

Comparison of physical properties of oxidative sintered pellets produced with UG2 or metallurgical grade South African chromite – a case study

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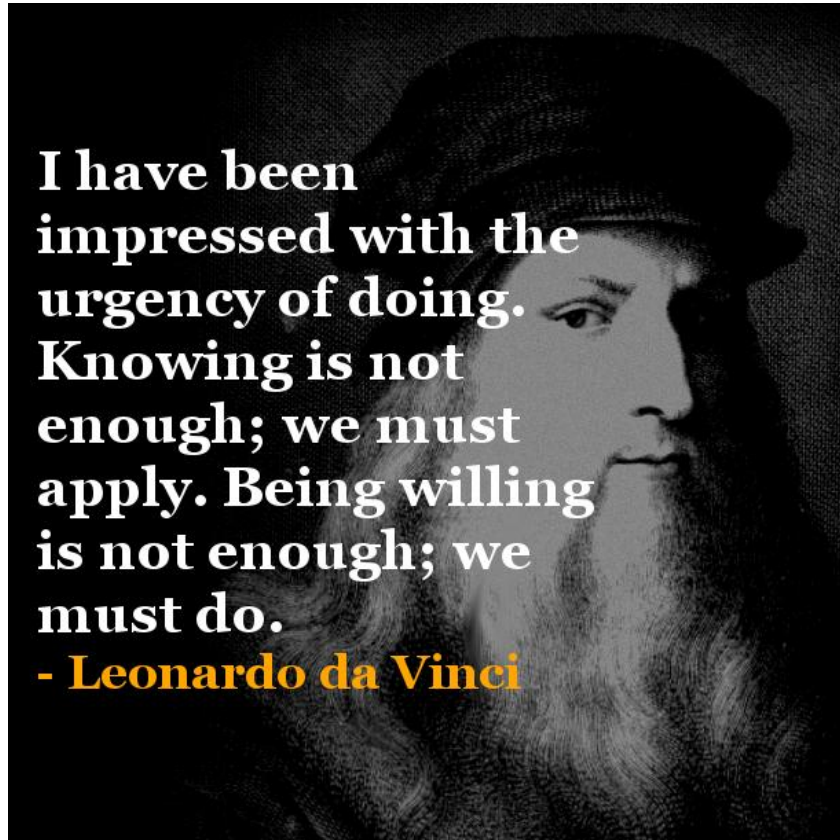
Dissertation submitted in partial fulfilment of the requirements for the degree *Magister Scientiae* in *Chemistry* at the Potchefstroom Campus of the North-West University

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May 2014



ACKNOWLEDGEMENTS



Firstly and most importantly I would like to thank my loving Father in heaven for blessing me in more ways than I could ever deserve. Through You all things are possible.

I would also like to thank my mother, Norma, and my father, Reg, my brother Reggie and my sisters Lisa and Daggie for helping me to get where I am today with their love and support.

Thank you to my mentors, Paul Beukes and Pieter van Zyl for all your guidance, patience and friendship with which you attend to each and every one of your students.

Special thanks to my friends, Monique Loock and Yolindi van Staden. Both of you always motivated and encouraged me when I needed it.

Last, but by no means least, I want to thank my grandmother Tienie Glastonbury for always believing in me.

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 for publication. The conventional experimental, 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 or similar text appearing in some of the chapters and in the article. The numbering of Chapter 3 (article) is also not consistent with the rest of the dissertation, since it was added in the exact format as it was submitted to the journal. The figures and tables of Chapter 3 are also added at the end of the text as prescribed by the journal.

Rationale in submitting dissertation in article format

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

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

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Contributions to article

The contributions of the various co-authors were as follows. The work was conducted by me, Ralph Glastonbury, 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. L.N. Sadiki assisted with the stirred mill test, A. Jordaan aided with the SEM analysis and Q.P. Campbell assisted with the particle size analysis. All three these afore-mentioned authors who assisted with analytical procedures also provided conceptual recommendations or comments on the draft article. H.M. Stewart and N.F. Dawson were mainly responsible for partial funding of the project and also gave conceptual recommendations or comments on the draft article.

Formatting and current status of article

The article was formatted in accordance with the journal specifications to which it was submitted, i.e. *Minerals Engineering*, which is an Elsevier journal. The guide to the authors 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).

Declaration by co-authors:

All the co-authors of the article had the opportunity to comment on the draft article as included in Chapter 3 and gave consent that it can be included in this MSc dissertation.

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ABSTRACT

The Bushveld Igneous Complex (BIC) in South Africa holds approximately three quarters of the world's viable chromite ore deposits. Most chromite is used for the production of ferrochromium (FeCr), which is a relatively crude alloy. Several chromite seams exist in the BIC. The most economically viable seams are the lower group 6 (LG6), the middle group 1 and 2 (MG1 and 2) and the upper group 2 (UG2) seams. The LG and MG seams are exploited specifically for their chromium content, whereas the UG2 seam is mainly exploited for platinum group minerals (PGM). However, the upgraded UG2 chromite in the PGM tailing is increasingly being used as a feedstock for FeCr production. Many different process variations exist for FeCr production. However, the process option applied in most green and brown field FeCr expansion projects during the last two decades in South Africa has been the oxidative sintered process (also referred to as the Outotec or Outokumpu process). Notwithstanding the common application of the oxidative sintered pelletised feed technology in the South African FeCr industry, and the increased utilisation of beneficiated UG2 ore, a direct comparison of the physical properties of oxidative sintered pellets produced from UG2 with the physical properties of that produced with conventional metallurgical grade chromite ore is currently lacking in the peer-reviewed scientific literature. Therefore, the physical properties of oxidative sintered pellets produced from a typical beneficiated South African UG2 ore were compared with the physical properties of that produced with conventional South African metallurgical grade chromite ore in this study.

The results indicated that the case study metallurgical grade chromite ore required 13 kWh/t more energy to mill than the case study UG2 ore prior to pelletisation, which can lead to substantial cost savings. The compressive strength of the oxidative sintered pellets of both case study ores statistically showed that oxidative sintered pellets made from UG2 ore

were the same or better than those prepared from metallurgical grade chromite ore. A comparison of the abrasion strengths of the oxidative sintered pellets of both case study ores indicated that the pellets prepared from UG2 ore were superior compared to the metallurgical grade pellets. The reasons for the superior UG2 pellet strength were investigated with backscatter-, secondary electron- and elemental X-ray mapping scanning electron microscopy (SEM), which indicated that differences in crystalline structures at least partially contributed to the differences observed. Results presented here can be utilised by FeCr producers to better quantify the advantages and disadvantages associated with the use of UG2 ore for FeCr production.

Keywords: South Africa; UG2 and metallurgical grade chromite; oxidative sintered pellets; compressive and abrasion strengths; milling energy requirements

CHAPTER 1

BACKGROUND, MOTIVATION AND OBJECTIVES

1.1 Project background and motivation

Since the discovery of chromite in 1798, it has remained the only commercially recoverable source of new chromium units (Niagru, 1988; Cowey, 1994; Riekköal-Vanhanen, 1999). Geologically, commercial chromite deposits in the world are found in three forms, i.e. alluvial-, podiform- and stratiform-type deposits (Murthy et al., 2011, Cramer et al., 2004). The chromite ore reserves in South Africa are the largest example of a stratiform-type chromite and are held in the Bushveld Igneous Complex (BIC) (Howat, 1994, Cramer et al., 2004), which holds between 74% (Cowey, 1994) and 80% (Riekköal-Vanhanen, 1999) of the world's viable chromite ore reserves.

Several chromite seams exist within the BIC. The most economically interesting seams are the lower group 6 (LG6), the middle group 1 and 2 (MG1 and 2) and the upper group 2 (UG2) (Cramer et al., 2004). The LG and MG seams are exploited specifically for their chromium content, whereas the UG2 seam is exploited for platinum group minerals (PGM) (Xiao and Laplante, 2004). The extraction of the PGMs from the UG2 ore usually involves the liberation of the sulphite-containing PGMs with milling and subsequent recovery of the PGM concentrates through floatation (Xiao and Laplante, 2004, Nel and Theron, 2004). The chromite present in the beneficiated PGM concentrate is unwanted and therefore mostly transpires in the tailings of the PGM recovery circuit. However, the chromite in the PGM tailings can potentially serve as feedstock for ferrochrome (FeCr) production, after beneficiation thereof to increase the chromium content and/or the chrome-to-iron ratio (Cr/Fe).

The price that a FeCr producer is prepared to pay for UG2 is determined by balancing the advantages and possible disadvantages associated with the use thereof. Advantages related to the use of UG2 by South African FeCr producers include:

- The utilisation of UG2 for FeCr production minimises tailing volumes for PGM producers, which also has associated financial benefits, e.g. tailing waste storage facilities can comparatively be smaller.
- The use of UG2 contributes to the optimum utilisation of natural resources, since additional mining is avoided. This also reduces the carbon footprint of FeCr producers.
- The overall safety risk associated with FeCr production is much lower if the mining of new chromite units can be reduced by the utilisation of upgraded UG2 tailing originating from PGM operations. Although this is not a direct financial or technical benefit, the safety-, health- and environmental (SHE)-related aspects are just as important as production volumes and profit margins in the modern-day industrial setting.

The disadvantages associated with the substitution of metallurgical grade chromite ore with UG2 during FeCr production include:

- The Cr/Fe ratio of UG2 ore is usually lower than that of metallurgical grade ore originating from LG6 or the MG1/2 BIC seams (Cramer et al., 2004). Chromite does not only contain Fe and Cr, but also magnesium (Mg) and aluminium (Al) in varying proportions that depend on the deposit. The chemical composition of chromite can be represented by the chemical formula $(\text{Mg}, \text{Fe}^{+2}) (\text{Cr}, \text{Al}, \text{Fe}^{+3})_2\text{O}_4$ (Murthy et al., 2011). In this spinel structure, Fe^{2+} can be replaced by Mg and similarly Cr can be replaced by Fe^{3+} and Al. This variation in composition can result in substantial differences in the Cr/Fe ratio of specific chromite deposits.

Since Fe oxides are reduced easier (at lower temperatures) than Cr oxide (Niemelä et al., 2004), Fe recovery from ore is higher than that of Cr recovery. Therefore, the lower Cr/Fe ratio of UG2 ores results in the lower Cr content of the FeCr produced. Since FeCr producers are only paid for the Cr content of FeCr, UG2 utilisation has a disadvantage in this regard.

- The above-mentioned dilution of Cr content in the FeCr produced from UG2 also results in higher transport cost per Cr unit. This is significant, considering that most of South Africa's FeCr is exported to stainless steel producers in Europe, Asia and North America. This additional transport cost also increases the overall carbon footprint of FeCr production in South Africa.
- Cramer et al. (2004) reported that the higher Ti content of UG2 could also be problematic, since some stainless steel producers have specifications for the Ti content of the FeCr.

FeCr in SA is produced with a variety of process combinations, which were recently reviewed (Beukes, 2010). Of the thirteen full-time South African FeCr smelters (there is also one part-time smelter) (Jones, 2011), at least eight utilise the oxidative sintered pelletised feed process (Beukes et al., 2012).

Notwithstanding the common application of the oxidative sintered pelletised feed technology in the South African FeCr industry, and the increased utilisation of beneficiated UG2 ore as an ore feedstock into this process, a direct comparison of the physical properties of oxidative sintered pellets produced from UG2 with the physical properties of that produced with conventional metallurgical grade chromite ore (from the LG6 or the MG1/2 seams) is currently lacking in the peer-reviewed scientific literature. Singh and Rao (2008) reported the impacts of properties of different chromite ores of Indian origin on pelletisation and sintering. Although knowledge can be gained from similar studies as presented by Singh and Rao

(2008), it cannot be used to exactly predict the performance of South African UG2 ore in the oxidative sintered process. This deficiency in knowledge was recently highlighted by a large South African FeCr producer that requested the candidate to investigate this topic. This FeCr producer indicated that some negative aspects associated with the physical properties of oxidative sintered pellets produced from UG2 ore were being reported by operational personnel. This has resulted in some operational resistance to the use of large fractions of UG2 ore in the oxidative sintered process, notwithstanding that these reports were not scientifically founded.

1..2 Project objectives

In this study, the properties of oxidative sintered pellets produced from a typical South African BIC metallurgical grade chromite ore will be compared to that produced from a typical South African BIC UG2 ore. The detailed objectives include:

- Detailed characterisation of the two case study ores.
- Production of oxidative sintered pellets from the case study ores with a procedure simulating the industrially applied process.
- Comparison of abrasion and breaking strengths of pellets produced with the above-mentioned procedure.
- Determination of the energy requirements for milling the two case study ores.
- Making recommendations with regard to the industrial use of UG2 ore in the oxidative sintered process.

CHAPTER 2

LITERATURE SURVEY

2.1 General information relating to chromium

2.1.1 Brief historical perspective

On 26 July 1761, Johann Gottlob Lehmann found an orange-red mineral in the Beryozovskoye mines in the Ural Mountains that he named *Siberian red lead*, which was later named Crocoite (Guertin *et al.*, 2005; Rosa, 2008). In 1797, the French chemist Louis Nicolas Vauquelin produced chromium trioxide (CrO_3) by mixing crocoite with hydrochloric acid. A year later, he isolated metallic chromium (Cr) by heating CrO_3 in a charcoal oven (Nriagru, 1998a; Roza, 2008; Vauquelin, 1798). He named this metal chromium, which is derived from the Greek word “chrōma” (χρῶμα), meaning colour (Emsley, 2003).

During the early 1800s, Cr was primarily used as a compound in paints and tanning salts (National Research Council (U.S), 1974; Guertin *et al.*, 2005). In 1821, French scientist Pierre Berthier found that when Cr was alloyed with iron (Fe), the new metal alloy was able to resist corrosion (Roza, 2008). Unfortunately, it was too brittle for practical applications. During the next fifty years, many scientists experimented with combinations of Cr, Fe and other metals and minerals. In 1872, two Englishmen, Woods and Clark, filed a patent for a weather-resistant Fe alloy that contained 30-35% Cr and 2% tungsten (W) (Roza, 2008), which was one step closer to the discovery of stainless steel. French chemist Henri Moissan heated ore that contained Cr and Fe in an electric furnace with coke (carbon) in 1893. The result was an alloy that he named ferrochrome (FeCr). This metal contained large amounts of Cr and small amounts of carbon (C) that made the metal stronger. Since then, many scientists

have experimented with various concentrations of C, Fe and Cr until stainless steel as we know it today was developed.

2.1.2 Natural occurrence

Cr is the 21st most abundant element in the earth's crust (Emsley, 2003; Nriagu, 1988), although chromite is the only source of Cr that is economically feasible to commercially exploit (Rosa, 2008; IETEG, 2005; Nriagu, 1988).

Most of the major Cr deposits known occur in three principal geological settings (Nriagu, 1988b):

- Stratiform-type deposits, such as the Bushveld Igneous Complex (BIC) of South Africa, the Great Dyke in Zimbabwe and the Kemi intrusion of Finland. These deposits account for over 90% of the identified Cr ore resources.
- Podiform-type or Alpine-type deposits generally associated with island-arcs and the major tectonic belts, such as the Tethyan mountain chains and Ural Mountains. These deposits account for 10% of the world's Cr ore resources.
- Lateritic deposits, which are generally derived from the weathering of Cr-bearing peridotites. Few of these deposits have been exploited profitably.

Mining of chromite deposits is carried out by open-pit and by underground mining. The most intensive mining occurs in the BIC in South Africa, which is one of the world's great mineral treasure chests. According to the United States Geological Survey (USGS), world resources of chromite exceed 11×10^{12} kg and are sufficient to meet world demand for many centuries to come.

