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## **Alteration of chrome-to-iron ratio in chromite ore by chlorination**

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## Abstract

The industrial importance of the chromium industry to South Africa is emphasised by the fact that it is considered the largest chromite (chromium ore) and ferrochrome (chrome-iron alloy) producing country in the world. Although South Africa holds three quarters of the world's chromite ore reserves, the chrome-to-iron (Cr-to-Fe) ratio of the local chromite ores is relatively low (1.47 to 1.55), compared to other deposits in the world (2.6 to 3.5). Additionally, iron is more readily reduced than chromium. The combination of these two factors implies that ferrochrome produced from South African chromite ore contains 47-53% chromium. Current pricing practises in the world ferrochrome industry dictate that ferrochrome producers are only paid for the chromium content in the ferrochrome, which implies that South African ferrochrome producers export a large percentage of their product without any financial benefit. Research to improve the Cr-to-Fe ratio is therefore essential to support sustainability of the local ferrochrome industry.

Conventional beneficiation methods such as gravity concentration, magnetic separation and floatation are unlikely to increase the Cr-to-Fe ratio, since both iron and chromium are part of the same mineral phase, i.e. the spinel, which requires structural dissociation. It has been proven on laboratory scale that high temperature carbochlorination (CO and Cl<sub>2</sub> atmosphere) can be used to selectively remove iron from chromite. However, such methods are unlikely to be implemented on an industrial scale due to health, environmental and cost considerations. In light of this, an alternative approach to chromite chlorination, avoiding the use of chlorine and other toxic gasses, was investigated during this study. Since it was found that NaCl addition significantly improved the effectiveness of carbochlorination of chromite, the effect of adding only NaCl during high temperature treatment of chromite was investigated.

The material utilised during this investigation consisted of local chromite, anthracite (source of carbon) and attapulgite clay (serving as a binder). These materials were mixed in a ratio and subsequently milled to  $D_{90} = 75\mu\text{m}$  to represent materials and specifications similar to those used during pelletisation of the chromite in the pre-reduction ferrochrome production process. This mixture could also be used to generate a partially reducing atmosphere (CO rich) during high temperature treatment, which was similar to the reaction conditions utilised during carbochlorination. The above-mentioned milled mixture was pelletised into cylindrical pellets with a die set and a hydraulic press.

This experimental investigation was based on a mono-variance procedure, in that the four different variables investigated, i.e. maximum pellet treatment temperature, exposure time, wt% NaCl addition to the pellets and the atmosphere the pellets were exposed to, were varied one at a time during experimentation. After each alteration of the afore-mentioned variables, the Cr-to-Fe ratios, together with other parameters, were measured. Analyses undertaken included Scanning Electron Microscopy, with Energy-Dispersive X-ray Spectroscopy (SEM-EDS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and cured breaking strength.

Although this investigation did not focus on the cured breaking strength of the pellets, it is a very important industrial parameter and was therefore measured. Results indicated that the addition of NaCl had a definite effect. In both oxidising and partially reducing atmospheres the cured breaking strength of the cured pellets increased up to 800°C exposure, whereafter it decreased. This was attributed to melting of NaCl at 801°C. In the oxidising atmosphere, the cured breaking strength increased again at temperatures higher than 1000°C, due to the formation of a thin oxidised layer on the outside of the pellets, which could be confirmed by SEM analysis.

Fine, metallic-like crystals were noticed inside and on the lids of crucibles in which pellets containing NaCl as an additive were cured at temperatures of

900°C or higher. SEM-EDS analysis and weight-ratio calculations revealed that these crystals were pure FeO. This indicated that some iron might have been liberated from the chromite spinel matrix. However, ICP-OES analyses revealed that Cr-to-Fe ratios did not change significantly under any of the experimental conditions (NaCl addition 5wt% to 15wt%, curing between 500°C and 1200°C, and oxidative/partially reducing atmospheres).

The observed FeO crystals did not make any meaningful difference to the Cr-to-Fe ratio of the chromite, but was of great academic interest as iron was extracted from the chromite spinel. This indicated that it is not only the formation of low melting point species, such as those proposed in previous mechanistic studies of carbochlorination of chromite, but that molten NaCl alone could also initiate the extraction of iron out of chromite. According to the knowledge of the author, this is the first report of its nature in open literature.

