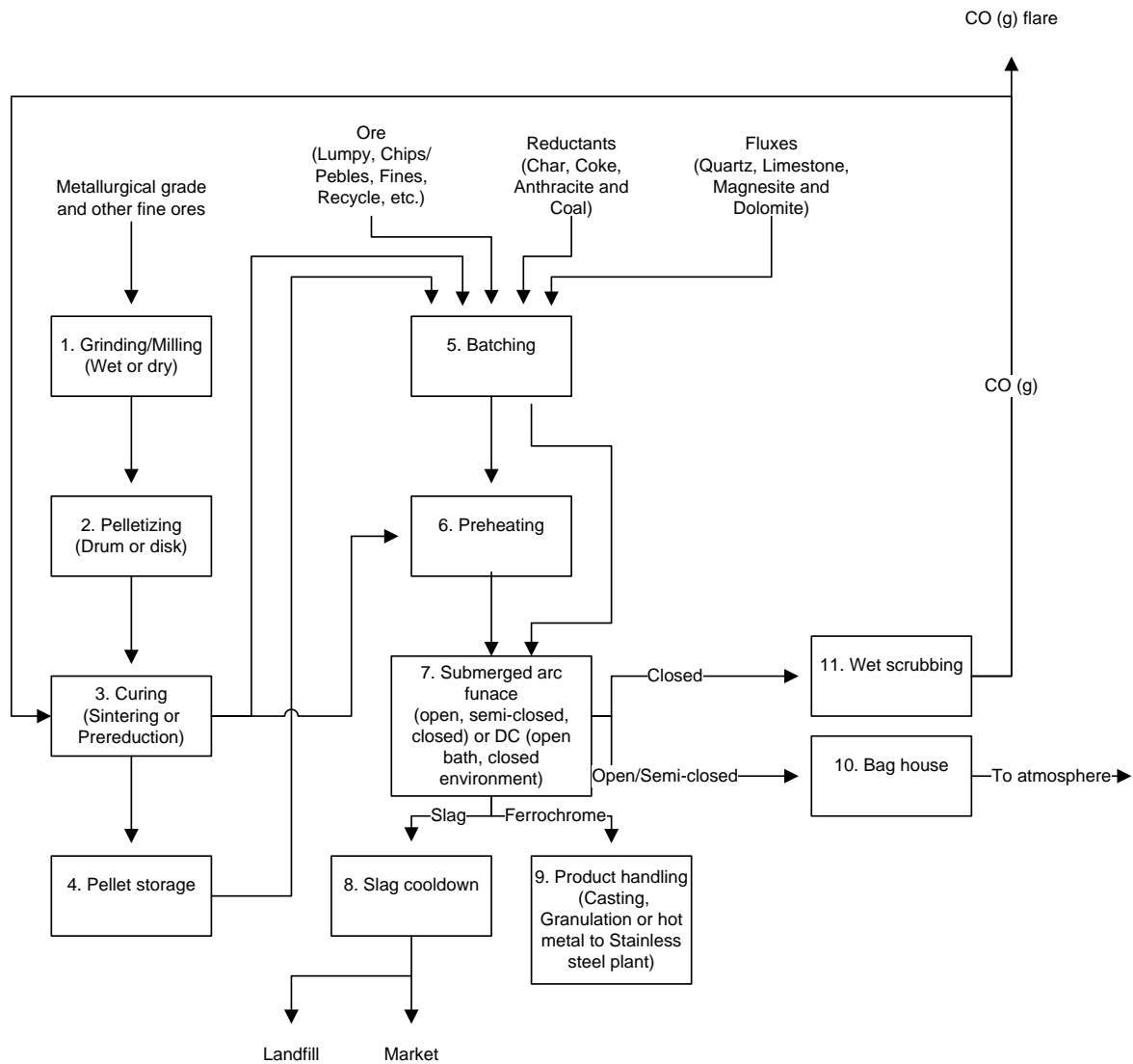
According to Gu and Wills (1988), lumpy ore is ideal for smelter feed. The chromite in South Africa is friable and can easily be broken down to the size of the chromite crystals (Gu and Wills, 1988). Low grade and friable or fine ores that are produced during the mining of the hard lumpy ores must be subjected to beneficiation before smelting. Several

beneficiation methods can be applied to the ore, such as gravity concentration, high-intensity magnetic separation, flotation, heavy medium separation and in some cases even simple screening, which depends on the type of product that is required. Spirals, jigs and shaking tables are common gravity separation techniques used to treat finer particles. Gravity separation methods are also more generally used to beneficiate coarse particles. However, heavy medium separation is the most economic method for the treatment of coarse particles. The recovery during the beneficiation process is usually 10 to 15% of lumpy ore (15 mm < typical size range < 150 mm) and 8 to 12% of chip/pebble ores (6 mm < typical size range < 15 mm) (Glastonbury et al., 2010). The fraction of the remaining fine ore (< 6 mm) is normally milled or crushed to < 1 mm. Gravity separation techniques are utilised to upgrade the < 1 mm ore to approximately 45% Cr₂O₃ content, which is termed metallurgical grade ore (Glastonbury et al., 2010). Very limited fractions of fine ore can be fed directly into SAFs and therefore these fine ores usually first undergo an agglomeration step (Gu and Wills, 1988).

2.2.2 *Production of FeCr*

The production of FeCr is a highly energy intensive process during which FeCr is pyrometallurgically produced by carbothermic reduction of chromite. Coke, char, anthracite or coal are added as reductants, while quartzite, bauxite, olivine, dolomite, limestone and calcite are used as slag additives (Riekola-Vanhanen, 1999). In Figure 3., the combination of the most commonly used steps in FeCr production in South Africa is presented as a process flow diagram.

Figure 3.3: A generalised flow diagram showing the combination of process steps most commonly utilised by the South African FeCr industry (Beukes et al., 2010).



Beukes et al. (2010) described four relatively well-defined FeCr process combinations that are utilised by South African FeCr producers, i.e.:

- i. Conventional semi-closed SAF operation, which is the oldest technology applied in South-Africa. Coarse (lumpy and chips/pebble ore, Par 2.2.1) and a small fraction of fine ores can be smelted in this type of operation, without an agglomeration process to form pellets from the fine ores. Although Riekkool-Vanhanen (1999) stated that fine ores

cannot be fed directly into an SAF without causing dangerous blow-outs or bed turnovers, a small fraction of fine ores do get fed into some semi-closed SAFs in South Africa. The process steps presented in Fig. 2.3 that are followed for this operation are 5, 7, 8, 9, and 10. Some semi-closed SAFs consume pelletised feed, in which case process steps 1 to 4 (Fig 2.3) would also be included. Most of the semi-closed SAFs in South Africa are operated on an acid slag with a basicity factor (BF) smaller than one. The BF is calculated with Eq. 2.1.

$$\text{BF} = \frac{\% \text{ CaO} + \% \text{ MgO}}{\% \text{ SiO}_2} \quad (2.1)$$

Some semi-closed SAFs might operate on $\text{BF} > 1$, which is less common and in certain instances only a temporary operation condition in order to compensate for refractory linings that are in poor condition due to the higher liquidus temperature of basic slags, or if enhanced sulphur (S) removing capacity by the slag is required. The latter is achieved since higher Ca and Mg containing slag results in more S being retained as CaS and MgS in the slag. Several South African FeCr producers operate semi-closed SAFs, which include furnaces at Lydenburg, Machadodorp, ASA, Tubatse, Wonderkop and Rustenburg (Table 2.1).

- ii. Closed SAF operations usually utilise oxidative sintered pelletised feed, which is the technology most commonly used in South Africa (Outotec, 2008). The process steps for this operation include steps 1, 2, 3, 4, 5, 7, 8, 9 and 11, including or excluding step 6 presented Fig. 2.3. In most of the greenfield FeCr developments, the pelletising (step 2) and sintering (step 3) steps were combined at closed SAFs. At plants where the pelletised feed is utilised by conventional semi-closed SAFs, pelletising and sintering sections have also been constructed. All the afore-mentioned SAFs are usually operated on an acid slag

($BF < 1$). Oxidative sintered pelletising plants have been constructed at several South African FeCr producers with semi-closed and closed SAFs, i.e. Machadodorp, Tubatse, ASA, Hercul, International Ferro-Metals, Ferrometals Witbank, Middelburg Ferrochrome, Wonderkop and SA Chrome (Boshoek) (Table 2.1).