2.1.3 Uses of Cr

Different industrial applications require different forms of Cr, such as chromite, FeCr, Cr metal, stainless steel, chromite refractory bricks, chromite foundry sands, chromic acid

and other Cr-containing compounds or alloys. The ~25 million tons of chromite produced in 2011 (ICDA, 2012) was distributed among three principal industrial end uses, i.e. metallurgical, refractory and chemical applications. Of these, metallurgical application was by far the largest, which was estimated to consume ~91% of all mined chromite (ICDA, 2012).

2.2 Cr in South Africa

2.2.1 Economic and market considerations

Although this dissertation is for the most part technically orientated, a small section is devoted to understanding the economic and market considerations impacting on the local FeCr industry, which are therefore briefly discussed.

Although chromite ore is mined in over 20 countries, approximately 80% of chromite originates from four countries, i.e. South Africa, India, Kazakhstan, and Turkey, with South Africa producing approximately 37% of the world's chromite ore (ICDA, 2010; Papp, 2009b; Papp, 2008).

As mentioned in Par. 2.1.3, the majority of chromite is converted into FeCr, which is predominantly consumed in the production of stainless steel (CRU, 2010; ICDA, 2012). It is therefore useful to consider the correlation between chromite, FeCr and stainless steel production volumes. Figure 2–1 indicates that there is a direct correlation, with some lags, between the production volume trends of these commodities.

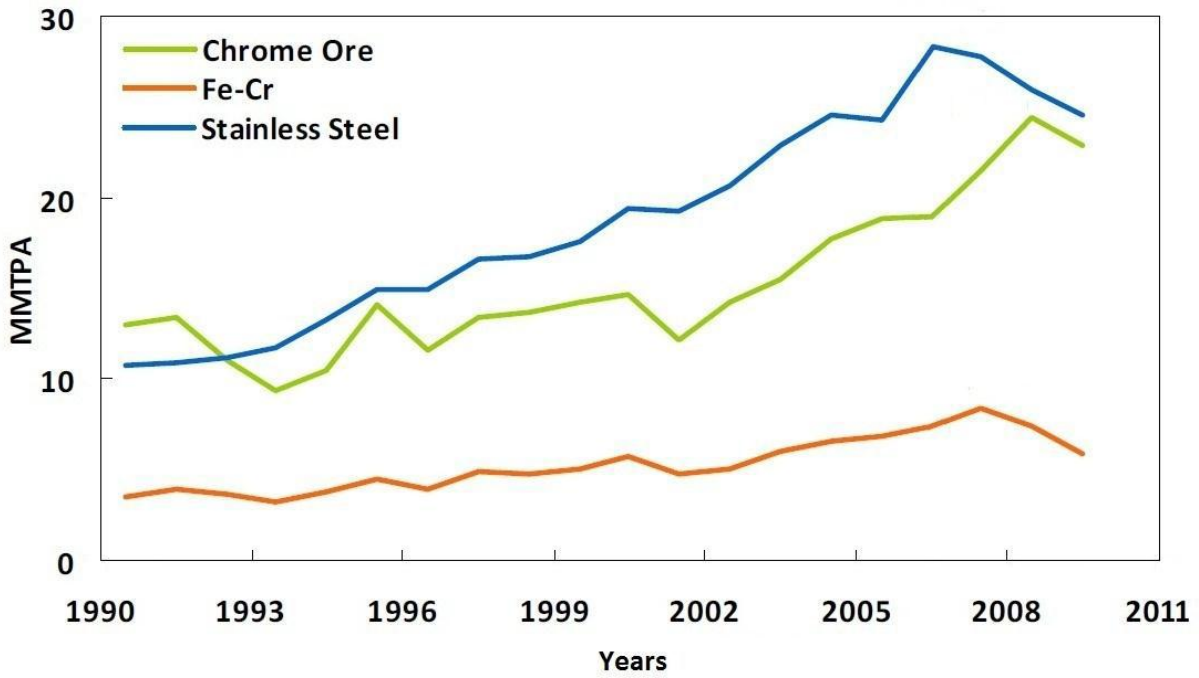


Figure 2–1: World production of chromite ore, FeCr and stainless steel in million metric tons per annum (MMTPA) for 1990-2009 (Ideas 1st Research, 2010)

From Figure 2–1, it is evident that an increase in the demand for stainless steel will escalate the demand for FeCr. This could either lead to a supply deficiency and a rise in FeCr prices or an increase in FeCr production, or both of these scenarios. Figure 2–2 indicates the correlation between the stainless steel and FeCr price indexes.

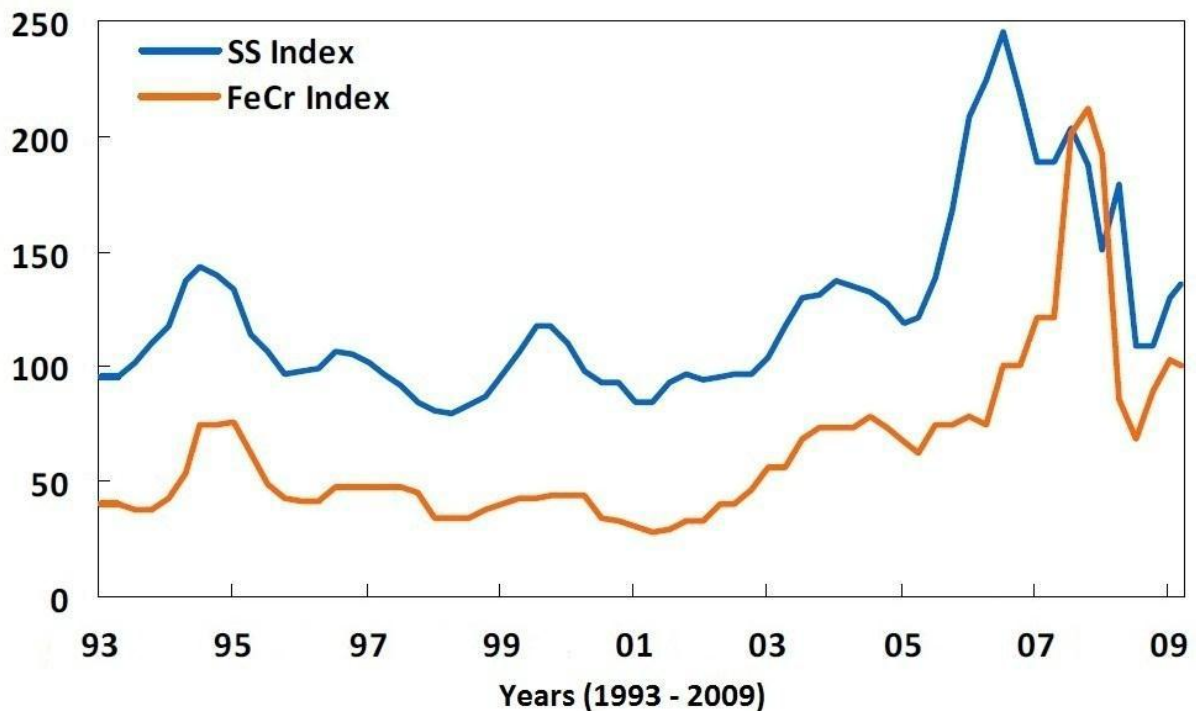


Figure 2–2: Stainless steel (SS) and FeCr price indexes (CRU, 2010; Ideas 1st Research, 2010)

The South African rand foreign exchange rate is a potential significant factor in the price of chromite ore and FeCr, since South Africa is a leading producer of these commodities (Papp, 2008). South Africa is also the largest and second largest exporter of platinum (Pt) and gold (Au), respectively, therefore it is expected that these two markets would also have a significant influence on the strength of South Africa’s currency (Ideas 1st Research, 2010). Figure 2–3 shows the monthly average exchange rate between the South African Rand (ZAR) and the United States dollar (US\$) between May 2005 and August 2013 (Pacific Exchange Rate Service, 2013). These exchange rate fluctuations clearly indicate the volatility of the ZAR and the possible financial impacts on the South African FeCr industry.

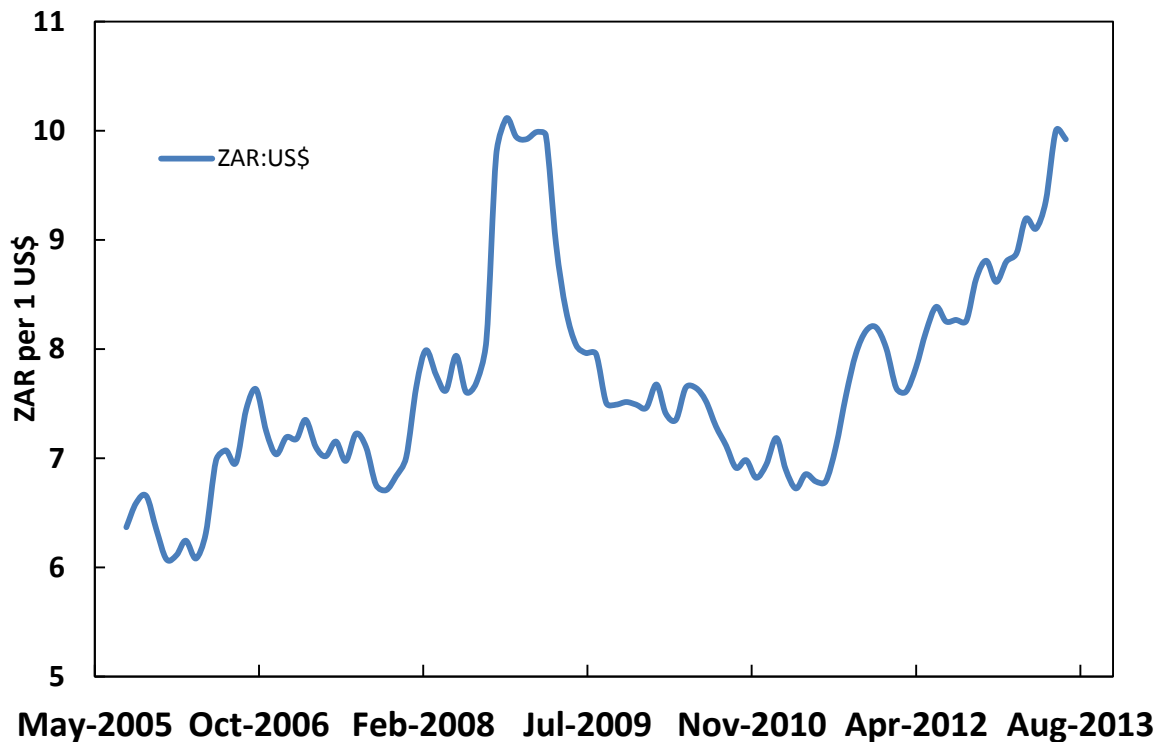


Figure 2–3: *Monthly average exchange rates between the South African rand (ZAR) and the US dollar (US\$) (Pacific Exchange Rate Service, 2013)*

Another factor that has a significant impact on the South African FeCr industry is the availability of suitable reductants, i.e. C, with coal, anthracite, char and coke being the main sources of C (Makhoba & Hurman Eric, 2010). Reductants with low ash, phosphorus (P) and sulphur (S) contents are required for FeCr production (Ideas 1st Research, 2010; Makhoba & Hurman Eric, 2010; Basson *et al.*, 2007). Due to the specific properties required, reductant availability is usually a concern for FeCr producers. Moreover, there is no regulation within reductant markets and therefore over-supply or shortages may occur regularly resulting in enormous price fluctuations. In addition, the steel industry has a major influence on the dynamics of coking coal prices (Ideas 1st Research, 2010; Makhoba & Hurman Eric, 2010).

2.2.2 Chromite ore reserves and production

The German explorer Karl Mauch first observed the occurrence of Cr in South Africa in 1865. He marked an outcrop of chromite in the Rustenburg district. One of the first

attempts to exploit the deposits was made in 1917 when a farmer in the Lydenburg district sent 200 tons of chromite ore to the British Munitions Board. However, the ore was rejected since the Cr/Fe ratio was too low. Serious chromite mining started only in 1921 in South Africa and by the start of the Second World War, production had reached levels of 180 000 tons per year (t·y⁻¹) (Mintek, 1994). Up until 1963, the majority of chromite mined in South Africa (approximately 93%) was exported without further beneficiation (South Africa Natural Resources Development Council, 1964).

The USGS defines shipping-grade chromite ore as the deposit quantity and grade normalised to a 45% Cr₂O₃ content. The total global shipping-grade chromite ore reserves are estimated by the USGS to be approximately 474 million tonnes (Papp, 2008; Basson *et al.*, 2007). It is generally accepted that South Africa holds between 68% (Howat, 1994) and 75% (Cramer *et al.*, 2004) of the world's viable chromite ore reserves. As stated in Par 2.1.2, the geological setting containing the most abundant chromite ore in the world is the Stratiform-type. These types of chromite deposits occur as parallel seams in large, layered igneous rock complexes. The layering is relatively regular and there is large lateral continuity. The largest and best example of this type of deposit in the world is the BIC. The extent of the BIC is presented in Figure 2-4. South Africa's entire chromite ore resources are located within the BIC that contains several chromite seams (Cramer *et al.*, 2004).

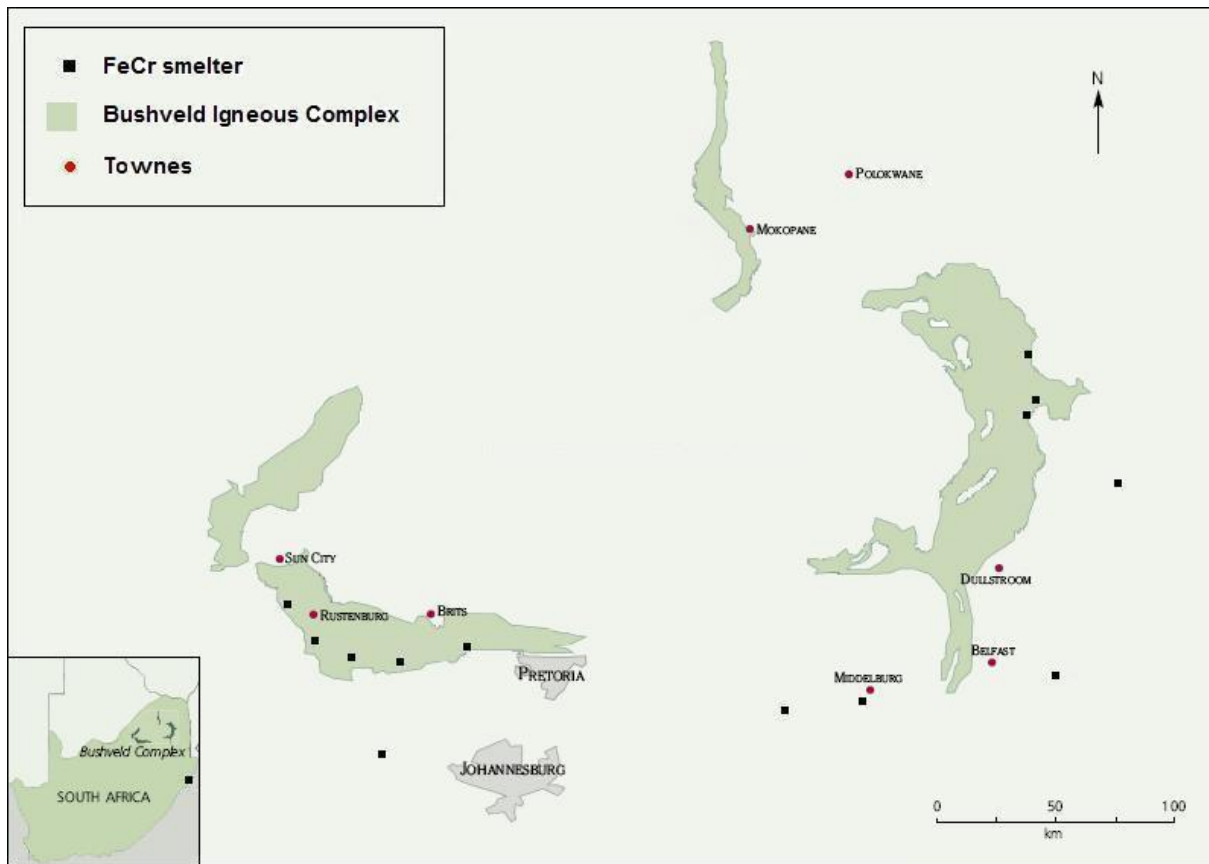


Figure 2-4: A graphical representation of the BIC and location of FeCr smelters (adapted from Johnson Matthey, 2008)

The economically exploitable seams in the BIC are the lower group 6 (LG6) with a Cr/Fe ratio of 1.5-2, the middle group 1 and 2 (MG1 and MG2) with Cr/Fe ratios of 1.5-1.8, as well as the upper group 2 (UG2) with a Cr/Fe ratio of 1.3-1.4. Chromite ores in South Africa are also associated with PGMs. The major reserves of PGMs are the UG2 and Merensky reefs that have the largest deposits of Cr, vanadium (V) and Pt in the world (Basson *et al.*, 2007; Cramer *et al.*, 2004; Xiao & Laplante, 2004; Cramer, 2001; Howat, 1986). UG2 chromite ore has gained acceptance by FeCr producers as a source for charge chrome (ChCr) production with the utilisation of several technological innovations (Basson *et al.*, 2007).