SEM and SEM-EDS analyses also proved that the addition of NaCl to the chromite/carbon/clay mixtures enhanced the rate of chromite pre-reduction. This finding was in agreement with earlier literature reports.

In conclusion, it can be stated that the addition of NaCl alone cannot alter the Cr-to-Fe ratio of chromite during high temperature treatment. NaCl addition did, however, have an effect on other important parameters i.e. initiation of iron removal, cured breaking strength and the rate of chromite pre-reduction. From the results and experience gained in this study, certain recommendations with regard to possible future studies could also be made. This included investigating i) other single component additives to possibly alter the Cr-to-Fe ratio during high temperature treatment, ii) the effect of industrially relevant additives such as CaO/CaCO<sub>3</sub>, MgO<sub>3</sub> and SiO<sub>2</sub> on the rate of chromite pre-reduction and iii) the effect of different clays (e.g. attapulgite, bentonite, etc.) on the rate of chromite pre-reduction.



## Opsomming

Die chroomindustrie in Suid-Afrika is belangrik aangesien Suid-Afrika die grootste produsent van chromiet (chromerts) en ferrochroom (chrom-ysteralooi) in die wêreld is. Alhoewel Suid-Afrika driekwart van die wêreld se chromietreserwes bevat, is die chroom-tot-yster (Cr-tot-Fe) verhouding van die erts relatief laag (1.47 tot 1.55) indien dit vergelyk word met ander reserwes in die wêreld (2.6 tot 3.5). Yster word ook makliker gereduseer as chroom. Hierdie twee faktore saam veroorsaak dat Suid-Afrikaanse ferrochroom 47-53% chroom bevat. Tans word ferrochroomvervaardigers slegs vir die chroominhoud van die ferrochroom betaal, wat beteken dat 'n groot persentasie van die produk uitgevoer word sonder enige finansiële voordeel. Navorsing om die Cr-tot-Fe verhouding van plaaslike chromiet te verhoog is dus noodsaaklik om die volhoubaarheid en groei van die plaaslike ferrochroomindustrie te bevorder.

Konvensionele verryking soos gravitasiekonsentrasie, magnetiese skeiding en flotasie kan nie gebruik word om die Cr-tot-Fe verhouding van chromiet te verbeter nie, as gevolg van die feit dat beide die yster en chroom deel is van 'n spinelstruktuur wat strukturele dissosiasie vereis. Laboratoriumstudies het aangetoon dat hoë-temperatuur karbochlorinering (CO en Cl<sub>2</sub> atmosfeer) suksesvol gebruik kan word om yster selektief uit chromiet te verwyder. As gevolg van gesondheid-, omgewings- en kostefaktore is dit egter onwaarskynlik dat hierdie skeidingsmetode op industriële skaal geïmplementeer sal word. Daar is dus besluit om tydens hierdie studie alternatiewe metodes, wat die gebruik van chloor- en ander skadelike gasse vir die chlorinering van chromiet uitsluit, te ondersoek. Aangesien daar in vorige karbochlorineringsondersoeke bevind is dat die byvoeging van NaCl die effektiwiteit van die chlorinering aansienlik verbeter het, is daar besluit om gedurende hierdie studie slegs die effek van NaCl, tydens hoë temperatuur behandeling van chromiet, te ondersoek.

Materiale wat gebruik is tydens hierdie ondersoek het ingesluit plaaslike chromient, antrasiet (bron van koolstof) en attapulgietskley (bindmiddel). Hierdie materiale is in 'n spesifieke verhouding gemeng en daarna vermaal tot  $D_{90} = 75 \mu\text{m}$ , om soortgelykemengselverhouding en partikelgroottes na te boots soos wat in die pre-reduksie vervaardiging van ferrochroom gebruik word. Hierdie mengsel was geskik om 'n gedeeltelike reduserende atmosfeer (CO ryk) te genereer gedurende die hoë temperatuur behandeling, wat soortgelyk was aan dié in die bogenoemde karbochlorineringsproses. Die gemaalde materiaalmengsel is in silindriese pilletjies met 'n matriks en hidroliese pers gedruk.