- iii. Closed SAF operation utilising a pre-reduced pelletised feed (Botha, 2003; Naiker, 2007, Kleynhans et al., 2012; Neizel et al., 2013). The process steps in Fig. 2.3 for this type of operation are 1, 2, 3, 4, 5, 7, 8, 9 and 11. The pelletised feeds are mostly fed hot into the SAFs directly after pre-reduction occurred in contour current rotary kilns. The SAFs are closed and operate on a basic slag ($BF > 1$). Two South African FeCr smelter operations use this process, i.e. Lion Ferrochrome and Lydenburg (Table 2.1).
- iv. DC arc furnace operation in which the feed consists exclusively of fine material (Curr, 2009; Denton et al., 2004). There are currently three of these furnaces that are in routine commercial operation for FeCr production in South Africa, i.e. furnaces at Middelburg Ferrochrome and Mogale (Table 2.1). These furnaces typically utilise a basic slag regime (Eq. 2.1). The process steps for this operation are 5, 7 (with a DC, instead of a SAF), 8, 9 and 11 (Fig. 2.3).

2.3 Waste generated by the FeCr industry

In the FeCr smelting industry, three types of generic Cr-containing wastes are generated utilising the afore-mentioned FeCr production processes (Par 2.2.), i.e. slag, venturi sludge and BFD. Slag is produced during the smelting process and is removed from the furnace through a tapping hole. Venturi sludge is generated during the scrubbing of the off-gas from closed SAFs, while BFD is formed from cleaning the off-gas originating from semi-

closed SAFs. Additional to the afore-mentioned three types of FeCr smelting-related wastes, there is also waste generated from the mined ore used for FeCr smelting.

Slag is by volume the largest waste produced during FeCr smelting. The amount of slag produced per ton of alloys ranges from 1.1 to 1.9 ton slag per ton of alloy produced, depending on the type of smelting technology applied and the quality of feed materials (Beukes et al., 2010). BFD is from an environmental perspective the most important waste, since it contains small amounts of Cr(VI) (Beukes et al., 2010). Cr(VI) is generally regarded as carcinogenic, although not all forms of Cr(VI) have been proven to be carcinogenic (IARC,1997). Venturi sludge is generated in similar volumes than BFD, but contains significantly less Cr(VI) (Beukes et al., 2010; Gericke, 1995). Beukes et al. (2012) provided an overview of Cr(VI) treatment strategies currently applied by South African FeCr producers. The treated wastes, consisting mostly of BFD and venturi sludge, are commonly stored in specially designed waste facilities.

2.4 Recovery of Cr units from FeCr wastes

All FeCr producers strive towards reduced waste generation, with associated lower Cr unit losses due to increased costs, efficiency and environmental pressures. However, the loss of Cr units through FeCr production wastes, i.e. slag, venturi sludge and BFD, contributes significantly to loss of revenue. Typical Cr recovery during FeCr smelting ranges between 70 and 93%, depending on the specific smelting technology applied (Naiker and Riley, 2006, Cramer et al., 2004).

The recovery of Cr units from FeCr wastes has mainly been performed with physical separation methods, such as jigging, magnetic separation, dense media separation (DMS), flotation, shaking tables and spirals (e.g. Sripriya and Murty, 2004; Shen and Forssberg, 2002; Coetzer et al., 1997; Visser and Barret, 1992). Most South African FeCr producers

have constructed FeCr metal recovery plants utilising some of the above-mentioned methods. The industrial application of these processes has predominantly been limited to the recovery of particles $> 75 \mu\text{m}$, with waste streams consisting of smaller particles being somewhat neglected.

Many studies have been conducted on the potential FeCr recovery from slag using different physical separation methods (Erdem et al., 2005; Shen and Forsberg, 2003; Mashanyare and Guest, 1997). However, potential hydrometallurgical recovery methods for Cr recovery from any of the FeCr waste materials have not been investigated that extensively. Shawabkeh (2010) and Strobos and Friend (2004) performed studies on the leaching of Zn from BFD. However, these authors did not consider the recovery of Cr units.

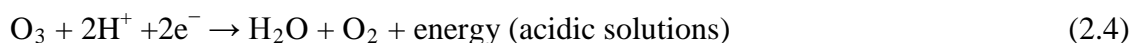
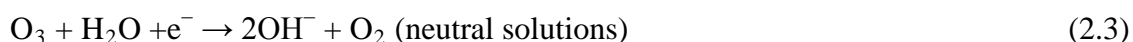
2.5 Aqueous ozonation and the advanced oxidation process as possible recovery methods of Cr units from FeCr wastes

Van der Merwe et al. (2012) indicated that aqueous ozonation or O_3 oxidation could be used to convert water-insoluble Cr(III) to water-soluble Cr(VI), while Rodman et al. (2006) indicated the conversion of Cr(III) propionate to Cr(VI) through the advanced oxidation process as a means of pre-treatment for an analytical technique. These two aqueous processes where Cr species are chemically converted could be considered as possible hydrometallurgical recovery methods of Cr from FeCr wastes.

In recent years, the interest in gaseous and aqueous phase O_3 chemistry has increased due to various reasons, which include the influence of O_3 chemistry on the atmosphere and the applications of O_3 in water-related topics due to its oxidising capacity in aqueous mediums. There is a significant difference in the gaseous and aqueous phase reactions of O_3 (Fábíán, 2006). O_3 is 10 to 12 times more soluble in water than oxygen is. Aqueous O_3 has

a wide range of applications, which are mostly based on its strong oxidising properties. Aqueous O₃ decomposes through a radical chain mechanism to form hydroxyl (OH[•]) radicals (Han et al., 2006; Fábíán, 1995). The OH[•] radical plays a major role in O₃ chemistry and is one of the strongest oxidising agents in aqueous mediums. According to Fábíán (2006) and Rosenfeldt et al. (2006), the aqueous phase O₃ oxidation can occur directly or indirectly, i.e. either oxidation through the chemical reaction of O₃ directly with the species or indirectly through the formation of OH[•] radicals.

Aqueous O₃ can react differently at different pH levels. In Eq. 2.2 to 2.3, the proposed initiation reactions of O₃ decomposition in acidic, neutral and basic aqueous solutions are indicated (Lin and Nakajima et al., 2002; Beltrán, 2003).



At low aqueous pH values, O₃ does not react with water and it is present as an O₃ molecule. At higher pH levels, O₃ decomposes spontaneously to form OH[•] radicals (Han et al., 2004; Gordon, 1995).

The decomposition of the O₃ in aqueous mediums can be initiated and accelerated by the presence of hydroxide ions, formate ions and various other species (Beltrán, 2003). Therefore, in order to enhance the oxidation ability of O₃ in aqueous mediums, several advanced oxidation processes have been developed. These advanced oxidation processes are based on the generation of radical intermediates (usually OH[•] radicals) that enhance regular

oxidation processes (Neyens and Baeyens, 2003; Andreozzi et al., 1999). There are many different variations of advanced oxidation processes, which include the addition of a peroxide or ultraviolet irradiation to an oxidation reaction (Bragg et al., 2012; Cortez et al., 2011 and Rodman et al., 2006). The formation of OH[•] radicals is usually enhanced by the addition of a peroxide with Fe²⁺, O₃ and/or ultraviolet irradiation to an oxidation reaction (Bragg et al., 2012; Cortez et al., 2011, Rodman et al., 2006). As an example to illustrate the principle of the advanced oxidation process, Eq. 2.5 indicates by what means O₃ decomposition can be accelerated by the addition of H₂O₂. The hydroxide anions formed from H₂O₂ initiate the decomposition of O₃ into OH[•] radicals (Von Gunten, 2003).



Various studies have been conducted on the applications of the advanced oxidation processes. Rosenfeldt (2006) compared different variations of the advanced oxidation process. As mentioned previously, Bragg et al. (2012) and Rodman et al. (2006) used the advanced oxidation process for the conversion of Cr(III) to Cr(VI) as part of the pre-treatment of samples for an analytical technique.. Many other authors (e.g. Chu et al., 2012; Wu et al., 2004; Andreozzi et al., 1999) also used different variations of the advanced oxidation process for a wide range of applications.

2.6 Conclusions

Literature relating to the hydrometallurgical recovery of Cr units from FeCr waste materials is very limited. Cr recovery has been mostly associated with physical separation methods. The studies of Van der Merwe et al. (2012) and Rodman et al. (2006) indicated that

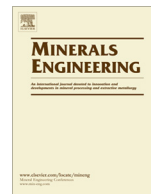
aqueous ozonation and the advanced oxidation process could be used to convert water-insoluble Cr(III) to water-soluble Cr(VI). Although the objectives of these studies did not entail the recovery of Cr units from waste material, these techniques could be applied to potentially leach Cr from FeCr waste materials.

Considering the magnitude of the South African FeCr industry, Cr liberation and recovery from ultra-fine waste materials could be beneficial for the local industry. Although it is not foreseen that this study will find the complete solution to the challenge, it is anticipated that the knowledge gained in this study will form the basis for subsequent investigations, which could eventually lead to feasible industrial-scale process options to recover Cr units from the ultra-fine FeCr waste materials.

Chapter 3

Article

Chapter 3 consists of the article which was added into the dissertation in the exact format in which it was published in *Minerals Engineering*: 56 (2014), 112–120. The journal can be found at www.elsevier.com/locate/mineng (Date of access: 3 March 2014).