It is evident from the above-mentioned paragraph that South Africa's *in situ* chromites are largely low grade ores (< 45% Cr₂O₃) with low Cr/Fe ratios (< 1.6), which are also

generally brittle. The resulting alloys produced from these ores are mostly charge grade (ChCr) with a Cr content < 55%. There is also a general requirement for agglomeration of the ore to render it suitable for efficient ChCr production. The production of ChCr with lower chromium content also influences the transport cost per Cr unit adversely, since FeCr producers are only paid for the Cr units (Basson *et al.*, 2007).

2.3 Core processes and techniques

2.3.1. Mining and beneficiation of chromite ores

Open-cast mining and underground mining techniques are used to obtain raw chromite ore. Specific mining techniques vary widely depending on the local resources and materials (Gediga & Russ, 2007; Nafziger, 1982).

The purpose of beneficiation is to render the ore physically (granulometry) and chemically suitable for subsequent treatments. Beneficiation operations typically serve to separate and concentrate mineral values from waste materials, to remove the impurities or prepare the ore for further refinement. Beneficiation activities do not change the mineral content, but either reduce (crushing and grinding) or enlarge (pelletising and briquetting) particle size to facilitate further processes. Several methods are applied to beneficiate chromite ore, which is determined by the ore source, end-use sector requirements, mineral characteristics of the ore deposits, gangue mineral assemblage and the degree of dissemination of constituent minerals. A general representation of a typical chromite ore beneficiation process is presented in Figure 2–5. It consists of two sections, i.e. comminution (preparing the material for subsequent unit operations) and concentration (Murthy *et al.*, 2011; Abubakre *et al.*, 2007).

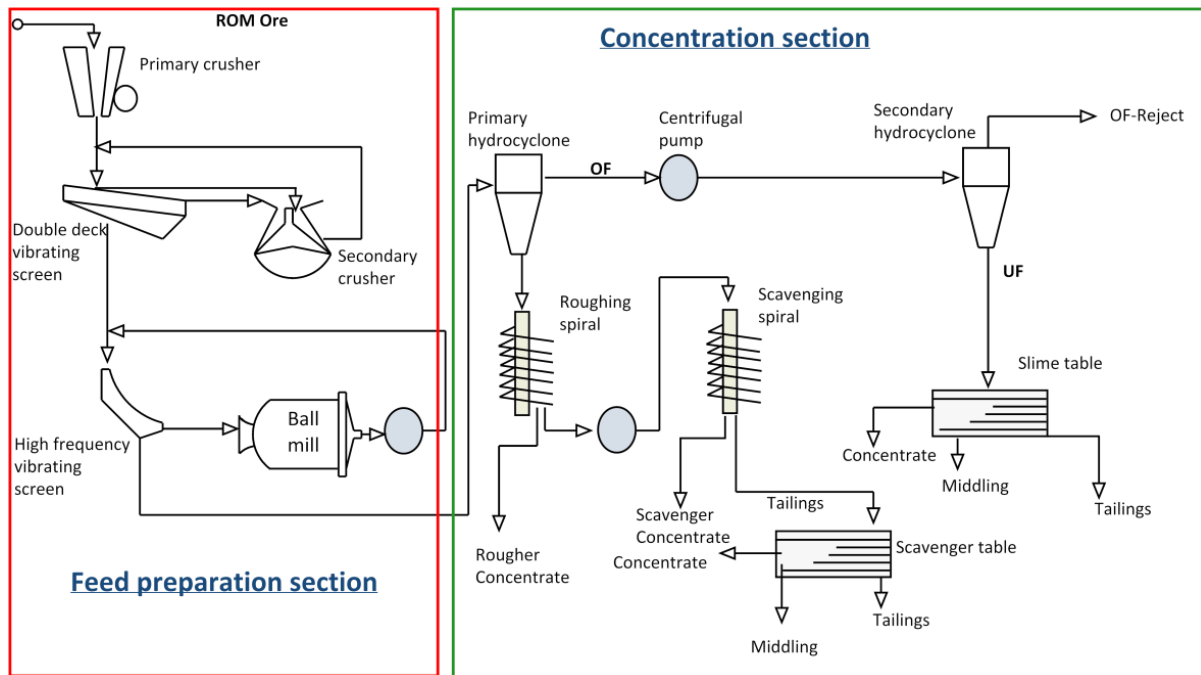


Figure 2–5: General process flow sheet for typical chromite ore beneficiation (Murthy *et al.*, 2011)

In the feed preparation section, the run-of-mine ore is screened from ± 220 mm to 75 mm. This is followed by a primary and secondary crushing stage that is separated by screening to produce an offset of less than 3 mm. The secondary crushers offset is recycled back and rescreened. The crushed ore is then further grounded to less than 1 mm. In the concentration section, the ore is upgraded using conventional gravity techniques such as spiral concentrators (Murthy *et al.*, 2011).

Although gravity techniques are well established and widely accepted for concentrating chromite ores, these techniques are inefficient and complex for the treatment of fine particles with sizes $< 75\mu\text{m}$. Each gravity separation technique delivers its maximum efficiency under specific operating conditions and for specific particle size ranges (Murthy *et al.*, 2011:377).

Heavy medium and gravity concentration methods are the most commonly used beneficiation processes. Heavy medium separation is the most economical method for the treatment of coarse particles ranging between 10 and 100 mm. Finer particles are usually

beneficiated with jigs, spirals and shaking tables. Spirals are currently the preferred choice gravity concentrators in industry. Cr can be recovered within the range of 80 to 85% when using these processes (Gu & Wills, 1988; Howat, 1986).

Although gravity separation methods are predominantly used for the beneficiation of chromite ores, other techniques are also utilised (Nafziger, 1982). Flotation techniques are used in certain instances, for instance to remove fatty acids, such as oleic acid. Chromite ores from different locations exhibit large variability in surface properties that causes major difficulties when utilising flotation techniques (Gu & Wills, 1988).

All chromites are paramagnetic at room temperature with their magnetic capacity depending on the Fe^{2+} content due to the non-uniform distribution of magnetic ions in the crystalline structure (Owada & Harada, 1985). Low-intensity magnetic separation (about 0.1 T) is used to separate magnetite from paramagnetic chromite material. It is, however, inefficient in separating chromites that are present in fine intergrowths with other materials. In a high-intensity magnetic field (about 1 T), chromite can be extracted as a magnetic product from the gangue material (Gu & Wills, 1988; Nafziger, 1982).

South African chromite ores are relatively friable and easily break down to the size of the chromite crystals (Gu & Wills, 1988). Due to this friability, it is common to only recover 10 to 15% lumpy ore (15 mm < typical size range < 150 mm) and 8 to 12% chip or pebble ores (6 mm < typical size range < 15 mm) during the beneficiation process employed directly after mining of the chromite. The remaining ore would typically be in the < 6 mm fraction, which is usually crushed and/or milled to < 1 mm and then upgraded utilising typical gravity separation techniques (e.g. spiral concentrators) to approximately 45% Cr_2O_3 content. This upgraded < 1 mm ore is commonly known as metallurgical grade chromite ore (Glastonbury *et al.*, 2010).

Although this dissertation does not focus specifically on comminution, milling energy requirements were considered during the experimental sections. Milling of the upgraded chromite ore is a prerequisite for the agglomeration of the fine ore prior to smelting in submerged arc furnaces (SAFs). In Equation 2–1, the Hall-Petch relation is presented as (DoITPoMS, 2013):

$$\sigma_y = \sigma_i + \frac{k}{\sqrt{d}} \quad 2-1$$

where σ_y is the tensile yield stress, d is the grain diameter, σ_i is the 'intrinsic' yield stress, and k is a constant for a particular material. The force required to break the crystal increases as the grain size gets smaller according to the Hall-Petch relation (DoITPoMS, 2013). Therefore, in theory, a grain can be infinitely strong if its grain size is infinitely small. This is, however, not possible since the smallest that a grain can be is a unit cell, which is the minimum number of atoms that makes up a crystal. The grain is no longer crystalline at single unit cell sizes since it becomes amorphous (Schuh & Nieh, 2003).

2.3.2. Ferrochromium production

A generalised process flow diagram that indicates the most common process steps utilised by South African FeCr producers is presented in Figure 2–5 (Beukes *et al.*, 2010). The different FeCr production processes utilised in South Africa are discussed in subsequent paragraphs.

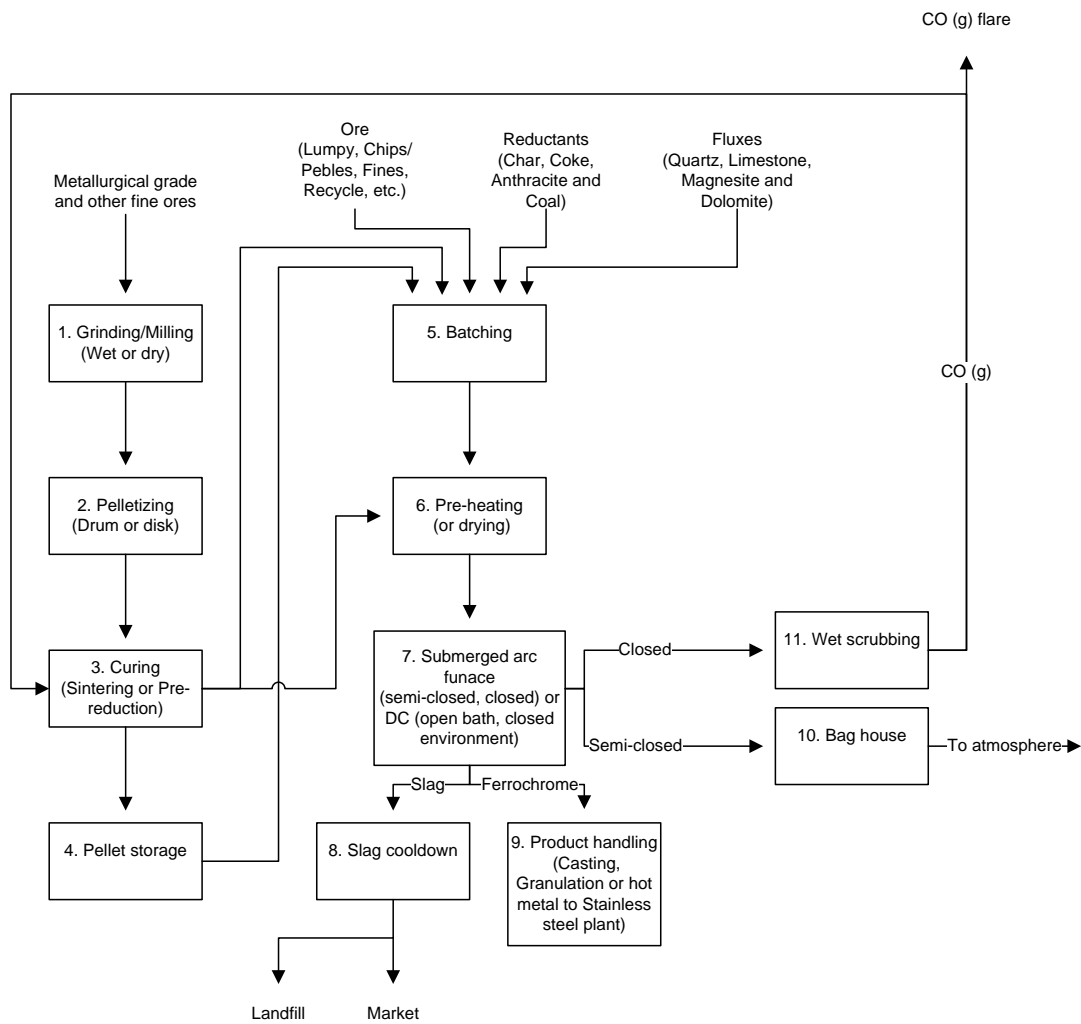


Figure 2–6: A flow diagram adapted by Beukes et al. (2010) from Riekkola-Vanhanen (1999), indicating the most common process steps utilised for FeCr production in South Africa

2.3.2.1 Conventional semi-closed SAF operation

Conventional semi-closed SAF operations with bag filter off-gas treatment are the oldest technology applied in South Africa, which still accounts for a considerable fraction of the total FeCr production (Gediga & Russ, 2007). In this operation, coarse (lumpy and chips/pebble ores) and a limited amount of fine ores without an agglomeration process undertaken to increase the size of fine ores can be smelted. Even though it has been stated that fine feed material cannot be fed directly into a FeCr SAF without causing dangerous

blow-outs or bed turnovers (Riekkola-Vanhanen, 1999), small amounts of fine chromite are fed into certain semi-closed FeCr SAFs in South Africa. With reference to the process flow diagram indicated in Figure 2–6, the process steps included in the semi-closed SAF operation are 5, 7, 8, 9 and 10. Certain semi-closed SAFs do consume pelletised feed, in which case process steps 1 to 4 would also be included. Most of the semi-closed FeCr SAFs in South Africa are operated on an acid slag, with a basicity factor < 1. Equation 2–2 defines the basicity factor (BF) (Beukes *et al.*, 2010) as:

$$BF = \frac{\%CaO + \%MgO}{\%SiO_2} \quad 2-2$$

Some semi-closed FeCr SAFs might operate on BF > 1. It is, however, less common and this type of operational mode is usually only temporarily undertaken to compensate for refractory linings being in poor condition or if enhanced S-removing capacity through the increased formation of CaS and MgS in the slag is required (Beukes *et al.*, 2010).

2.3.2.2 DC arc process

This type of furnace uses a single solid or hollow carbon electrode that produces a DC arc to an anode in the bottom of the furnace. These furnaces can be fed with raw materials either on the side of the electrode or through the hollow electrode (Geldenhuis, 2013). One major advantage of this process is that the raw materials, including only fines, can be used with minimum or no pre-processing requirements. The Cr recovery obtained using this process is also very high. A disadvantage of this operation is that specific electricity consumption is relatively high.

