



SEM image processing as an alternative method to determine chromite pre-reduction

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Declaration

I, **Given Terrance Mpho Mohale**, hereby declare that the dissertation entitled:
SEM image processing as an alternative method of determining chromite pre-reduction,
is my own work and has not been submitted to any other tertiary institution in whole or in
part.



Given Terrance Mpho Mohale

Potchefstroom

November 2014

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Worthy are you, our Lord and God,
to receive glory and honor and power,
for you created all things, and by your will
they existed and were created.

Revelation 4:11
truthforlife.org/pray



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Soli Deo Gloria

Contents

DECLARATION	I
ACKNOWLEDGEMENTS	II
NOMENCLATURE	VI
LIST OF FIGURES	IX
LIST OF TABLES	XIII
ABSTRACT	XIV
CHAPTER 1: BACKGROUND, MOTIVATION AND OBJECTIVES	1
1.1. BACKGROUND AND MOTIVATION	1
1.2. OBJECTIVES	3
CHAPTER 2: LITERATURE SURVEY	4
2.1. GENERAL INFORMATION ON CHROMITE ORE	4
2.1.1. <i>Locality of chromite ore reserves</i>	<i>4</i>
2.1.2. <i>Beneficiation of chromite ore</i>	<i>7</i>
2.2. FERROCHROMIUM PRODUCTION	9
2.2.1. <i>FeCr production trends</i>	<i>9</i>
2.2.2. <i>FeCr production in SA and processes applied</i>	<i>11</i>
2.3. ASPECTS OF CHROMITE PRE-REDUCTION	15
2.3.1. <i>Fundamentals of chromite pre-reduction</i>	<i>15</i>
2.3.2. <i>Effects of temperature on chromite pre-reduction</i>	<i>21</i>
2.3.3. <i>Effects of additives on chromite pre-reduction</i>	<i>22</i>
2.3.4. <i>Benefits of chromite pre-reductions</i>	<i>23</i>

2.3.5.	<i>General technique used to determine chromite pre-reduction</i>	25
2.4.	SEM	29
2.5.	IMAGE PROCESSING	33
2.5.1.	<i>Fundamental principles of digital image analysis</i>	33
2.5.2.	<i>Types of digital images</i>	34
CHAPTER 3: EXPERIMENTAL		36
3.1.	MATERIALS	36
3.2.	METHODS	36
3.2.1.	<i>Proximate analysis</i>	37
3.2.2.	<i>Elemental analysis</i>	38
3.2.3.	<i>Pre-reduction analysis</i>	38
3.2.4.	<i>Sample material preparation prior to SEM analysis</i>	39
3.2.4.1.	<i>Milling of laboratory prepared pellets mixtures</i>	39
3.2.4.2.	<i>Molding and metallographic polishing</i>	40
3.2.5.	<i>EDS analysis</i>	44
3.2.6.	<i>SEM image acquisition</i>	44
3.2.7.	<i>Image processing and analysis</i>	45
CHAPTER 4: RESULTS AND DISCUSSION		49
4.1.	RAW MATERIAL ANALYSIS	49
4.2.	HYPOTHESIS FOR THE DEVELOPMENT OF THE NEW ANALYTICAL METHOD	50
4.3.	BASIC ALGORITHM	52
4.4.	VALIDATION OF THE ANALYTICAL TECHNIQUE	56
4.4.1.	<i>Analysis of laboratory prepared pellets mixtures</i>	56
4.4.2.	<i>Analysis of industrially pre-reduced pellets</i>	58

4.4.3. <i>Possible industrial application of the method</i>	62
CHAPTER 5: PROJECT EVALUATION AND FUTURE PERSPECTIVES	64
5.1. PROJECT EVALUATION	64
5.2. FUTURE PERSPECTIVES	67
5.3. FINAL REMARKS	68
REFERENCES	70
APPENDIX A: PRE-REDUCTION CALCULATIONS	84
APPENDIX B: IMAGES	88

Nomenclature

Measure units and abbreviations used in this dissertation

Symbol	Description	Unit
MWh/ton	Mega-watt hour per tonne	power per weight
kwh	Kilo-watt hour	Power
kV	Kilo volts	energy
keV	Kilo electron volts	energy
mbar	millibar	pressure
mm	millimetre	length
nm	nanometre	length
ml	Millilitre	volume
L	litre	volume
M	Molar	Mole per volume
μm	micrometre	length
rpm	Revolutions per minute	speed
g	Gram	weight
Mill t	Million tonnes	weight
D ₉₀	90 % of the particles to be smaller than a specified size	length
FC	Fixed carbon	%
% Sol Cr	Percentage of soluble chromium	%
% Sol Fe	Percentage of soluble iron	%
w/v	Weight per volume	%

R^2	Correlation factor
AOD	Argon Oxygen Decarburisation
BIC	Bush Ingenious Complex
ASTM	American Society for Testing and Materials
BSE	Backscatter electron
Cr^0	Chromium at zero state
Cr_{tot}	Total chromium
DC	Direct current
EDS	Energy Dispersive X-ray Spectroscopy
	Combined abbreviation for Electricity Supply Commission (ESCOM)
ESKOM	and Elektrisiteitsvoorsieningskommissie
FC	Fixed carbon
Fe^0	Iron at zero state
$FeCr$	Ferrochromium
Fe_{tot}	Total iron
HC	High Carbon
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IR	Infrared
LG-6	Lower group 6
$M(\%)$	Metallisation percentage
MATLAB®	Matrix Laboratory
n	Quantum number
NERSA	Nation Energy Regulator of South Africa
NWU	North-West University

PC	Pulverised Carbon
PGM	Precious Group Metal
R(%)	Reduction percentage
RGB	Red Green Blue
RSA	Republic of South Africa
SAF	Submerged Arc Furnace
SARM 8	Certificate of analysis for chromium ore (Reference Material)
SARM 18	Certificate of analysis for coal (Reference Material)
SEC	Specific Electricity Consumption
UG-2	Upper group 2
WD	Working Distance
Z	Atomic number
ZAR	South African currency (rand)

List of Figures

Chapter 2: Literature survey

Figure 2-1:	Global chromite resources map (adapted from Pariser, 2013)	5
Figure 2-2:	The extent of the BIC and the location of FeCr smelters in South Africa	6
Figure 2-3:	General process flow sheet for chromite ore beneficiation (adapted from Murthy <i>et al.</i> , 2011)	8
Figure 2-4:	World HC/charge FeCr production in metric tonnes (10^6) (adapted from Fowkes, 2013)	11
Figure 2-5:	Process flow diagram of essential and common process steps utilised for FeCr production in South Africa adapted from Beukes <i>et al.</i> , (2010)	13
Figure 2-6:	The relationship between pre-reduction and metallisation, based on South African LG-6 (lower group) chromite treated at 1200 °C (adapted from Dawson & Edwards, 1986)	17
Figure 2-7:	Standard free energies of reduction of metal oxides with carbon and carbon monoxide (adapted from Niemelä <i>et al.</i> , 2004)	19
Figure 2-8:	Diagram illustrating the reduction mechanism of chromite (adapted from Ding & Warner, 1997b)	20
Figure 2-9:	The effect of time and temperature on the rate of chromite reduction (adapted Barnes <i>et al.</i> , 1983)	22
Figure 2-10:	The influence of various additives on the rate of chromite reduction at 1200 °C (adapted from Katayama <i>et al.</i> , 1986)	23
Figure 2-11:	SEC for the production of FeCr as a function of the pre-reduction level and charging temperature reconstructed from Takano <i>et al.</i> (2007) and Niayesh & Fletcher (1986)	25

Figure 2-12:	General wet chemical analysis procedure for analysing pre-reduction in pre-reduced material (adapted Baker & Siple, 1990)	27
Figure 2-13:	Signals emitted from a solid sample when struck by incident electron beam reconstructed from Viljoen & Johnson, (1983) and Goldstein <i>et al.</i> (2003)	30
Figure 2-14:	Schematic diagram of inner atomic electron shells	31
Figure 2-15:	Typical K shell spectra	32
Chapter 3:	Experimental	
Figure 3- 1:	A Speedivac vacuum degassing chamber model VDC 12	41
Figure 3- 2:	An image of a SS20 Spectrum System Grinder polisher, polishing three molded chromite pre-reduced pellets at the same time with diamond paste suspension dripping at a set flow rate while the disc rotates at 139 rpm	42
Figure 3- 3:	Inspection of sample scratches using a Nikon stereo-spectroscopy	43
Figure 3- 4:	Typical molded, polished and carbon coated samples of pre-reduced pellet mixtures	44
Figure 3- 5:	Steps for image analysis processing wherein decision are taken before pursuing the next step (adapted from Grande, 2012)	46
Chapter 4:	Results and discussion	
Figure 4 -1:	Identification of greyscale levels related to elements composition in respective particle using EDS, of a laboratory pre-reduced pellet mixture	51
Figure 4-2:	An example of a SEM micrograph image processing scheme wherein (a) is the original SEM micrograph image, (b) a zoomed-in area showing	

	actual pixels, (c) showing greyscale color numbers of the corresponding pixels and (d) is the converted binary black and white image	54
Figure 4-3:	An example of (a) ten SEM micrograph images stitched together and (b) shows a histogram of pixel numbers as a function of greyscale color and the corresponding threshold values	55
Figure 4-4:	Correlation between white pixel (%) and chromite pre-reduction (%) whereby the diamonds, triangles and crosses represent 1, 3 and 5% carbon content, respectively	56
Figure 4-5:	Polished sectional SEM micrograph image of a typical laboratory prepared pellet mixture	57
Figure 4-6:	Polished sectional SEM micrograph image of a typical industrial pre-reduced pellet mixture	59
Figure 4-7:	The pre-reduction of chromite in terms of the of metallisation rates of iron, Cr and their combination, adapted from Dawson & Edwards (1986). The evaluated pre-reduction range in this study is illustrated by the red line, corresponding (approximated) to the black dotted straight line	60
Figure 4-8:	Correlation between white pixels (%) and chromite pre-reduction levels (%) of industrial pre-reduced pellets originating from two different kilns	61

Appendix B

Figure B- 1:	A typical binary image of a flower with zoomed in pixel region showing 0's and 1's, acquired in MATLAB	88
Figure B- 2:	Greyscale image of a flower shown with zoomed in pixel region from 0 to 255 acquired in MATLAB	89

List of Tables

Chapter 2: Literature survey

Table 2-1:	The main commercial grades of ferrochromium according to ISO-standard 5448-81 (Lyakishev & Gasik, 1998; Downing <i>et al.</i> , 1986)	10
Table 2-2:	Production capacities of South African FeCr smelters adapted from Beukes <i>et al.</i> (2010) and Jones (2014)	12

Chapter 3: Experimental

Table 3-1:	Matlab syntax and their respective general descriptions (MathWorks, 2014)	47
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Chapter 4: Results and discussions

Table 4-1	Chemical characterisation of the metallurgical grade chromite (<1 mm), anthracite breeze (<1 mm) and fine FeCr (<1 mm) received from a large FeCr producer. These materials were used to prepare pre-reduced pellet mixtures synthesized in the laboratory, described in the text	50
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Abstract

Ferrochrome (FeCr) is a crude alloy containing chromium (Cr) and iron (Fe). FeCr is mainly used for the production of stainless steel, which is an important modern-day alloy. FeCr is produced from chromite ore through various smelting methods. In this study, the focus was on the pelletised chromite pre-reduction process, which is also referred to as the solid state reduction of chromite. In this process, fine chromite ore, a clay binder and a carbon reductant are dry milled, agglomerated (pelletised) and pre-reduced (solid state reduction) in a rotary kiln. The pre-reduced pellets are then charged hot, immediately after exiting the rotary kiln, into a closed submerged arc furnace (SAF). This production process option has the lowest specific energy consumption (SEC), i.e. MWh/ton FeCr produced, of all the FeCr production processes that are commercially applied. Other advantages associated with the application of the pelletised chromite pre-reduction process are that it eliminates the use of chromite fines, has a high Cr recovery, and produces low sulphur- (S) and silicon (Si)-containing FeCr. The main disadvantage of the pelletised chromite pre-reduction process is that it requires extensive metallurgical control due to the variances in the levels of pre-reduction achieved and carbon content of the pre-reduced pelletised furnace feed material. This implies that the metallurgical carbon balance has to be changed regularly to prevent the process from becoming carbon deficient (also referred to as ‘under coke’) or over carbon (also referred to as ‘over coke’). The analytical technique currently applied to determine the level of chromite pre-reduction is time consuming, making it difficult and expensive to deal with large numbers of samples. In an attempt to develop a technique that would be faster to determine the level of chromite pre-reduction, a new analytical method using a combination of scanning electron microscopy (SEM), image processing and computational techniques was investigated in this study.

Metallurgical grade chromite (<1 mm), anthracite breeze (<1 mm), and fine FeCr (<1 mm) that were used to prepare pellets in the laboratory, as well as industrially produced pre-reduced pellets that had already been milled in preparation for the determination of the pre-reduction level with wet chemical analysis were received from a large South African FeCr producer. These laboratory prepared pellets and the industrially produced pellet mixtures were considered in this investigation. Samples were moulded in resin and polished in order to obtain SEM micrographs of the polished cross sections. Elements with higher molecular weights are indicated by lighter greyscale, while elements with lower molecular weights are indicated by darker greyscale in SEM micrographs. This basic principle was applied in the development of the new analytical technique to determine the level of chromite pre-reduction, with the hypothesis that the pixel count of white pixels (representing metallised particles), divided by the combined pixel count of white (representing metallised particles) and grey (representing chromite particles) pixels would be directly related to the level of chromite pre-reduction determined with the current wet chemical method. This hypothesis can be mathematically expressed as:

$$\text{chromite prereduction \%} \cong \text{white pixel \%} = \frac{\text{white pixel count}}{\text{white pixel count} + \text{grey pixel count}}$$

The newly-developed analytical method was validated by correlating the white pixel% calculated with the chromite pre-reduction levels (%) determined with wet chemical analysis of laboratory prepared and industrially produced pellet mixtures, which had R² values of 0.998 and 0.919, respectively. This suggests that the method can be used to determine chromite pre-reduction accurately.

Keywords: *Metallurgical carbon balance, chromite pre-reduction, solid state reduction of chromite, scanning electron microscopy (SEM), image processing*

Chapter 1: Background, motivation and objectives

A brief background on the study, as well as the motivation for conducting this research, is outlined in Section 1.1. Subsequently, the objectives of the study are presented in Section 1.2.

1.1. Background and motivation

The ability of chromium (Cr) to be resistant against oxidation, i.e. prevent corrosion through the formation of a thin oxide layer on the surface of the metal, makes it a critical commodity in metallurgical, chemical and refractory industries. Ferrochrome (FeCr), which is a crude alloy that essentially consists of Cr and iron (Fe), is predominantly used for the manufacturing of stainless steels (metal alloys that resist oxidation), which contains ≤ 1.2 wt. % carbon (C) and $\geq 10.5\%$ Cr, with or without other elements. Stainless steels are predominantly used in the transport, process equipment, construction and catering appliances sectors (Pariser, 2013; Heikkinen & Fabritius, 2012; Murthy *et al.*, 2011; Akyüzü & Eric, 1992).

FeCr is produced from chromite ore, which is the only Cr-containing ore that is commercially viable for the recovery of Cr. The FeCr industry utilises various pre-processing and smelting methods of chromite ore, with the following processes being the most well defined (Beukes *et al.*, 2010; Daavittila *et al.*, 2004; Otani & Ichikawa, 1975): (a) Conventional semi-closed or open submerged arc furnace (SAF) operation that mainly utilises coarse chromite, flux and reductant feed materials. This process has the lowest capital input, since minimal pre-processing of the feed materials is necessary. However, it is the least environmentally friendly process and is also the least efficient in terms of Cr

recovery; (b) Closed SAF operation (e.g. Outotec process) that mainly uses oxidative sintered chromite pellets, as well as coarse flux and reductant as feed materials; (c) Closed SAF operation combined with pre-reduction of pelletised chromite ore, as well as coarse fluxes and reductants as feed material (e.g. Premus process applied by Glencore-Xstrata Alloys); (d) Closed SAF operation with plasma or direct current (DC) arc operation that can be fed fine feed material exclusively, thereby eliminating the pre-processing of raw materials. However, this process option has the highest specific electricity consumption (SEC), i.e. MWh/ton FeCr produced. According to Kleynhans (2012), the pelletised chromite pre-reduction process will become an even more attractive FeCr process option, as energy costs and environmental consciousness increase.

In the pelletised chromite pre-reduction process, extensive operation control is required to ensure optimal operation (Naiker, 2007; Otani & Ichikawa, 1975). Chromite pre-reduction levels and the amount of free C remaining in the pre-reduced pellets that are fed into the closed SAF vary over time. This influences the C balance of the process, which has to be changed regularly to prevent the smelting process from becoming C deficient (commonly referred to as ‘under coke’) or over C (commonly referred to as ‘over coke’). Both these imbalances can significantly affect Cr-recovery, production volume, tapping operation and general furnace stability. An unstable furnace could also have negative operational safety and environmental impacts. Therefore, the implementation of a robust and precise analytical technique to determine the level of chromite pre-reduction of the pellets being fed to the furnace is essential. The currently applied analytical method is an extensive and tedious procedure. The time between sampling the pellets and the availability of the analytical results become available is at least eight to 16 hours, which significantly contribute to metallurgical imbalance.

In an attempt to have a faster turn-around between the sampling of the pre-reduced pellets and the availability of the analytical results that indicate the level of chromite pre-reduction, a new analytical method using scanning electron microscopy (SEM) along with image processing was investigated as an alternative method.

1.2. Objectives

The specific objectives of this study were to:

- a) conduct a thorough literature survey to contextualise the work and indicate scientific gaps;
- b) develop an alternative method to determine chromite pre-reduction, using SEM image acquisition and image processing;
- c) validate the new analytical method by comparing it to pre-reduction levels of laboratory prepared and industrially produced pellets mixtures; and
- d) make recommendations with regard to the industrial relevance of the developed method and possible future research.

Chapter 2: Literature survey

The first section (Section 2.1) of this literature chapter provides a review of the general aspects of chromite ore, in particular the global and local reserves, as well as the various beneficiation processes of chromite ore. Ferrochrome (FeCr) production trends, FeCr production in South Africa and the production processes utilised are discussed in section 2.2. Significant aspects of the pelletised chromite pre-reduction process are discussed in section 2.3, wherein the focus is directed towards the fundamental characteristics, effects of temperature and additives, advantages, and the general analytical techniques applied to determine the level of chromite pre-reduction. The essential features of scanning electron microscopy (SEM) and image processing analyses are discussed in sections 2.4 and 2.5, respectively.

2.1. General information on chromite ore

2.1.1. *Locality of chromite ore reserves*

The first known and mined source of Cr was from lead chromate (PbCrO_4), which was found in the Ural Moldains in the former Union of Soviet Socialist Republics (U.S.S.R.) and was initially used for pigmentation. Since the discovery of high-grade chromite ore in Turkey during 1848, it has remained the only commercially viable source of new Cr units. Commercially viable chromite ore reserves exist in mafic hosting PGMs and ultramafic/ultrabasic rocks, which are subdivided into two types of ore deposits, i.e. stratiform and irregular podiform. These ultramafic rocks are generally found in countries such as South Africa, Zimbabwe, India, Kazakhstan, Turkey, Australia, Brazil, Finland, Russia, Vietnam, Oman and Pakistan. Stratiform seam deposits are particularly found in South Africa, Madagascar and India, whereas the podiform deposits that are relatively minor

(but contain a high Cr-to-Fe ratio) can be found in Kazakhstan, Turkey and Albania (ICDA, 2013; Murthy *et al.*, 2011; Schouwstra *et al.*, 2000; Howat, 1986). Figure 2-1 shows the global chromite ore resources, i.e. the stratiform and podiform deposits.

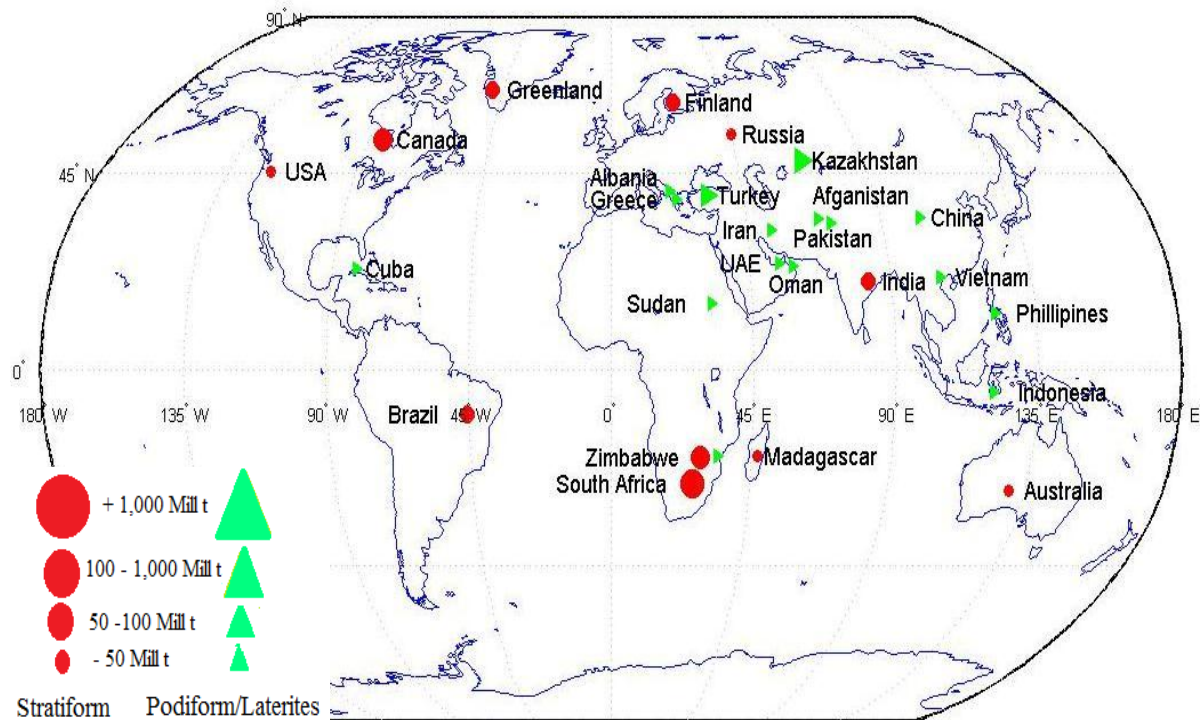


Figure 2-1: A global map of chromite reserves reconstructed from (Pariser, 2013)

From Figure 2-1, it is evident that South Africa holds the majority of the world's exploitable chromite ore reserves (approximately 75%). South Africa exports chromite ore to China, Europe, USA, Turkey, South America and India. China is the leading importer of chromite ore, whereas South Africa and Turkey are the main exporters (Pariser, 2013; Papp, 2011).