Characterisation and liberation of chromium from fine ferrochrome waste materials [☆]



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ABSTRACT

Three types of generic chromium (Cr)-containing wastes are generated during ferrochrome (FeCr) production, i.e. slag, bag filter dust (BFD) and venturi sludge. Slag is by volume the largest waste; however, fine FeCr waste materials (e.g. BFD, venturi sludge) are from an environmental perspective the most important. The loss of Cr units to FeCr waste streams represents both an added cost burden (related to disposal/storage) and a loss of revenue in terms of contained Cr units. In this paper, the novel idea of the liberation of Cr units from FeCr BFD and the ultra-fine fraction of slag (UFS) with aqueous ozonation and the advanced oxidation process was investigated. Several techniques were used to characterise both case study waste materials, i.e. particle size distribution, chemical composition, chemical surface composition and crystalline content analysis. Results indicated that limited Cr liberation could be obtained from the waste materials utilising aqueous ozonation. For BFD, only a maximum of 4.2% of total Cr liberation was achieved. However, the Cr liberation of BFD was substantially higher than that achieved for the UFS, which was attributed to the difference in characteristics of the two materials. Cr liberation observed was related to the formation of the OH[•] radicals during the spontaneous decomposition of aqueous O₃. Application of the advanced oxidation process by the addition of H₂O₂ during ozonation increased Cr liberation dramatically. More than 21% of total Cr liberation could be achieved for both the waste materials used in this investigation. Although the afore-mentioned Cr liberation level is unlikely to be commercially viable, the investigation proved that further research could optimise this process.

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1. Introduction

Chromium (Cr) is an essential element in modern-day society. The only commercially recoverable source of Cr is chromite (Murthy et al., 2011; Riekkola-Vanhanen, 1999). Approximately 90% of all mined chromite is used in the manufacturing of ferrochrome (FeCr) (Rao, 2010), which is mostly produced by the carbothermic reduction of chromite (Riekkola-Vanhanen, 1999). Various grades of FeCr can be produced, with high carbon FeCr being the most common. FeCr is mainly used in the production of stainless steel (Murthy et al., 2011), of which the application and demand are growing at a significant rate (ISSF, 2011).

South Africa holds approximately three quarters of the world's viable chromite reserves (Cramer et al., 2004) and, in 2009,

produced approximately 39% of the global annual high carbon FeCr (ICDA, 2010). Beukes et al. (2010) presented an overview of the processes utilised by the South African FeCr industry. Although this review (Beukes et al., 2010) referred specifically to the South African FeCr industry, similar processes are also applied internationally. According to this review, FeCr is currently mainly produced with (i) conventional semi-closed/open submerged arc furnace (SAF) operation, with bag filter off-gas treatment; (ii) closed SAF operation that usually utilises oxidative sintered pelletised feed, with venturi scrubbing of off-gas; (iii) closed SAF operation consuming pre-reduced pelletised feed, with venturi scrubbing of off-gas; and (iv) closed direct current (DC) arc furnace operation, with venturi scrubbing of off-gas.

Three types of generic Cr-containing wastes are generated during FeCr production utilising the afore-mentioned FeCr production processes. Slag is generated during the smelting process, bag filter dust (BFD) during the cleaning of the off-gas originating from semi-closed/open furnaces, and venturi sludge during the scrubbing of the off-gas from closed furnaces. Although slag is by volume the largest waste produced during FeCr production, BFD is environmentally considered to be the most important waste, since it

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contains small amounts of Cr(VI) (Beukes et al., 2010). Venturi sludge is generated in similar volumes than BFD, but contains significantly smaller amounts of Cr(VI) (Beukes et al., 2010; Gericke, 1995). Cr(VI) is generally regarded as carcinogenic, although not all forms of Cr(VI) have been proven to be carcinogenic (IARC, 1997). Beukes et al. (2012) provided an overview of the Cr(VI) treatment strategies currently applied by South African FeCr producers.

Typical Cr recovery during FeCr smelting is 70–93%, depending on the specific smelting technology applied (Naiker and Riley, 2006; Cramer et al., 2004). Due to increased cost, efficiency and environmental pressures, all FeCr producers strive towards reduced waste generation with associated lower Cr unit losses. The loss of Cr units in FeCr production wastes, i.e. slag, BFD and venturi sludge, is a significant contributor to loss of revenue.

The recovery of Cr units from FeCr wastes has up to now mainly been associated with physical separation methods, such as jigging, magnetic separation, dense media separation (DMS), flotation, shaking tables and spirals (e.g. Sripriya and Murty, 2004; Shen and Forssberg, 2002; Coetzer et al., 1997; Visser and Barret, 1992). These processes have also predominantly been limited to the recovery of >75 µm particles, with waste streams consisting of smaller particles being somewhat neglected.

Van der Merwe et al. (2012) indicated that aqueous ozonation could be used to convert water insoluble Cr(III) to soluble Cr(VI). These authors only focused on the possible health and environmental impacts associated with such conversion during water treatment. Additionally, Rodman et al. (2006) indicated that the conversion of Cr(III) propionate to Cr(VI) by the advanced oxidation process could be used as a means of pre-treatment for an analytical technique. The advanced oxidation processes are based on the generation of radical intermediates (usually OH· radicals) to enhance regular oxidation techniques (Neyens and Bayens, 2003; Andreozzi et al., 1999). There are many different variations of the advanced oxidation process. Popular examples of this process include the combination of hydrogen peroxide (H₂O₂) with Fe²⁺ and H₂O₂ in combination with ozone and/or UV (Cortez et al., 2011; Wu et al., 2004). From the studies presented by Van der Merwe et al. (2012) and Rodman et al. (2006), it seems possible that the conversion of insoluble Cr(III) to soluble Cr(VI) could be considered as an alternative method for Cr recovery from wastes. Although this route for Cr recovery seems counterintuitive, since Cr(VI) is generally considered to be carcinogenic, the risks associated with aqueous Cr(VI) is certainly much less than airborne Cr(VI) and these risks can be mitigated (Beukes et al., 2010). Therefore, the possible recovery of Cr units from BFD and the ultra-fine slag fraction (UFS) with aqueous ozonation and the advanced oxidation process was considered in this study.

2. Materials and methods

2.1. Materials

In this paper, two case study waste materials were used, i.e. BFD and the UFS. Both these materials were sampled at one of the large FeCr smelters in South Africa. The BFD was obtained from the bag filter of a semi-closed furnace at this smelter. The UFS originated from the <1 mm circuit at the metal recovery plant, where slags from both semi-closed and closed furnaces of this specific FeCr producer were treated. At the metal recovery plant, the 1–8 and the 8–20 mm slag fractions were treated in air-pulsed jigs to recover the FeCr in these two size fractions. Numerous papers have described similar FeCr recovery systems (Sripriya and Murty, 2004; Visser and Barret, 1992). The <1 mm slag fraction was treated in spirals to recover the liberated FeCr, unaltered chromite and

partially altered chromite, which was fed back to the pelletising section at this specific FeCr producer and smelted again. However, before the <1 mm slag fraction was treated in the spirals, the ultra-fine fraction was removed with a cyclone (cyclone overflow). This ultra-fine fraction was then dewatered with a filter press to form a filter cake. This filter cake was sampled from its stockpile and used as the case study UFS.

SARM 8, supplied by Industrial Analytical (Pty) Ltd., was used as a reference material in the determination of total Cr. A reference standard containing 1009 ± 2 µg/mL chromate (CrO₄²⁻), obtained from Spectrascan, was used to prepare standard solutions to construct a calibration line for Cr(VI) analysis. Sodium hydroxide (NaOH) (Merck) and 98% sulphuric acid (H₂SO₄) (Sigma-Aldrich) were used to adjust the pH. All other chemicals used were of analytical grade (AR). These were received from various suppliers and used without further purification or treatment. In all experiments requiring water, ultra-pure water (resistivity 18.2 MΩ cm⁻¹) was used, which was produced by a Milli-Q water purification system. The medical grade oxygen (O₂) that was used for ozone (O₃) production was supplied by Afrox.

2.2. Case study waste characterisation

The particle size distributions of the case study waste materials were determined by utilising laser diffraction particle sizing (Saturn DigiSizer II 5205). A diluted suspension of each material was ultra-sonicated for 60 s prior to the measurement, in order to disperse the particles and to avoid the use of a chemical dispersant.