The process steps presented in Figure 2–6 include 5, 7, 8, 9 and 11. In certain instances, a drying step (process step 6) might also be included. These furnaces typically utilise a basic slag regime (BF > 1). Currently, three such furnaces are in routine commercial operation for FeCr production in South Africa.

2.3.2.3 Closed SAF operations with pre-reduced pelletised feed

This FeCr production operation is commonly referred to as the Premus process (applied by Glencore-Xstrata Alloys) and is also known as the solid state reduction of chromite (SRC process). It was developed by Showa Denko (Japan) in the 1970s, with subsequent improvements made by Glencore-Xstrata Alloys. With reference to Figure 2–6, the process steps included are 1, 2, 3, 5, 7, 8, 9, 11, as well as step 4 if all pellets cannot be fed immediately into the SAF. In this operation, approximately 3.5 to 4.5% clay binder and 12 to 16% fixed carbon (from a reductant) are added to the ore mixture. The material mixture is then milled to 90% <75 μm , where after it is pelletised. The pelletised feed differs substantially from the oxidative sintered type (Paragraph 2.3.2.4) since the pellets are pre-reduced and mostly fed hot, directly after pre-reduction, into the closed SAF. The relatively high level of reductant in the composite pellets, compared to the oxidative sintered process of Outotec (Paragraph 2.3.2.4), is essential to achieve pre-reduction. The SAFs operate on a basic slag ($\text{BF} > 1$) (Botha, 2003; Naiker, 2007; Beukes *et al.*, 2010). At present, only two FeCr smelters, i.e. Glencore-Xstrata Lydenburg operations and Glencore-Xstrata/Merafe Lion Ferrochrome, use this process.

2.3.2.4 The oxidative sintered process

The oxidative sintered process for chromite is also known as the Outotec or Outokumpu process. In this type of FeCr production operation, closed SAFs utilise oxidative sintered pelletised feeds (Outotec, 2011). This technology has been the most commonly employed in South Africa, with the majority of green and brown field expansions utilising this process during the last two decades. The process steps presented in Figure 2–6 usually include steps 1, 2, 3, 4, 5, 7, 8, 9 and 11, which can include or exclude step 6. These furnaces are usually operated on an acid slag ($\text{BF} < 1$) (Beukes *et al.*, 2010). In all green field FeCr

developments, the pelletising and sintering (steps 2 and 3) sections were combined with closed SAFs. However, pelletising and sintering sections have also been constructed at plants where the pelletised feed is utilised by conventional semi-closed SAFs (Paragraph 2.3.2.1). A visual representation of the oxidative sintered process is presented in Figure 2-7.

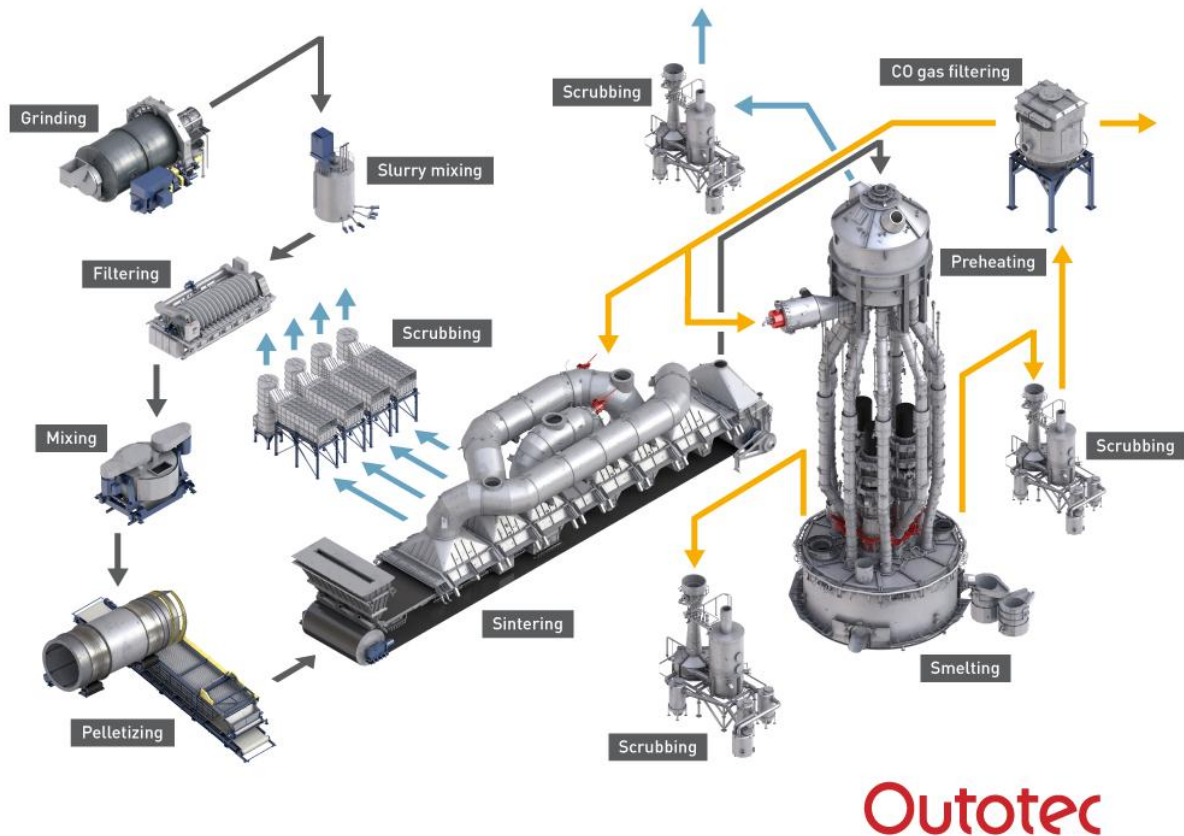


Figure 2-7 Visual representation of Outotec/Outokumpu FeCr process (Outotec, 2013)

Since oxidative sintered pellets were specifically investigated in this study, selected studies that focused specifically on relevant aspects of this process are additionally discussed. The green pellets (pre-sintered pellets, step 2, Figure 2–6) of this process consist of chromite ore fines (0-25mm) that are milled in a wet ball mill until the desired size is reached, 4 to 5% coke that provides a heat source during sintering and bentonite that acts as a binder for the pellets. These three materials are mixed and pelletised in a pelletising drum. The over- and undersized green pellets are removed and recycled, while the appropriate-sized green pellets

are layered on a sintering belt. The sintering belt is protected by a layer of already sintered pellets and moves through a grate furnace for the sintering process (drying, preheating, sintering and cooling). A counter-current gas flow implies that the drying and preheating of these green pellets occur in oxidising conditions. When these pellets approach the peak temperature (1300 °C) of the furnace, the coke ignites. This partially fuses the pellets and creates a porous yet mechanically strong material. At the exit of the furnace, the pellets are cooled by inflowing air (Singh & Rao, 2008; Zhao, 2010; Beukes *et al.*, 2010).

2.4 UG2 ore and the platinum industry

2.4.1 A brief history

In June 1924 H.C. Dunne sent a small bottle of greyish-white concentrates to the Johannesburg office of the consulting geologist Dr Hans Merensky. The analysis confirmed the presence of Pt, as well as rhodium (Rh) and iridium (Ir). Dr Merensky went to investigate Dunne's brother-in-law, Andries Lombaard's farm Maandagshoek, to the north of Lydenburg. He had located the basic mineral in a reef running parallel to the mountain range in a north-south direction, extending some sixty miles with great geological insight and deductive reasoning within a few weeks. Merensky's first thought was to christen it "The Lombaard Reef" (after Andries Lombaard on whose farm the discovery was made). However, his colleagues overruled him and it was named "The Merensky Reef". Today, the PGM industry in South Africa is the world's largest producer of Pt and the world's second largest producer of palladium (Pd) (McDonald & Hunt, 1982).

2.4.2 UG2 ore

Historically, the Merensky Reef was the only source of PGMs in the BIC. The UG2 reef, which is close to and largely parallel to the Merensky Reef (Figure 2.8), was an enticing source of PGMs, but metallurgical difficulties delayed the extraction and processing of PGMs

(Nel & Theron, 2004). However, since 2000, all three major South African PGM producers, Anglo Platinum, Impala Platinum and Lonmin Platinum, have moved increasingly into mining the UG2 Reef horizon (Rule, 2011). Today, UG2 ore is the second most mined source of PGM in the BIC (Nel & Theron, 2004). In Figure 2–8, the stratigraphic column showing the position of the UG2 Reef relative to the Merensky Reef is presented. The UG2 Reef is a platiniferous chromitite layer that, depending on the geographic location within the BIC, is developed between 20 to 400 metres below the Merensky Reef. The chromitite layer is usually 1 m thick, but can vary from 0.4 up to 2.5 m (Schouwstra & Kinloch, 2000)

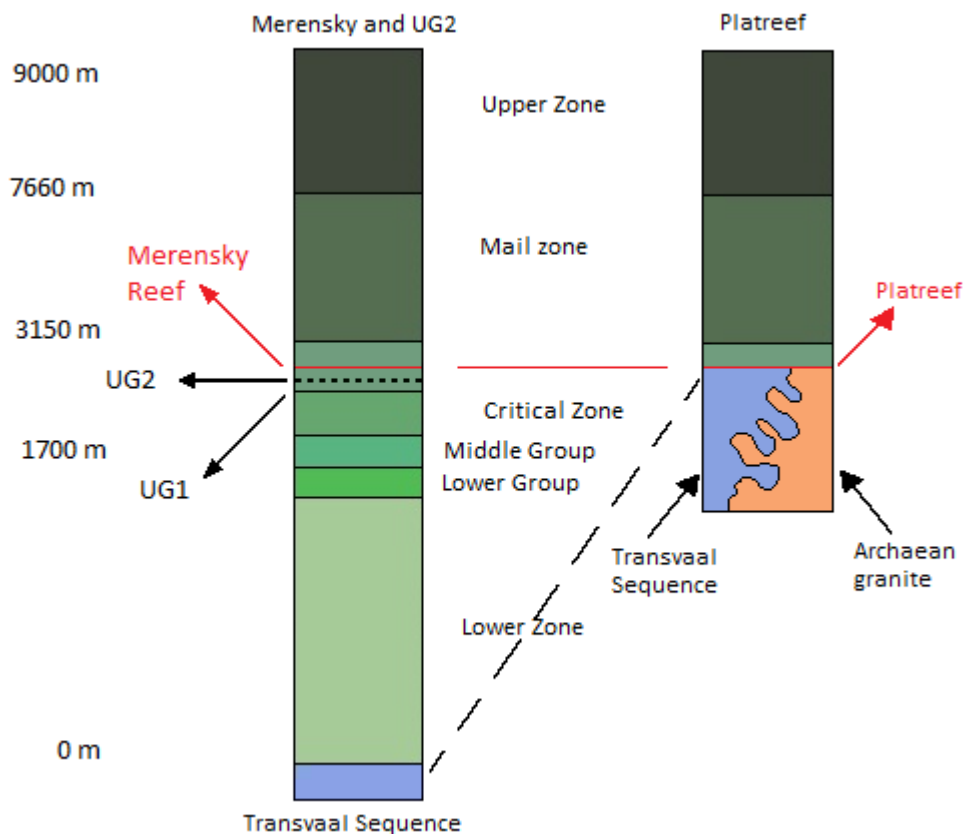


Figure 2–8: Stratigraphic column showing the position of the UG2 Reef relative to the Merensky Reef: The Platreef is interpreted as a Merensky equivalent (modified after Vermaak, 1995)

The majority of UG2 consists by volume of 60 to 90% chromite, 5 to 30% pyroxene, and 1 to 10% plagioclase. There are also other silicates, oxides and base metal sulphides

present (Vermaak, 1995). The Cr_2O_3 content of the UG2 Reef varies from 30 to 35% (Schouwstra & Kinloch, 2000).

The PGM containing minerals are highly variable and mostly occur as PGM sulfides, predominantly as laurite (RuOsIr sulfide), cooperite (PtS), braggite (Pt, Pd, NiS) and an unnamed PtRhCuS mineral. These minerals are usually present as ~12 μm particles, with particles larger than 30 μm being extremely rare. Most of these minerals occur with the base metal sulfides and silicates, with only laurite mostly associated with chromite grains. On average, the total PGMs in UG2 ore range between 4 and 7 g / ton ore (Schouwstra & Kinloch, 2000).

2.4.3 PGM process

The conventional process for the extraction of PGMs from the Merensky Reef and the Platreef involves:

- smelting of a flotation concentrate to remove gangue material and to produce an Fe-nickel (Ni)-copper (Cu)-PGM matte;
- converting this matte by blowing air through to oxidize iron sulphide and to transfer the oxidized iron to the slag; and
- leaching the resulting Cu-Ni-PGM matte to dissolve the Cu and Ni, as well as obtain a residue for feed to the refinery (Green *et al.*, 2004).

A disadvantage of the above-mentioned process is that if there is Cr in the concentrate, chromium-bearing insoluble spinels form in the furnace. This would periodically necessitate the shutdown and dig out of the furnace, which, from an economic perspective, is not desirable. Most refineries therefore did not use ores such as UG2 that have high Cr content (Green *et al.*, 2004; Bryson, 2004). Historically, there was no real driving force to use UG2 ore due to the availability of the ore from the Merensky Reef. The global Pt demand was sufficiently met from just the Merensky ore. However, increases in the price of PGMs with

an associated increase in the demand of these commodities led to the commissioning of processes to extract PGMs from UG2 ores (Bryson, 2004). Most of the PGM production operations that started since 1998 focused more on the use of UG2 reef (Bryson, 2004). An example of an operation that utilises UG2 ore is indicated in Figure 2-9 (Nel & Theron, 2004).

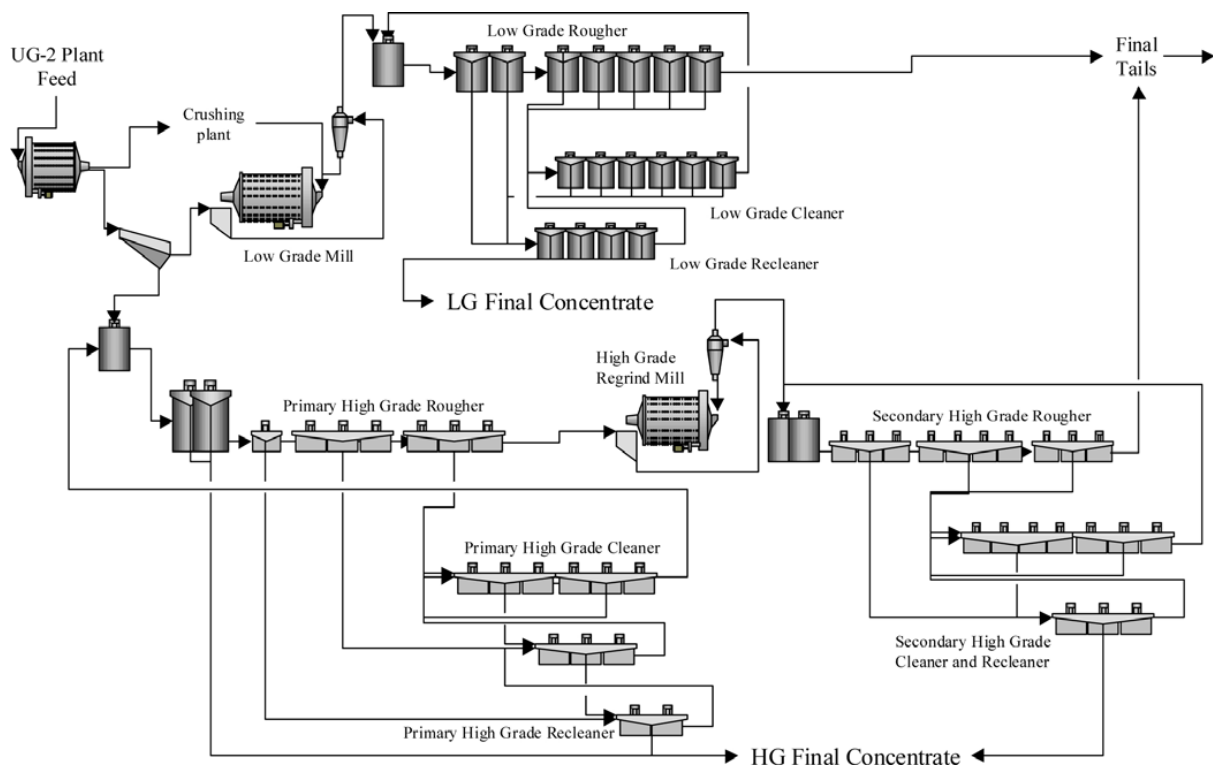


Figure 2-9: UG2 ore separation basic flow sheet (Nel & Theron, 2004)

UG2 ore has two unique characteristics that assist in creating the UG2 ore separation procedure (Figure 2-9) (Nel & Theron, 2004), viz.