Die eksperimentele ondersoek was gebaseer op 'n monovariante-prosedure. Vier verskillende veranderlikes, naamlik maksimum temperatuur waaraan pilletjies bloot gestel is, blootstellingstyd, persentasie byvoeging van NaCl in die pilletjies en die atmosfeer waarin die pilletjies behandel is, is afsonderlik ondersoek. Na afloop van elke eksperiment is die Cr-tot-Fe verhouding saam met ander parameters gemeet. Die pilletjies is geanaliseer met 'n Skandereer Elektron Mikroskoop gekoppel aan 'n Energiedispersie X-straal Spektrometer (SEM-EDS), Induktief Gekoppelde Plasma Optiese Emissie Spektrometer (IGP-OES), asook 'n breeksterkte instrument.

Alhoewel die primêre fokus van hierdie studie nie op die verharde breeksterktemeting van die pilletjies was nie, is dit wel ondersoek aangesien dit belangrik in die industrie is. NaCl-byvoeging het 'n beduidende effek op verharde breeksterkte gehad. In beide oksiderende en gedeeltelike reduserende atmosfere het die breeksterkte van die verharde pilletjies toegeneem tot in met 'n temperatuur van  $800^{\circ}\text{C}$ , waarna dit afgeneem het. Hierdie verskynsel is toegeskryf aan die smeltpunt van NaCl by  $801^{\circ}\text{C}$ . In die oksiderende atmosfeer het die verharde breeksterkte weer toegeneem by temperature hoër as  $1000^{\circ}\text{C}$ . Dit kon toegeskryf word aan die vorming van sintering in die dun geoksideerde laag aan die buitekant van die pilletjies wat deur SEM-analises bevestig is.

Fyn, metaalagtige kristalle is waargeneem binne-in en op die deksels van kroesies waarin pilletjies met NaCl behandel is by temperature van 900°C en hoër. SEM-EDS-analises, asook gewigsverhouding berekeninge, het aangetoon dat die kristalle suiwer FeO was. Hierdie waarneming het daarop gedui dat van die yster wel uit die chromietspinelmatriks verwyder kon word. IGP-OES-analises het egter aangetoon dat geen waarneembare verbetering in die Cr-tot-Fe verhouding onder enige van die eksperimentele kondisies (5% tot 15% NaCl bygevoeg, verhit tussen 500°C en 1200°C in oksiderende/gedeeltelike reduserende atmosfeer), plaasgevind het nie.

Alhoewel die waarneming van die bogenoemde FeO-kristalle geen verskil aan die Cr-tot-Fe verhouding gemaak het nie, was hierdie waarneming wel wetenskaplik belangrik. Die vorming van FeO-kristalle impliseer dat gesmelte NaCl die verwydering van yster uit chromiet kan inisieer. Dit is in teenstelling met vorige karbochlorinerings meganistiese studies waarin beweer is dat verbindings met 'n lae-temperatuur smeltpunt verantwoordelik is vir die inisiasie van yster verwydering uit chromiet. Volgens die skrywer se kennis, is hierdie die eerste keer wat hierdie verskynsel waargeneem word.

SEM- en SEM-EDS-analises het albei aangetoon dat die byvoeging van NaCl by chromiet/koolstof/klei mengsels die tempo van chromiet pre-reduksie verbeter. Die bevinding is in ooreenstemming met vorige ondersoek.

Die byvoeging van NaCl alleen het nie die Cr-tot-Fe verhouding van chromiet tydens die hoë-temperatuur behandeling gewysig nie. Dit het wel ysterverwydering geïnisieer, verharde breeksterkte beïnvloed en die tempo van chromiet pre-reduksie verander. Vanuit die resultate en ondervinding wat tydens hierdie studie opgedoen is kon sekere voorstelle met betrekking tot toekomstige studies gemaak word wat insluit die ondersoek van i) ander enkelkomponent byvoegmiddels wat moontlik die Cr-tot-Fe verhouding van chromiet kan verbeter gedurende hoë temperatuur behandeling, ii) die effek van industrieelrelevante byvoegmiddels soos CaO/CaO<sub>3</sub>, MgO<sub>3</sub> en SiO<sub>2</sub> op die tempo van chromiet pre-reduksie en iii) die effek van verskillende

kleisoorte (attapulgië, bentoniet, ens.) op die tempo van chromiet pre-reduksie.