A Spectro Ciros vision inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the majority of elements present in the two case study materials. The materials were digested prior to ICP-OES analysis with hydrofluoric acid (HF), perchlorate (HClO₄) and nitric acid (HNO₃). Thereafter, the solution was made up to the required volume with hydrochloric acid (HCl). The elemental carbon (C) and sulphur (S) contents of the two case study materials were determined by means of combustion and infrared (IR) spectrophotometry utilising a LECO CS 200 and an Eltra CS 2000. A 1:1 mixture of tungsten (W) and iron (Fe) chips was used as the accelerator flux. The phosphorus (P) content was determined by dissolution of the case study material in concentrated HNO₃ and HClO₄, followed by P complexation with a metavanadate/molybdate colouring agent. The P was then determined colourimetrically in a UV-visible instrument (SHIMADZU 400). Atomic absorption spectroscopy (AAS) was conducted with a Varian spectra 10 to determine the Na content. The materials were prepared for AAS analysis by digestion in HNO₃ and HClO₄, where after the solution was made up to the required volume with HCl.

X-ray diffraction (XRD) using a Röntgen diffraction system (PW3040/60 X'Pert Pro) and a back loading preparation method was used to determine the crystalline phases present in the case study FeCr waste materials. The samples were scanned using X-rays generated by a copper (Cu) Kα X-ray tube. The measurements were carried out between variable divergence- and fixed-receiving slits. The phases were identified using X'PertHighscore plus software. The relative phase amounts were estimated using the Rietveld method (Autoquan programme). A limitation of the method applied was that ferrochrome metal was not detected as crystalline phases. In addition, X-ray fluorescence (XRF) was used to determine the concentration of elements present in the case study materials. The same instrument was used, but a rhodium (Rh) X-ray tube was used to irradiate the samples and a Super Q database was used to determine the multi-elemental concentrations.

Surface analysis of the two case study materials was performed with an FEI Quanta 200 scanning electron microscope (SEM) with an integrated Oxford Instruments INCA 200 energy dispersive

X-ray spectroscopy (EDS) microanalysis system. SEM micrographs were taken at various magnifications to characterise the physical attributes of the two case study materials. SEM–EDS was used to conduct chemical analysis of the surface of the samples. In order to mitigate the negative impact of surface roughness and porosity on SEM–EDS analysis, the area considered during an analysis was moved to cover almost the entire area of the button covered with the material analysed. Such analysis of almost the entire sample button area was referred to as “entire surface” analysis in the results. Additionally no samples were coated with carbon prior to SEM–EDS analysis. However, after the EDS analyses were completed, the same sample buttons were coated with carbon in order to facilitate better micrographs.

2.3. Experimental procedures for chromium liberation

2.3.1. Ozonation experimental procedure

O₃ was produced using a P-HP 250 Sterizone ozone generator. O₂ feed at a flow of 500 NL/h was maintained throughout all experiments. The gaseous O₃ concentration was determined with a Cary 50 Conc UV–visible spectrophotometer. The absorption of O₃ was measured at a wavelength of 254 nm and an absorption coefficient of 3024 L cm⁻¹ mol⁻¹ was used in the calculation of the gaseous O₃ concentrations (McElroy et al., 1997; Dohan and Masschelein, 1987).

A predetermined mass of the case study material, i.e. BFD or UFS, was suspended in 150 ml of pH-adjusted water. O₃ was bubbled through the solution with a bubble diffuser for a pre-selected ozonation contact time. The particles were kept in suspension by means of continuous stirring with a magnetic stirrer. The sealed glass beaker containing the particle suspension was placed in a water jacket in which the water temperature was controlled. The experimental set-up is similar to that used by Van der Merwe et al. (2012). This experimental setup enabled the monovariance investigation of the influence of different process controlling parameters, e.g. pH, ozonation contact time, waste material solid loading, gaseous O₃ concentration and temperature, on the liberation of Cr from the waste materials.

After each ozonation experiment, the 150 ml Cr(VI)-containing solution was filtered off by means of milli-pore filtering (0.45 μm). The remaining solid residue was washed with 50 ml pH-adjusted water, with the pH correlating to the pH of the specific experiment conducted. The combined solution (filtrate and wash water) was then adjusted to a pH of 12.6 (see Section 2.3.3), transferred to a 250 ml volumetric flask and filled to the mark with water adjusted to a pH of 12.6. The Cr(VI) content of this solution was then determined with the method described in Section 2.3.3. Blank experiments, during which all reaction conditions were kept the same with the O₃ generator switched off, were also performed.

2.3.2. Advanced oxidation process experimental procedure

In the advanced oxidation process, a peroxide and/or ultraviolet (UV) irradiation can be used in conjunction with O₃ to increase the oxidation potential (Bragg et al., 2012; Rodman et al., 2006). In this study, H₂O₂, combined with aqueous ozonation, was used. The experimental procedure was the same as discussed for ozonation (Section 2.3.1), with the exception that H₂O₂ was also added. The fraction of H₂O₂ added, as a fraction of the total aqueous solution ozonated, was varied between 3.3 and 20 vol.%. H₂O₂ was added either at the beginning of the experiment only, or throughout the duration of ozonation contact time.

2.3.3. Cr liberation determinations

In order to calculate the liberation of Cr from the waste materials, the total Cr content of the initial material and Cr(VI) content of the aqueous solution after treatment with ozonation (Section 2.3.1)

or the advanced oxidation process (Section 2.3.2) had to be determined.

Total Cr content present was determined by converting all Cr, irrespective of the oxidation state, to water-soluble Cr(VI) (Vogel, 1978). Approximately 2 g of sodium peroxide (Na₂O₂) and 0.5 g of sodium carbonate (Na₂CO₃) were weighed into a zirconium (Zr) crucible. Approximately 0.2 g of the sample was also accurately weighed into the crucible. The materials were then thoroughly mixed. Thereafter, the crucible was fused over a Bunsen flame and swirled continuously until the entire mixture melted. After cooling, the fusion was tapped loose from the crucible and transferred to a 500 ml beaker, where 80 ml of distilled water was added. The solution was then filtered using milli-pore filtering (0.45 μm) in order to separate the Cr(VI) solution from the insoluble fraction. The pH of the above-mentioned Cr(VI) aliquot was measured prior to determining the Cr(VI) content and found to be approximately 12.6. The pH was measured using a Hanna Instrument (HI) 2211 pH/ORP meter with an HI 1131B pH electrode and an HI 7662 temperature probe. The Cr(VI) content in the aliquot was quantified using a Pharmacia Biotech Ultrospec 3 000 UV–visible spectrophotometer with a 10 cm quartz cell. Since the UV–visible spectra of Cr(VI) solutions are pH sensitive, the pH of all the standard solutions was 12.6. A five-point calibration curve for Cr(VI) was determined at 350 nm with concentrations ranging from 200 to 4500 pbb.

In order to verify the accuracy and to determine the precision of the above-mentioned method to determine total Cr content, a certified SARM 8 chromite ore reference material was analysed. The average percentage Cr₂O₃ content with an associated confidence interval of the reference material was certified as 48.9 ± 0.1%. Applying the experimental method used to determine the total Cr-content described above on the reference material and performing six analyses yielded a Cr₂O₃ content of 49 ± 0.8%.

The percentages Cr liberated from the two waste materials were calculated for each experiment from the Cr(VI) content in the solution after ozonation or the advanced oxidation process. This liberation was expressed as a percentage of the total Cr content in the original case study material. All the experiments were repeated at least three times to ensure repeatability. The results reported for each set of unique reaction conditions were the mean obtained from these iterations. Error bars/whiskers indicated on graphs represent the maximum and minimum values obtained experimentally.

3. Results and discussion

3.1. Case study waste material characterisation

The particle size, chemical and surface chemical, and crystalline content characterisation of BFD and the UFS are presented in Tables 1–3, respectively.

In order to quantify the particle size distribution of the BFD and UFS, the *d*₉₀, *d*₅₀ and *d*₁₀ particle sizes are presented in Table 1. From these results, it is evident that both these materials are too fine for conventional physical separation methods to effectively separate Cr-containing particles from the gauge. In addition, the

Table 1
Particle size analysis of BFD and UFS.

Particle size (μm)	BFD	UFS
<i>D</i> ₉₀	29.5	83.1
<i>D</i> ₅₀	3.3	14.4
<i>D</i> ₁₀	–	0.6

BFD is substantially finer than the UFS, with d_{90} values of 29.5 and 83.1 μm , respectively. The BFD was so fine that the d_{10} could not be determined accurately with the specific instrument utilised.