- The ore itself is very friable with the PGMs in an inter-granular location. This implies that after underground blasting and primary milling, most of the ore is relatively fine and most of the PGMs are well liberated.

- The lower PGMs that have high silicate fractions (mainly norite, anorthosite) originate from the hanging- or footwall of the stope face. This material can therefore be easily separated from the richer material during primary grinding.

The primary grinding and classification circuit maximises the exploitation of the mineralogical characteristics. This grinding is fully autogenous instead of semi-autogenous, meaning that the breaking characteristics ore is used instead of using steel balls/rods to pulverise the ore. The sizeable stream of silicate pebbles from the UG2 ore can be crushed with this method, reducing the risk of crusher damage through misdirected grinding media. The primary mill's capacity increases by approximately 40%, since there is no other component in the grinding process. The two products obtained from this circuit, i.e. the chromite/PGM-rich material (which is finer), and the silicate materials (which are coarser) are treated in separate circuits (Nel & Theron, 2004).

For both these circuits, any material over 12mm is milled in a cone crushing plant and used in the low grade circuit feed. The material < 12mm is screened at 600µm with the oversized material being fed back to the crushed material in the low-grade circuit feed. The undersized material from these screens is used in the high-grade circuit feed. The low-grade circuit feed is milled in a ball mill to a grind size of approximately 65% < 75µm (Nel & Theron, 2004). The circuits are treated similarly but separately. Tank cells ranging from 10 to 50m³ are used for primary flotation with sodium isobutyl xanthate, sodium dithiophosphate and copper sulphate added as reagents to activate the Fe sulphides. A polyglycol ether frother and a CMC-based polymeric depressant are also used to assist in the extraction of PGMs. After this flotation procedure, the tailings of high-grade circuit feed are grinded again in a single ball mill to a grind size of approximately 65% < 75µm to liberate more PGMs that might be trapped in the crystalline structure of this material. The secondary flotation is the same as the primary flotation, although only in smaller capacity (Nel & Theron, 2004). The

final tailings of this circuit and the tailings of the low-grade circuit feed primary flotation are then discarded.

2.5. Conclusion

Although the oxidative sintered pelletised feed technology is commonly used in the South African FeCr industry and UG2 ore is increasingly used as an ore feedstock in this process, there is no direct comparison of the physical properties of oxidative sintered pellets produced from UG2 with the physical properties of those produced with conventional metallurgical grade chromite ore (from the LG6 or the MG1/2 seams) in peer-reviewed scientific literature. The pelletisation and sintering properties of different chromite ores of Indian origin were reported by Singh and Rao (2008), and although knowledge from these types of studies can be useful, it cannot be used to predict how pellets made from the aforementioned two South African ores would perform in the oxidative sintered process.

CHAPTER 3

Comparison of physical properties of oxidative sintered pellets produced with UG2 or metallurgical grade South African chromite: A case study

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Abstract

In this paper, the physical properties of oxidative sintered pellets produced from typical South African UG2 ore are compared with the physical properties of that produced with conventional South African metallurgical grade chromite ore (from the Lower Group 6 or the Middle Group 1/2 seams). A statistical evaluation of the cured (sintered) compressive strength results obtained from the case study ores proved that pellets prepared from UG2 ore are likely to have the same or better compressive strength than pellets prepared from metallurgical grade chromite ore. The cured abrasion strength of the UG2 ore pellets was also superior compared to the metallurgical grade pellets.

Scanning electron microscopy (SEM) backscatter, secondary electron and elemental X-ray mapping were used to determine the reasons for the general superior strength of the UG2 ore pellets. The case study UG2 ore also required 13 kWh/t less energy to be milled to the required particle size distribution prior to pelletisation, which can lead to substantial cost savings. Results presented in this paper can be utilised by ferrochromium (FeCr) producers to better quantify the advantages and disadvantages associated with the use of UG2 ore for FeCr production.

Keywords: South Africa; UG2 and metallurgical grade chromite; oxidative sintered pellets; compressive and abrasion strengths; milling energy requirements

1. Introduction

Chromite, a mineral of the spinel crystal type, is the only commercially viable source of virgin chromium units. Geologically, commercial chromite deposits in the world are found in three forms, i.e. alluvial-, podiform- and stratiform-type deposits (Murthy et al., 2011; Cramer et al., 2004). Alluvial deposits were formed by weathering of chromite-bearing rock with the subsequent release of chromite and gravity concentration thereof by flowing water. However, these deposits are relatively small and of comparatively minor commercial interest. Podiform-type chromite deposits are usually present in irregular shaped pods or lenses. The distribution of podiform-type chromite deposits within a mineralised zone is usually relatively erratic and unpredictable, making the exploration of these chromite deposits difficult and costly (Cramer et al., 2004). Stratiform-type chromite deposits geologically occur as parallel seams in large, layered igneous rock complexes with more regular layering and lateral continuity (Cramer et al., 2004). The largest example of a stratiform-type chromite deposit is the South African Bushveld Igneous Complex (BIC), which holds an estimated three quarters of the world's viable chromite ore resources (Cramer et al., 2004).

Several chromite seams exist in the BIC. The seams with economic interest are the lower group 6 (LG6), the middle group 1 and 2 (MG1 and 2) and the upper group 2 (UG2) seams (Cramer et al., 2004). The LG and MG seams are specifically exploited for their chromium content, while the UG2 seam is primarily mined as a source of platinum groups minerals (PGMs) (Xiao and Laplante 2004). Extraction of the PGMs from the UG2 ore usually involves the liberation of the sulphite-containing PGMs with milling and subsequent recovery of the PGM concentrate through flotation (Xiao and Laplante 2004). Chromite in the PGM concentrate is undesirable; therefore, PGM

recovery circuits are specifically designed to ensure maximum rejection of the chromite to the tailings stream. However, the chromite in the PGM tailings can potentially serve as ore feedstock for ferrochrome (FeCr) production, after beneficiation thereof to increase the chromium content.

South Africa has dominated the global production of FeCr in the recent past (Kleynhans et al., 2012 and references therein) due to its vast chromite resources and past history of relatively inexpensive electricity. FeCr is a relatively crude alloy consisting predominantly of iron (Fe) and chromium (Cr), which is mainly utilised for the production of stainless steel. In South Africa, FeCr is generally produced from metallurgical chromite ore originating from LG or MG seams. However, due to increases in the availability of UG2, as well as technical innovations in the FeCr and stainless steel industry, an increasing volume of UG2 feed material is being utilised by South African FeCr producers (Cramer et al., 2004). However, there are certain advantages and disadvantages that need to be considered. The price that a FeCr producer is prepared to pay for UG2 is determined by balancing these advantages and possible disadvantages. Advantages related to the use of UG2 by South African FeCr producers include:

- The utilisation of UG2 for FeCr production minimises tailing volumes for PGM producers, which also has associated financial benefits, e.g. tailing waste storage facilities can comparatively be smaller.
- The use of UG2 contributes to the optimum utilisation of natural resources, since additional mining is avoided. This also reduces the carbon footprint of FeCr producers.
- The overall safety risk associated with FeCr production is much lower if the mining of new chromite units can be reduced by the utilisation of upgraded UG2

tailing originating from PGM operations. Although this is not a direct financial or technical benefit, environmental-, health- and safety-related aspects are as important as production volumes and profit margins in the modern-day industrial setting.

- UG2 ore is usually cheaper than conventional metallurgical chromite ore, originating from LG6 or the MG1/2 BIC seams.

The disadvantages associated with the substitution of metallurgical grade chromite ore with UG2 during FeCr production include:

- The Cr/Fe ratio of UG2 ore is lower than that of metallurgical grade ore originating from LG6 or the MG1/2 BIC seams (Cramer et al., 2004). Chromite does not only contain Fe and Cr, but also magnesium (Mg) and aluminium (Al) in varying proportions, depending on the deposit. The chemical composition of chromite can be represented by the chemical formula $(\text{Mg}, \text{Fe}^{+2}) (\text{Cr}, \text{Al}, \text{Fe}^{+3})_2\text{O}_4$ (Murthy et al., 2011). In this structure, Fe^{2+} can be replaced by Mg and similarly Cr can be replaced by Fe^{3+} and Al. This variation in composition can result in substantial differences in the Cr/Fe ratio of chromite deposits. Specifically within the BIC, the composition variation within a particular seam is relatively small across the whole complex, but there is a progressive shift in composition between the sequential reef horizons. Since Fe oxides are reduced easier (at lower temperatures) than Cr oxide (Niemelä et al., 2004), Fe recovery from ore is higher than that of Cr. Therefore, the lower Cr/Fe ratio of UG2 ores results in a lower Cr content of the FeCr produced. Since FeCr producers are only paid for the Cr content of FeCr, UG2 utilisation has a disadvantage in this regard.
- The above-mentioned dilution of Cr content in the FeCr produced from UG2 also results in higher transport costs per Cr unit. This is significant, considering that

most of South Africa's FeCr is exported to stainless steel producers in Europe, Asia and North America. This additional transport cost also increases the overall carbon footprint of FeCr production in South Africa.

- Cramer et al. (2004) reported that the higher Ti content of UG2 could also be problematic, since some stainless steel producers have specifications for the Ti content of the FeCr.

FeCr is produced in South Africa with various different process combinations, which were recently reviewed (Beukes et al., 2010). However, at least eight of the 14 South African FeCr smelters utilise oxidative sintered pelletised feed. As described by Beukes et al. (2010), this process entails the wet milling of chromite that is thereafter de-watered. Refined clay, which serves as a binder, together with a small percentage of carbonaceous material, is then added and mixed into the moist milled ore. The mixture is then pelletised in a pelletising drum. The over- and undersized green pellets are removed and recycled, while the appropriate-sized green pellets are layered on a sintering belt, which is protected by a layer of already sintered pellets. The green pellets are then ignited in a furnace, where after air is pulled through the pellet bed to sinter the pellets. The amount of carbon present in the green pellets is limited to supply just enough exothermic energy to sinter the pellets properly (Beukes et al., 2010).

Notwithstanding the common application of the oxidative sintered pelletised feed technology in the South African FeCr industry and the increased utilisation of beneficiated UG2 ore as an ore feedstock into this process, a direct comparison of the physical properties of oxidative sintered pellets produced from UG2 with the physical properties of that produced with conventional metallurgical grade chromite ore (from the LG6 or the MG1/2 seams) is currently lacking in the peer-reviewed scientific literature. Singh and Rao (2008) reported the impacts of properties of different

chromite ores of Indian origin on pelletisation and sintering. Although knowledge can be gained from similar studies, as presented by Singh and Rao (2008), it cannot be used to exactly predict the performance of South African UG2 ore in the oxidative sintered process. This knowledge gap was recently highlighted by a large South African FeCr producer that requested the authors to investigate this matter. This producer indicated that some negative aspects associated with the physical properties of oxidative sintered pellets produced from UG2 ore were being reported by operational personnel. This has resulted in some operational resistance to the use of large proportions of ore from the UG2 ore horizon in the oxidative sintered process. In this paper, the physical properties of oxidative sintered pellets produced from a typical South African BIC metallurgical grade ore are compared to the physical properties of oxidative sintered pellets produced from a typical South African BIC UG2 ore.

2. Experimental

2.1. Materials

A UG2 ore sample and a metallurgical grade ore sample (from the LG6 seam) were received from one of the largest FeCr smelters situated in the western limb of the BIC. At the time when this study was initiated, these specific ores were used for the production of oxidative sintered pellets at this smelter. Refined bentonite (G&W Base (Pty) Ltd., 2013), which was used as a binder during the pelletisation process associated with the oxidative sinter pellet production, was also obtained from the same FeCr producer. Anthracite (Nkomati Anthracite (Pty) Ltd, Mpumalanga Province, South Africa) (Sentula, 2013) was used as a carbonaceous source in the pellets.

In addition, 10 milled chromite ore samples were obtained from a large FeCr producer applying the oxidative sintered process. These samples were only used to

determine the particle size requirement during milling of chromite ore in preparation for the production of oxidative sintered pellets.

2.2. *Surface, crystalline and chemical analyses*

An FEI Quanta 200 scanning electron microscope (SEM) with an integrated Oxford Instruments INCA 200 energy dispersive x-ray spectroscopy (EDS) microanalysis system was utilised to perform surface analysis of the case study materials, i.e. visual inspection and surface chemical characterisation. Chemical characterisation of chromite ore samples was performed with a Spectro Ciros Vision inductively coupled plasma optical emission spectrometer (ICP-OES). Both semi-quantitative and quantitative X-ray diffraction (XRD) analyses were conducted with a Philips X-ray diffractometer (PW 3040/60 X'Pert Pro) to determine the mineral composition of the UG2 and metallurgical grade chromite ores. The samples were scanned using x-rays generated by a copper (Cu) $K\alpha$ x-ray tube. The measurements were carried out between variable divergence- and fixed receiving slits. The crystalline phases were identified using X'Pert Highscore plus software, while the relative phase amounts were estimated using the Rietveld method (Autoquan programme). X-ray fluorescence (XRF) was also used to determine the concentration of elements present in the case study materials. The same instrument described above for XRD analysis was used with a rhodium (Rh) x-ray tube and a Super Q database.

2.3. *Milling*

A Siebtechnik mill was used to reduce the particle size of the materials (ore, anthracite and bentonite) to the required particle size, prior to pelletisation. All parts of this mill that made contact with the materials milled were made of tungsten carbide,

which prevented possible Fe contamination of the milled material. Prior to milling, the materials were dried at 40 °C for one day and then cooled in airtight containers to avoid possible moisture absorption. The three components were mixed in a ratio of 97 wt % ore, 2 wt % anthracite and 1 wt % bentonite. Batches of 170 g of this dried material mixture were then milled. After a batch was milled, the milled material mixture was collected in a sample bag and stored for future usage. The mill was cleaned before milling of a new batch commenced.

In order to quantify the energy requirements during the milling of the two different case study ores, stirred mill tests were conducted. This was carried out by utilising a mill with a 5 L stationary vertical chamber and a stirrer comprising of a shaft fitted with pins to agitate the grinding media. The stirrer rotational speed was held constant at 400 rpm (3.7 m/s). The grinding chamber is 18 cm in diameter and 23 cm high. The mill was equipped with a variable speed drive and a torque sensor to facilitate the accurate determination of energy absorbed by the charge. All the key operating conditions of this mill were monitored with a computer that also calculated the energy consumption. The grinding chamber was equipped with a water jacket for cooling. 1 kg of ore was milled with 1.5 kg of water and 20 kg of 6 mm steel balls. For each case study ore, from five different milling energy inputs were tested experimentally, i.e. 10, 20, 40, 80 and 160 kWh/ton. In practice (industrial application), a relatively narrow energy input range would be expected. However, this relatively large range was tested in order to identify possible trends.