The South African Bushveld Igneous Complex (BIC) is a mineral rich area, which is a saucer-like intrusion that stretches from the western limb located in the North West Province to the eastern limbs in Mpumalanga and Limpopo (Schouwstra *et al.*, 2000; Howat, 1986).

Most of the chromite mines and FeCr smelters in South Africa are situated within the BIC. In Figure 2-2 presented below, the extent of the BIC and the locality of FeCr smelters in South Africa are indicated. Apart from chromite, the BIC also holds various other minerals, e.g. tin (Sn) in the acidic phase and fluorspar, vanadium, titanium, as well as platinum group metals (PGMs).

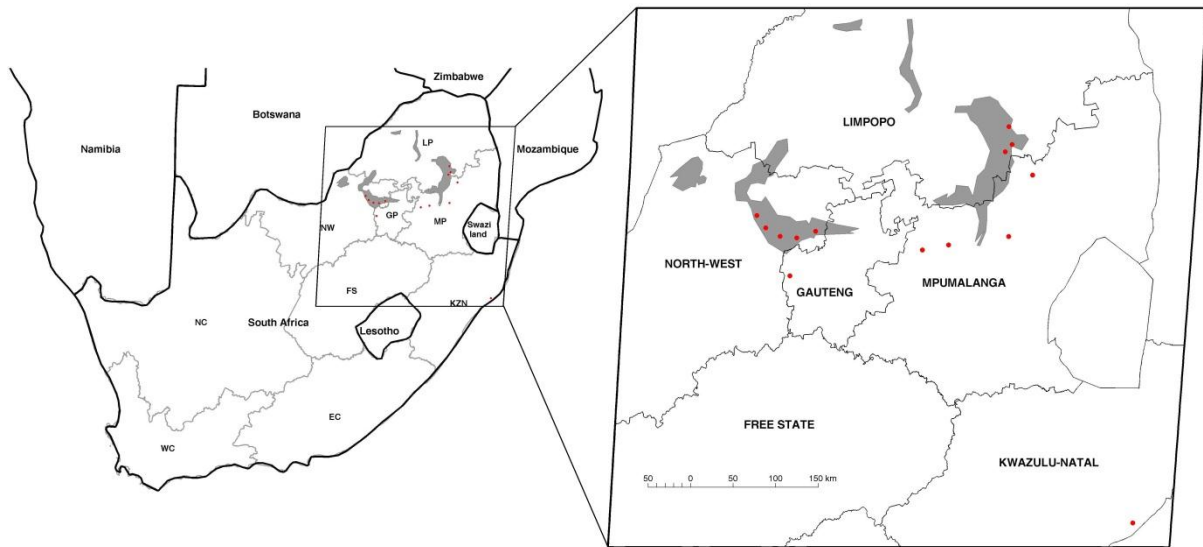


Figure 2-2: The extent of the BIC and the location of FeCr smelters in South Africa

Typical South African chromite ore located in the BIC can be chemically represented by a chromite spinel (complex mineral) structure of the following form $(\text{Fe}_{0.74}^{2+}\text{Mg}_{0.27})_{\Sigma=1.01}(\text{Cr}_{1.42}\text{Al}_{0.40}\text{Fe}_{0.15}^{3+}\text{Ti}_{0.01}\text{V}_{0.01})_{\Sigma=1.99}\text{O}_4$. The majority of the Cr reserves are present in the upper group 2 (UG-2) Reef and Merensky Reef of the BIC. Consequently, significant chromite ore mining operations and smelters are located in these regions. Within the BIC, the chromite ore containing the highest Cr oxide (Cr_2O_3) content (approximately 55 %) and having the highest Cr-to-Fe ratios (an average of 2.5) is located in the Zeerust and Potgietersrus districts, although these reserves are limited. However, areas within the BIC that contain the majority of the reserves have a lower grade ore, i.e. 45 % of Cr_2O_3 and Cr-to-Fe of 1.4 to 1.55 (Niemelä *et al.*, 2004; Schouwstra *et al.*, 2000; Howat, 1986).

2.1.2. Beneficiation of chromite ore

The objective of beneficiation is to have the ore concentrate physically (granulometry) and chemically suitable for subsequent treatments and refinement. Mineral processing techniques depend on the source of the ore, mineral characteristics of the ore deposits specified by the end-use sector, gangue mineral composition, as well as the degree of propagation of constituent minerals. Beneficiation activities do not change the value of the mineral, but typically serve to separate and concentrate valuable minerals from waste materials, to remove the waste discard and to prepare the ore for further refinement (Abubakre *et al.*, 2007). Processing and mineral beneficiation of ores can generally be outlined by the following steps (Murthy *et al.*, 2011; Wills, 2006):

- i. **Mining:** Depending on the distribution of the ore and location resources, open-cast mining, as well as underground mining methods can be employed to obtain chromite ore (Gediga & Russ, 2007; Nafziger, 1982).
- ii. **Liberation:** The first step of mineral processing, subsequent to mining and prior to concentration and extraction from ores, is the release of valuable minerals from their gangue waste minerals. The latter is accomplished by means of comminution, which includes crushing and/or grinding to a particle size wherein the product is a relatively clean mixture of the mineral and gangue containing liberated particles.
- iii. **Concentration:** This is the actual physical separation of the valuable minerals from their waste gangue or discard. Techniques such as heavy medium and gravity concentration are commonly employed for chromite.
- iv. **Extraction:** Extraction of metals from metal oxides, wherein pyrometallurgy, hydrometallurgy and electrometallurgy processing techniques can be employed. For FeCr production, pyrometallurgical smelting is required.

According to Riekkola-Vanhanen (1999), 30 % of natural chromite ore resources can be recovered as lumpy/coarse ore (typically between 6 mm and 150 mm) and 70 % as fine ore typically < 5 mm. The liberation (comminution) and concentration of fine chromite ore concentrate, such as metallurgical or chemical grade chromite ore (typically ≤ 1 mm), are presented in Figure 2-3. The production of pebble/chip and lumpy/coarse chromite ore is much less complicated, consisting mostly of crushing and heavy medium separation.

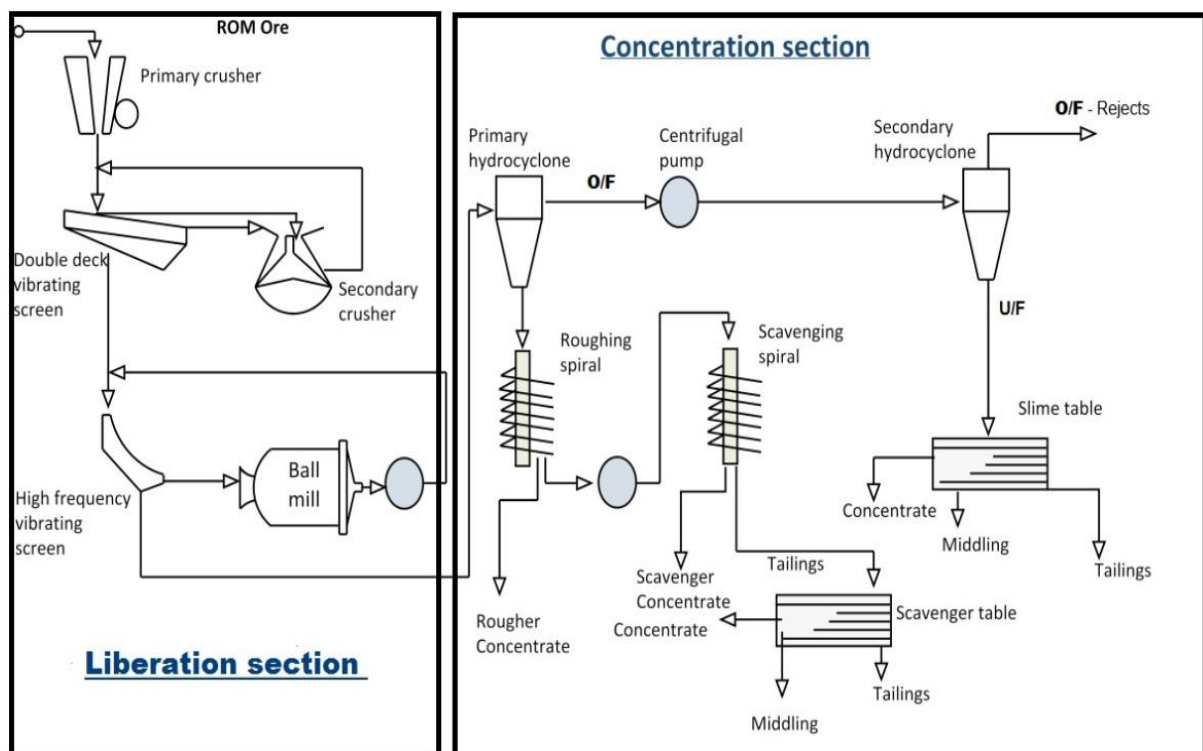


Figure 2-3: General process flow sheet for fine chromite ore beneficiation adopted from (Murthy *et al.*, 2011)

Gravity separation methods dominate flotation techniques for the production of chromite concentrate (typically ≤ 1 mm) (Nafziger, 1982). Froth flotation is therefore not a major method of beneficiation for chromite ores, although fatty acids, such as oleic acid, have been used where flotation has been adopted as a method of separation (Gu & Wills, 1988). South African chromite ores are comparatively friable and easily break down to the size of

the chromite crystals (Basson *et al.*, 2007; Gu & Wills, 1988). Due to this friability, it is common to only recover 10 to 15% lumpy ore (ranging between 15 mm and 150 mm) and 8 to 12% chip or pebble ores (range between 6 mm and 15 mm) during the beneficiation process employed after chromite mining. The remaining chromite ore would typically be less than 6 mm, which would usually be crushed and/or milled to less than 1 mm and then upgraded utilising typical gravity separation techniques (e.g. spiral concentrators) to approximately 45% Cr₂O₃ content (Glastonbury *et al.*, 2010).

The chromite ore produced globally each year is divided into three major industrial end-uses, i.e. the metallurgical, refractory and chemical applications, which consume approximately 94 %, 4 % and 2 % chromite ore, respectively (ICDA, 2013; Murthy *et al.*, 2011; CRU, 2010; Abubakre *et al.*, 2007; Xstrata, 2006; IETEG, 2005).

2.2. Ferrochromium production

2.2.1. FeCr production trends

The main commercial grades of FeCr can be classified as high, medium and low C FeCr, as presented in Table 2-1.

Table 2-1: The main commercial grades of ferrochromium according to ISO-standard 5448-81 (Lyakishev & Gasik, 1998; Downing *et al.*, 1986)

	% Cr	%C	%Si	%P	%S
High carbon FeCr (HC FeCr)	45-70	4-10	0-10	< 0.05	< 0.10
Medium carbon FeCr (MC FeCr)	55-75	0.5-4	< 1.5	< 0.05	< 0.05
Low carbon FeCr (LC FeCr)	55-95	0.01-0.5	< 1.5	< 0.03	< 0.03
Charge grade	53-58	5-8	3-6		

High carbon (HC) FeCr is the most common grade produced. Approximately 90 % (~9 million tonnes) of the global HC FeCr production occurs in four countries, i.e. China, South Africa, Kazakhstan and India, as presented in Figure 2-4 (Fowkes, 2013). Since the introduction of argon-oxygen decarburisation (AOD) in 1954 that prompted the expansion of South Africa's FeCr industry, South Africa has become the world leader in FeCr production by some margin (Basson *et al.*, 2007; Featherstone & Barcza, 1982). This was primarily due to an abundance of good quality raw materials (ore, reductants and fluxes), historically inexpensive electricity costs, adequate infrastructure and reasonably low-cost capital (Basson *et al.*, 2007). However since 2012, China surpassed South Africa as the largest FeCr producer. This trend is set to continue, even though China's production is dependent on imported feed material (Pariser, 2013). South Africa's pre-eminent position in FeCr production is being eroded as a result of high electricity costs and -shortages, as well as labour unrest (Creamer, 2013; Kleynhans *et al.*, 2012). Since 2007, South Africa's electricity prices increased by 221% from 19 ZAR cents/kWh for 2006/07 to 61 ZAR cents/kWh for 2012/13 (NERSA, 2009a; NERSA, 2009b). ESKOM recently applied for another rate increase of 16% on average per year over the next five years. This would lead to another 110% increase from 61 ZAR cents/kWh for 2013/14 to 128 ZAR cents/kWh for 2017/18 (ESKOM, 2011). The exponential increase in the demand for electricity in South Africa has also led to ESKOM implementing a 'buy-back policy' programme, where major smelting plants are compensated to turn off their operations in order to maintain the supply of electricity to the national grid and to avoid load shedding and/or power cuts (Esterhuizen, 2012).

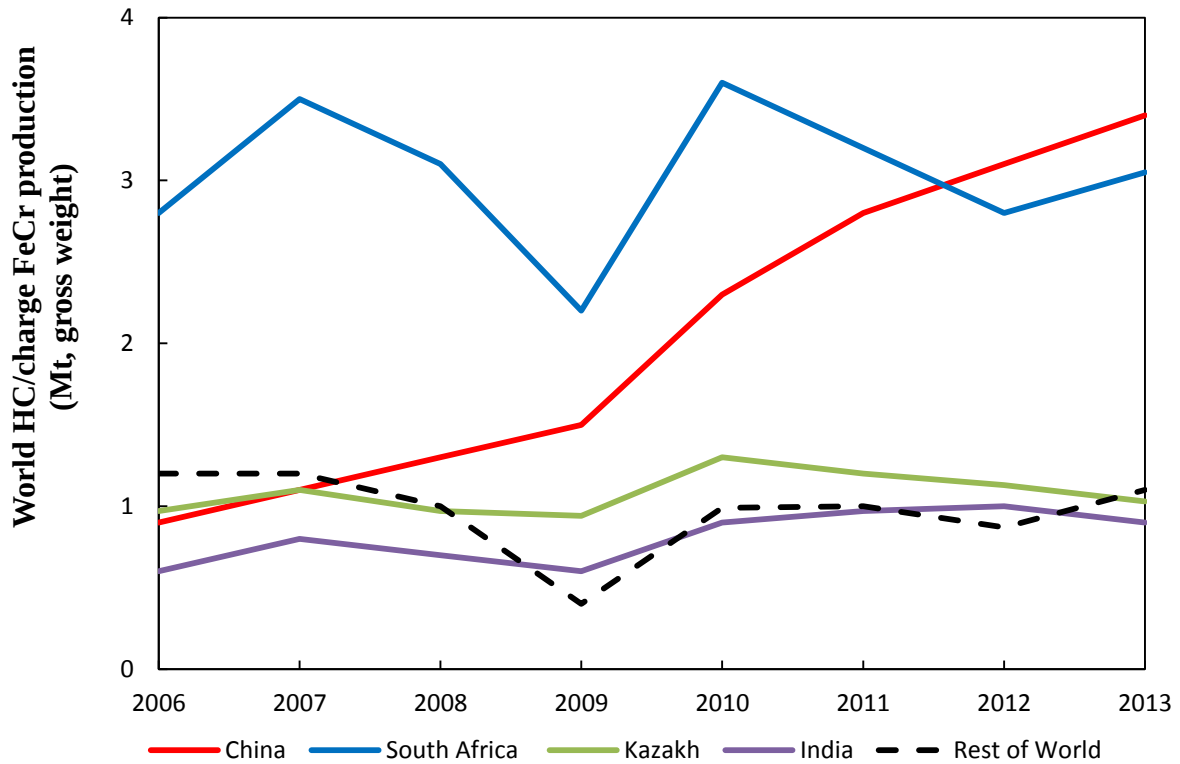


Figure 2-4: World HC/charge FeCr production in metric tonnes (10⁶) reconstructed from (Fowkes, 2013)

2.2.2. FeCr production in SA and processes applied

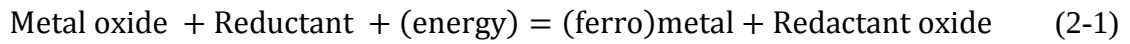
At present, South Africa has fourteen FeCr smelters (Beukes *et al.*, 2010) of which the locations are indicated in Figure 2-2. In Table 2-2, the production capacities of all the FeCr smelters in South Africa are listed. These plants have the capacity to jointly produce approximately 5.4 million tons of FeCr per annum (Beukes *et al.*, 2011; Jones, 2014).

Table 2-2: Production capacities of South African FeCr smelters adapted from Beukes *et al.* (2010) and Jones (2014)

Plant	Locality	Production capacity (ton/year)
ASA Metals Dilokong	Burgersfort	400 000
Assmang Chrome	Machadodorp	300 000
Bathlako Ferrochrome – Samancor	Rustenburg	25 000
Ferrometals	Witbank	550 000
Hernic Ferrochrome	Brits	260 000
International Ferro-Metals	Rustenburg-Brits	267 000
Middelburg Ferrochrome	Middelburg	285 000
Mogale Alloys	Krugersdorp	130 000
Tata Ferrochrome	Richards Bay	270 000
Sinosteel Tubatse Chrome	Steelpoort	380 000
Glencore Lydenburg	Lydenburg	400 000
Glencore-Merafe Boshoeck	Rustenburg-Sun City	430 000
Glencore-Merafe Lion	Steelpoort	724 000
Glencore Rustenburg	Rustenburg	430 000
Glencore Wonderkop	Rustenburg-Brits	545 000
TOTAL		5 396 000

The production of FeCr is an energy intensive process through which FeCr is pyrometallurgically produced by the carbothermic reduction of chromite. Primarily, electricity provides the energy, while carbon is used as a reductant in this process, as illustrated by Equation 2- 1. Carbon-based reductants, such as coke, char, anthracite or coal

are usually added, while quartzite, bauxite, olivine, dolomite, limestone and calcite are used as slag additives (Riekkola-Vanhanen, 1999).



In Figure 2-5, the combination of the most commonly applied process steps in FeCr production in South Africa (and indeed internationally) are presented as a generalised process flow diagram.

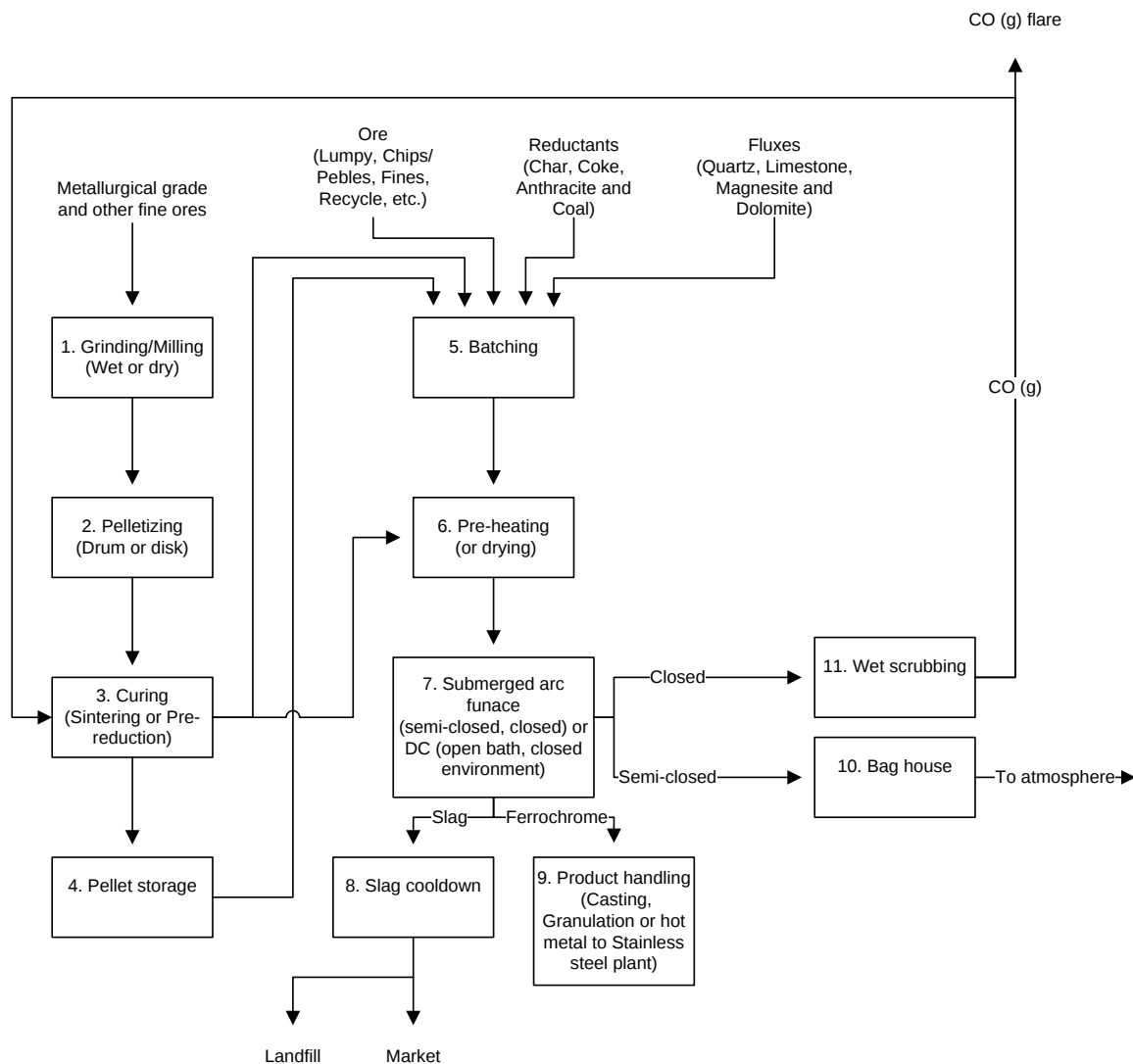


Figure 2-5: Process flow diagram of essential and general process steps applied for FeCr production in South Africa (adapted from Beukes *et al.* 2010)

The FeCr industry utilises various pre-processing and smelting methods, with the following processes being the most well defined (Beukes *et al.*, 2010; Daavittila *et al.*, 2004):

(a) Conventional semi-closed or open SAF operation that accounts for a significant fraction of FeCr production globally and is the oldest technology utilised in South Africa. It mainly utilises coarse chromite ore, flux and reductant as the process feed materials. This process requires the lowest capital input, since minimal pre-processing of the feed materials is necessary. However, this process is the least efficient in terms of Cr recovery and is also the least environmentally friendly process. The process steps followed are 5, 7, 8, 9 and 10, as indicated in Figure 2-5. In some instances, semi-closed furnaces do consume pelletised feed material, which also includes process steps 1-4.