The chemical compositions of the two case study FeCr waste materials were determined with destructive (ICP–OES, LECO and AAS) and non-destructive (XRF) methods. In general, there is a relatively good correlation between the results of the two different methods (Table 2), although the destructive method is likely to provide more accurate quantitative chemical compositional results. Both these methods indicate that there is still a noteworthy amount of Cr in both these waste materials. Currently, these materials are discarded without any Cr units being recovered. Alumina, magnesium and silicates seem to be the dominant species present apart from the Cr content. This is to be expected, since these species occur in significant fractions in the chromite ore, as well as the fluxes (e.g. quartz, dolomite, magnesite, limestone) utilised in the smelting process. The Cr/Fe ratio of the BFD was 1.42 and for the UFS 1.34. These ratios are a bit lower than that of typical South African metallurgical grade chromite ore of approximately 1.5 and similar to the ratios of the UG2 process residue of approximately 1.4 (Cramer et al., 2004; Howat, 1994). However, these Cr/Fe ratios are not critical in this study since the objective was to liberate only Cr and not Fe. More Na was present in the BFD, which was expected since Na and other volatile metal species are concentrated in particles present in the off-gas of smelters. S was higher in the UFS than the BFD. This is due to the presence of calcium and magnesium in the slag phase during smelting, which results in the formation of calcium sulphide (CaS) and magnesium sulphide (MgS). In fact, all FeCr producers strive to reduce the S content of the FeCr metal. Therefore, the capturing of S in the slag phase is promoted if possible, e.g. basic slag operation that requires the addition of Ca- and/or Mg-containing materials (e.g. dolomite, magnesite, limestone). Surprisingly, the C content of the UFS was relatively

high. This could be due to two reasons. Firstly, it is likely that unreacted C-containing reductants (e.g. coke, char and anthracite) are tapped out of the taphole occasionally. This is a relatively common occurrence during periods of metallurgical instability and when the electrode closest to the taphole is short. Secondly, C enrichment in the UFS is likely due to the low density of the carbonaceous particles that will result in these particles mostly reporting to the cyclone overflow during the separation of the ultra-fine slag fraction from the coarser <1 mm slag. Zinc (Zn) was not included in the ICP–OES analysis. However, the XRF analysis clearly indicates the presence of relatively significant concentrations of Zn in both the BFD and UFS. Strobos and Friend (2004) reported a similar level of Zn in another South African FeCr BFD.

The XRD results (Table 3) show the crystalline phase compositions of the materials. The mineral names give the mineral group composition, rather than the actual compositions of the minerals identified. The most significant outcome from these XRD results is the fractional occurrences of chromite in the two case study materials, i.e. 40.1% in BFD and only 8.1% in the UFS. This indicates that the Cr content indicated by the chemical analyses of the BFD originates mostly from unreacted chromite particles. In contrast, the Cr content of the UFS is likely to be a combination of unreacted and/or recrystallised chromite, as well as FeCr particles. Due to limitations of the methods applied FeCr particles was not detected by the XRD analysis. Caution also has to be taken in the comparison of chemical (Table 2) and XRD results (Table 3). XRD only detects the crystalline phases of the sample, within the limitations of the method applied. As an example, the chromite determined with XRD only indicates the crystalline phase materials identified as chromite, and not the concentration of chromite in the overall sample. Thus, the XRD results will not necessarily be consistent with the chemical analysis.

The SEM–EDS results in Table 2 reflect the entire surface area composition of the materials (as defined in Section 2.2). Small amounts of Cr were detected on the surface of both materials, with 2.5% Cr in the BFD and 2.9% in the UFS. The Cr contents determined with chemical analysis (Table 2) were higher than that obtained with SEM–EDS. SEM–EDS could give lower Cr contents for the BFD, since Cr-containing particles could be partially or totally coated by more volatile species condensing on the surface of these particles (Beukes et al., 1999). Therefore, there were larger differences between the SEM–EDS and the chemical analysis results for the Cr content of BFD, than for the UFS. Similar to the chemical analysis, high concentrations of alumina, magnesium and silicates were found in both materials. A Na content of 2.7% was obtained for the BFD, while no Na was observed in the UFS. This also indicates the presence of volatile species condensing on the surface of BFD particles. SEM–EDS also confirmed the higher C and S contents in the UFS, as indicated by the chemical analysis. In general, the surface chemical results corresponded relatively well with the chemical analysis, except for species that could be expected to be concentrated on the surface of particles.

Fig. 1 presents SEM micrographs indicating the general surface characteristics of the two case study materials (Fig. 1a and c) and

Table 2
Chemical and surface chemical characterisation of BFD and UFS.

	BFD	UFS		BFD	UFS
ICP (%)			LECO C, S and P contents (%)		
Cr ₂ O ₃	7.66	6.04	C	1.8	14.4
FeO	4.75	3.98	S	1.3	4.2
MgO	23.60	10.30	P2O ₅ (ppm)	928	999
Al ₂ O ₃	5.85	5.86	AAS Na contents (%)		
SiO ₂	47.90	42.10	Na	2.4	1.9
CaO	0.66	0.95	XRF (%)		
TiO ₂	0.16	0.14	O	–	0.03
MnO	0.48	0.42	MgO	19.70	11.40
ICP (ppm)			Al ₂ O ₃	3.36	5.27
As	81	80	SiO ₂	33.20	36.60
Co	37	35	P ₂ O ₅	0.01	0.05
Cu	52	43	SO ₃	3.61	12.30
Mo	55	59	Cl	0.35	0.11
Ni	127	103	K ₂ O	2.07	2.55
Pb	520	1460	CaO	0.40	0.80
V	251	180	TiO ₂	0.14	0.15
Cd	<10	<10	Cr ₂ O ₃	6.52	5.30
SEM–EDS (%)			MnO	0.46	0.424
C	4.6	17.2	Fe ₂ O ₃	4.41	3.86
O	46.9	32.6	NiO	0.02	0.02
Na	2.7	–	CuO	–	0.01
Mg	13.3	5.6	ZnO	4.20	13.60
Al	2.0	1.9	Ga ₂ O ₃	0.06	0.13
Si	18.5	15.6	GeO ₂	–	0.01
S	1.7	5.2	Rb ₂ O	0.02	0.02
Cl	0.3	–	SrO	0.01	0.01
K	1.9	2.5	ZrO ₂	0.01	0.01
Ca	0.3	0.3	PbO	0.06	0.15
Cr	2.5	2.9	SnO ₂	–	0.02
Mn	0.4	0.5	Tl ₂ O ₃	–	0.03
Fe	2.0	2.2			
Zn	3.2	13.9			

Table 3
XRD analysis of BFD and UFS.

Crystalline content (%)		
	BFD	UFS
Chromite	40.1	8.1
Forsterite	52.8	22.9
Magnesioferrite	2.6	19.9
Cristobalite	3.3	
Liebenbergite	1.3	
Wurtzite	–	40.9
Quartz	–	6.6

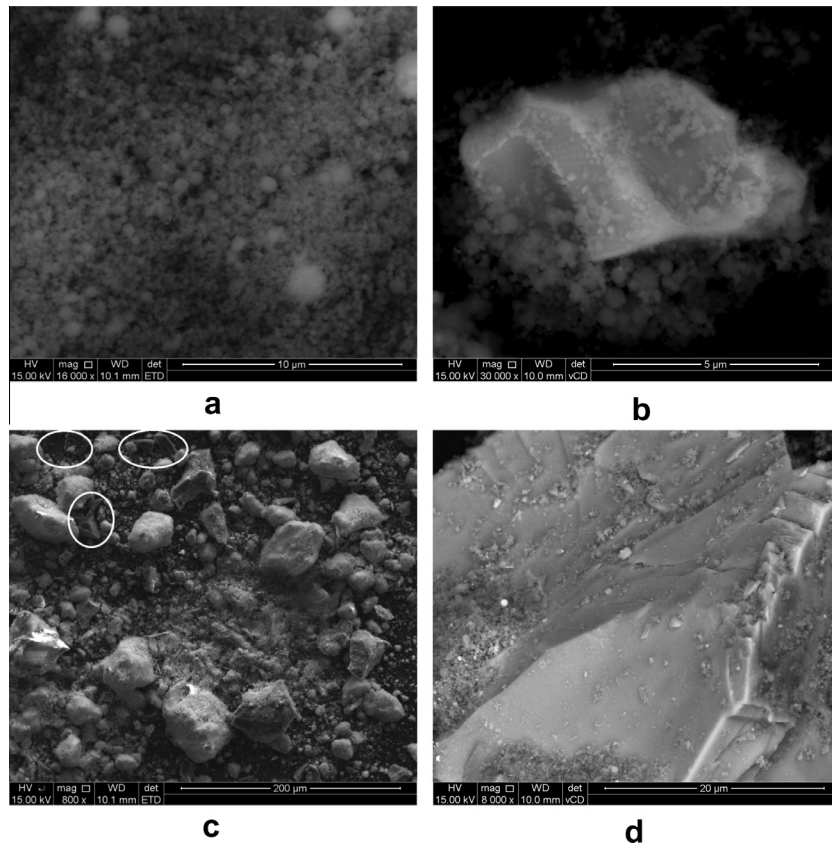


Fig. 1. SEM micrographs of: (a) a BFD sample, (b) an uneven-shaped particle in the BFD, (c) an UFS sample with the white ovals indicating C particles and (d) an uneven-shaped particle in the UFS.