2.4. Particle size analysis

Particle size distribution of the as-received case study ores was determined by wet screening. The particle size distribution of the milled chromite ore samples generated

with the two different milling methods was determined with laser diffraction particle sizing using a Malvern Mastersizer 2000. A diluted suspension of milled material was treated ultra-sonically for 60 s prior to the particle size measurement in order to disperse the individual particles and to prevent the use of a chemical dispersant.

2.5. *Pelletisation*

The milled material mixtures (obtained from the Siebtechnik mill) were pressed into cylindrical pellets in a Specac PT No. 3000 13 mm die with an LRX Plus strength testing machine (Ametek Lloyd Instruments) equipped with a 5 kN load cell. Each pellet consisted of 3 g dry milled material to which two drops of water was added prior to pressing the pellet, i.e. correlating to a moisture content of approximately 4.1 wt %. The compression rate was controlled at 10 mm/min, until a load of 1.5 kN was reached, where after this load was held for 30 s. Although time consuming (each pellet made individually), this technique was preferred over conventional disc or drum pelletisation that can result in the formation of pellets with different densities and sizes. Pressing the pellets according to the procedure described here ensured consistent density and size, allowing a monovariance investigation of other process parameters.

2.6. *Oxidative sintering*

A camber furnace (Lenton Elite, UK model BRF 15/5) with a programmable temperature controller was used to conduct all oxidative sintering experiments. The temperature profile used in this experimental study was compiled in an attempt to simulate conditions occurring in the industrially applied oxidative sintering process. In Fig. 1, the temperature profile that was utilised is presented. The furnace was heated up at the maximum rate to 1 400 °C, where after this temperature was maintained for

20 min. Thereafter, the furnace was switched off and the pellets were allowed to cool down inside the furnace. 100 min after the furnace was switched off, the furnace door was opened to accelerate the cooling of the pellets.

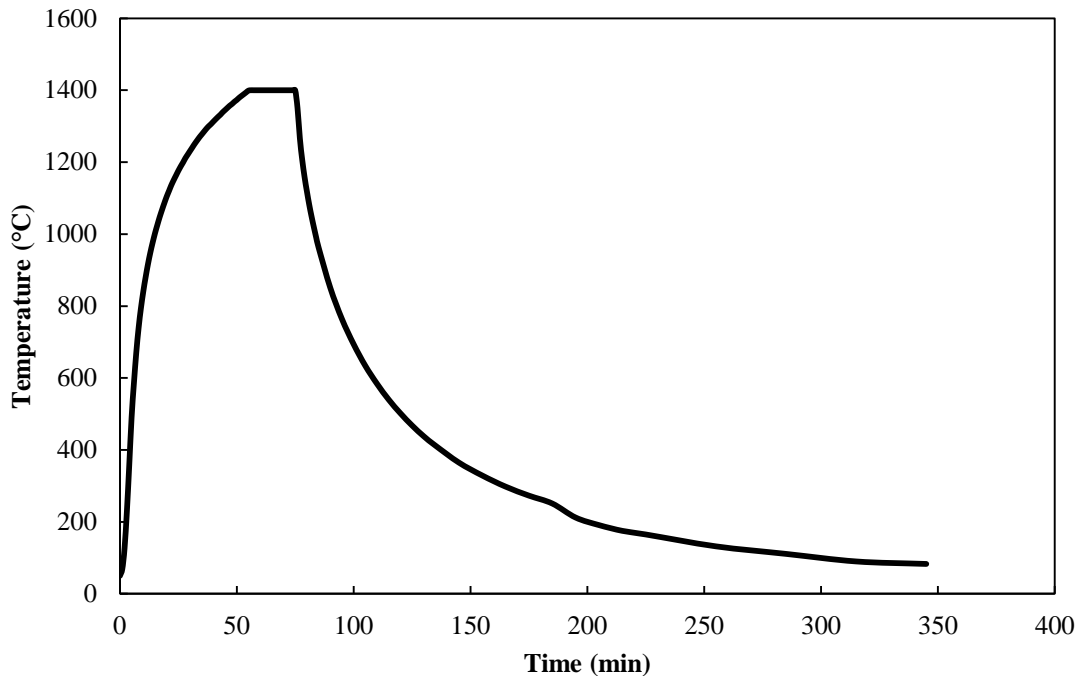


Fig. 1. Temperature profile used to cure oxidative sintered pellets.

2.7. Compressive strengths testing

The compressive strength of the oxidative sintered pellets was tested with an Ametek Lloyd Instruments LRXplus strength tester. The speed of the compression plates was maintained at 10 mm/min during crushing to apply an increasing force on the pellets. The maximum force applied to incur breakage was recorded for each pellet.

2.8. Abrasion resistance testing

Similar to test work conducted by Kleynhans et al. (2012) and Neizel et al. (2013), the abrasion resistance test apparatus utilised was based on a downscaled version of the European standard EN 15051 rotating drum. The drum was designed

according to specifications provided by Schneider and Jensen (2008). Abrasion resistance tests were conducted at drum rotational speeds of 33, 55 and 77 rpm. A batch of ten oxidative sintered pellets, generated under specific experimental conditions, was abraded for different time periods, i.e. 1, 2, 4, 8, 16, 32 and 64 min. After each time interval, the material was screened at 9.5 mm. The over- and undersized material was then weighed and all the material returned to the drum for further abrasion until the final abrasion time interval was achieved.

2.9. Statistical handling of data

The compressive strength tests were repeated 50 times for each of the experimental conditions investigated. In order to determine whether the differences in mean values between the compressive strength of the two case study ores were meaningful, the t Test was applied (Skoog et al., 2004).

3. Results and discussions

3.1. Material characterisation

The particle size distributions of the as-received case study UG2 and metallurgical grade chromite ore samples are presented in Table 1. It is evident from these results that the case study UG2 ore was substantially finer than the case study metallurgical grade chromite ore. This was expected, since the UG2 ore originated from the process residue of the PGM industry where it was already milled to liberate the PGMs. The relevance of the difference in size distribution of the as-received case study ores will be discussed later.

Table 1 Size distribution of as-received case study ores.

Particle size (μm)	Wt.%	
	Metallurgical grade chromite ore	Beneficiated UG2 process residue
<90	1.66	10.54
90-106	0.39	2.58
106-150	2.54	23.44
150-300	20.17	42.23
300-600	69.3	20.78
>600	5.94	0.43
TOTAL	100	100

In Table 2, the chemical, surface chemical and crystalline compositions of the two case study ores are presented. Chemical analysis (ICP-OES) indicated that the Cr_2O_3 compositions of the metallurgical grade and UG2 case study ores were 44.19 and 41.82 %, respectively, which is typical for these ores (Cramer et al., 2004). Slightly lower Cr_2O_3 compositions were obtained for both case study ores with XRF analysis, which can be expected since results obtained from the destructive chemical analysis technique (ICP-OES) will be more accurate. As expected, the XRD analyses indicated that chromite was the dominant Cr-containing mineral phase. All chemical analytical techniques (ICP-OES, SEM-EDS and XRF) indicated that the Fe-content of the UG2 ore was higher than that of the metallurgical grade chromite ore, which was reflected in the Cr/Fe ratios that were 1.4 and 1.58, respectively. These Cr/Fe ratios are quite typical of South African metallurgical grade and UG2 ores that are used in FeCr production (Cramer et al., 2004).

Table 2 Characterisation of the two case study ores in terms of the chemical (ICP-OES and XRF), surface chemical (SEM-EDS) and crystalline (XRD) contents.

XRF	Metgrade	UG2	XRD semi-quantitative	Metgrade	UG2
Na ₂ O	-	0.12	Magnetite	9	-
MgO	8.46	9.1	Chromite	38	32
Al ₂ O ₃	11.0	11.7	Enstatite	32	58
SiO ₂	4.48	5.46	Magnesioferrite	16	4
P ₂ O ₅	0.01	0.01	Tetrataenite	-	2
SO ₃	0.02	0.03	Trevorite	4	4
Cl	0.01	0.01	SEM-EDS	Metgrade	UG2
K ₂ O	0.02	0.01	Cr	28.1	28.1
CaO	0.24	0.35	Fe	16.0	18.0
TiO ₂	0.67	0.78	Al	6.5	6.7
Cr ₂ O ₃	40.7	37.8	Mg	6.3	5.7
MnO	-	0.28	Si	2.4	2.0
Fe ₂ O ₃	26.4	27.3	Ca	-	0.3
Co ₃ O ₄	-	0.09	Ti	0.4	0.4
NiO	0.13	0.17	V	-	0.3
ZnO	-	0.0849	O	40.3	38.5
ZrO ₂	-	0.01			
ICP-OES	Metgrade	UG2			
Cr ₂ O ₃	44.19	41.82			
FeO	24.68	26.2			
SiO ₂	2.96	3.38			
Al ₂ O ₃	14.71	16.21			
MgO	10.31	10.47			
CaO	0.16	0.27			
P	0.001	0.001			
Cr/Fe	1.58	1.4			

The bentonite used as a binder and the anthracite used as a carbonaceous source in the oxidative sintered pellets were exactly the same sample materials utilised by Kleynhans et al. (2012). These authors (Kleynhans et al., 2012) conducted detailed characterisation of these two materials (chemical, surface chemical and crystalline contents) and it is therefore not presented in this paper. In summary, the bentonite

consisted mostly of smectite mineral groups, which were made up of montmorillonite. On an air-dried basis, the anthracite sample had 75.08 % fixed carbon, 17.79 % ash and 6.87 % volatiles.

3.2. Particle size requirement

For the pelletised chromite pre-reduction process, Kleynhans et al. (2012) stated that the milled particle size requirement is 90 % of the particles (d_{90}) to be smaller than 75 μm . However, definitive information regarding the particle size requirement for oxidative sintered pellets could not be obtained in the peer-reviewed public domain. Laser diffraction particle sizing analyses of 10 milled chromite ore samples obtained from a large FeCr producer applying the oxidative sintered process yielded an average d_{90} of 108 μm . This value was therefore adopted as the required particles size target during subsequent milling experiments.

In Fig. 2, the d_{10} , d_{50} and d_{90} values obtained with laser diffraction particle sizing analysis of the two case study ores milled for different time periods with the Siebtechnik mill are presented. Additionally, the solid lines in this figure indicate trends of each data series. Although the d_{50} of both the case study ores was the same after approximately 95 s of milling, the d_{90} at this milling time of the metallurgical grade chromite ore was still higher than the targeted value of 108 μm . After approximately 120 s of milling, both case study ores had a d_{90} close to the aforementioned target value. However, at this milling time, the d_{50} values of the two case study ores differed substantially. This data indicated that it would be impossible with this specific mill to find a milling time that would yield a d_{90} value of 108 μm for both ores, with both ores also having the same particle size distribution. Achieving this might have been possible if the composition of the milling media could have been

changed, but this was impossible with the mill utilised. It was therefore decided to mill the case study ore mixtures at both 95 and 120 s in preparation for pelletisation.

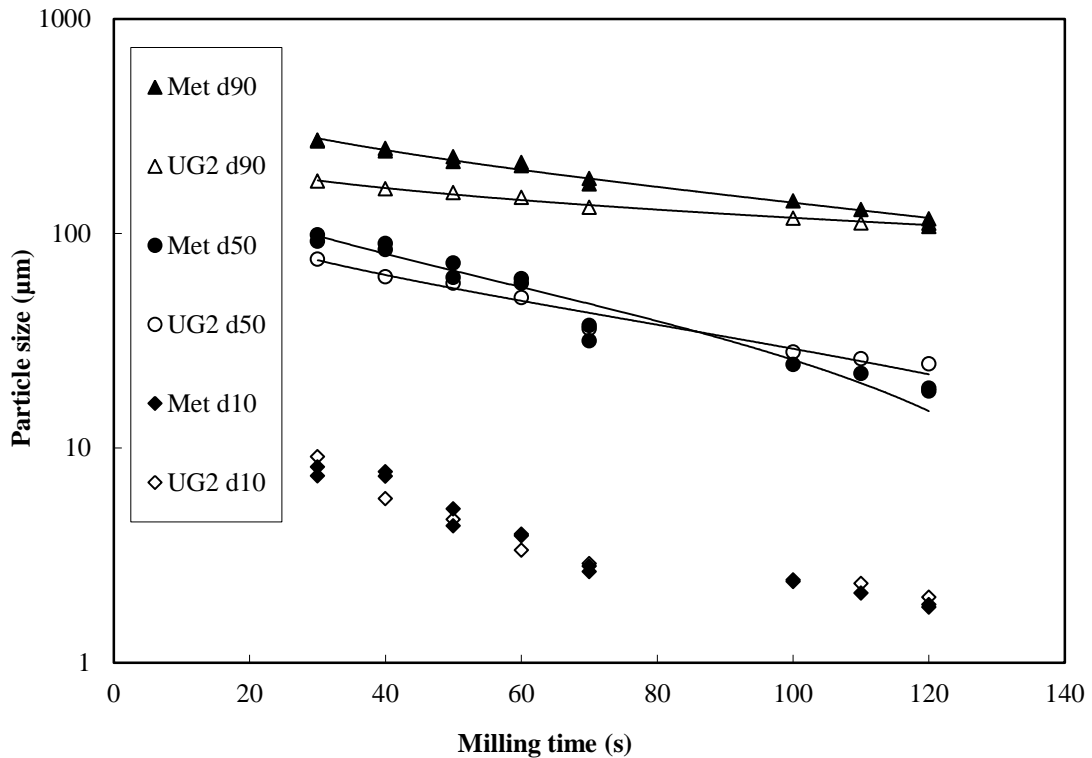


Fig. 2. Particle size of the two case study ores milled with the Siebtechnik mill used to prepare oxidative sintered pellets.

3.3. Compressive strengths comparison

In Fig. 3, the compressive strength of oxidative sintered pellets prepared from the two case study ores milled with the Siebtechnik mill at 95 s, i.e. where the d_{50} values were the same and at 120 s, i.e. where the d_{90} values were similar, is presented. In this box and whisker plot, the short horizontal line inside the box indicates the median of each dataset, the dot the mean, the upper and lower ends of the boxes the 25th and 75th percentiles and the whiskers 2.7σ (99.3 % coverage if it is assumed that the data has a normal distribution). Although there are significant overlaps between the datasets, it

seems that the oxidative sintered pellets prepared from UG2 ore milled for 95 s were slightly stronger, i.e. higher median and mean values, in relation to the oxidative sintered pellets prepared from the metallurgical grade chromite ore milled for 95 s. The calculation of the t-Test values with and comparison of these to standard t-values at a 95 % probability (Skoog et al., 2004), proved that the differences in the mean pellet compressive strengths between these two datasets were meaningful. However, for pellets prepared from ore milled for 120 s, there was no meaningful difference in the pellet compressive strengths. Considering these results, it can be stated with a high level of confidence that oxidative sintered pellets prepared from UG2 ore are likely to have similar or better compressive strength compared to pellets prepared from metallurgical grade chromite ore.