(b) Closed SAF operation (e.g. Outotec process) that mainly uses oxidative sintered chromite pellets that are air cooled and stockpiled. Thereafter, the sintered pellets, as well as coarse fluxes and reductants are fed cold (excluding step 6), or hot (including preheating in step 6) into the closed SAFs. General process steps include 1, 2, 3, 4, 5, 7, 8, 9 and 11, with or without the addition of step 6.

(c) Closed SAF operation, where fine chromite ore, clay binder and a carbon-based reductant are dry milled, pelletised and preheated before being fed into rotary kilns wherein the partial reduction of iron (Fe) and Cr oxides occurs. The hot pelletised pre-reduced chromite pellets, as well as coarse fluxes and reductants are fed into the closed SAFs (e.g. Premus process applied by Glencore-Xstrata Alloys). The process steps included are 1, 2, 3, 4, 5, 7, 8, 9 and 11.

(d) Closed SAF with plasma or direct current (DC) arc operation that can be fed fine feed material exclusively, thereby eliminating the pre-processing of raw materials. Although this process has the advantage that material is not pre-processed, this process option has the highest SEC (MWh/ton FeCr produced). Process steps include 5, 7 (with a DC, instead of an

SAF), 8, 9 and 11. A drying process, i.e. step 6, is sometimes included (Beukes *et al.*, 2010; Naiker, 2007; Riekkola-Vanhanen, 1999; Otani & Ichikawa, 1975).

2.3. Aspects of chromite pre-reduction

2.3.1. Fundamentals of chromite pre-reduction

In the chromite pre-reduction process, particular terms are used to describe the pre-reduction rate, degree of pre-reduction and metallisation. Therefore, it is of paramount importance that these terms are defined before continuing the discussion on chromite pre-reduction. Barnes *et al.* (1983) suggested definitions for the terms ‘degree of pre-reduction’ and ‘metallisation’ that have since been used by numerous researchers (e.g. Kleynhans *et al.*, 2012; Weber & Eric, 2006; Soykan *et al.*, 1991a). By accepting that pre-reduction is associated with the removal of oxygen, the degree of pre-reduction, R (%), was defined as (Barnes *et al.*, 1983):

$$R(\%) = \frac{\text{Mass of oxygen removed}}{\text{Original removable oxygen}} \times 100 \quad (2-2)$$

In addition, since solid carbon is a reductant in the chromite pre-reduction process, carbon monoxide (CO) is formed as a reduction reaction product (illustrated in Equation 2–5, Equation 2–6 and Equation 2–7). Therefore, the degree of pre-reduction can also be defined as (Barnes *et al.*, 1983):

$$R(\%) = \frac{\text{Mass of CO evolved}}{\frac{28}{16} \times \text{Original removable oxygen}} \times 100 \quad (2-3)$$

The amount of original removable oxygen used in both Equation 2–2 and Equation 2–3 is determined from the oxygen loss associated with the metal oxides, namely hematite (Fe₂O₃), Wüstite (FeO) and Cr oxide (Cr₂O₃).

The degree of metallisation, M (%), is defined as by Barnes *et al.* (1983) as:

$$M(\%) = \frac{Cr^0 + Fe^0}{Cr_{tot} + Fe_{tot}} \times 100 \quad (2-4)$$

where Cr^0 and Fe^0 denote metallic Cr and Fe in their zero oxidation state, respectively. The Cr_{tot} and Fe_{tot} are the total Cr and Fe present in all their respective oxidative states. Complete oxygen removal can be related to complete metallisation; therefore, 100 % reduction corresponds to 100 % metallisation. However, the relationship between metallisation and pre-reduction is not linear. This can be ascribed to the following aspects (Barnes *et al.*, 1983):

- 1) In the initial stages of reduction, Fe_2O_3 is reduced to FeO without any metallisation:



- 2) FeO is reduced to Fe^0 , producing 1 mole of CO for every mole of Fe produced:



- 3) Cr_2O_3 is reduced to Cr^0 , producing 1.5 mole of CO per mole of Cr produced:



The above-mentioned difference in metallisation and pre-reduction of Fe and Cr was further explained by Dawson and Edwards (1986), who graphically illustrated the relationship between pre-reduction and metallisation, as indicated in Figure 2–6.

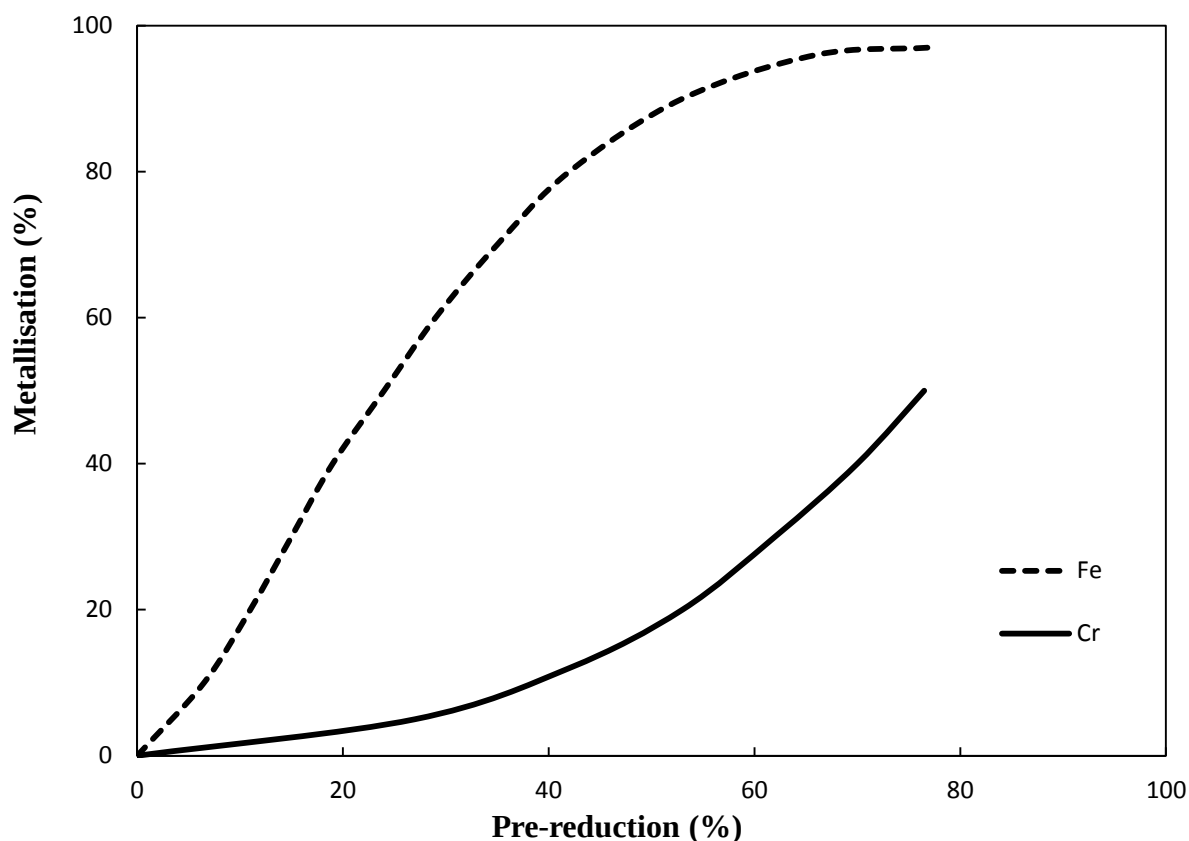


Figure 2-6: The relationship between pre-reduction and metallisation, based on South African LG-6 (lower group) chromite treated at 1200°C (adapted from Dawson & Edwards, 1986)

As previously stated in section 2.1.1, chromite ore is composed of a chemically complex spinel structure, resulting in a complicated reduction mechanism. Takano *et al.* (2007) and Sahajwalla *et al.* (2004) proposed three main ways through which the reduction of chromite ore utilising a carbothermic process can generally occur, i.e. i) solid-state reduction of chromite ore with a solid or gaseous reductant; ii) direct interface reaction of slag and metal, wherein dissolution of C in the smelted metal reduces dissolved chromite in the slag; and iii) direct reaction between floating carbon particles and chromite dissolved in the slag. In the case of SAF smelting, mechanisms (ii) and (iii) are dominant, whereas (i) is dominant in the chromite pre-reduction process, since it is expected that chromite will be reduced by

solid and/or gaseous reductants prior to liquid phase formation. Equations 2-8 and 2-9 illustrate the carbon-based reductant reactions necessary to start a solid or gaseous chromite pre-reduction process (Takano *et al.*, 2007):



The reducibility of metal oxides utilising CO gas that is formed during the carbothermic reduction of chromite was investigated by Niemelä *et al.* (2004) and is presented in an Ellingham diagram indicated in Figure 2–7. From this diagram, it is evident that hematite (Fe_2O_3) is the easiest to reduce at 250 °C by utilising solid C. The reduction of Fe_3O_4 to FeO that occurs kinetically, and FeO to Fe^0 both occur at temperatures of approximately 710 °C, while the reduction of Cr_2O_3 occurs at temperatures of higher than 1250 °C. Fe_2O_3 to Fe_3O_4 is reduced by CO over the entire calculated temperature range. Considering the calculations illustrated in the Ellingham diagram it is apparent that Cr_2O_3 and $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ (indicated as Cr_2FeO_4 in the figure) reduction is not possible with CO alone.

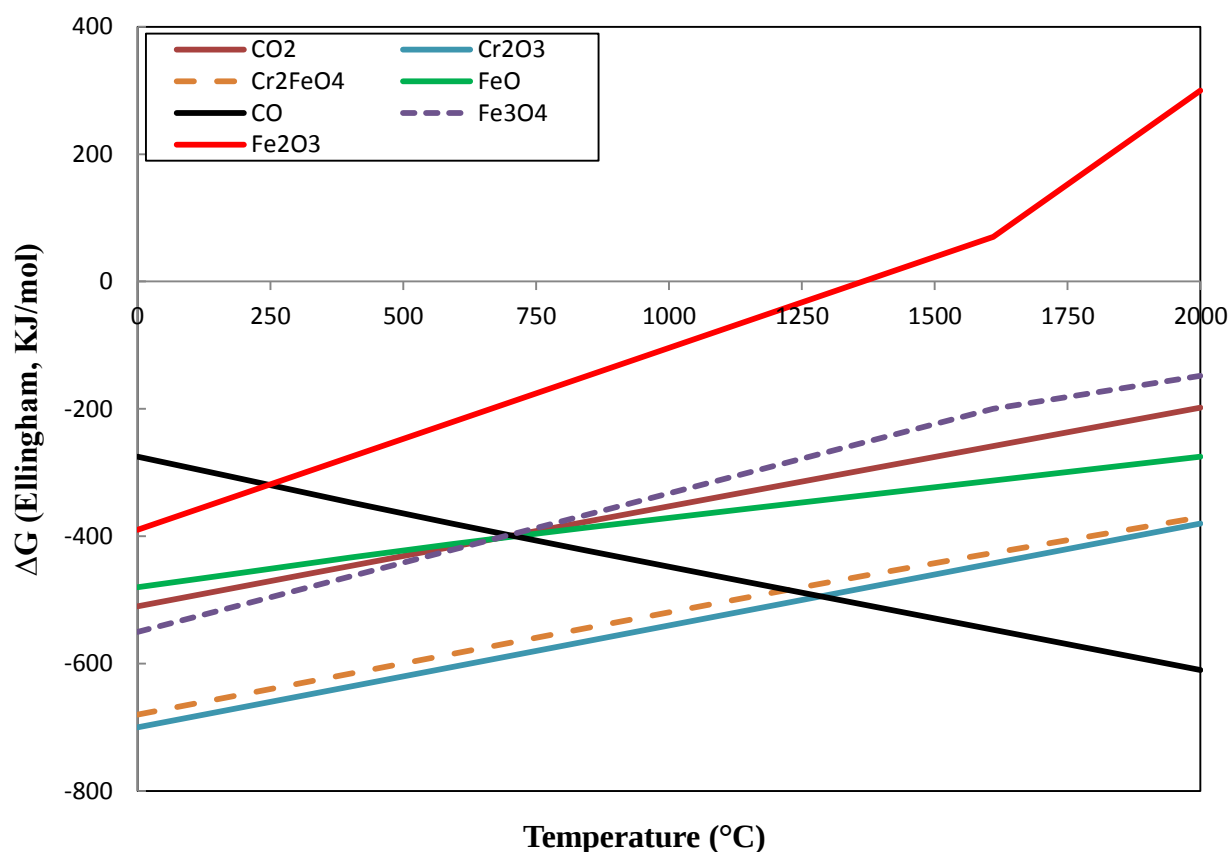


Figure 2-7: Standard free energies of reduction of metal oxides with C and CO, reconstructed from Niemelä *et al.* (2004)

Hayes (2004) presented an overview of South African chromite ore reduction mechanisms. Sykan *et al.* (1991a&b) published the results of the solid-state carbothermic reduction of chromite mined from the LG6 (lower group) in the BIC. Among other mechanisms, Sykan *et al.* (1991a&b) proposed a swap mechanism between the Cr^{2+} ion of the surface unit cell and the Fe^{2+} ion of the unit cell just below the surface. It was also observed that localisation occurred in partially reduced chromites and that, with an increase in Cr and Fe reduction, all the oxygen from the surface is removed. Ding and Warner (1997b) proposed a similar mechanism, as illustrated in Figure 2-8. From this it is evident that the inner core of the chromite is Fe rich, whereas the outer most part of the core is Fe deficient.

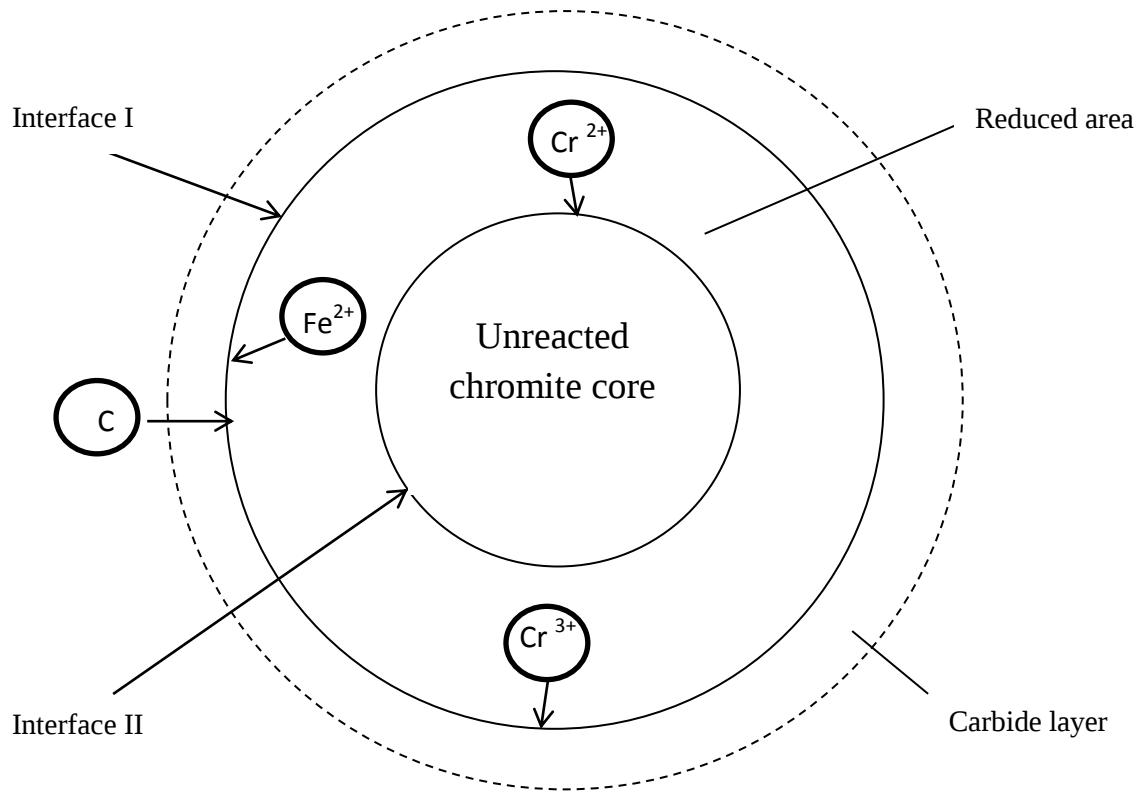


Figure 2-8: Diagram illustrating the pre-reduction mechanism of chromite, reconstructed from (Ding & Warner, 1997b)

Soykan *et al.* (1991a&b) hypothesised that the outwards diffusion of Fe^{2+} and Cr^{3+} ions occurred on the outer core (Reduced area, Figure 2–8), while Cr^{2+} diffused inward. Primarily, Fe^{2+} and Fe^{3+} ions at interface 1 (Figure 2–8) of the chromite particle are reduced to the Fe^0 after which the reduction of Cr^{3+} to Cr^{2+} occurs. The reduction of Fe^{3+} ions in the spinel to Fe^{2+} at the reduction area occurs due to the Cr^{2+} ions migrating toward the inner core of the particle. Fe^{2+} ions diffuse toward the surface, whereby it is reduced to its metallic state, as previously stated. Only after the completed reduction of Fe, the Cr^{3+} ion and some of the Cr^{2+} ions are reduced to the metal state. Consequently, an MgAl_2O_4 spinel structure remains, which is Fe and Cr free. The carburisation of metallic Fe^0 and Cr^0 during chromite pre-reduction into $(\text{Fe,Cr})_7\text{C}_3$ is illustrated by Equations 2–10 and 2–11.





2.3.2. *Effects of temperature on chromite pre-reduction*

Chromite pre-reduction levels of up to 80 % have been achieved at higher temperatures in an industrial operation. However, since Cr oxide reduces at higher temperatures than Fe oxide (as illustrated in Figure 2-7), chromite pre-reduction levels above 60 % are less feasible on a commercial scale, since elevated temperatures and longer retention time would be required. The pre-reduction kinetics of chromite is dependent on the temperature of the operation, which is limited to a maximum of approximately 1350 °C. At temperatures above 1350 °C, pellets start to partially melt, which leads to the formation of dam-rings in the rotary kiln that affects the efficiency of the operation (Dawson & Edwards, 1986; Barnes *et al.*, 1983). Therefore, relatively low levels of pre-reduction are achieved in the current industrial operation, which can be ascribed to the slow reduction kinetics of the Cr species. The effect of temperature on chromite pre-reduction is illustrated in Figure 2-9.

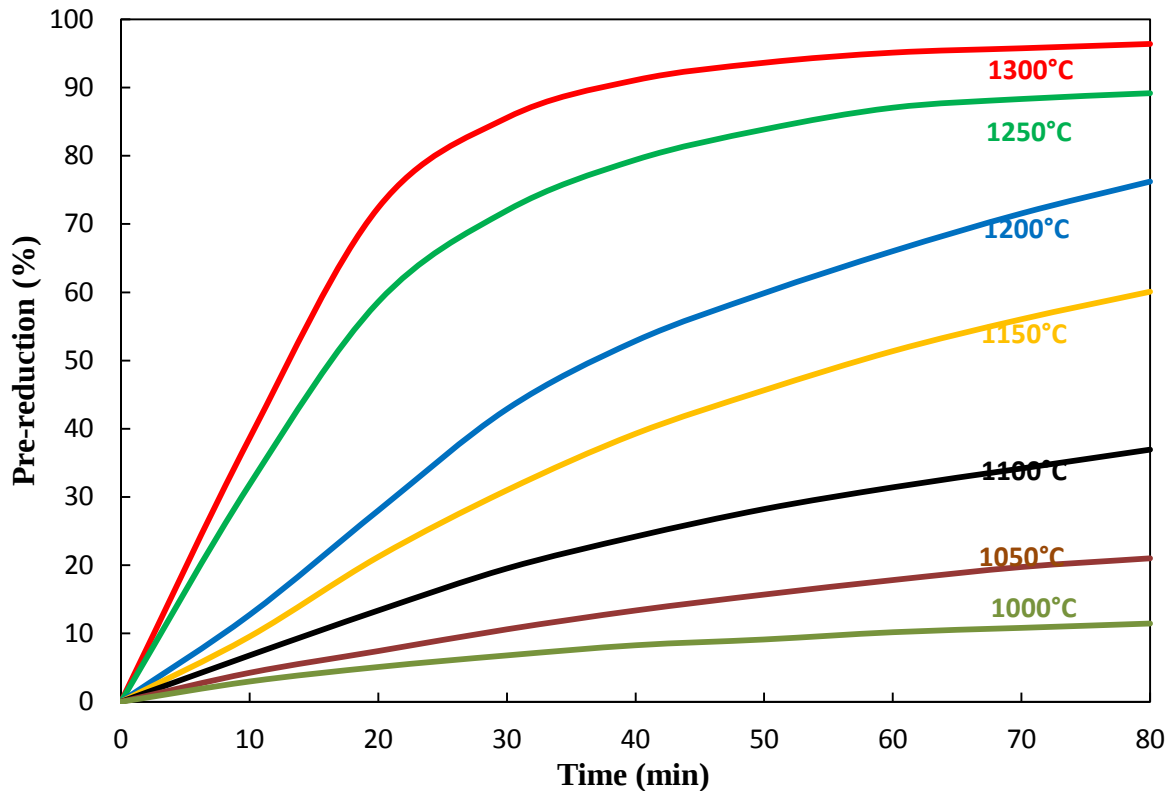


Figure 2-9: The effect of time and temperature on the rate of chromite reduction (adapted from Barnes *et al.*, 1983)

2.3.3. Effects of additives on chromite pre-reduction

The effects of several additives on chromite pre-reduction, e.g. CaO, Na₂B₄O₇, NaF, NaCl, CaB₄O₇, B₂O₃, CaF₂ and CaCO₃, have been intensively investigated (Dawson & Edwards, 1986; Katayama *et al.*, 1986; Nunnington & Barcza, 1989; Ding & Warner, 1997; Lekatou & Walker, 1997; Weber & Eric, 2006; Takano *et al.*, 2007; Neizel *et al.*, 2013). Additions of additives, which can also be referred to as catalysts, or even fluxes, to the chromite pre-reduction process may have either an enhancing (positive) or inhibiting (negative) influence on the reducibility of the chromite ore (Katayama *et al.*, 1986; Dawson & Edwards, 1986). For instance, the addition of CaO can enhance reduction, since CaO has the ability to enter the spinel lattice and release the FeO from the tetrahedral sites (Ding &

Warner, 1997). In Figure 2-10, an example of the influence of additives on pre-reduction is presented. Since no additives were considered in this study, they are not discussed further.