Table 4
SEM-EDS analyses of: (a) the entire surface area of a BFD sample, (b) an unreacted chromite particle in the BFD, (c) the entire area of a UFS sample and (d) an unreacted chromite particle in the UFS.

Analysis number	Cr	Fe	Mg	Al	Si	S	O	Zn	Mn	C	Na	Ti	K	Ca	Cl
<i>a</i>	2.5	2.0	13.3	2.0	18.5	1.7	46.8	3.2	0.4	4.4	2.7	–	1.9	0.3	0.3
<i>b</i>	18.6	13.6	6.4	7.5	3.6	–	45.0	4.3	–	–	0.3	0.7	–	–	–
<i>c</i>	2.9	2.2	5.6	2.0	15.6	5.2	32.6	13.6	0.5	17.2	–	–	2.5	0.3	–
<i>d</i>	26.1	15.3	5.3	5.2	2.6	1.9	33.9	9.4	–	–	–	–	0.3	–	–

specific particles identified in these materials (Fig. 1b and d). In Table 4, the surface chemical composition of the two case study materials and the specific particles indicated in Fig. 1b and d are listed.

It is evident from Fig. 1a that the BFD consisted mostly of very small spherical particles. This micrograph visually confirms the earlier findings (with laser diffraction particle sizing, Table 1) that the BFD particle size distribution is very fine. The spherical shapes of most of the BFD particles suggest that these particles had formed as a result of melting or during condensation. However, the BFD particle matrix did not exclusively consist of spherical particles, since some unevenly shaped particles also occurred. An example of such an uneven-shaped BFD particle is presented in Fig. 1b. SEM-EDS analysis of this particle (Table 4, number b) indicates that it had a significantly higher Cr content than the overall surface analysis (Table 4, number a). This indicates that it is likely to be an unreacted or partially altered chromite particle. In contrast to the BFD matrix that was dominated by spherical-shaped particles, the UFS (Fig. 1c) consisted mostly of uneven-shaped particles.

The difference in particle size distribution between the two case study materials is also evident by comparing Fig. 1a with Fig. 1c (note the 20 times difference in magnification). C particles, as indicated by the white ovals in the upper left corner of Fig. 1c, are clearly present in the UFS. This agrees with the chemical analysis results, which indicated a relatively high C content in UFS. In Fig. 1d, a magnification of a particle within the UFS is presented. SEM-EDS analysis of this particle is shown in Table 4 (number d). The higher Cr content of this particle, i.e. 26.1% Cr, compared to the total UFS matrix surface analysis, i.e. 2.9% Cr, indicates that it is likely to be an unreacted chromite particle. Although not specifically shown in the SEM micrographs presented in Fig. 1, FeCr particles were also present in the UFS.

Considering all the above-mentioned characterisation results of the UFS material, it is evident that its composition differs substantially from conventional FeCr slag. This can be expected, since it was recovered from the overflow of a fine material cyclone at a typical metal recovery plant (Section 2.1). By nature the cyclone overflow material might not be representative of the bulk of the

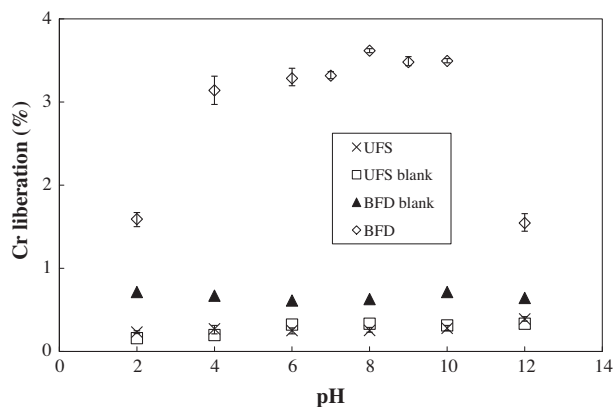


Fig. 2. The effect of aqueous media pH on Cr liberation for both the BFD and UFS. Ozonation contact time = 30 min; solid loading = 2.5 g per 150 ml; gaseous O_3 concentration = 4.5 mg/L; temperature = 24 °C.

FeCr slag, since it consists of ultra-fine particles and particles with lower density that also reported to the cyclone overflow (e.g. the unusually high C content of the UFS).

3.2. Cr liberation with aqueous ozonation

The Cr(VI) generation with aqueous ozonation that indicated Cr liberation from the waste materials was investigated as a function of pH, ozonation contact time, waste material solid loading, gaseous O_3 concentration and temperature.

3.2.1. pH dependence

Fig. 2 shows the influence of pH on the liberation of Cr(VI) from the two waste materials through the oxidation of Cr(III) and/or Cr(0) to soluble Cr(VI) during aqueous ozonation.

For the BFD, there was a substantial difference in Cr liberation between the blank and ozonation experiments. The Cr liberation from the BFD during ozonation increased with an increase in pH, reaching a maximum at pH 8. Similar levels of Cr liberation were maintained up to pH 10, where after the liberation decreased. The effect of pH on Cr liberation from the BFD during ozonation can be explained by considering previously published data. Ratpukdi et al. (2010) and Lovato et al. (2009) showed that aqueous O_3 is relatively stable at low pH levels, while its spontaneous decomposition to OH^\cdot radicals accelerate at higher pH levels. Although aqueous O_3 is a strong oxidant, the OH^\cdot radical is a stronger oxidant (Lovato et al., 2009; Von Gunten, 2003; Huang et al., 1993). Therefore, due to higher OH^\cdot radical concentrations at elevated pH levels, increased Cr liberation was observed for BFD. However, the increase in Cr liberation associated with increased pH seems to diminish for $pH > 10$. The exact reason for this observation is currently unclear. However, the extent of Cr liberation from the BFD was not very high, i.e. maximum 3.6%. It is therefore unlikely that this process would be feasible on an industrial scale.

For the UFS there was no meaningful difference in Cr liberation between the blank and ozonation experiments. This implies that neither aqueous O_3 nor its decomposition products, i.e. OH^\cdot radicals, were able to liberate Cr from the UFS by oxidation. The differences in the ability of aqueous ozonation to liberate Cr from the two case study materials can be explained by considering their characteristics (Tables 2 and 3). From the chemical and crystalline characteristics of Cr in the two waste materials it is evident that the Cr in the BFD was contained mostly in chromite or partially altered chromite particles, while the Cr in the UFS was contained mostly in FeCr particles. It is therefore feasible to postulate that the Cr(III) present in the chromite and/or partially altered chromite might

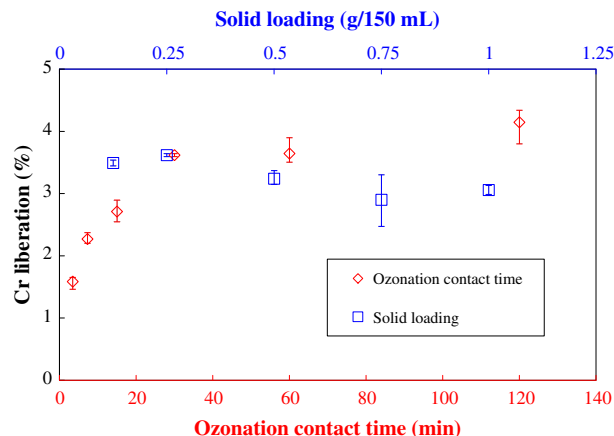


Fig. 3. The effect of ozonation contact time (primary x-axis) and solid loading (secondary x-axis) on Cr liberation for BFD. pH = 8; ozonation contact time = 30 min (for solid loading only); solid loading = 2.5 g per 150 ml (for ozonation contact time only); gaseous O_3 concentration = 4.5 mg/L; temperature = 24 °C.

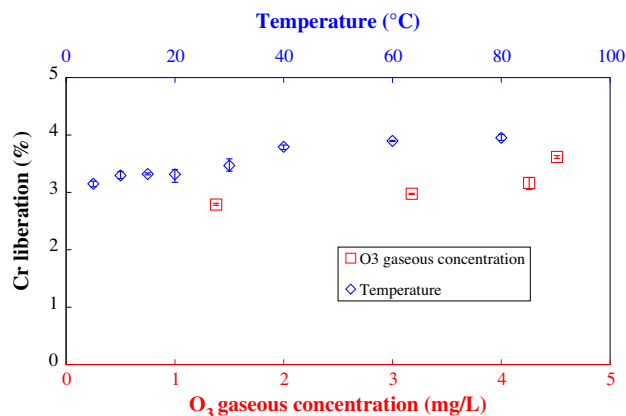


Fig. 4. The effect of O_3 concentration (primary x-axis) and temperature (secondary x-axis) on Cr liberation for BFD. pH = 8; ozonation contact time = 30 min; solid loading = 2.5 g in 150 ml; gaseous O_3 concentration = 4.5 mg/L (for temperature only); temperature = 24 °C (for O_3 concentration only).

be more susceptible to oxidation to Cr(VI) than the metallic Cr(0) present in the FeCr. It is well known that Cr(0) enhances the corrosion resistance of materials. Due to the inability of aqueous ozonation to liberate Cr from the UFS, only the liberation of Cr from the BFD was considered in subsequent sections (Section 3.2.2 to 3.2.5), focusing on the effect of other process-controlling parameters.