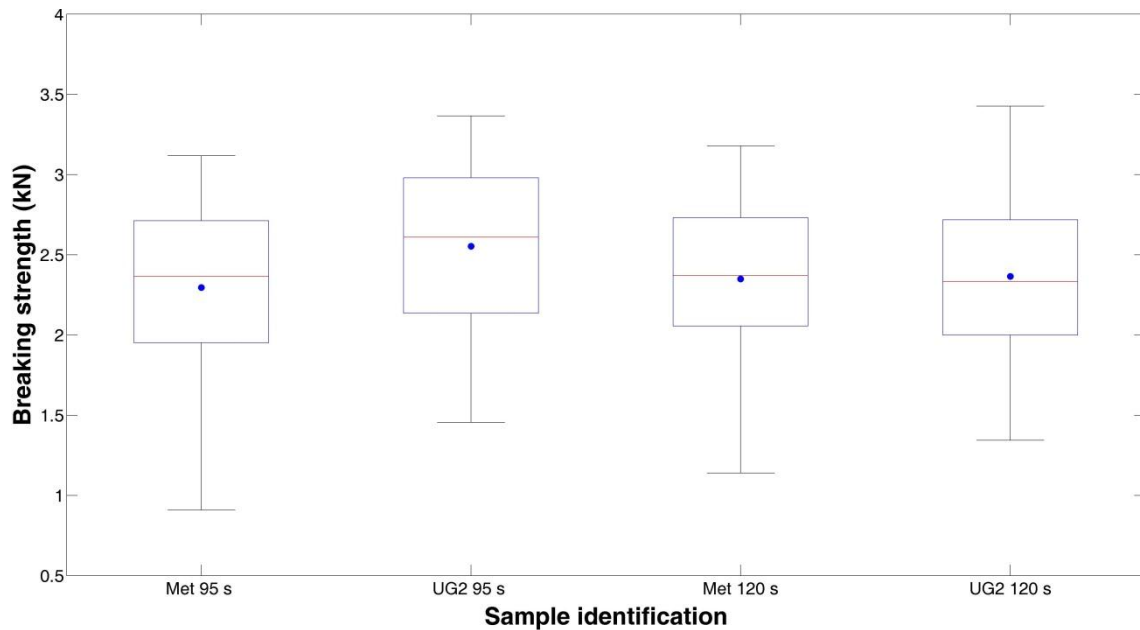


Fig. 3. Statistical comparison of compressive strength of oxidative sintered pellets prepared from the two case study ores milled for 95 s and 120 s with the Siebtechnik mill.

3.4. Abrasion strength comparison

The comparison of abrasion strengths at different rotational drum speeds for oxidative sintered pellets prepared from UG2 and metallurgical grade chromite ore is presented in Fig. 4. All of these pellets were prepared from ore milled for 120 s in the Siebtechnik mill. It is evident from this data (Fig. 4) that the abrasion strength of the UG2 oxidative sintered pellets was better than that of the oxidative sintered pellets prepared from metallurgical grade chromite ore.

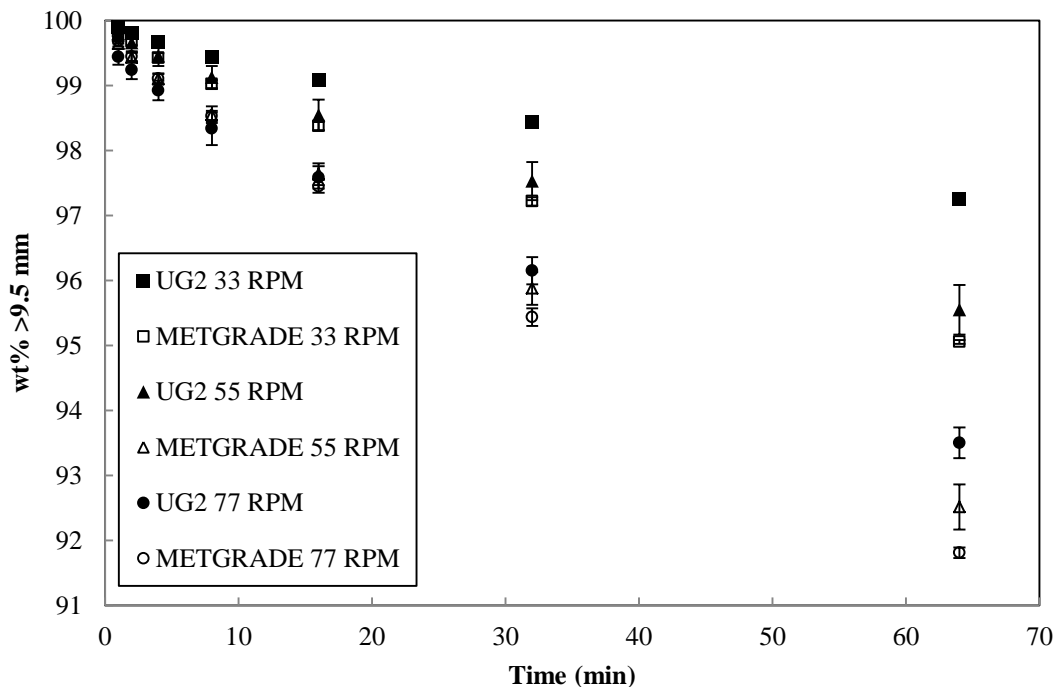


Fig. 4. Abrasion resistance strength indicated in weight percentage remaining above 9.5 mm versus abrasion time

3.5. Microstructural analysis

In order to assess why the compressive (Section 3.3) and abrasion (Section 3.4) strengths of oxidative sintered pellets prepared from UG2 ore were in general better than that of oxidative sintered pellets prepared from the metallurgical grade chromite

ore, microstructural analysis was performed. In Fig. 5, SEM backscatter micrographs of polished sections at two magnifications of oxidative sintered pellets prepared from metallurgical grade and UG2 chromite ore are presented. All these pellets were prepared from ore milled for 120 s with the Siebtechnik mill. From the backscatter micrographs (Fig. 5), it is evident that the oxidative sintered pellets prepared from both case study ores revealed a crystalline structure. However, the crystalline structure of the oxidative pellets prepared from the metallurgical grade chromite ore had a much finer and better defined crystalline structure than that of the pellets prepared from UG2 ore.

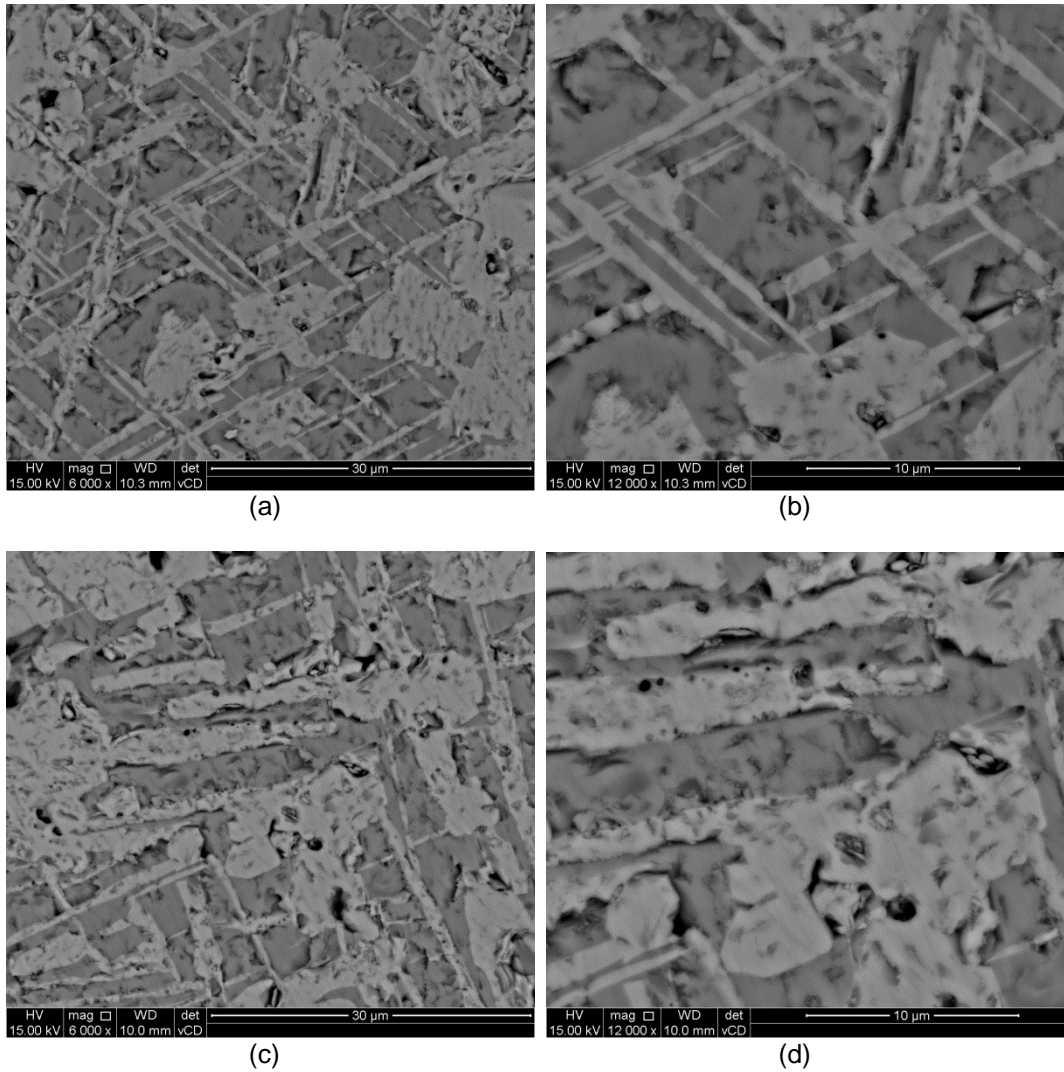


Fig. 5. Backscatter SEM micrographs at two different magnifications of oxidative sintered pellets prepared from metallurgical grade chromite ore ((a) and (b)), and oxidative sintered pellets prepared from UG2 ore ((c) and (d)).

According to the Hall-Petch law, Eq. (1), structures with smaller grain size require higher force before breaking (DoITPoMS, 2013).

$$\sigma_y = \sigma_i + \frac{k}{\sqrt{d}} \quad (1)$$

where σ_y is the tensile yield stress, d grain diameter, σ_i is the 'intrinsic' yield stress, and k is a constant for a particular material.

If the Hall-Petch law (Eq. 1) is applied, it would have been expected that the pellets prepared from metallurgical grade chromite would have been stronger. This was clearly not the case (Figs. 3 and 4). However, the Hall-Petch law only applied to grain structures of materials with the same composition. As indicated in Table 2, the chemical and crystalline content of the two case study ores differed from one another. It is therefore unlikely that this law can be applied.

SEM secondary electron micrographs of the same areas shown in Fig. 5 are presented in Fig. 6. In contrast to SEM backscatter micrographs (Fig. 5), secondary electron micrographs (Fig. 6) give a topographic perspective. Since these figures indicate polished sections of both pellet types, limited depth perspective information can be derived from Fig. 6. However, it seems as if the crystalline structure occurring in the oxidative sintered pellets prepared from the metallurgical grade chromite is better defined (Figs. 6(a) and 6(b)) than the crystalline structure occurring in the pellets prepared from the UG2, which blends into the general matrix (Figs. 6(c) and 6(d)). This indicates that the crystals formed in the oxidative sintered pellets prepared from the metallurgical grade chromite was a well-defined separate phase from the matrix, while in the pellets prepared from the UG2 ore, the crystal had assimilated better into the general matrix. The better assimilation of the crystalline growth into the matrix of the pellets prepared from the UG2 ore could at least partially explain why this type of pellet was stronger than that prepared from metallurgical grade chromite (Fig. 3 and 4).

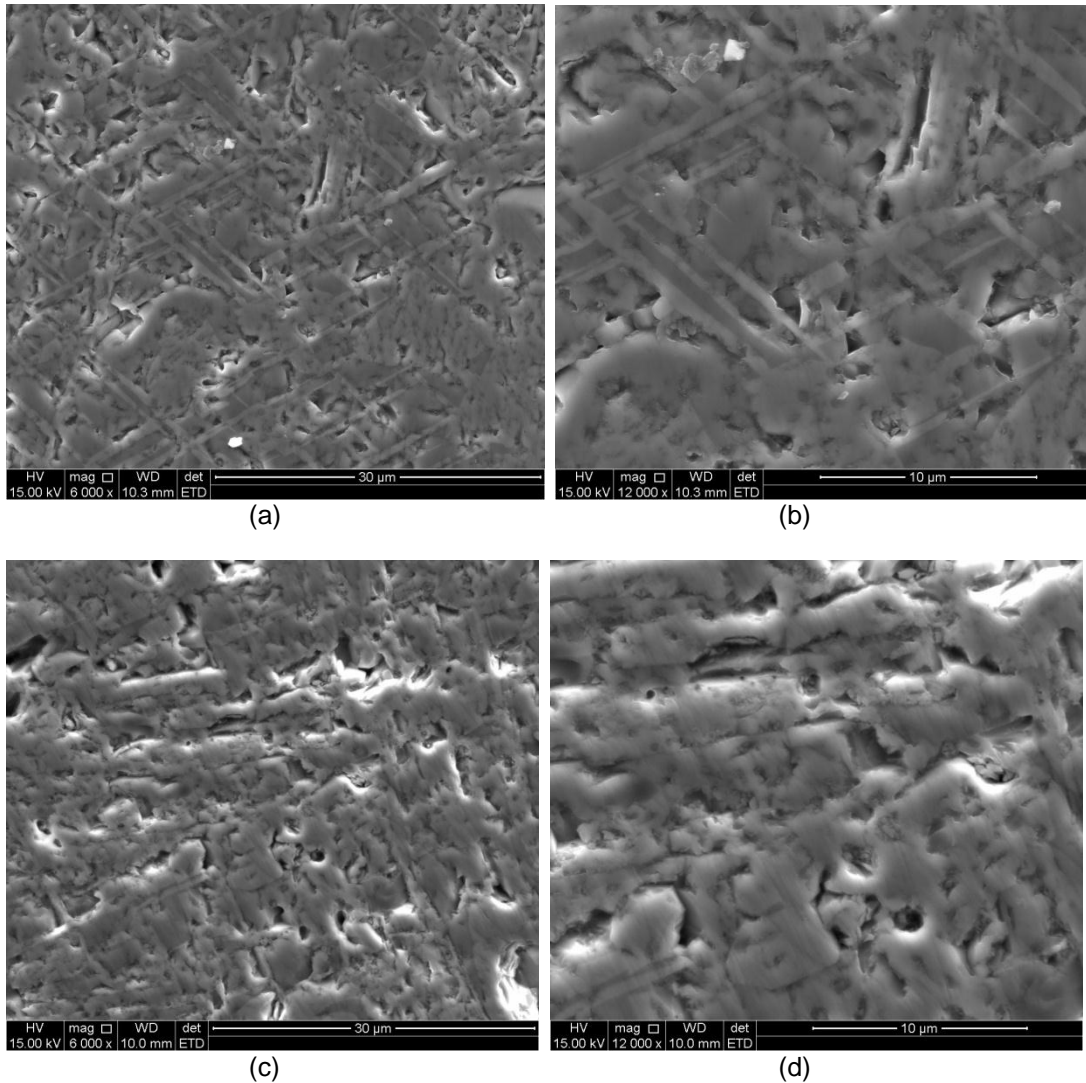
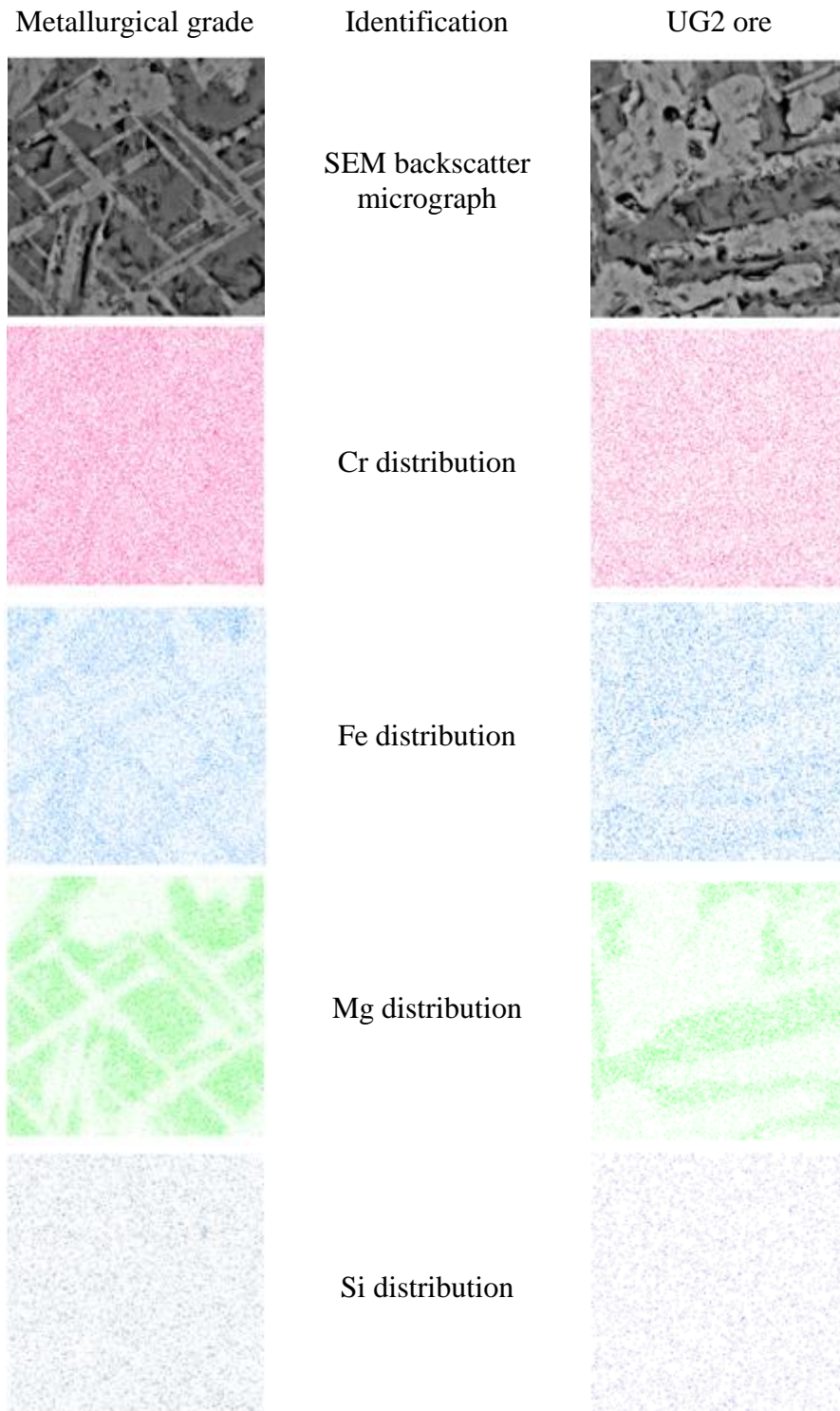