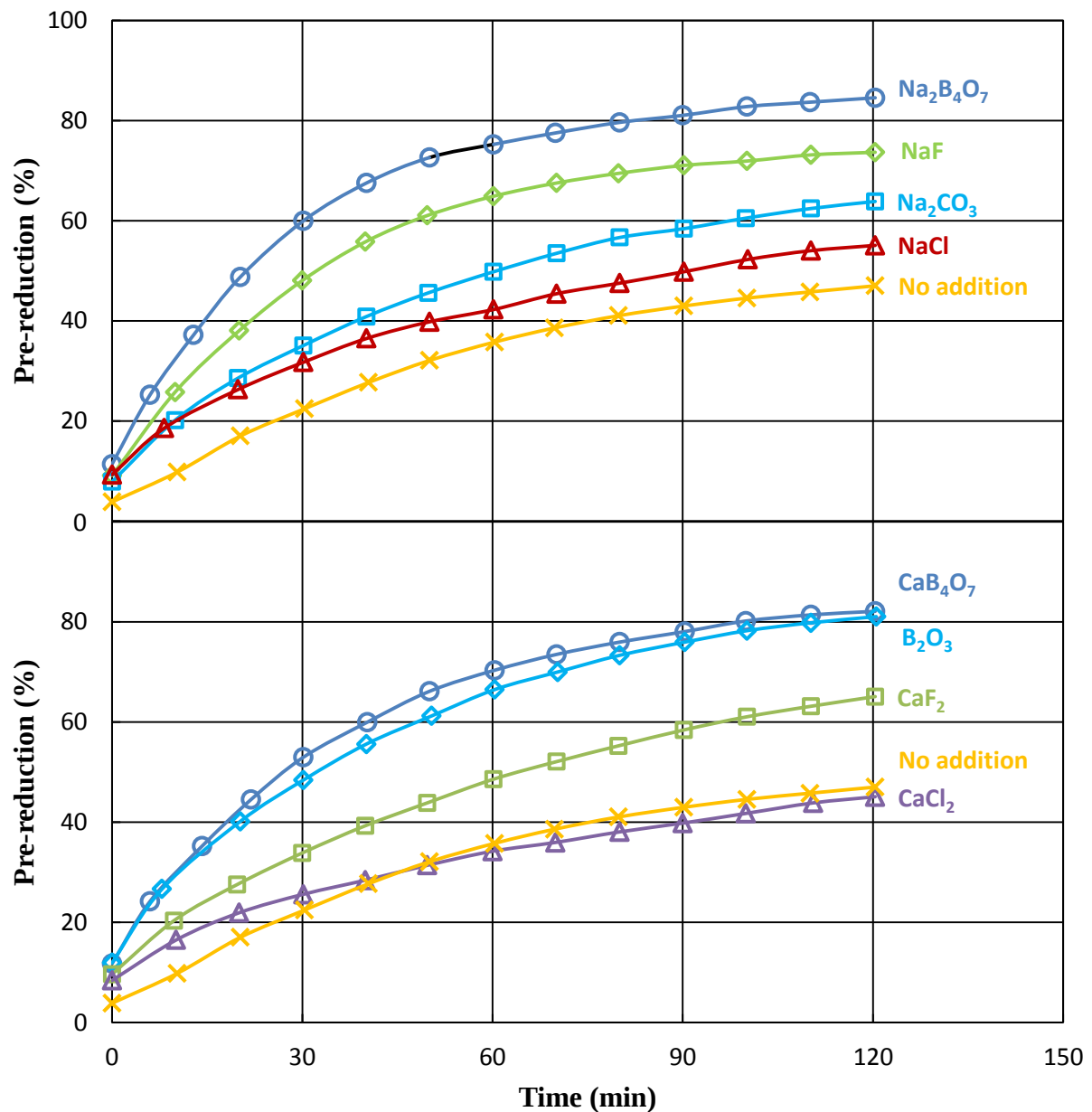


Figure 2-10: The influence of various additives on the rate of chromite pre-reduction at 1200 °C (adapted from Katayama *et al.*, 1986)

2.3.4. Benefits of chromite pre-reductions

The significant benefits of the pelletised chromite pre-reduction process include the following:

- a) In general, the price of electricity is increasing, particularly in South Africa. The most significant advantage of the pelletised chromite pre-reduction process above the conventional, oxidative sintering and the DC arc processes is certainly the overall lower SEC (Ugwuegbu, 2012; Naiker, 2007). The SEC required to produce FeCr from pre-reduced pellets with 90 % Fe and 50 % Cr metallisation is approximately 2.4 MWh/t, which is 40 % less when compared to the conventional processing method (3.9 MWh/t) (McCullough *et al.*, 2010). The relationship between the SEC and the level of chromite pre-reduction for different charging temperatures is presented in Figure 2-11.
- b) The pre-reduction process has a high metallic oxide recovery above 90%, with a low Si content in the FeCr produced (typically below 2%) (Kleynhans *et al.*, 2012; Naiker, 2007; Botha, 2003).
- c) The pelletised chromite pre-reduction process utilises only fine material (chromite ore and low cost reductants such as anthracite), thereby maximising beneficiation of the friable chromite ore mined in South Africa (Naiker & Riley, 2006).
- d) The increased contact area of the reagents significantly improves the extent of pre-reduction (Takano *et al.*, 2007). This is also the reason why this process option utilises dry, instead of wet milling.
- e) Agglomeration (pelletising) reduces possible fatal risks and production disruptions attributed to bed turnovers and blowouts that occur as a result of evolving gas that is trapped by a sintered bed in the SAF (Naiker & Riley, 2006; Riekkola-Vanhanen, 1999).
- f) The low consumption of lumpy metallurgical grade coke in the smelting process, which is the most expensive type of reductant. Coke consumption can be reduced by up to 65 % (Fowkes, 2013; McCullough *et al.*, 2010).

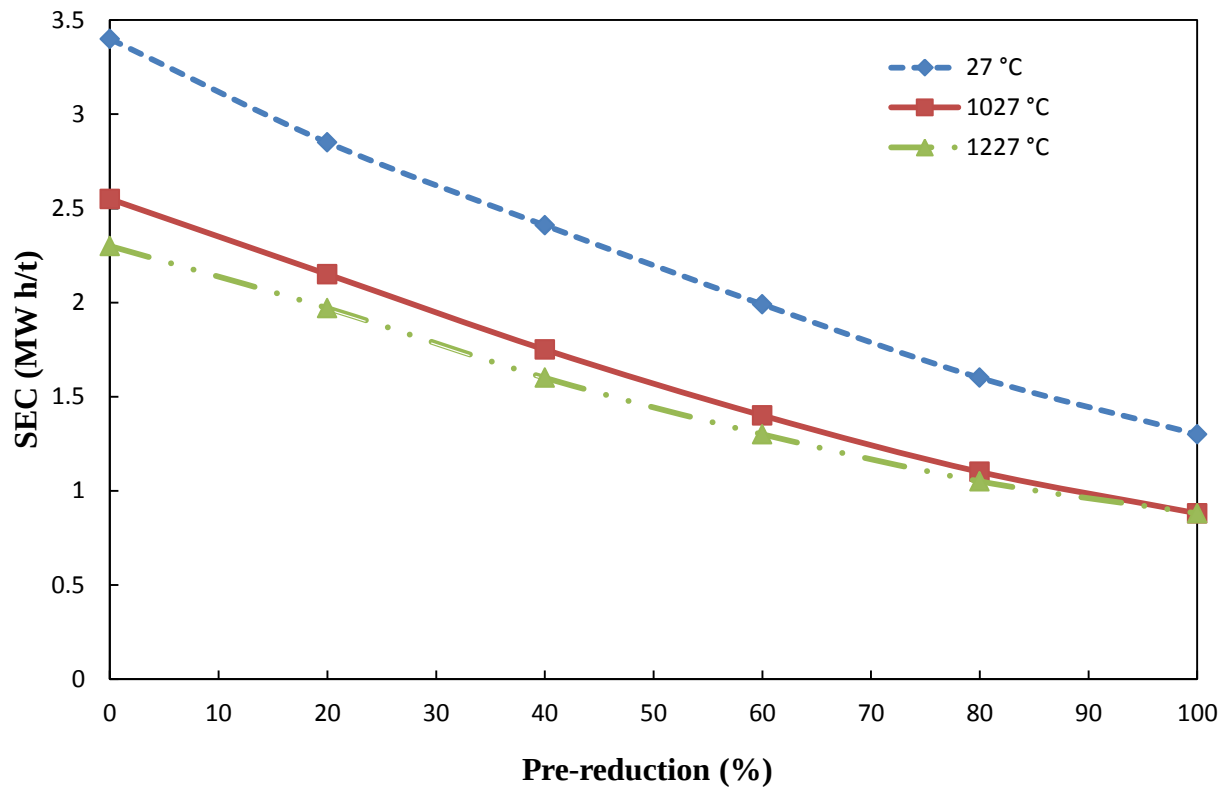


Figure 2-11: SEC for the production of FeCr as a function of the pre-reduction level and charging temperature, reconstructed from Takano *et al.* (2007) and Niayesh & Fletcher (1986)

2.3.5. General technique used to determine chromite pre-reduction

Rodgers (1972) conducted a thorough review on published techniques for the decomposition and analysis of the chromite spinel structure. Up until that time, the chromite spinel, as well as the high concentrations of Fe^{2+} and Cr^{2+} have always presented serious problems in obtaining reliable analytical results (Rodgers, 1972). It must be noted that the techniques, i.e. wet chemical methods utilised to calculate total Cr and Fe in chromite minerals, differ slightly from those utilised to determine reduction or metallic Cr and Fe in FeCr slag (and in the pre-reduced pellets). When chromite material is smelted or pre-reduced, the crystal structure is changed, and once the spinel structure is opened, Fe and Cr

become more susceptible to acid attack. Partially reduced Cr species (also referred to as ‘metallic Cr’) in the form of silicates, carbonates, or other carbon compounds, as well as Cr metal are subject to acid attack. Baker and Siple, (1990), Rodgers, (1972) and Dinnin (1959) described the techniques of analysing mineral chromites and FeCr slags for i) total Cr in mineral chromite and ferrochrome slags; ii) acid-soluble or ‘metallic’ Cr in FeCr slags; iii) total iron in mineral chromite and FeCr slags; iv) ferrous ion in mineral chromite and FeCr slag; and v) metallic Fe in FeCr slags. The afore-mentioned analytical techniques (i), (iii) and (iv) are not suitable for the purpose of determining the degree of metalisation. Therefore, only techniques (ii) and (v) are discussed further. The general wet chemical analysis procedure typically applied is summarised in Figure 2-12 and the relevant steps in techniques (ii) and (v) are also discussed.

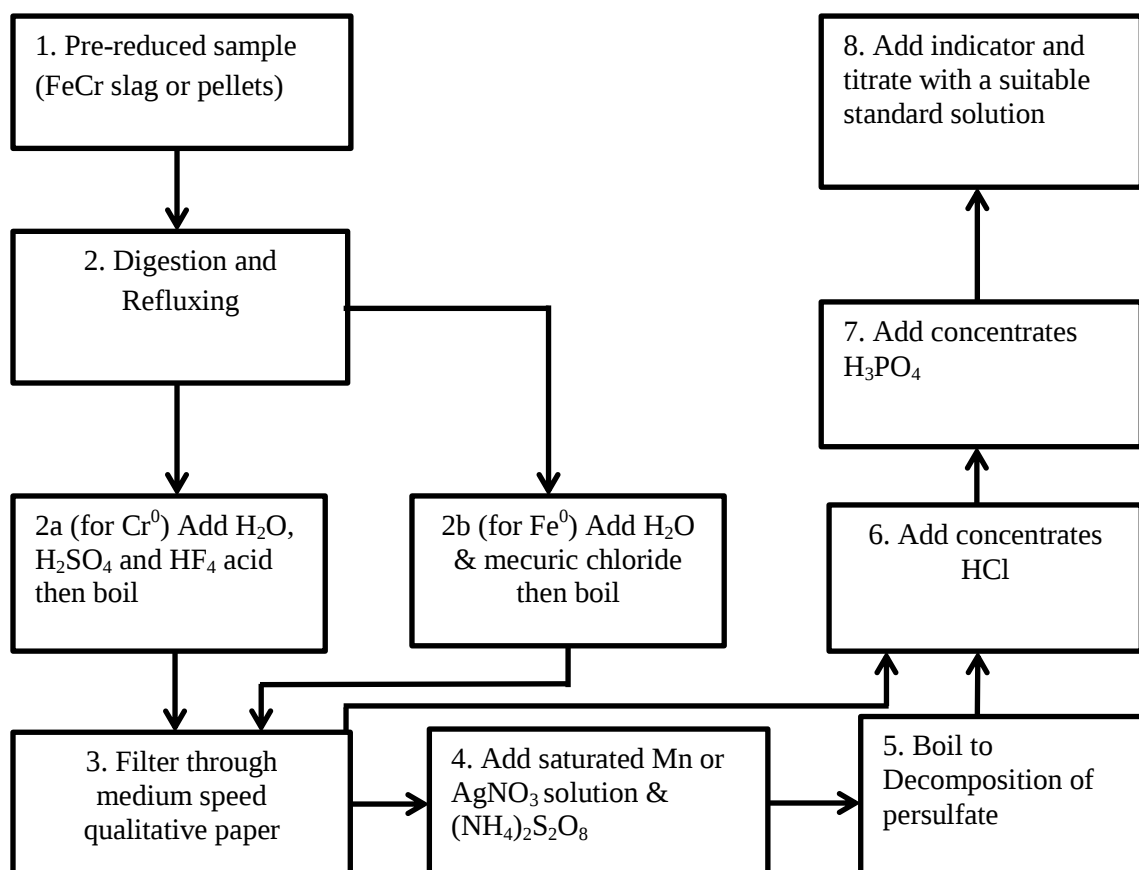


Figure 2-12: General wet chemical analysis procedure for analysing pre-reduction in pre-reduced material (adapted from Baker & Siple, 1990 and Dinnin, 1959)

Method (ii)

Baker and Siple (1990) stated that they used this technique, i.e. “the acid soluble or metallised Cr in FeCr slag technique” to determine the degree of reduction from smelter charge, rather than the level metallisation of Cr. However, according to Barnes *et al.* (1983), the method actually determines the metalisation of Cr that is then related to pre-reduction (see Equation 2-16). This technique is reliable and yields high quality results with a reproducibility well within 1%. The relevant steps in Figure 2-12 that are included in this method are steps 1, 2a, 3, 4, 5, 6, 7 and 8 for determining the metallic Cr (Cr⁰). In order to obtain the metallic Cr⁰ titration volume, titration with a standard ferrous iron solution and

approximately four drops of sodium diphenylamine sulfonate indicator is required. The titration equation is:



Method (v)

Since it would be unusual that the chromite mineral will contain metalised Fe, this technique is utilised for pre-reduced smelter charges, wherein the level of metalised Fe determined is used to calculate reduction/pre-reduction (see Equation 2-14). In Figure 2-12, procedure steps 1, 2b, 3, 6, 7 and 8 are included in this method. A standard solution of potassium dichromate solution and approximately four drops of sodium diphenylamine sulfonate indicator are used in this method. The titration equation is:



After performing the above-mentioned individual titrations (methods (ii) and (v)), the total pre-reduction can be calculated with Equation 2-14. The mathematical derivation of this equation is presented in Appendix A.

$$\text{chromite prereduction \%} = \frac{\frac{\% \text{ Sol Cr}}{34.67} + \frac{\% \text{ Sol Fe}}{55.85}}{0.0121} \quad (2-14)$$

It is evident from the above-mentioned paragraphs that the method currently used in determining the level of chromite pre-reduction is relatively old, with few improvements made over the last couple of decades.

2.4. SEM

In this study, scanning electron microscopy (SEM) was used extensively in the development of the new analytical technique developed. Therefore, some principles of this technique are considered in detail. In 1913, Mosely discovered that the frequency of emitted X-radiation excited by an electron beam correlates with the atomic number (Z) of the analysed element. However, it was only during the 1950s that the precursors of the electron microanalysers used today were invented, on which the development of the SEM is based.

The SEM - Energy Dispersive X-ray Spectroscopy (SEM-EDS) microanalysis technique is utilised in several research fields, such as physical and biological science, engineering and forensic investigations. The SEM utilises a high-energy electron beam to generate various signals at the surface of the solid specimen or object under investigation. The signal that derives from the interaction between the high-energy electron beam (incident electrons beam) and the specimen (cathodoluminescence, X-ray, secondary electrons, backscatter electrons and Auger electrons) provides information on the sample that, although not limited to, includes morphology (texture), chemical composition, crystalline structure and positioning of materials composition (Pareek & Pareek, 2013; Goldstein *et al.*, 2003). On the left of Figure 2-13, the various types of signals that are emitted after interaction of the constituent atoms of the specimen or sample and incident electron beam are presented. The excitation volumes or volume of generation (within the sample) from which the respective signals are generated are shown on the right of Figure 2-13 (Goldstein *et al.*, 2003; Viljoen & Johnson, 1983).

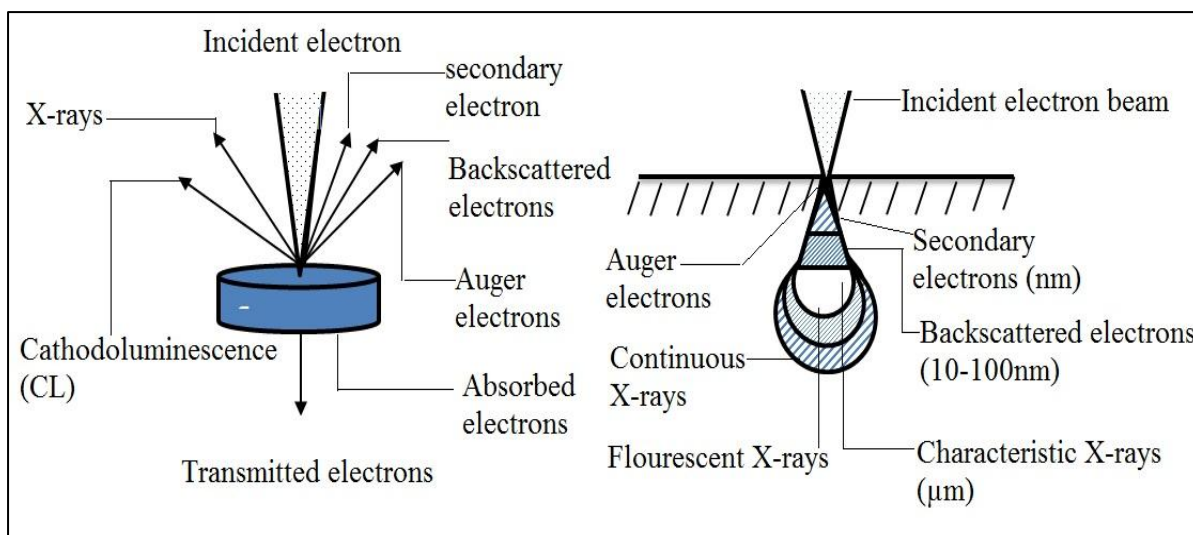


Figure 2-13: Signals emitted from a solid sample when struck by an incident electron beam, reconstructed from Viljoen & Johnson, (1983) and Goldstein *et al.* (2003)

Principal quantum numbers (n) are usually used to determine energy orbitals. Typically, X-ray signals are generated by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample, i.e. the K shell ($n=1$, the closest shell to the nucleus), L shell ($n=2$) and the M shell ($n=3$). The L shell and M shells are subdivided into three subshells (L1, L2 and L3) and five subshells (M1 to M5), respectively. All the subshells of the L- and M shells have different quantum configurations with marginally different energies, whereas the K shell is unitary, as represented by Figure 2-14. Pauli's principal of exclusion governs the inner shell filling, which states that only one electron may possess a given set of quantum numbers. This implies that the filling of the shell is equivalent to the possible states possessing the relevant quantum number. Electrons contained in the outermost shells are generally not involved in the production of X-ray spectra, and therefore are also not significantly affected by aspects such as chemical bonding. When the excited electrons return to lower energy states, X-rays are produced at fixed wavelengths (that are associated to the change in energy levels of electrons in different shells for a particular element). Consequently, distinctive X-rays are produced for each element in

a mineral that is ‘excited’ due to the incident electron beam. SEM electrons, e.g. 20 keV, will excite (or kick out) electrons from the K shell. SEM analysis is a ‘non-destructive’ analytical technique, i.e. X-rays generated by electron interactions do not cause volume loss of the sample (Goldstein *et al.*, 2003).