3.2.2. Ozonation contact time dependence

In order to establish the influence of ozonation contact time on the liberation of Cr, the contact time was varied from 4 to 120 min. The effect of contact time was only investigated at pH 8, since it was the optimum pH for Cr liberation from BFD (Fig. 2). The results presented in Fig. 3 on the primary x-axis indicate that longer contact times increase the liberation of Cr. However, after 30 min, the Cr liberation started to stabilise with no significant increases in Cr liberation at longer contact times.

3.2.3. Waste material solid loading dependence

The effect of the amount of BFD solid loading in the aqueous medium at pH 8 (optimal pH) during ozonation is presented in Fig. 3 on the secondary x-axis. From these results, it is evident that there was almost a linear relationship with lower solid loading

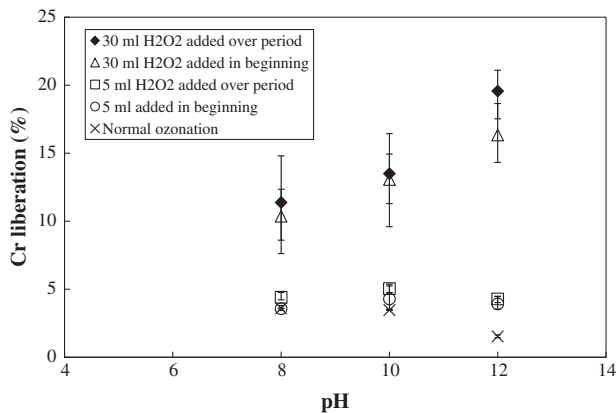


Fig. 5. Cr liberation for BFD with the advanced oxidation process. pH = 8–12; ozonation contact time = 30 min; solid loading = 2.5 g in 150 ml; gaseous O₃ concentration = 4.5 mg/L; temperature = 24 °C.

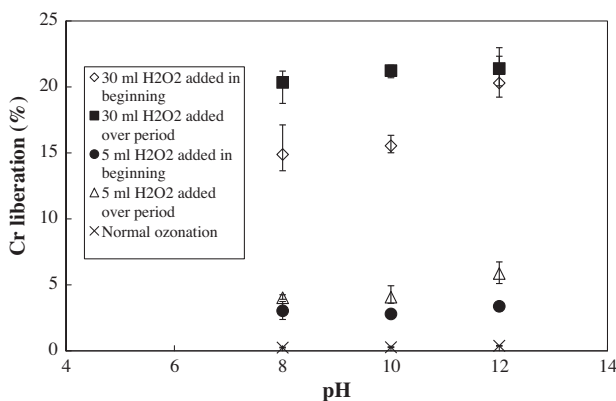


Fig. 6. Cr liberation for UFS with the advanced oxidation process. pH = 8–12; ozonation contact time = 30 min; solid loading = 2.5 g in 150 ml; gaseous O₃ concentration = 4.5 mg/L; temperature = 24 °C.

resulting in higher Cr liberation. This was expected, since higher oxidant concentrations per particle will result in more oxidation.

3.2.4. O₃ concentration dependence

In Fig. 4 on the primary x-axis, the effect of O₃ gaseous concentration on Cr liberation at pH 8 (optimum pH) from the BFD is shown. Four different O₃ concentrations were considered. The highest concentration that could be generated by the O₃ generator used was 4.5 mg/L, which was considered to be an experimental limitation. However, notwithstanding the limited O₃ concentration range evaluated, it is evident from the results that Cr liberation increased with increasing gaseous O₃ concentration. The increased O₃ concentration resulted in a higher OH[•] radical concentration from O₃ decomposition, thereby increasing the amount of Cr liberated through oxidation to Cr(IV).

3.2.5. Temperature dependence

In Fig. 4 on the secondary x-axis, the effect of the aqueous ozonation reaction temperature (between 5 and 80 °C) on the liberation of Cr from the BFD at pH 8 (optimum pH) is presented. It can be seen that Cr liberation increases with an increase in temperature. An increase in temperature will lead to an increase in O₃ decomposition (Elovitz et al., 2008; Beltrán, 2003), which will therefore increase the concentration of OH[•] radicals. As indicated previously,

OH[•] radicals are likely to be the species that are mainly responsible for the oxidation and liberation of Cr in this reaction system.

3.3. Cr liberation with the advanced oxidation process

Since the maximum liberation of Cr with aqueous ozonation was relatively low, i.e. 4.2%, Cr liberation with the advanced oxidation process was also investigated. The advanced oxidation process can be applied in various ways (Bragg et al., 2012; Wu et al., 2004). In this specific study, it was decided to add H₂O₂ during ozonation. According to Rosenfeldt et al. (2006) and Beltrán (2003), the addition of H₂O₂ accelerates the decomposition of aqueous O₃ into OH[•] radicals. Additionally, the H₂O₂ itself also decomposes to form OH[•] radicals causing an even higher OH[•] radical concentration (Bragg et al., 2012; Rodman et al., 2006). If our earlier postulation, i.e. that OH[•] radicals are mainly responsible for the liberation of Cr through oxidation to Cr(VI), was valid, then the addition of H₂O₂ should enhance Cr liberation.

Since the decomposition of H₂O₂ is favoured at high pH levels (Rosenfeldt et al., 2006), it was decided to perform the advanced oxidation process with H₂O₂ addition during ozonation at pH 8, 10 and 12. H₂O₂ can also serve as a reducing agent for Cr(VI) to Cr(III) at low pH levels (Perez-Benito and Arias, 1997). The liberation of Cr with the advanced oxidation process is presented in Fig. 5 for the BFD and in Fig. 6 for the UFS at the selected pH values. By comparing these results with the liberation results obtained by only utilising aqueous ozonation, it can be stated that Cr liberation was increased significantly. Cr liberation from the BFD was up to five times higher, while up to 20 times higher Cr liberations were achieved from the UFS.

Figs. 5 and 6 illustrate three different process controlling parameters that were tested for each waste material, i.e. the influence of pH, volume H₂O₂ added and method of H₂O₂ addition. From both these figures, three important deductions can be made. Firstly, increased pH resulted in higher Cr liberation. As previously stated, this is related to higher OH[•] radical concentrations at higher pH levels, which was due to H₂O₂ decomposition (Bragg et al., 2012; Rodman et al., 2006; Rosenfeldt et al., 2006). Secondly, higher volumes of H₂O₂ addition resulted in substantially higher Cr liberation. This was due to higher concentrations of OH[•] radicals formed as a result of the combined decomposition of O₃ and added H₂O₂ into OH[•] radicals. Lastly, improved Cr liberation was obtained if H₂O₂ addition was made over the entire contact time, instead of the addition of the total volume at the beginning of the experiment. The latter observation can be attributed to the decomposition of H₂O₂ that occurs relatively fast (Rosenfeldt et al., 2006). In addition, the half-life of the OH[•] radicals formed is also short (Staehelin and Hoigné, 1982; Rosenfeldt et al., 2006). Therefore, the addition of H₂O₂ over the entire experiment ensured consistently higher OH[•] radical concentrations in the aqueous medium, which allowed the liberation of more Cr through oxidation.

4. Conclusions

In this paper, two relatively novel procedures to liberate Cr from fine FeCr waste materials were investigated. Limited Cr liberation could be attained from the waste materials by utilising aqueous ozonation to form soluble Cr(VI). For BFD, a maximum of only 4.2% Cr liberation was achieved by studying the influence of several process controlling factors, which included pH, ozonation contact time, waste material solid loading, gaseous O₃ concentration and aqueous media temperature. However, the Cr liberation of BFD was substantially higher than that achieved for the UFS, which was attributed to the difference in characteristics of the two mate-

rials, i.e. the Cr content in BFD was mostly related to chromite and/or altered chromite particles, while the Cr content of the UFS was mostly related to FeCr particles. Comparison of the results presented in this paper with that of Van der Merwe et al. (2012) indicated that Cr liberation from UG2 chromite ore with aqueous ozonation, was much worse than what was achieved for BFD and UFS. It can therefore be concluded that it is more difficult to liberate Cr from unaltered chromite, than from waste materials wherein the Cr occurs in an altered form. The Cr liberation observed was attributed to the formation of OH[•] radicals during the spontaneous decomposition of aqueous O₃. These radicals are extremely strong oxidising agents.

Although not investigated in such detail, application of the advanced oxidation process by the addition of H₂O₂ during ozonation increased Cr liberation dramatically. 21.1% and 22.3% Cr liberation could be achieved for the BFD and UFS, respectively. The advanced oxidation process provided significantly better results than the aqueous ozonation process, since the addition of H₂O₂ resulted in substantially higher OH[•] radical concentrations that promoted Cr(VI) formation by oxidation.