Fig. 6. SEM secondary electron micrographs at two different magnifications of oxidative sintered pellets prepared from metallurgical grade chromite ore ((a) and (b)), and oxidative sintered pellets prepared from UG2 ore ((c) and (d)).

In addition to the backscatter (Fig. 5) and secondary electron (Fig. 6) micrographs already discussed, X-ray mapping of elemental distribution of the two pellet types is presented in Fig. 7. From these figures, it is evident that the Mg distribution correlated best with the crystalline structures observed (Figs. 5 and 6), with low Mg content in the crystals compared to the general matrix. Although not that well defined, Fe was enriched in the crystals observed. However, both pellet types exhibited these elemental

distribution differences and it can therefore not be used to explain the differences in pellet strengths observed (Figs. 3 and 4).



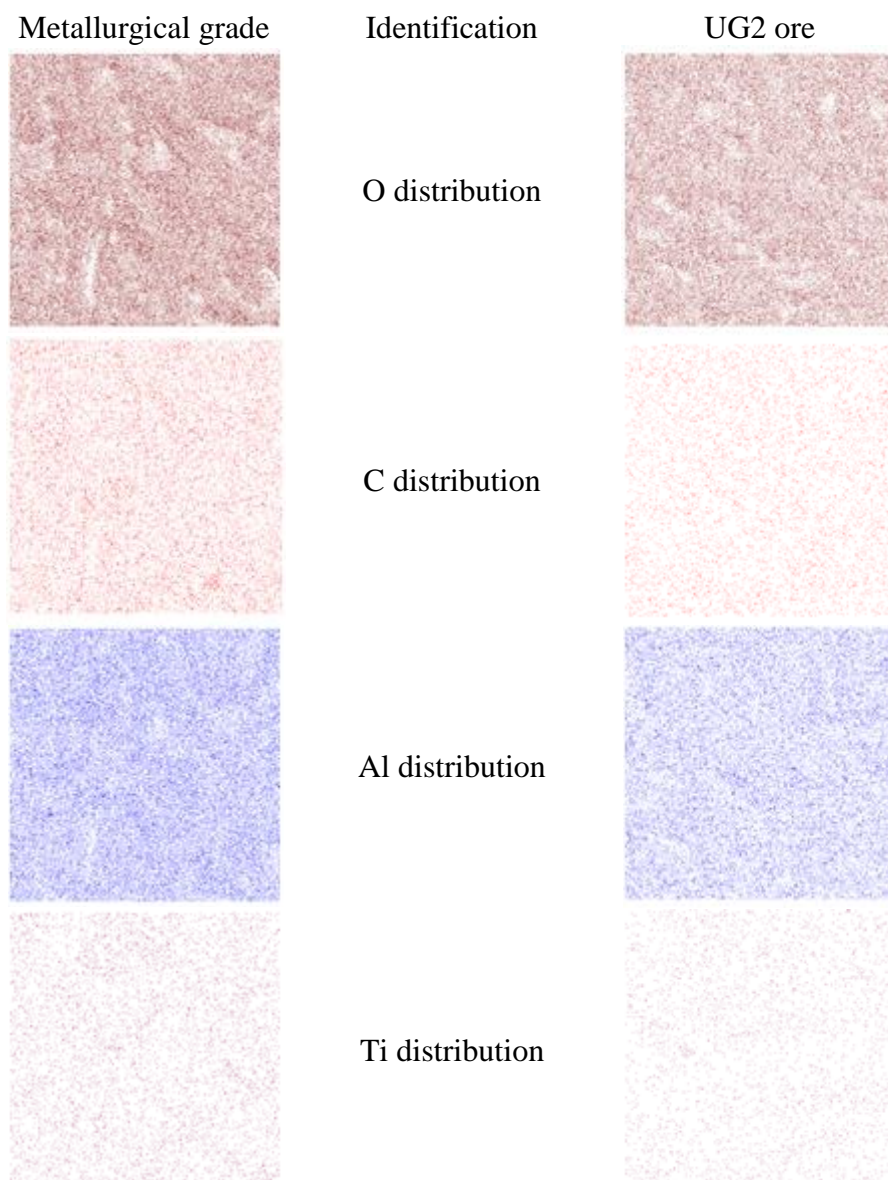


Fig. 7. SEM elemental X-ray mapping micrographs of oxidative sintered pellets prepared from metallurgical grade chromite ore and oxidative sintered pellets prepared from UG2 ore.

3.6. *Milling energy requirements*

In Fig. 8, the energy input measured during the stirred mill tests is presented as a function of particle size, i.e. d_{90} and d_{50} , for both case study ores. The targeted particle size, i.e. d_{90} of 108 μm (Section 3.2), is also indicated as a solid horizontal line in this figure. From these results, it is evident that the case study UG2 ore required 13 kWh/t less energy than the case study metallurgical grade chromite to reach the targeted particle size. This is plausible since the as-received UG2 ore particle size distribution was substantially finer than that of the as-received metallurgical grade chromite (Table 1). Although Cramer et al. (2004) mentioned that less energy is required to mill UG2 ore than metallurgical grade ore, this advantage has not yet been quantified in the public peer-reviewed domain. With electricity costs rising rapidly in South Africa (Kleynhans et al., 2012) and electricity being the single largest cost component during FeCr production (Daavittila et al., 2004), this possible electricity saving during milling prior to pelletisation could be significant for large FeCr producers. For example, if a generic FeCr producer with a production capacity of 300 000 t FeCr/y is considered and it is assumed that 2.1 t oxidative sintered pellets are consumed to produce 1 t FeCr, it can be calculated that approximately 4.15 million ZAR can be saved if the case study UG2 ore instead of the case study metallurgical grade chromite ore was used exclusively. This calculation was based on an electricity unit cost of R0.523/kW h (Eskom, 2011).

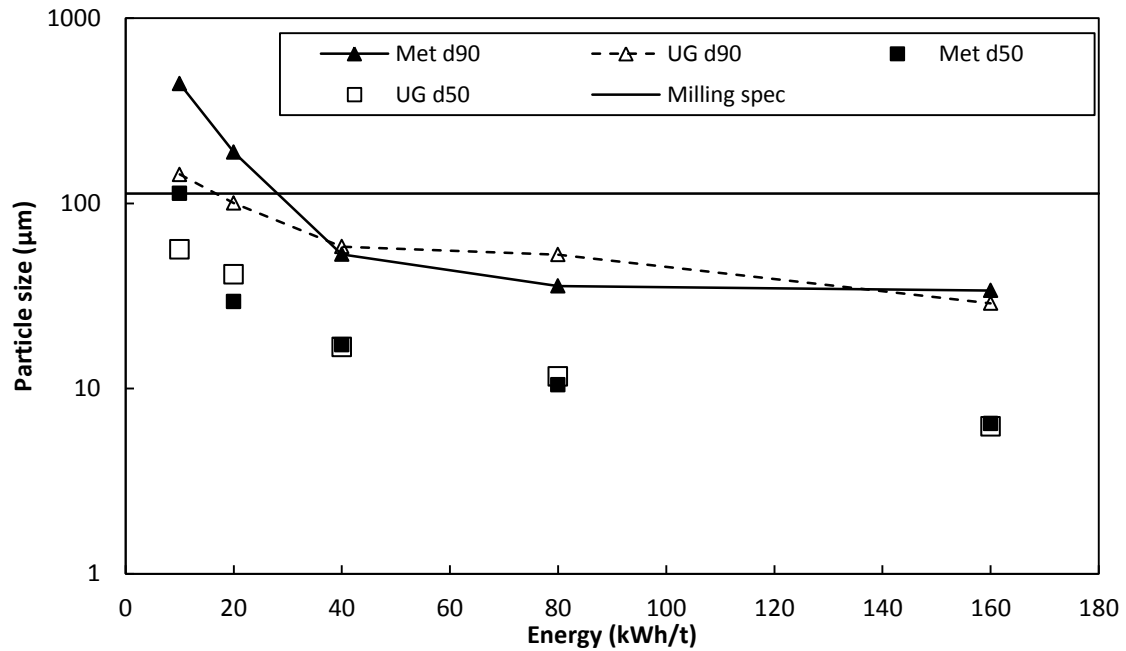


Fig. 8. Energy consumption as a function of particle size during stirred mill experiments for the two case study ores. The solid horizontal line indicates the targeted d_{90} value of 108 μm .

4. Conclusions

The results presented for the case study ores proved that the compressive strength of pellets prepared from the UG2 ore was the same, or stronger, than pellets prepared from the metallurgical grade chromite. The UG2 pellets also had superior abrasion strength. It can therefore be stated that the use of UG2 ore, instead of metallurgical grade chromite ore, is unlikely to result in the formation of additional fines (e.g. 0 to 6 mm) during material handling and feeding into submerged arc furnaces (SAF). Limited fine materials can be accommodated in SAFs, since fines can lead to unstable operation, as well as increased safety risks and equipment damages. SEM backscatter, as well as secondary electron and elemental X-ray mapping indicated that the cured oxidative sintered pellets prepared from both the case study ores had developed a relatively well-

defined crystalline structure. The crystalline structure of the pellets prepared from the UG2 ore was, however, better assimilated into the matrix, which could explain its general superior strength. The results further proved that less energy was required to mill the case study UG2 to the desired particle size, which can lead to substantial cost savings.

Results presented in this paper can be used by South African FeCr producers to better quantify the advantages or disadvantages associated with UG2 ore consumption. Considering the size of the South African FeCr industry, decisions impacting the local FeCr industry also have a global influence on the FeCr market. Additionally, substantial volumes of UG2 ore are currently being exported for FeCr production outside South Africa. Therefore, the results can also assist these FeCr producers to contextualise the use of South African UG2 ore.

Acknowledgements

The authors wish to thank Glencore Alloys for financial assistance and Mintek for the use their stirred mill.

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CHAPTER 4

PROJECT EVALUATION AND FUTURE PROSPECTIVE

4.1 Project evaluation

The general aim of this study was to compare the physical properties of oxidative sintered pellets produced from a typical South African BIC metallurgical grade chromite ore to oxidative sintered pellets produced from a typical South African BIC UG2 ore. In Chapter 1, specific objectives were set in order to achieve this main objective. These objectives are critically evaluated in this section in view of the successes and shortcomings of the study.

Objective 1: Detailed characterisation of the two case study ores

An extensive material characterisation was performed on both the UG2 ore and the metallurgical grade chromite ore. The particle size distribution was determined for both materials and it was found that the case study UG2 ore was substantially finer than the case study metallurgical grade chromite ore. This was expected, since the UG2 ore originated from the process residue of the PGM industry where it was already milled to liberate the PGMs. All chemical analytical techniques (ICP-OES, SEM-EDS and XRF) indicated that the Fe content was higher and the Cr content lower for the UG2 ore compared to that of the metallurgical grade chromite ore.

Objective 2: Production of oxidative sintered pellets from the case study ores with a procedure simulating the industrially applied process

Although no definitive information regarding the particle size requirements for oxidative sintered pellets could be obtained in the peer-reviewed public domain, the candidate analysed 10 milled chromite ore samples obtained from a large FeCr producer that

applies the oxidative sintered process. An average d_{90} of 108 μm was determined for the milled ore, which was utilised as the required particles size target for the milling experiments. Identical cylindrical pellets were pressed with a computer controlled hydraulic press, as previously indicated in literature (Kleynhans et al., 2012; Neizel et al., 2013). The consistent size and density of the pellets prepared using the afore-mentioned procedure enabled the monovariance investigation of other factors.

Objective 3: Comparison of abrasion and breaking strengths of pellets produced with the above-mentioned procedure

The abrasion and breaking strength experiments revealed that oxidative sintered pellets made from the case study UG2 ore are at least as strong as oxidative sintered pellets made from the case study metallurgical grade chromite ore.

Objective 4: Determination of the energy requirements for milling the two case study ores

It was concluded that the case study UG2 ore requires less energy (13 kWh/ton ore) to be milled to the appropriate size (108 μm) for the oxidative sintered process than the case study metallurgical grade chromite ore.

Objective 5: Making recommendations with regard to the industrial use of UG2 ore in the oxidative sintered process

The results obtained in this investigation can be utilised by South African FeCr producers to better quantify the advantages and/or disadvantages associated with UG2 ore consumption. Considering the size of the South African FeCr industry, decisions impacting the local FeCr industry also have a global influence on the FeCr market.

4.2 Future prospective

Although the physical attributes of oxidative pellets prepared from the two case study ores were investigated in relative detail in this study, a complementing study on the smelting characteristics of oxidative pellets prepared from these case study ores would enable FeCr producers to better evaluate the full extent of the use of UG2 ore.

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