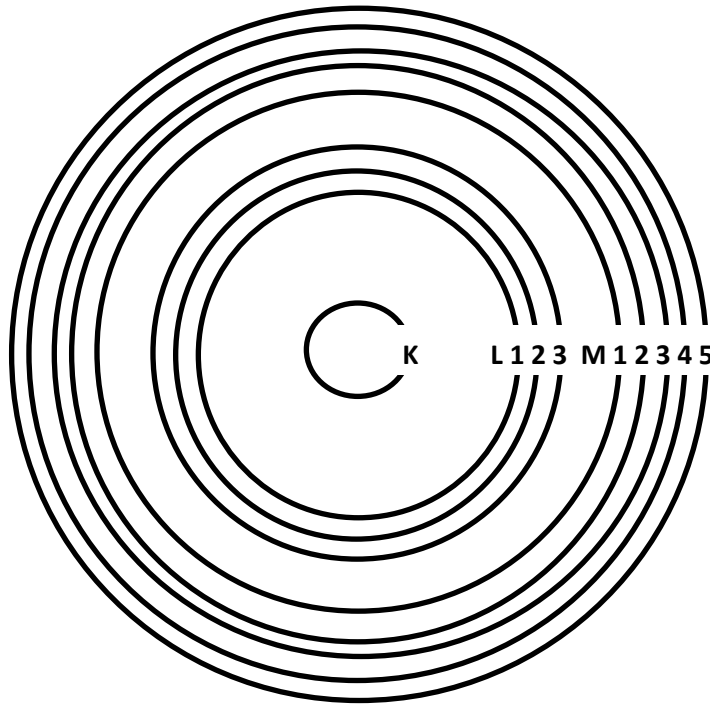


Figure 2-14: Schematic diagram of inner atomic electron shells

Since X-ray spectral lines originate in transitions between inner shells, the energy of a particular line shows a dependence on atomic number, which varies as Z^2 increases (Moseley’s law), and this principal is illustrated in Figure 2-15.

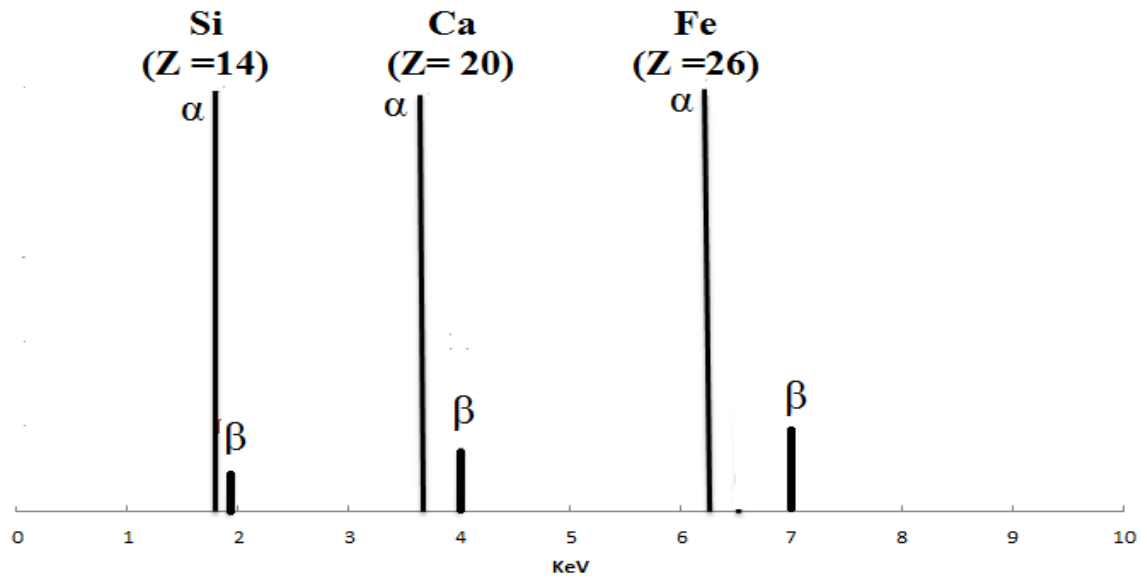


Figure 2-15: Typical K shell spectra

In most applications, data are collected over a selected area of the surface of the sample and a two-dimensional image that displays spatial variations is generated. By utilising conventional SEM techniques in a scanning mode, areas ranging from approximately 1 cm to 5 μm in width can be acquired as images (magnification of $\sim 20\text{X}$ to 30,000X with spatial resolution ranging between approximately 50 and 100 nm). SEM is also capable of performing analyses of selected point locations on the sample. This approach is especially useful to qualitatively or semi-quantitatively determine chemical compositions (using EDS), crystalline structure, and crystal orientations (Swapp, 2013; Sustiyadi, 2011).

In the mineral and metallurgical industry, SEM and/or SEM-EDS have been applied extensively in areas of mineral processing, hydrometallurgy, pyrometallurgy, physical metallurgy and corrosion. However, these techniques are primarily applied for mineral quantification and degree of liberation, as well as ore characterisation for mineral processing (Andrews, 2007).

2.5. Image processing

2.5.1. Fundamental principles of digital image analysis

A digital image differs significantly from a film photo since it contains discrete values, which are typically represented by integers. Therefore, a digital image can be considered as a large array of discrete dots or mosaics with very small areas, i.e. pixels, with each pixel having a level of reflectance associated with it (McAndrew, 2004). When thousands of these pixels are clustered together, they provide an impression of a genuine smooth picture. The nature of these pixels allows images to be saved and transformed as matrices of numbers (Wojnar, 1998; Graig *et al.*, 1982).

Digital image analysis has been applied in various disciplines. According to Graig *et al.* (1982), ore microscopy was developed approximately 200 years ago the 1800s. However, it remained manually intensive up until the 1950s when significant advances were made in the quantitative measurement of reflectance, after which the process was improved when the evaluation of colour was quantified in the 1970s. Approximately ten years later, after the development of automated image analysers, the application of digital image processing to deal with problems in material science and civil engineering gained rapid prominence (Bentz, 1999; Graig *et al.*, 1982). The development of a quantimet image analyser, which is an automated image analyser for quantitative mineralogical analysis, was described by Petruk in 1976. The National Institute for Metallurgy in South Africa, known as MINTEK in the present day, installed a Lietz-T.A.S (texture analysis system). automatic image analyser in 1978 (Pong *et al.*, 1983).

The specific process steps involved in analysing a visualised scene leads to either i) an enhanced image for human interpretation or ii) data that is suitable for autonomous

machine/computer perception (Jingzhong *et al.*, 2013; McAndrew, 2004). Images that are sharp, clear and detailed are preferred for human eye assessment, while machines/computers prefer simple and uncluttered images (McAndrew, 2004). Therefore, the purpose of image processing needs to be clearly outlined.

2.5.2. *Types of digital images*

There are in principal three types of images, i.e. binary, greyscale and true colour or RGB (red green blue) (Grande, 2012; Bhuiyan, 2011; McAndrew, 2004; Papasaika-Hanusch, 2004; Wojnar, 1998):

1. In a binary image, a pixel can only be represented as either black (0) or white (1) pixel. An example of such an image is presented in Figure B-1, in Appendix B.
2. A greyscale digital image (Figure B-) consists of a two-dimensional array of pixels, whereby each pixel is assigned a grey level value typically ranging between 0 (black) and 255 (white), indicating the reflectance or more specifically the strength of the measured signal (e.g. in a SEM image).
3. In true colour images (Figure B-), each pixel has a certain colour that is described by the amount of red, green and blue within it. Each of these three components has a range of 0 to 255 that indicates the strength of the measured colour. Therefore, i.e. $255^3 = 16,777,216$ different possible combinations of colours are present in the image. This is also referred to as 24 bit colour images due to the total number of bits (24) required for each pixel.

These types of digital images were used for various applications and/or research purposes. Some of the published studies conducted in recent years are briefly introduced here:

- Bentz (1999) conducted a study on the microstructure and physical cement hydration properties by making use of a three-dimensional digital-based computer model.
- Kahn *et al.* (2002) showed routine coupling of backscatter electron BSE, and X-ray dot-mapping images produced a proper mineral discrimination for quantitative phase and mineral liberation degree analysis.
- Bhuiyan (2011) demonstrated that a morphological image analysis of SEM micrographs (greyscale images) of epoxy impregnated pellets is an efficient technique for the characterisation of *bubble porosity* and *packing porosity*, as well as for the quantification of the latter.
- Melissa *et al.* (2013) recently showed the significance of computer techniques for advancing process control systems in the mining and mineral processing industry where textural image analysis was used to monitor mineral process systems.

Chapter 3: Experimental

The materials utilised and experimental methodologies are discussed in this chapter. Section 3.1 describes the raw materials utilised. The sample preparation procedures for proximate, elemental, level of pre-reductions and SEM analysis, as well as SEM image acquisition procedure and image processing method will be discussed in section 3.2.

3.1. Materials

The raw materials utilised in the industrial application of the pelletised chromite pre-reduction process consist of fine chromite ore, a carbonaceous reducing agent and a clay binder. Samples of metallurgical grade chromite (<1 mm), anthracite breeze (<1 mm), fine ferrochromium (FeCr) (<1 mm) and industrially produced pre-reduced pellets that have already been milled in preparation for determining pre-reduction levels using wet chemical analysis were obtained from a large South African FeCr producer applying the pelletised chromite pre-reduction process. Geologically, all the raw materials, excluding the clay binder, were from Mpumalanga. The chromite ore and anthracite breeze were mined in the eastern limb of the Bushveld Igneous Complex (BIC) and south of eMangweni, respectively.

3.2. Methods

A spectroscopic vision inductively coupled plasma (ICP) coupled to an optical emission spectroscopy analyser (OES) was utilised for the analyses of the metallurgical grade chromite ore, anthracite, as well as the pre-reduced pellets. For the anthracite determination, precisely 1 g of sample and 1g of SARM 18 (reference) were placed on silica dishes and exposed to 815 °C for 1½ hour in a muffle furnace. The ash residues were then separately transferred into zirconium crucibles each containing 2 g sodium peroxide (Na_2O_2) and 0.5 g

sodium carbonate (Na_2CO_3) that were used as fluxes, which were then mixed thoroughly using a spatula. A Bunsen flame was used to bring the mixtures to a complete melt, after which the crucibles were allowed to cool down. The melt fusions were tapped loose from the crucibles and transferred to 500 mL beakers. Four parts of 20 mL 1:1 water:nitric acid were used to wash out the remaining fusion residue from the crucible. The sample solutions in the beakers were heated on a hot plate until they became clear, near boiling point. They were then removed from the hot plate and allowed to cool down. 10 mL yttrium (Y) solution was then added to each sample solution and the combined solutions transferred to 200 mL volumetric flasks, wherein they were diluted. The diluted solutions were then used for ICP analysis. In preparation of the Y solution, 0.635 g Y oxide was dissolved in 50 mL 1:1 water:nitric acid by slightly heating the solution. The Y solution was then diluted to 5 L in a volumetric flask. The chromite and pre-reduced pellet ICP analyses were also conducted using the same procedure, although these samples were not reduced to ash at 815 °C. For chromium analysis, the same procedure was performed, although precisely 0.2 g of the sample was weighed as starting material and SARM 8 was used as a reference.

3.2.1. Proximate analysis

Proximate analysis, i.e. inherent moisture, ash, volatile contents and fixed carbon (FC) of the anthracite, was determined according to ASTM standard method D3172-07A (ASTM, 2007). In order to determine the inherent moisture, 1 g of the sample was dried at 110 °C for 1½ hours and the weight loss measured was used to calculate the inherent moisture content. Similarly, the ash content was determined by heating a 1 g sample to 815 °C for 1½ hour using a muffle furnace. To determine the volatile content of the anthracite, four drops of methyl isobutyl ketone/acetone were added to a 1 g sample, after which it was heated to 900 °C for exactly 7 min. The FC was determined by subtracting the ash, moisture and volatile contents from the total weight (combined total 100%).

3.2.2. *Elemental analysis*

Elemental carbon (C) and sulphur (S) contents were determined to characterise the anthracite. The pre-reduced pellets were also analysed to confirm an excess of free carbon, to ensure that the reduction rates were not affected by a lack of reducing agent. This was conducted by means of infrared (IR) spectrophotometry utilising a LECO CS 244. Tungsten (W) and iron (Fe) chips at a 1:1 ratio were used as the accelerator flux.

3.2.3. *Pre-reduction analysis*

The method utilised to determine the level of chromite pre-reduction was conducted in accordance with the method applied by laboratories associated with FeCr smelters in South African presently applying the chromite pre-reduction process, which is derived from the general pre-reduction analysis technique presented in section 2.3.5.

The metallic Fe and chrome (Cr), i.e. the % soluble Fe and Cr that is required to calculate the total pre-reduction %, was obtained by initially leaching the pulverised pre-reduced pellets in an acidified water solution. 1 g of pulverised pre-reduced pellet sample was weighed into a 500 mL Erlenmeyer beaker and 50 mL leaching solution was added. The leaching solution was made up of 100 ml concentrated phosphoric (H_3PO_4) acid, 400 ml concentrated sulphuric acid (H_2SO_4) together with 500 ml distilled water. The sample was leached under reflux for 1½ hours at approximately 100 °C on a hot plate. Then the sample solution was diluted to 250 mL in a volumetric flask, after which it was filtered. The leachate was split into two portions for the determination of soluble Cr and Fe, respectively.

For the determination of soluble Cr, 50 mL (20% aliquot) of the filtrate solution was pipetted into a 250 mL beaker. 5 mL potassium permanganate (KMnO_4).solution, 3% w/v

(weight by volume), was added and the solution was brought to boil for 4 min. 25 mL sodium chloride (NaCl) solution, 20% w/v, is then added and the solution boiled until clear. The solution was removed, allowed to cool and 100 mL water added. The % soluble Cr was determined volumetrically by a ferrous ammonium sulphate-potassium dichromate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$) titration. Two to three drops of diphenylamine sulphonate were added as indicator. The indicator was prepared by dissolving 0.5 g diphenylamine sulphonate in 100 mL water. The solution was then titrated against a 0.1 M potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution until a definite purple colour was reached.

The determination of % soluble Fe was conducted by pipetting 100 mL (40 % aliquot) of leached filtrate solution into a 500 mL Erlenmeyer flask. Two to three drops of diphenylamine sulphonate was then added as an indicator. The entire solution was then titrated against 0.1 M of ($\text{K}_2\text{Cr}_2\text{O}_7$).

3.2.4. Sample material preparation prior to SEM analysis

In this study, both laboratory prepared pellet mixtures, as well as industrially produced pre-reduced chromite ore pellets were considered to validate the new analytical technique developed.

3.2.4.1. Milling of laboratory prepared pellets mixtures

The laboratory prepared mixtures, consisting of FeCr, chromite ore and anthracite were dry milled to the particle size specifications applied for industrial pre-reduction feed material, i.e. 90% of the particles smaller than 75 μm ($D_{90} = 75 \mu\text{m}$). The laboratory prepared mixture compositions were prepared in such a manner that the mixtures mimicked different pre-reduction levels, i.e. 15, 30, 45 and 60% pre-reduction. Three sets of these mixtures were prepared with each set containing varying carbon contents, i.e. 1, 3 and 5 wt. % FC. A Siebtechnik laboratory disc mill equipped with a tungsten carbide grinding

chamber was used to avoid possible iron contamination (Kleynhans *et al.*, 2012). Additionally, after milling each batch, the grinding chamber was cleaned thoroughly with water and wash acetone. 50 g mixtures of the raw materials were milled for 2 min to obtain the desired size specification. The particle size distribution was verified with laser diffraction particle size analysis utilising a Malvern Mastersizer 2000. For this purpose, a much diluted suspension of milled material mixture was ultra-sonicated for 60 s prior to the particle size measurement, in order to disperse the individual particles without the use of a chemical dispersant.

3.2.4.2. *Mounting and metallographic polishing*

The laboratory prepared pellet mixtures, as well as the industrially produced pre-reduced pellets that had already been milled in preparation for determining pre-reduction levels were mounted in resin and polished for cross-sectional SEM micrograph imagery. 1 g of the respective mixtures was placed in 25 mm diameter moulding cups. The epoxy resin solution ratio was 100 g of resin to which 12 g of slow curing agent was added. The epoxy resin solution was stirred thoroughly in a plastic beaker for 3 min, before it was placed in a Speedivac vacuum degassing chamber model VDC 12 (see Figure 3-1). The pressure in the chamber was allowed to reach ~200 mbar near the epoxy resin's boiling point, whereby it became less viscous, which ensured the elimination of air bubbles in the epoxy resin solution. A few drops of epoxy resin were added to each of the 1 g mixtures in the moulding (mounting) cups and mixed slowly to avoid stirring air into the mixture, but thoroughly to ensure homogenous mixing. The moulding cups were then placed back into the vacuum chamber to remove any air bubbles that may have formed during stirring. The homogenous mixture was allowed to set for a few hours (12 hours), additional epoxy resin was then added on top of this mixture (over the designated sample label) to fill the 25 mm moulding cup. The mixtures in the moulding cups were then allowed to set over night.



Figure 3- 1: A Speedivac vacuum degassing chamber model VDC 12

The epoxy resin moulded samples were polished using a SS20 Spectrum System Grinder polisher, operated at an average speed of 150 rpm for polishing (see Figure 3-2). A 250 mm platinum 2 green cameo magnetic disc (comparable to 220-280 grit), a 250 mm platinum 4 red cameo magnetic disc (comparable to 600 grit), as well as 9, 3 and 1 μm diamond paste, on polishing cloths were used, respectively. The two rough/abrasive grits were operated using continuous water flow as cleaner and lubricant, whereas diamond paste suspension poly lubricant was applied on the diamond paste cloths/discs to ensure a smooth polished surface. Analytical grade ethanol was used to wipe the surfaces clean after polishing.



Figure 3- 2: An image of a SS20 Spectrum System Grinder polisher, polishing three moulded chromite pre-reduced pellets at the same time with diamond paste suspension dripping at a set flow rate while the disc rotates at 139 rpm

The bottle from which the diamond paste was dispensed during polishing was custom made, with a control valve, to ensure the consistent flow rate of the diamond paste suspension. An excessively low diamond paste flow rate resulted in increased friction between the samples and the cloth, which led to the polishing cloth tearing up and sample scratches, whereas over dispensing of the paste resulted in inadequate polishing. The speed during grinding (i.e. with an abrasive discs and water as the lubricant) was usually set higher (~250 rpm) than the polishing speed of ~150 rpm. Figure 3-3 shows a microscope being used to inspect moulded samples for any scratches or artefacts.



Figure 3- 3: Inspection of sample scratches using a Nikon stereo-spectroscopy

A Nikon stereo-microscope, as indicated in Figure 3-3, was utilised to inspect the surface of all the moulded samples prior to SEM analysis for any scratches or artefacts. This was done to avoid the evaluation of samples that had defects or scratches, which could then result in a misrepresented SEM image. Typical moulded, polished and carbon-coated samples of pre-reduced pellet mixtures are shown in Figure 3-4.



Figure 3- 4: Typical moulded, polished and carbon-coated samples of pre-reduced pellet mixtures

3.2.5 EDS analysis

Elemental analysis in this study was solely used to reaffirm the main elements contained within the chromite particles on the scanning electron microscopy (SEM) micrographs generated.

3.2.6. SEM image acquisition

Prior to scanning electron microscopy (SEM) analysis, polished samples were made conductive by carbon coating in a Dentom vacuum DV-502A. An FEI QUANTA 250 FEG SEM with integrated OXFORD X-max electron dispersive spectrometer (EDS) system, using a backscattered electron compositional signal, operating with a 15 kV electron beam (suitable for metals), at a working distance of 10 mm, 300 ns scan speed and magnification of 800X

was used to acquire the SEM micrographs. A substantial amount of kinetic energy is carried within the accelerated electrons in a SEM, and as mentioned in section 2.4.1, this energy is dissipated as a variety of signals produced by electron specimen interaction when the incident electrons are decelerated in the moulded chromite pellet mixture (see Figure 2-13). These signals include secondary electrons (that produce SEM micrographs). Secondary electrons are most valuable to show morphology and topography on samples, and backscattered electrons are most valuable to illustrate contrasts in composition in multiphase samples (i.e. for rapid phase discrimination) (Goldstein *et al.*, 2003; Swapp, 2013). Ten micrograph images were captured for every sample from random areas, so that they were representative of the entire sample.

3.2.7. *Image processing and analysis*

Grey-level image processing is often used to enhance features in an image either for visualisation purposes, or for subsequent quantification (Grande, 2012). In an ideal situation, a digitalised image can be directly binarised (converted to black and white) in order to obtain the desired features. However, several image acquisition aspects such as brightness setting, contrast setting, working distance (WD) between sample and detector, as well as artefacts often prevent straightforward feature analysis (McAndrew, 2004). Subsequently, these effects influence the data that is acquired from the image.

The following image analysis technique, as illustrated in Figure 3-5, suggested by Grande (2012) and McAndrew (2004), was used as the basic image analysis procedure followed in this study.