Although the above-mentioned levels of Cr-liberation are unlikely to be industrially feasible at present, the investigation proved that further research of especially the advanced oxidation process could optimise Cr-liberation further. During this investigation, O₃ concentrations were limited by the O₃ generator used and only H₂O₂ addition was tested as an example of the advanced oxidation process. The H₂O₂ volume addition was also limited. In future studies, several other peroxide compounds could be considered, while UV radiation and Fe²⁺ addition could also be used to further enhance the process. From the results, it was also evident that the level of Cr liberation depended on the nature of the waste material. Large differences might occur in fine FeCr waste materials between different smelters, due to different smelting technologies (e.g. closed or open/semi-closed SAF, DC arc furnaces, pelletised or ore fed furnaces) and different process control philosophies (e.g. slag basicity) being applied. It is therefore possible that research focusing on a specific fine FeCr waste material, with optimised advanced oxidation process conditions, might result in substantially better Cr liberation. Additional milling of waste materials might also enhance Cr liberation, but that was not considered in this paper. An important future perspective should be to investigate the actual mechanism of Cr liberation by the OH[•] radical, especially for the advanced oxidation process options. Such mechanistic information would further enable optimisation of the process.

If higher Cr liberation levels can technically be achieved, future research could also consider the techno-economic aspects. The Cr(VI) liberated from the FeCr waste material could be reduced to non-soluble Cr(III) hydroxides in the aqueous media, where after these Cr units could be fed back to the FeCr smelting process. If an aqueous reducing agent other than Fe(II) is used, such Cr(III) hydroxide material could theoretically contain no Fe, which could boost the overall Cr/Fe ratio of the feed material.

In addition, it is well known that the alkaline roasting process to produce Cr(VI) chemicals is not considered to be environmentally friendly and also not ideal from an occupational health perspective. Generating Cr(VI) in aqueous media, as indicated here, could be considered as an alternative in the production of Cr(VI) chemicals, especially since such Cr(VI) compounds could be produced from waste material instead of chromite ore.

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Chapter 4

Project evaluation and future prospective

4.1 Project evaluation in relation to objectives

The specific objectives of this project were stated in Chapter 1, Par 1.2. The project evaluation was discussed in accordance with these objectives. A future perspective is presented in the evaluation of the final objective of this study.

- i) *Obtaining case study waste materials (BFD and UFS) from a large South African FeCr producer and perform a detailed characterisation of both these materials.*

BFD and UFS were obtained from ASA Metals – a large South African FeCr producer. Extensive material characterisation was conducted on both waste materials obtained. The particle size distribution was determined for both materials and it was found that BFD consists of much smaller particles than UFS. XRD was also performed, which provided more information on the crystalline content of the waste materials. The surface and total chemical analyses presented more information on what the waste materials consisted of. All the afore-mentioned characterisation information was used to interpret observations during subsequent Cr liberation experiments.

ii) *Determining the liberation of Cr units from BFD and the UFS through the use of aqueous ozonation.*

A limited fraction of Cr could be liberated from BFD with aqueous ozonation, while almost no Cr could be liberated from the UFS. An explanation for the weaker Cr liberation from UFS could be attributed to the differences in the characteristics of the two materials. The results presented by Van der Merwe et al. (2012) clearly indicate that Cr liberation from UG2 chromite ore was much less compared to the Cr liberation achieved from BFD and UFS. The Cr content of BFD was mainly retained in chromite and/or partially altered chromite, while the Cr content of the UFS was mostly related to FeCr particles. Therefore, it is possible that the Cr(III) present in the chromite and/or partially altered chromite might be more susceptible to oxidation to Cr(VI) than the metallic Cr(0) present in the FeCr. The Cr liberated through this process was attributed to the formation of OH[•] radicals from the spontaneous decomposition of aqueous O₃, which is a very strong oxidant in water. The OH[•] radicals could oxidise the Cr(III) present in the waste material to water soluble Cr(VI), leading to the liberation of Cr from the waste material.

iii) *The investigation of the above-mentioned reaction system as a function of pH, ozonation contact time, waste material solid loading, gaseous O₃ concentration and temperature.*

Cr liberation from BFD increased with an increase in pH, with the highest liberation of 3.6% achieved at a pH 8 with aqueous ozonation. The decomposition of O₃ into OH[•] radicals accelerates at higher pH levels, leading to higher liberations achieved at higher pH levels. The Cr liberation from the UFS showed no meaningful differences at different pH levels with almost no Cr liberation occurring. Therefore, the influence

of the other parameters on Cr liberation was only investigated for BFD. Longer ozonation contact times resulted in the liberation of more Cr from BFD. The effect of solid loading correlated linearly with higher Cr liberation for larger solid loads. An increase in O₃ concentration also resulted in higher levels of Cr liberation. Temperature had a significant influence on the Cr liberation with higher Cr liberation occurring at higher temperatures. O₃ decomposes faster at higher temperatures, which will result in a higher OH[•] radical concentration. The maximum Cr liberation that could be achieved with aqueous ozonation was 4.2% for BFD.

- iv) *Determining the liberation of Cr units from BFD and UFS through the use of the advanced oxidation process.*

Various process combinations of the advanced oxidation process can be applied. In this study, H₂O₂ was added during aqueous ozonation. The Cr liberation from both waste materials was substantially higher with the advanced oxidation process compared to only applying aqueous ozonation. The advanced oxidation process enhances the formation of OH[•] radicals, which are responsible for the oxidation of Cr. Cr liberation achieved with the advanced oxidation process for the BFD was approximately 5 times higher than that achieved with aqueous ozonation and approximately 20 times higher for UFS. Therefore, the added H₂O₂ makes a substantial difference in the oxidation process.

- v) *The investigation of the above-mentioned reaction system as a function of pH, volume H₂O₂ added and the method of H₂O₂ addition.*

For the advanced oxidation process, the influence of pH was investigated by conducting the experiments at pH 8, 10 and 12. Similar to aqueous ozonation, higher

Cr liberation was achieved at higher pH levels due to an increase in concentrations of OH[•] radicals that enhances the oxidation of Cr. The addition of larger volumes of H₂O₂ resulted in higher Cr liberations, which was also ascribed to the associated higher OH[•] radical concentrations with the larger volume of H₂O₂. The influence of the method of addition of H₂O₂ was also investigated. The differences between adding the entire volume of H₂O₂ at the beginning of the experiment or by adding the H₂O₂ over the entire duration of the experiment were determined. The addition of the H₂O₂ over the entire duration of the experiment resulted in higher levels of Cr liberation. Since the decomposition of H₂O₂ occurs relatively fast, the addition of H₂O₂ throughout the entire experiment ensured consistently higher OH[•] radical concentrations during the advanced oxidation process.

- vi) *Making recommendations with regard to the industrial relevance of this process and/or environmental implication thereof.*

Although the Cr liberation achieved with the advanced oxidation process was much higher compared to the level of Cr liberation achieved with aqueous ozonation, the highest Cr liberation that could be achieved was still relatively low (21.1% for BFD and 22.3% for UFS). Therefore, the industrial application of this process is still unlikely to be feasible. However, since a significant increase in Cr liberation was observed with the advanced oxidation process, the possibility exists that with further investigation the process could be optimised to yield higher levels of Cr liberation. O₃ concentrations applied in the experiments were also limited by the O₃ generator used and higher O₃ concentrations could result in more Cr liberation. The addition of larger volumes of H₂O₂ to the process could also possibly produce better results. The

advanced oxidation process could also be conducted by adding other peroxide compounds or by utilising UV radiation. There are many alternative ways in which the advanced oxidation process can be conducted. A thorough investigation of the mechanism of Cr liberation by OH^\bullet radicals during the advanced oxidation process would provide more knowledge on the optimisation of the process. If the liberation of Cr can substantially be increased, there are several different methods through which such a process could be integrated with current operations. For instance, the Cr(VI) liberated from the waste material could be reduced to non-soluble Cr(III) hydroxides in the aqueous media, where after these Cr units could be fed back to the FeCr smelting process. The aqueous Cr(VI) generated from the waste materials can also be used as an alternative method for the production of Cr(VI) chemicals. The alkaline roasting process used in the production of Cr(VI) chemicals is not a particularly environmentally friendly process and with many health risks involved. Therefore, the utilisation of FeCr waste materials instead of chromite ore that is currently used to produce these chemicals is an optimistic future prospective.

4.2 Overall project evaluation

As indicated in the previous section, the project outcomes successfully met the specific objectives that were set for this study. Furthermore, the results obtained were published in a peer-reviewed journal, which exceeds the minimum requirements of an MSc study prescribed by the NWU. Although there are certain shortcomings in this investigation, the project can generally be regarded as being successful.

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