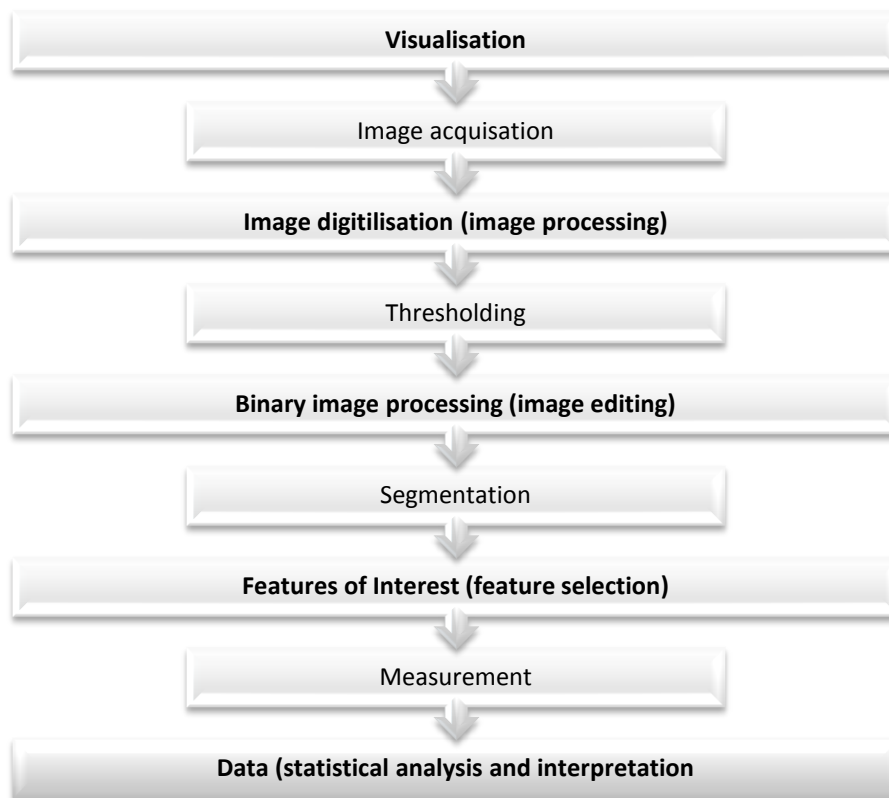


Figure 3- 5: Steps for image analysis processing wherein decisions are taken before pursuing the next step (adapted from Grande, 2012)

As previously described, an image that has 255 greyscale values should be processed in such a way as to allow quantification by lowering the available grey values in an image to only the features of interest. The process in which 255 grey values were reduced to two values (black and white, or 0 and 1) is called thresholding. It was accomplished by selecting the grey-level range of the features of interest. Pixels within the selected grey-level range were assigned as foreground, or detected features, and everything else as background, or undetected features. Primarily, thresholding basically converts the image into a series of 0s and 1s, which represent undetected and detected features, respectively. Matlab, which was used as the programming language used for image processing, which, like most programming tools, has various commands (syntax) that can be used to achieve a single objective. However, the most essential concept is that images loaded onto Matlab are viewed as

matrices. Table 2-3 presents a few commands that were used in the image processing analysis in this study.

Table 3-1: Matlab syntax and their respective general descriptions (MathWorks, 2014)

Matlab operators/ functions	Brief Description of functions
<i>imread</i>	This function loads images into MATLAB
<i>num2str</i>	Converts numbers and arrays to string representations
<i>imtool</i>	Displays image and allows observation of the pixel region (greyscale and true colour)
<i>imshow</i>	Displays image
<i>Im2bw(x,i)</i>	Converts greyscale and or RGB image to black and white. where 'x' denotes the image name and 'i' denotes the threshold
<i>Bwareaopen</i>	Morphologically open binary image, filters all connected or clustered pixels in a binary image which are less than 'p' pixels. The default clustering for a 2-D image is 8 and 26 for 3-D. Useful for noise filtering on images.
<i>Imadjust</i>	Increases the contrast of a 2-D image
<i>Imopen</i>	Same as bwareaopen, but can cause morphological opening in greyscale images as well (not only black and white)
<i>Cell2mat</i>	Converts a cell into matrix
<i>Sum (image,:)</i>	Counts all detectable features
<i>Numel(image)</i>	Counts all the pixels on the image

Since the human eye can only differentiate between 30 and 40 grey levels, this makes utilising image processing an essential tool. From these grey level (intensity) matrices,

mathematical manipulations (*Im2bw(x,i)* and *Numel(image)* etc.) were performed to enhance the images and to discriminate various greyscales to effectively quantify the white, grey and black pixels within the image. Pixel counting in digital greyscale images can also be used to analyse various quantities, for instance phase volume fractions, surface areas as well as sizes and stereological properties of individual particles (MathWorks, 2014; Grande, 2012; McAndrew, 2004); however, in this study, it was used to count the % of certain pixels on a SEM micrograph.

Chapter 4: Results and discussions

The results of the newly-developed analytical technique to analyse chromite pre-reduction are discussed in this chapter. The results of the raw material utilised to prepare laboratory pre-reduced chromite ore pellets are discussed in section 4.1. The hypothesis from which the study was derived is discussed in section 4.2, after which the basic process or algorithm developed is discussed in section 4.3. The results obtained for the laboratory prepared and industrially pre-reduced pellets, as well as possible recommendations to enable industrial application or feasibility are discussed in section 4.4.

4.1. Raw material analysis

The chemical compositions of the chromite, anthracite and ferrochrome (FeCr) samples from which the laboratory prepared pellet mixtures were made up are listed in Table 4-1. If these raw material analyses are compared to relatively recent studies related to chromite pre-reduction, e.g. Kleynhans *et al.* (2012) and Neizel *et al.* (2013), it is evident that the raw materials utilised in this study are typical of raw materials utilised by South African FeCr producers applying the pelletised pre-reduction process.

Table 4-1 Chemical characterisation of the metallurgical grade chromite (<1 mm), anthracite breeze (<1 mm) and fine FeCr (<1 mm) received from a large FeCr producer. These materials were used to prepare pre-reduced pellet mixtures synthesised in the laboratory, described in the text

FeCr							
	%Cr	%Si	%Fe	%P	%SLAG	%C	%S
Wt. %	50.32	3.07	36.65	0.01	2.08	7.20	0.05
Chromite				Anthracite			
ICP Wt. %		EDS Wt. %		ICP Wt. %		EDS Wt. %	
Cr ₂ O ₃	45.37	Cr	27.21	SiO ₂	10.09	Si	2.53
FeO	25.39	Fe	15.33	Al ₂ O ₃	3.13	Al	0.89
Al ₂ O ₃	15.21	Al	6.39	FeO	1.62	Fe	1.19
MgO	9.83	Mg	6.37	CaO	0.8	Ca	0.18
SiO ₂	1.72	Si	3.70	MgO	0.35	-	-
CaO	0.22	Ca	0.48	P	0.011	-	-
P	<0.01	Ti	0.37	S	0.59	S	0.68
-	-	O	40.16	-	-	C	76.9
				-	-	O	17.63
				Proximate analysis (air-dried basis) %			
				FC		75.08	
				Inherent Moisture		0.26	
				Ash		17.79	
				Volatiles		6.87	

4.2. Hypothesis for the development of the new analytical method

In scanning electron microscopy (SEM) micrographs, elements with higher molecular weights are indicated by lighter greyscale, while elements with lower molecular weights are indicated by darker greyscale. In the composite chromite pellets considered in this study, unaltered chromite ore particles are therefore typically indicated as grey particles since they contain both heavy (e.g. Cr and Fe) and light elements (e.g. Si, Al and Mg). In contrast, metallised particles/droplets that form as a result of chromite pre-reduction are typically

indicated as white particles, consisting mostly of Fe and Cr. Figure 4-1 is a SEM micrograph of a laboratory prepared pre-reduced chromite ore pellet indicating this principle.

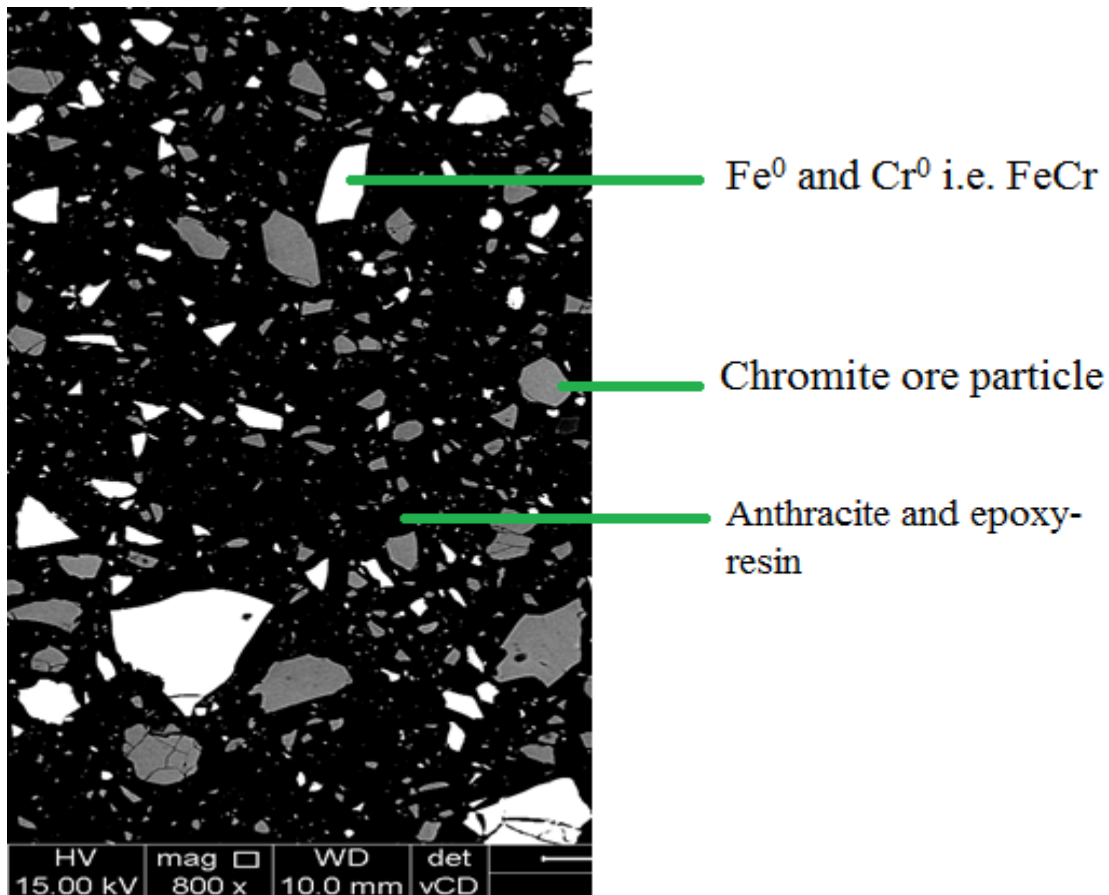


Figure 4 -1: Identification of greyscale levels related to elements composition in respective particle using EDS, of a laboratory pre-reduced pellet mixture

As previously stated, the EDS feature of the SEM-EDS used in this study was also used to confirm that particles appearing white on the moulded polished samples contained mostly Fe and Cr. Considering all the afore-mentioned, the basic hypothesis applied in the development of this new analytical technique was that the pixel count of white pixels (representing metallised particles), divided by the combined pixel count of white (representing metallised particles) and grey (representing chromite particles) pixels would be

directly related to the level of chromite pre-reduction determined by the current wet chemical method. This hypothesis is mathematically expressed in Equation 4-1:

$$\text{chromite pre-reduction \%} \cong \text{white pixel \%} = \frac{\text{white pixel count}}{\text{white pixel count} + \text{grey pixel count}} \quad (4-1)$$

4.3. Basic algorithm

The above-mentioned basic approach was refined into a general algorithm consisting of several steps, i.e.:

- i) Firstly, all ten of the SEM micrographs of a specific polished sample were cropped to the same size to remove the footer information (e.g. working distance, magnification) from each image.
- ii) Secondly, all ten cropped micrographs were stitched together into one image. This was done to ensure that image processing was not done on a single micrograph, which might not be statistically representative of the overall sample.
- iii) Thereafter, the pixel count of white pixels in the above-mentioned stitched image was determined. According to the hypothesis applied in this method, this represented metallised particles. A typical example of this determination is shown in Figure 4-2. Figure 4-2a indicates an original SEM micrograph in greyscale, while Figure 4-2b is a zoomed-in portion for illustration purposes. On this zoomed-in image, the actual pixels in greyscale colour can be seen. This greyscale colour map was then converted into a matrix in Matlab containing the actual greyscale number array that ranges from 0 to 255, with 0 being black and 255 white, as is indicated in Figure 4-2c. This greyscale number matrix was then converted into a binary matrix of black and white, which is indicated by 0 and 1 in Figure 4-2d, respectively. This was done by applying a fixed threshold value of 0.98. In Figure 4-2a, an example of an image consisting of

ten stitched SEM micrographs is presented, together with a histogram (Figure 4-2b) indicating the number of pixels as a function of the greyscale numbers 0 to 255, as well as the correlating threshold values from 0 to 1. Practically, the afore-mentioned fixed threshold value of 0.98 implies that the number of white pixels was regarded as the pixels occurring at greyscale values larger than the correlating threshold number of 0.98.

- iv) SEM micrograph image acquisition is subjected to minor artefacts, e.g. noise from the SEM detector. Therefore, noise filtering was applied on the white pixel areas to avoid random white pixels from contributing to the white pixel count. Any individual white pixel, not neighboured by another white pixel, was discarded in this step.
- v) The number of greyscale pixels, representing the unaltered and altered chromite ore particles, was then determined. For this purpose, two threshold values were determined, with the number of greyscale pixels in-between these threshold values regarded as appropriate. However, these threshold values could not be fixed, since the degree of metallisation achieved influenced the range of greyscale colours observed for altered chromite particles. The selection of the two threshold values can be explained, by again considering the example presented in Figure 4-3b. The epoxy resin, wherein the sample material was moulded, and the carbon reductant (anthracite in this case) formed part of the black pixel areas that are typically represented by greyscale colours correlating with a threshold value of less than 0.2. Therefore, these pixels were not considered in this greyscale pixel count calculation. The actual range of appropriate greyscale colours was determined by varying the threshold value between 0.2 and 0.98 in steps of 0.02. This was done in an iterative loop in Matlab, which enabled the testing of all possible greyscale threshold ranges between 0.2 and 0.98. This approach will be further explained in the method validation section, when

both laboratory prepared pellet mixtures, as well as the industrially produced pre-reduced pellet samples are considered.

- vi) The last step in the method was to determine the white pixel %, as indicated in Equation 4-1.

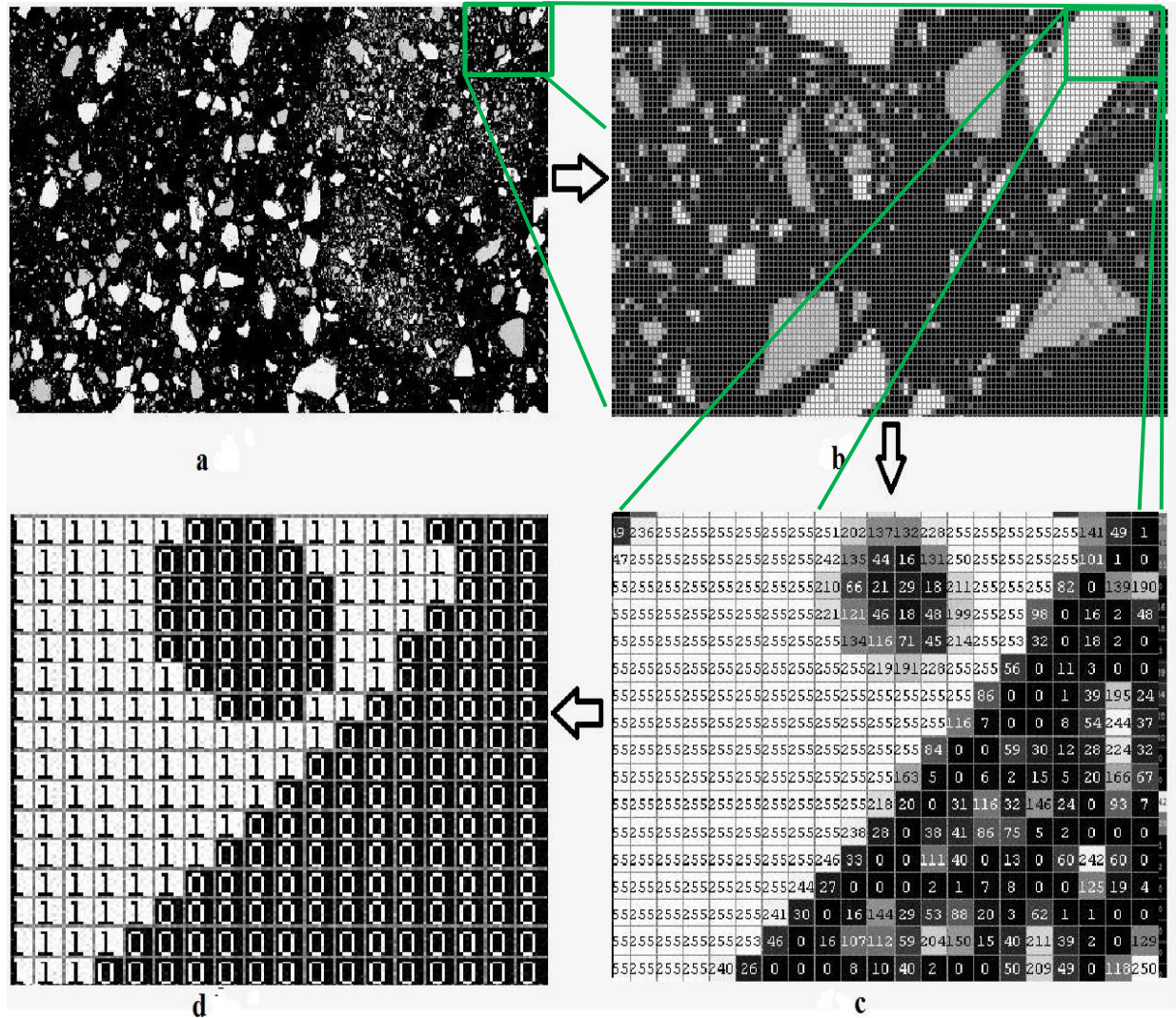


Figure 4-2: An example of a SEM micrograph image processing scheme wherein (a) is the original SEM micrograph, (b) a zoomed-in area showing actual pixels, (c) showing greyscale intensity numbers of the corresponding pixels and (d) is the converted binary (black and white) image

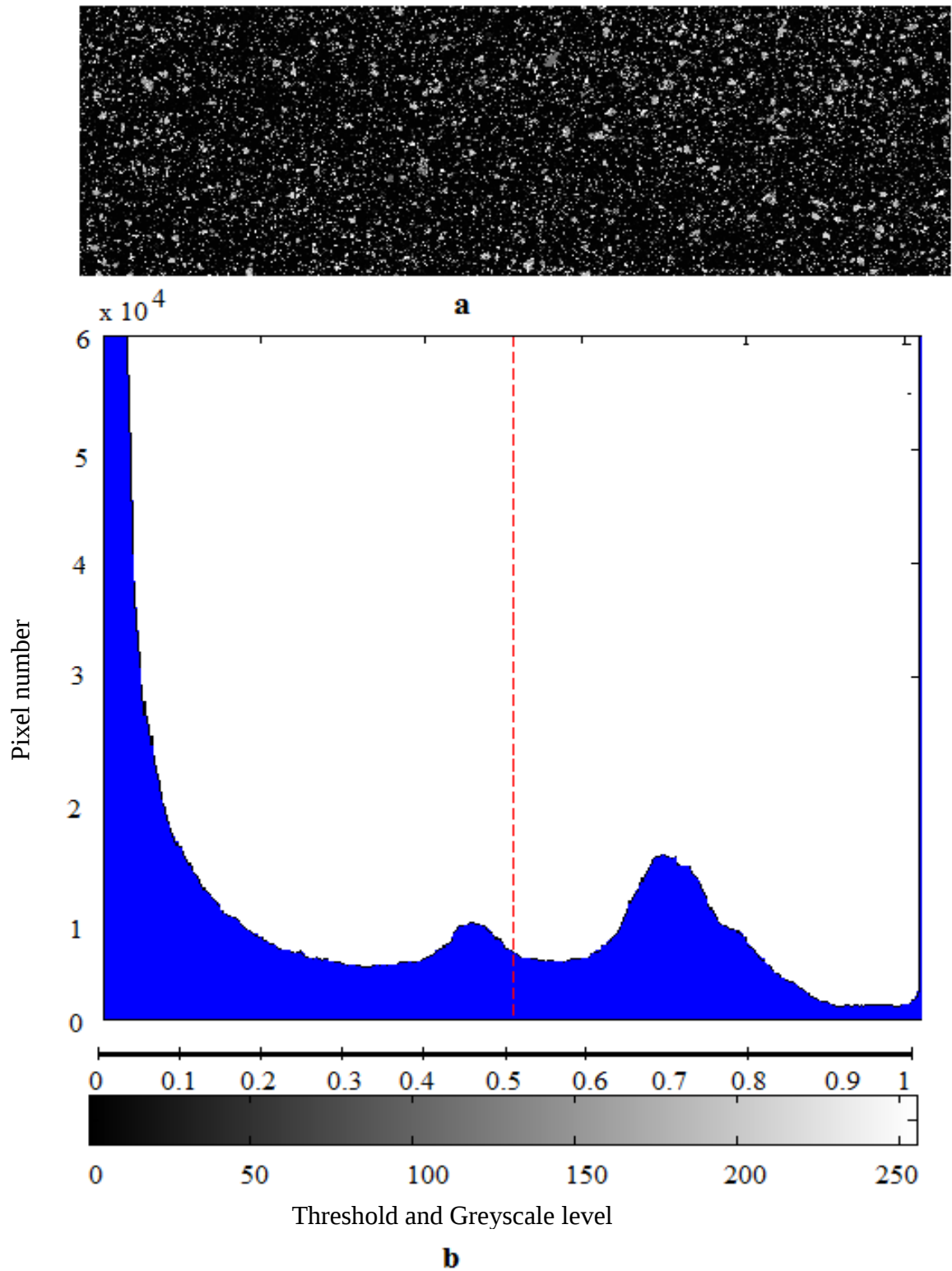


Figure 4-3: An example of (a) ten SEM micrograph images stitched together and (b) shows a histogram of pixel numbers as a function of greyscale level and the corresponding threshold values

4.4. Validation of the analytical technique

4.4.1. Analysis of laboratory prepared pellets mixtures

In Figure 4-4, the correlation between the white pixel % (Equation 4-1), as determined with the algorithm described earlier and the chromite pre-reduction levels (%) of the laboratory prepared pellet mixtures is presented. As is evident from these results there was a strong linear relationship ($R^2 = 0.998$) between the white pixel % and the level of pre-reduction determined chemically.

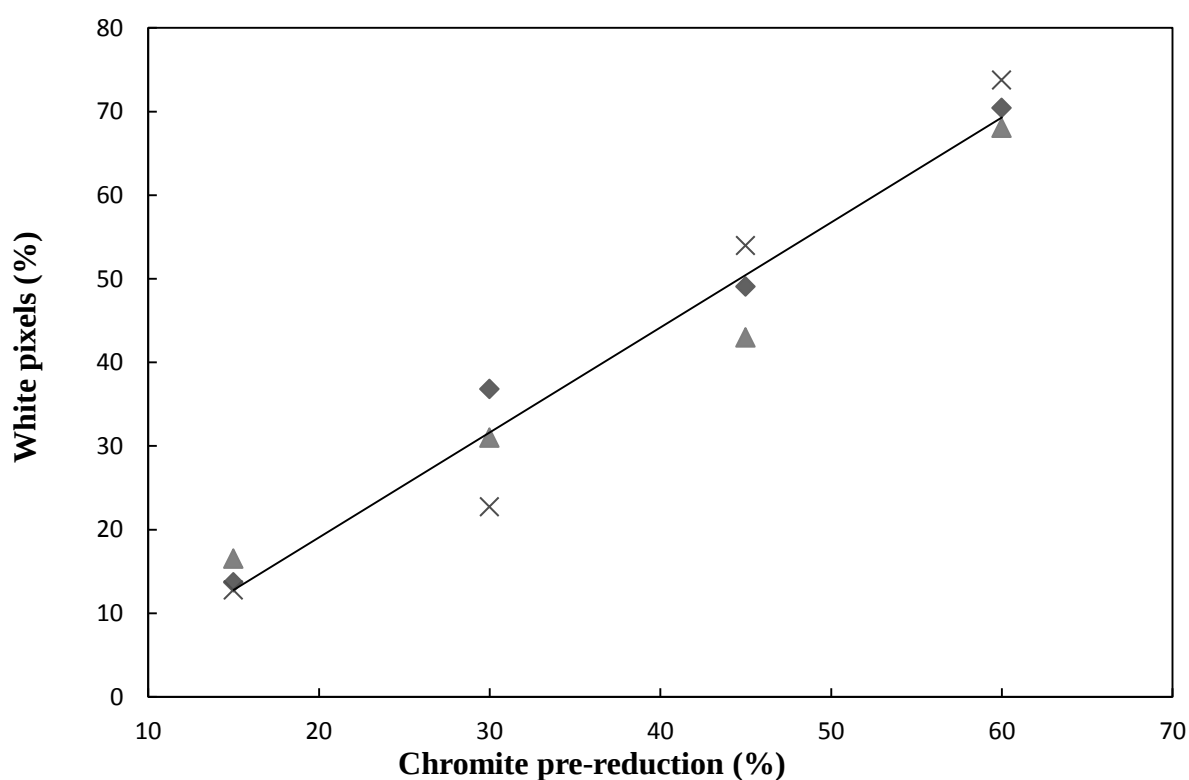


Figure 4-4: Correlation between white pixel (%) and chromite pre-reduction (%), whereby the diamonds, triangles and crosses represent 1, 3 and 5 % carbon content, respectively

From Figure 4-4, it can be seen that the method can be applied successfully to determine the level of chromite pre-reduction, at least for laboratory prepared samples.

However, these laboratory prepared samples do not accurately represent the real-world situation. Firstly, the metallised particles represented by FeCr particles in these laboratory prepared samples were totally liberated from the chromite particles, as is illustrated in Figure 4-5. Additionally, the greyscale level of the chromite particles included in these laboratory prepared samples was relatively constant, since these laboratory prepared samples were not actually pre-reduced at elevated temperatures. This implies that the greyscale threshold ranges (step ‘v’ in the algorithm), which should be representative of the chromite particles, could have been chosen by manually checking the greyscale level numbers of a couple of chromite particles. Therefore, testing the method on these laboratory prepared samples was only the first step in method validation.

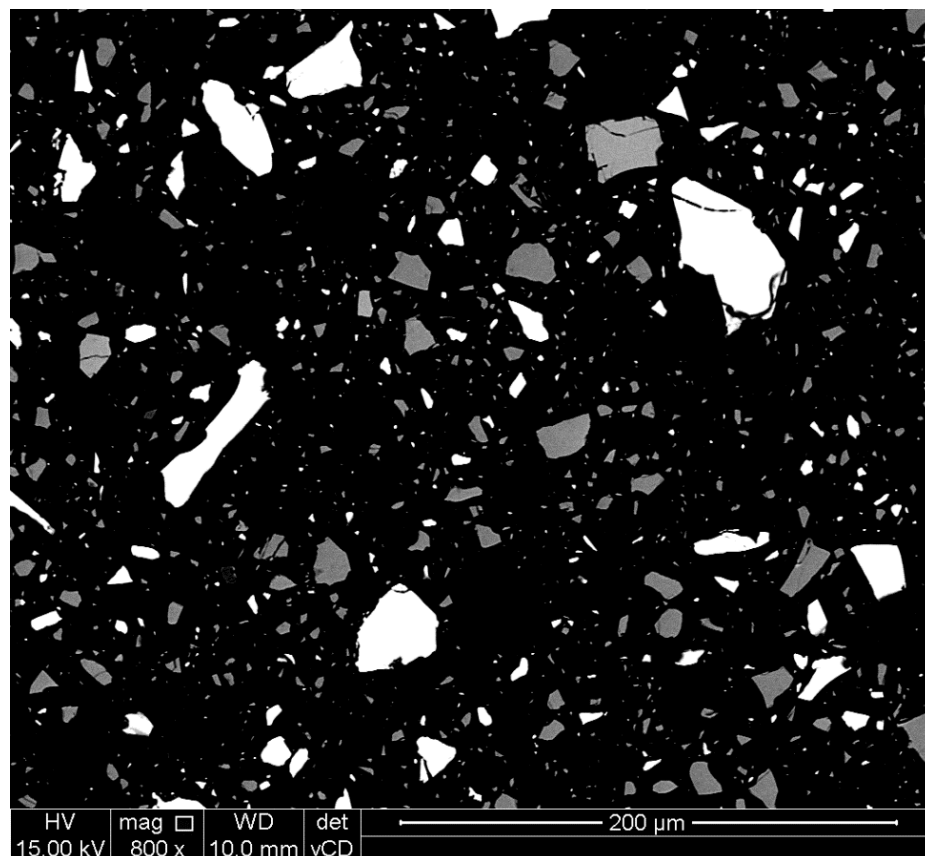


Figure 4-5: Polished sectional SEM micrograph of a typical laboratory prepared pellet mixture

4.4.2. Analysis of industrially pre-reduced pellets

In Figure 4-6, a typical SEM micrograph of a moulded polished industrial pre-reduced pellet mixture is presented. In contrast to the laboratory prepared mixture (Figure 4-5), most metallised particles (white areas) are associated with chromite grains, since the metallised particles actually form from the chromite during pre-reduction at elevated temperatures. Furthermore, the greyscale of the chromite particles varies substantially. When Cr and Fe migrate from the chromite spinel to the metallised phase, the remaining chromite particle(s) will consist of a higher percentage of elements with lower molecular weights, and consequently appear darker than the unaltered chromite particle(s), as explained in section 2.3.1. Therefore, the importance of selecting an appropriate greyscale range, between two matching threshold values, as indicated in Figure 4-3 and step 'v' of the algorithm, becomes apparent. The selection of these two threshold values cannot be done manually, since the range of appropriate greyscale intensity to match altered and unaltered chromite particles cannot be easily predicted.

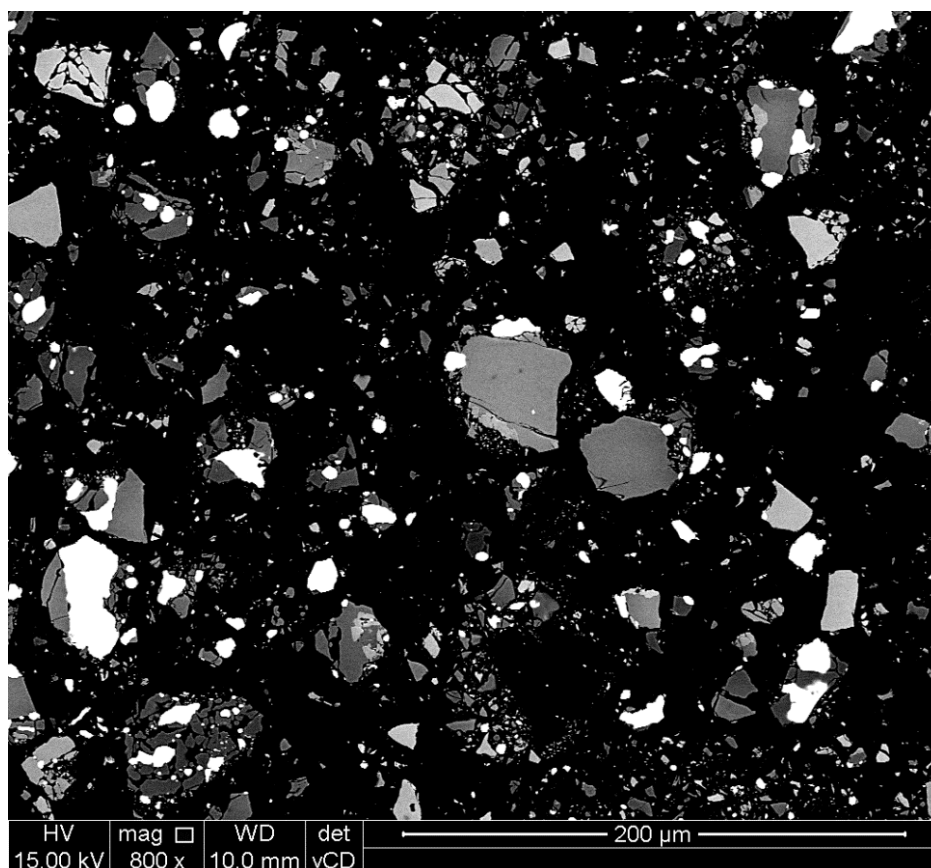


Figure 4-6: Polished sectional SEM micrograph of a typical industrial pre-reduced pellet mixture

Actual chromite pre-reduction levels up to 80 % have been achieved commercially on an industrial scale. However, Cr oxides reduce at higher temperatures than Fe oxides do (Niemelä *et al.*, 2004; Dawson & Edwards, 1986). Therefore, chromite pre-reduction above 60 % is relatively uncommon in an industrial setting, since this would require elevated temperatures and exposure periods that become less feasible on a commercial scale. The industrial pre-reduced pellet mixtures received from the FeCr producer applying this process had pre-reduction levels varying between 38 and 50 %. Figure 4-7 indicates the relationship between Cr and Fe metallisation with chromite pre-reduction, as a function of exposure time during pre-reduction at 1200 °C, adapted from Dawson & Edwards (1986). In this figure, the metallisation and pre-reduction of the industrial pre-reduced pellet mixtures received are also

indicated (as the range of investigation). As is evident from Figure 4-7, the increase in pre-reduction is not linear. However, for the purpose of developing the alternative analytical technique considered in this investigation, it was assumed that the level of pre-reduction over the range of the industrial pre-reduced pellet received can be approximated by a straight-line correlation as indicated in Figure 4-7.

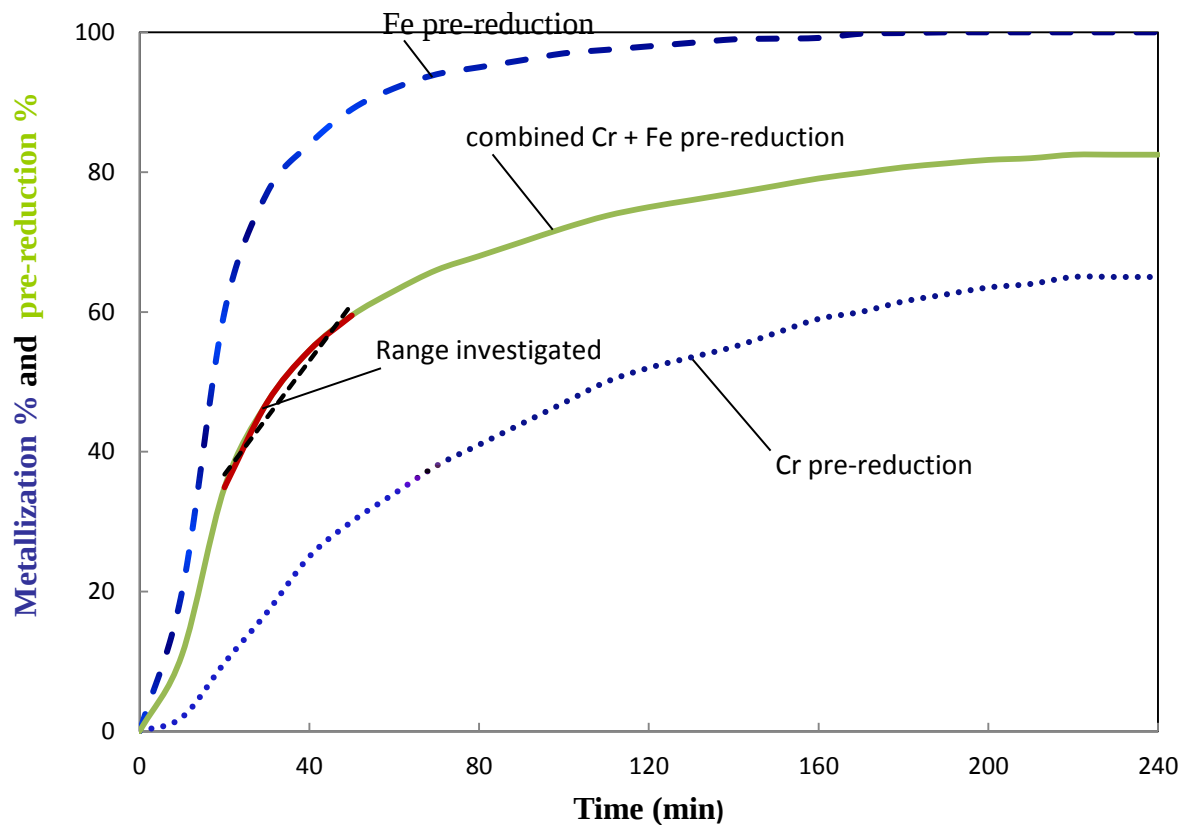


Figure 4-7: The pre-reduction of chromite in terms of the of metallisation rates of iron, Cr and their combination, adapted from Dawson & Edwards (1986). The evaluated pre-reduction range in this study is illustrated by the red line, corresponding (approximated) with the black dotted straight line

If the above-mentioned assumption is valid, the white pixels % (according to Equation 4-1) would be correlated with the chromite pre-reduction levels (%) determined

using the wet chemical technique (Equation 4-1). This implies that the two threshold values determined in an iterative manner in step ‘v’ of the algorithm to represent the optimal range of greyscale of the unaltered and altered chromite particles must stay constant to determine the white pixels % for the entire range of pre-reduction levels of the industrial pre-reduced pellet mixtures received from the FeCr producer. From the results presented in Figure 4-8, it is evident that this is indeed the case. The level of chromite pre-reduction (Equation 4-1) of the industrial pellet mixtures originating from two different rotary kilns correlated very well with the white pixel % calculated according to Equation 4-1 ($R^2 = 0.919$) for both sets of data.

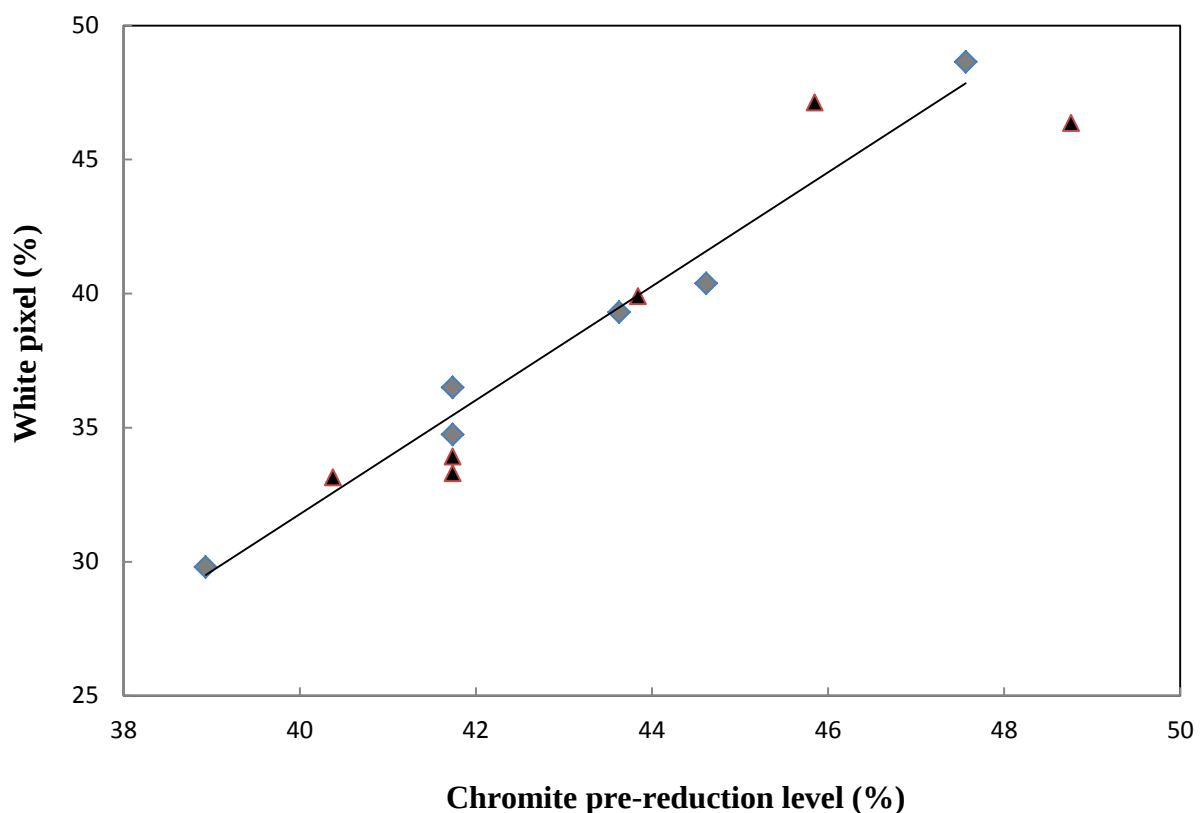


Figure 4-8: Correlation between white pixels (%) and chromite pre-reduction levels (%) of industrial pre-reduced pellets originating from two different kilns

4.4.3. Possible industrial application of the method

The objective of this study was to investigate the possible development of a SEM image processing method that would enable the faster determination of chromite pre-reduction than the currently applied wet chemical method. From the results presented, it seems feasible that the developed method can be applied to determine chromite pre-reduction. However, two issues need to be addressed. Firstly, how can the method be applied to deliver quicker results, and secondly to be valid over a wider range of pre-reduction levels than what was considered in this study, i.e. 38 to 50 % chromite pre-reduction.

Although not investigated as part of this study, it is suggested that, in order to address the two aforementioned issues, actual pre-reduced pellets (see Figure B-4) can be split into halves, after which these halves can be polished in a relatively short period. Industrial chromite pre-reduced pellets are strong enough to be polished in this manner (Neizel *et al.*, 2013; Kleynhans *et al.*, 2012). These polished cross-sectional pellets can then be moulded in a fit-for-purpose aluminium moulding stub, with metal grub screws to hold the pellets in place. This would eliminate the need to carbon coat the pellets, since such cross-sectional polished pellets would be conductive. SEM micrographs can then be taken of these polished pellets, without the need to set the sample material in a resin matrix prior to polishing. In this study, only milled pre-reduced pellets were received and this facet of method development was therefore not considered in the current scope of work.

As was indicated in Figure 4-7, the industrial pre-reduced material mixtures considered in this study were within a limited range of pre-reduction, i.e. 38 to 50 %. However, the result indicated that this range of pre-reduction could be linearly related to the white pixels % (Figure 4-8). However, according to the non-linear progress of chromite pre-

reduction presented in Figure 4-7, it might not be possible to accurately relate the white pixels % to the level of pre-reduction with only a single set of optimally determined greyscale threshold values (step 'v' in the algorithm). Therefore, it is proposed that reference standards be prepared to cover various ranges of pre-reduction. These standard samples could be prepared by splitting pellets into halves. One half could be analysed using the wet chemical method to determine pre-reduction, while the other half could be polished and moulded as described in the previous paragraph. If a pellet with an unknown level of pre-reduction is analysed, it should be analysed simultaneously (and at the same SEM settings) with a set of standard pellets with known pre-reductions. This would imply that a two-value threshold greyscale range (as indicated in step 'v' of the algorithm), applicable to the pre-reduction range covered by that specific set of standard pellets, would be determined. If the level of pre-reduction that was derived from the white pixels % of the unknown sample fell outside the range of pre-reduction covered by the standards, then the unknown sample should be re-analysed with another set of standard samples that do cover the appropriate range. Adaptations of the investigated method, which include polishing of pre-reduced pellets without being set in epoxy resin and the preparation of standards that have to be analysed with an unknown sample, were proposed to make the method industrially applicable.

Chapter 5: Project evaluation and future perspectives

The specific objectives of the project were described in Chapter 1, section 1.2. In this chapter, the project evaluation is discussed in relation to the afore-mentioned objectives. Furthermore, future perspectives and industrial relevance are discussed.

5.1. Project evaluation

- a) *Conduct a thorough literature survey to contextualise the work and to indicate scientific gaps.*

A thorough literature survey was conducted (Chapter 2). The global significance of South Africa's ferrochrome industry was justified in terms of chromite resources (section 2.1.1) and ferrochrome production (section 2.2.1). From the various processes and techniques discussed in section 2.2.2, it was evident that the pre-reduction process is likely to be the most viable option for the production of ferrochromium (FeCr) in order to lower the specific energy consumption (SEC) of smelting plants. The fundamentals (section 2.3.1), as well as numerous important aspects that relate to chromite pre-reduction, were considered in sections 2.3.2, 2.3.3 and 2.3.4, respectively. The general technique used to analyse the pre-reduction of pre-reduced chromite ore in FeCr plants is presented in section 2.3.5, which indicated that this is a relatively old technique that is very time consuming.

- b) *Develop an alternative method to determine chromite pre-reduction, using image acquisition and image processing.*

As far as the author could assess, the method described in this study is the first SEM image processing method developed for the determination of chromite pre-reduction

described in the peer-reviewed public domain. The technique consisted of several steps, which included:

- i. Milling of the laboratory prepared pellet mixtures to 90 % size less than 75 μm ($D_{90} = 75 \mu\text{m}$).
- ii. Moulding both the laboratory and industrially pre-reduced pellets mixtures into epoxy resin.
- iii. Polishing the moulded samples with various grinding discs to ensure smooth cross-sectional samples.
- iv. Carbon coating the samples to ensure conductivity prior to SEM analysis.
- v. Acquisition of representative, i.e. ten SEM micrographs per sample, at constant SEM settings (WD-working distance, magnification, contrast, brightness).
- vi. Importing the ten SEM micrographs and stitching them into one representative image of a specific sample.
- vii. Cropping of micrograph (matrix) to eliminate footer and removal of artefacts.
- viii. Thresholding (upper bound – 0.98) and subsequently transforming greyscale images into black and white (for % white pixel counting, representing FeCr).
- ix. Thresholding (lower bound - 0.2) and subsequently transforming greyscale images into black and white (for % black pixel counting, representing anthracite and resin).
- x. Thresholding (varying between 0.2 and 0.98 with 0.02 increments) and subsequently transforming greyscale images into black and white (for % grey pixel counting, representing chromite ore).

- xi. Performing steps viii, ix and x simultaneously and iteratively to achieve an optimal threshold combination, where the optimal is determined by comparing % white pixels (FeCr) and % of pre-reduction with a correlation factor (R^2).

c) *Validate the new analytical method by comparing it to pre-reduction levels of laboratory prepared and industrially produced pellets mixtures.*

The developed analytical method was validated for both laboratory prepared and industrially produced pellets mixtures. The validation in both cases was observed by correlating chromite pre-reduction (%) determined by wet chemical analysis and white pixel % determined using the developed method. A strong linear correlation, $R^2 = 0.998$ and 0.919 , was observed for laboratory prepared pellet mixtures, as well as industrially pre-reduced pellets obtained from two different kilns, respectively. This demonstrated that the developed method can be applied to determine chromite pre-reduction accurately.

d) *Make recommendations with regard to the industrial relevance of the developed method and possible future research.*

As indicated in section 4.4.3, several further improvements can be made in order to make the method industrially applicable. The milling, moulding and conductive coating steps can be excluded, since industrial chromite pre-reduced pellets are strong enough to withstand polishing in this manner, as explained in section 3.2.4 (Neizel *et al.*, 2013; Kleynhans *et al.*, 2012). The polished cross-sectional pellets can then be mounted in fit-for-purpose aluminium moulding stubs with metal grub screws to hold the pellets in place, eliminating the need to carbon coat the samples.

It could be assumed that the range of pre-reduction levels for which the technique was used to determine the level of pre-reduction was linear, i.e. 38 to 50 %. However, this assumption cannot be made for ranges outside these limits (Figure 4-8). Determination of pre-reduction over a wider range utilising this technique could be achieved by making reference samples. These reference samples could be prepared by splitting pellets into halves. One half could be analysed using the wet chemical method to determine pre-reduction %, while the other half could be polished and mounted for SEM analysis as described in the previous paragraph. This implies that a different threshold combination (as indicated in step 'v' of the algorithm) suitable for the pre-reduction range covered by that specific set of reference pellets will be determined. Reference samples should be simultaneously analysed at similar SEM settings when determining % white pixels. If the level of pre-reduction that was derived from the white pixels % of the unknown sample (sample under investigation) fell outside the range of pre-reduction covered by the standards samples, then the unknown sample should be re-analysed with another set of reference samples that do represent the appropriate range. The aforementioned adaptations were recommended in order to ensure the industrial feasibility of the developed analytical technique. The implementation of these minor modifications to the newly-developed method will definitely result in this method being faster than the conventional wet chemical analysis.

5.2. Future perspectives

In this study, a new method to determine chromite pre-reduction was presented. If successfully implemented, it could significantly reduce the instabilities that are currently associated with the carbon (C) balance of FeCr submerged arc furnace (SAF) operating on the pelletised pre-reduced process. However, it would be ideal if the actual C content of the pre-reduced pellets could be determined at the same time. This should be considered as an

important future perspective to further complement the method developed. The applicability of the method to other pre-reduction processes, such as iron ore pre-reduction, should be explored.

5.3. Final remarks

In closure, the candidate would like to evaluate this dissertation that is submitted for an MEng degree, by applying the programme outcomes prescribed for an MSc (ENG) degree by the North-West University. In short, the programme outcomes that an MSc (ENG) dissertation should comply with are listed:

- i. Identification of research problem and setting clear objectives.
- ii. A thorough investigation of critical and relevant literature survey on the study.
- iii. Development of crucial research methodology and experimental tools or numerical models.
- iv. Implementation of either an empirical or numerical investigation in order to address the research problem.
- v. Validation and substantiation of the results obtained.
- vi. Evaluations of results.
- vii. Conclusions, generalisation and recommendations.

From the candidate's perspective, the programme outcomes were successfully achieved. Furthermore, a relevant scientific contribution was made in developing an alternative method to enhance the pelletised chromite pre-reduction process. Since the true measure of scientific contribution is the acknowledgment of the research by peers, the candidate has submitted the results obtained for publishing in an accredited research journal. Therefore, since it is not compulsory that a significantly new scientific contribution is made in order to obtain an MEng degree, the aforementioned contribution can therefore be viewed

as sufficient proof that this study surpassed the requirements of an MSc (ENG) as prescribed by the North-West University.

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Appendix A: Pre-reduction calculations

Reduction is associated with the removal of oxygen, thus reduction (R) is defined as:

$$R(\%) = \frac{\text{Mass of oxygen removed}}{\text{Total original removable oxygen}} \times 100 \quad (1)$$

If carbon is the reducing agent, carbon monoxide is the reaction product



The following deduction can therefore be made:

$$n = \frac{m}{M}$$

$$\text{Mass of oxygen removed} = m_{O_\omega} = n_{O_\omega} M_O \quad (3)$$

$$\text{Total original removable oxygen} = m_{O_\tau} = n_{O_\tau} M_O$$

$$\frac{R(\%)}{100} = \frac{n_{O_\omega} M_O}{n_{O_\tau} M_O} = \frac{n_{O_\omega}}{n_{O_\tau}} \quad (4)$$

From equation (Barnes *et al.*, 1983) 1 mole C reacts with 1 mole O to produce 1 mole CO

$$1n_{O_\omega} = 1\text{mol CO produced} = 1n_{CO_\rho}$$

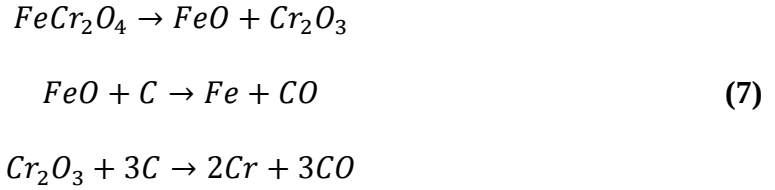
$$\frac{R(\%)}{100} = \frac{n_{CO_\rho}}{n_{O_\tau}} = \frac{\frac{m_{CO_\rho}}{M_{CO_\rho}}}{\frac{m_{O_\tau}}{M_{O_\tau}}} \quad (5)$$

$$M_{CO_\rho} = 28; M_{O_\tau} = 16$$

$$\frac{R(\%)}{100} = \frac{\frac{m_{CO_\rho}}{28}}{\frac{m_{O_\tau}}{16}} = \frac{m_{CO_\rho}}{28} \times \frac{16}{m_{O_\tau}} = \frac{m_{CO_\rho}}{\frac{28}{16} m_{O_\tau}}$$

$$\frac{R(\%)}{100} = \frac{\text{Mass of CO produced}}{\frac{28}{16}(\text{Total original removable oxygen})} \quad (6)$$

The reducible oxides in the chromite spinel are FeO and Cr₂O₃. These oxides are reduced with C to their metallic phases with the generation of gaseous intermediates, CO, according to the following reactions:



$$\begin{aligned} \frac{R(\%)}{100} &= \frac{m_{CO\rho}}{\frac{28}{16}m_{O\tau}} \\ \frac{R(\%)}{100} &= \frac{m_{CO\rho}^{Cr} + m_{CO\rho}^{Fe}}{\frac{28}{16}(m_{O\tau}^{Cr} + m_{O\tau}^{Fe})} \\ m &= nM \\ \therefore \frac{R(\%)}{100} &= \frac{n_{CO\rho}^{Cr}M_{CO} + n_{CO\rho}^{Fe}M_{CO}}{\frac{28}{16}(n_{O\tau}^{Cr}M_O + n_{O\tau}^{Fe}M_O)} \\ \frac{R(\%)}{100} &= \frac{M_{CO}(n_{CO\rho}^{Cr} + n_{CO\rho}^{Fe})}{\frac{28}{16}M_O(n_{O\tau}^{Cr} + n_{O\tau}^{Fe})} \\ \frac{R(\%)}{100} &= \frac{n_{CO\rho}^{Cr} + n_{CO\rho}^{Fe}}{n_{O\tau}^{Cr} + n_{O\tau}^{Fe}} \end{aligned} \quad (8)$$

FeO is reduced to Fe, producing 1 mole of CO for every mole of Fe produced and Cr₂O₃ is reduced to Cr, producing 1,5 mole of CO per mole of Cr produced. From leaching experiments the following was determined:

$$Cr_{sol} = \text{Soluble Cr}; Cr_{Tot} = \text{Total Cr} \quad (9)$$

$$Fe_{sol} = \text{Soluble Fe}; Fe_{Tot} = \text{Total Fe}$$

$$1\text{mol Cr} \rightarrow 1.5\text{mol CO}$$

$$1\text{mol Fe} \rightarrow 1\text{mol CO}$$

$$\therefore n_{CO\rho}^{Cr} = 1.5(n_{Cr_{sol}})$$

$$n_{CO\rho}^{Fe} = 1(n_{Fe_{sol}})$$

$$n_{O_t}^{Cr} = 1.5(n_{Cr_{Tot}})$$

$$n_{O_t}^{Fe} = 1(n_{Fe_{Tot}})$$

$$\frac{R(\%)}{100} = \frac{\frac{3}{2}(n_{Cr_{sol}}) + n_{Fe_{sol}}}{\frac{3}{2}(n_{Cr_{Tot}}) + n_{Fe_{Tot}}}$$

$$n = \frac{m}{M}$$

$$\therefore \frac{R(\%)}{100} = \frac{\frac{3}{2}\left(\frac{m_{Cr_{sol}}}{M_{Cr_{sol}}}\right) + \frac{m_{Fe_{sol}}}{M_{Fe_{sol}}}}{\frac{3}{2}\left(\frac{m_{Cr_{Tot}}}{M_{Cr_{Tot}}}\right) + \frac{m_{Fe_{Tot}}}{M_{Fe_{Tot}}}}$$

$$\frac{R(\%)}{100} = \frac{\frac{3}{2}\left(\frac{m_{Cr_{sol}}}{51.996}\right) + \frac{m_{Fe_{sol}}}{55.845}}{\frac{3}{2}\left(\frac{m_{Cr_{Tot}}}{51.996}\right) + \frac{m_{Fe_{Tot}}}{55.845}} \quad (10)$$

$$\frac{R(\%)}{100} = \frac{\frac{m_{Cr_{sol}}}{34.664} + \frac{m_{Fe_{sol}}}{55.845}}{\frac{m_{Cr_{Tot}}}{34.664} + \frac{m_{Fe_{Tot}}}{55.845}}$$

$$R(\%) = \frac{\frac{m_{Cr_{sol}}}{34.664} + \frac{m_{Fe_{sol}}}{55.845}}{\frac{m_{Cr_{Tot}}}{34.664} + \frac{m_{Fe_{Tot}}}{55.845}} \times 100$$

$$\frac{\frac{m_{Cr_{Tot}}}{34.664} + \frac{m_{Fe_{Tot}}}{55.845}}{100} = \text{Total Cr\&Fe Factor}(Tot_{CrFe_{Fac}}) = 0.0121$$

$$R(\%) = \frac{\frac{m_{Cr_{sol}}}{34.664} + \frac{m_{Fe_{sol}}}{55.845}}{0.0121}$$

Appendix B: Images

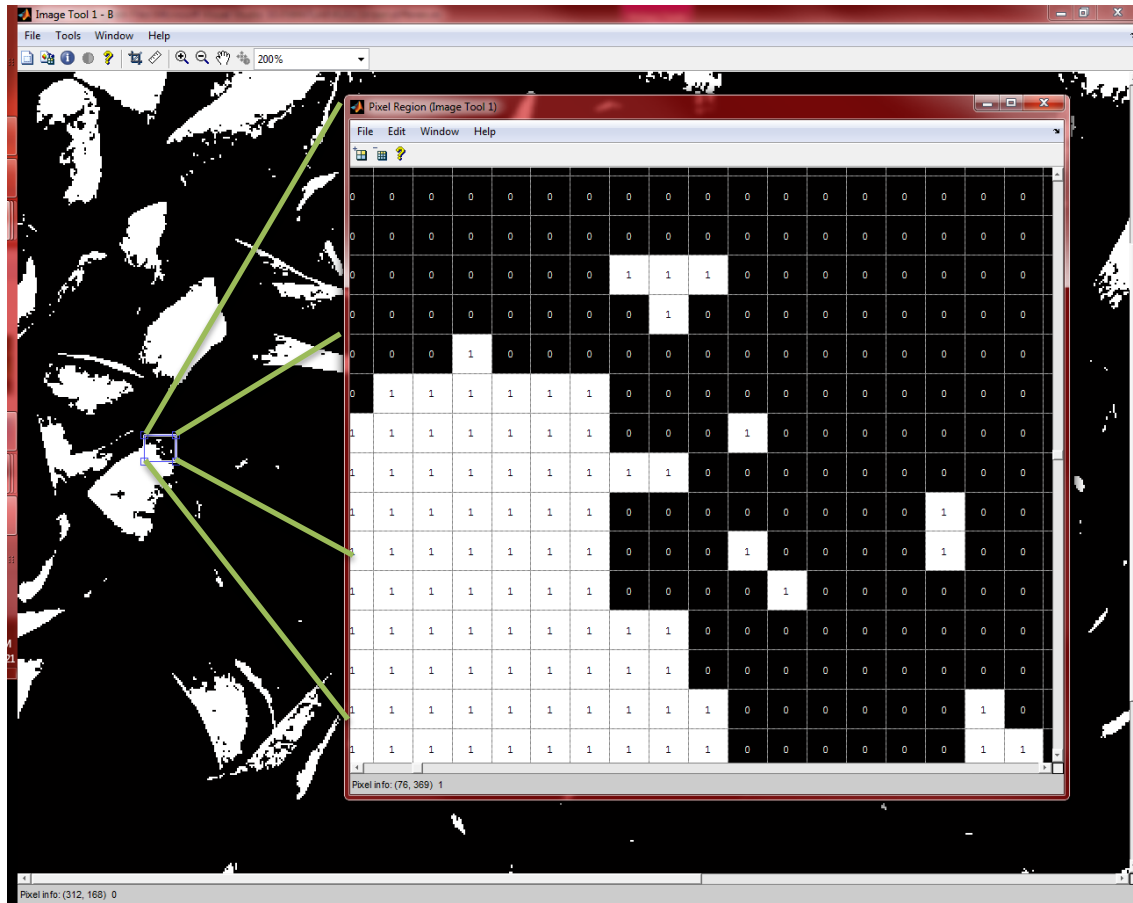


Figure B- 1: A typical binary image of a flower with zoomed in pixel region showing 0's and 1's, acquired in MATLAB

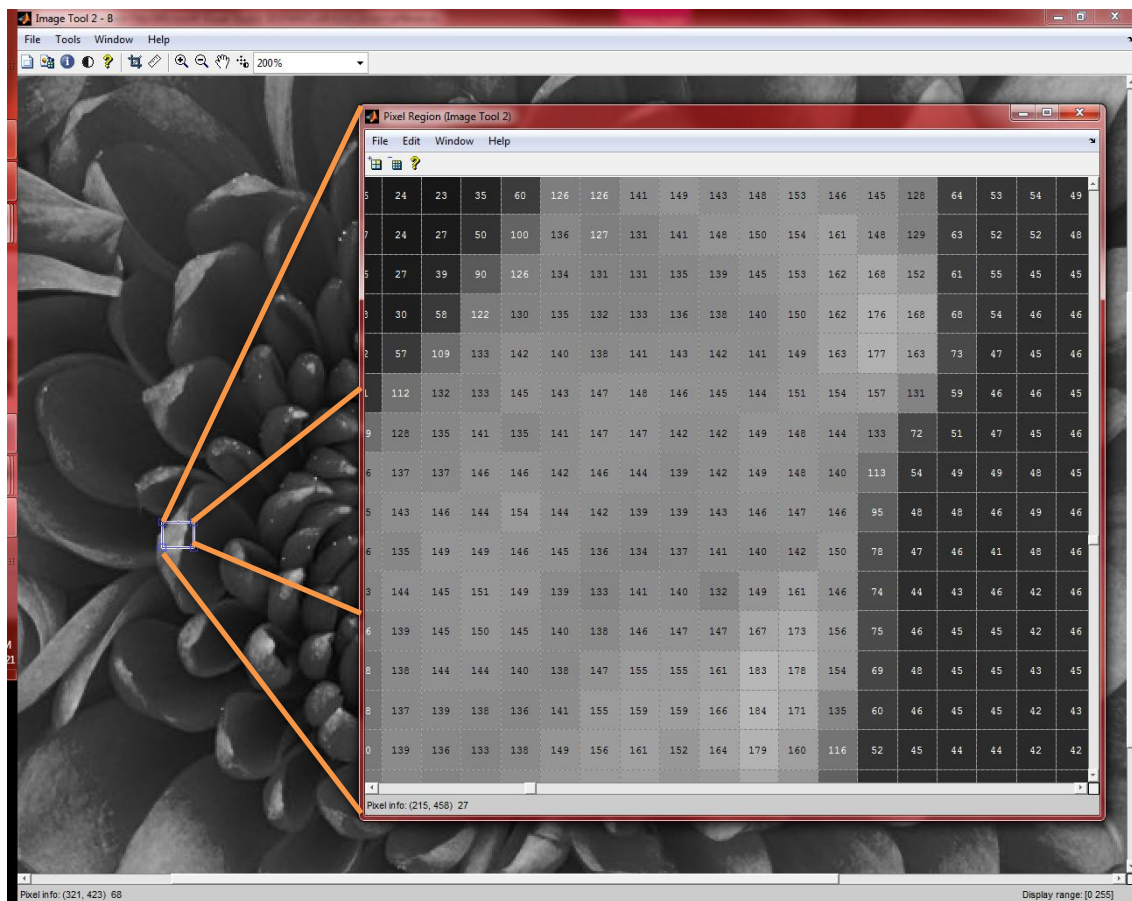


Figure B- 2: Greyscale image of a flower shown with zoomed in pixel region from 0 to 255 acquired in MATLAB

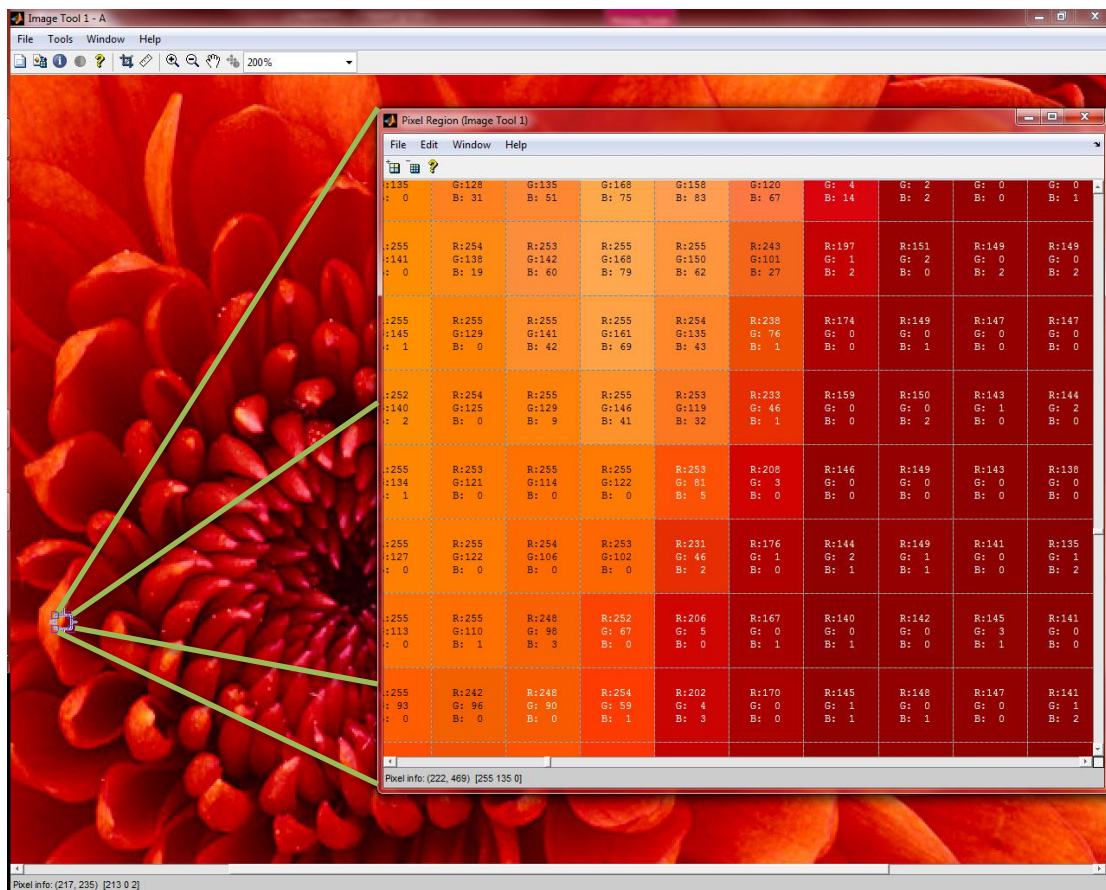


Figure B- 3: A true colour image of a flower with a zoomed in pixel region showing a combination of RGB represented in each pixel, acquired in MATLAB



Figure B-4: Typical industrially prepared chromite ore pellets