# Chapter 1

## Motivation and objectives

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In this chapter, the project motivation is briefly discussed, as well as the importance of this investigation to South Africa's chromium industry. It also provides a short overview of the principle of this investigation and lists the objectives of this study.

---

### 1.1 Motivation

Since its discovery in 1798, chromite has been the only commercially-recoverable source of chromium (Niagru, 1988a; Cowey, 1994; Riekkool-Vanhanen, 1999). It is generally accepted that South Africa holds between 74% (Cowey, 1994) to 80% (Riekkool-Vanhanen, 1999) of the world's viable chromite ore reserves. The South African chromite reserves are situated within the Bushveld Complex (Howat, 1994). This geological phenomenon consists of an enormous saucer-like intrusive igneous mass, which extends for approximately 400km from east to west and roughly the same distance from north to south. It is located in the central and western parts of the South African Highveld (Howat, 1994).

Chromite is primarily utilised for the production of ferrochrome, which is a crude alloy produced during the pyrometallurgical carbo-thermic reduction of chromite (Riekkool-Vanhanen, 1999). Ferrochrome is mostly utilised for the manufacturing of stainless steel, which is a very important alloy in modern-day living. According to the 2007 production statistics of the International Chromium Development Association (ICDA), South Africa produced

approximately 46.2% of the world's charge chromium, which is the most common ferrochrome grade containing typically 48.5-53.5%Cr (ICDA, 2008).

Although South Africa holds three quarters of the world's chromite ore reserves, the chrome-to-iron (Cr-to-Fe) ratio of the local chromite ores is relatively low. The deposits in the Zeerust and Potgietersrus areas, where the resources are limited, have Cr-to-Fe ratios of 2 to 2.9 (Howat, 1994). The major deposits in the western and eastern Bushveld, where the deposits are vast, have Cr-to-Fe ratios of 1.5 to 1.6 (Howat, 1994). The local ferrochrome industry also receives significant volumes of UG2 chromite, which is a process residue from the platinum group metals (PGM) industry in South Africa (Cramer et al., 2004). This UG2 chromite ore usually has Cr-to-Fe ratios of 1.3 to 1.4 (Cramer et al., 2004). Significant, but smaller, chromite resources are found in countries such as Zimbabwe and the former USSR states. Those deposits have Cr-to-Fe ratios of 2.6 to 3.5 and 2.8 to 3.0, respectively (Howat, 1994).

The low Cr-to-Fe ratios of the South African chromite deposits imply that the ferrochrome produced from these deposits usually has a chromium content of less than 52%. Because iron reduces more readily than chromium, almost all the iron present in the chromite ore ends up in the ferrochrome. Therefore, locally produced ferrochrome contains 35-39% iron. Current pricing practises in the world ferrochrome industry dictate that ferrochrome producers are only paid for the chromium content.

Approximately 90% of the global ferrochrome production is utilised for stainless steel production (Riekkola-Vanhanen, 1999). Since South Africa is only the sixth largest stainless steel producer, most of the locally produced ferrochrome is exported to stainless steel producers in Europe, Asia and America. This implies that South African ferrochrome producers export 35-39% of their product, i.e. the iron content of the ferrochrome, without any benefit.

In order to further enhance the growth and profitability of the South African ferrochrome industry, possible improvements to the Cr-to-Fe ratios of the local chromite ore need to be investigated. In this study, the improvement of the Cr-to-Fe ratio will be investigated by utilising halogenation. Halogenation, where chlorine and hydrochloric acid gasses were used, has been successfully conducted on laboratory scale (Shen et al., 2009a; Shen et al., 2009b, Kanari et al., 2001a; Kanari et al., 2001b; Kanari et al., 2000; Kanari et al., 1999). However, halogenation under such extreme conditions is unlikely to ever be implemented industrially, because the ferrochrome industry is regarded as a large-volume, low-profit commodity driven business. An alternative approach to halogenation, to avoid the use of chlorine and hydrochloric gases, will be investigated during this study.

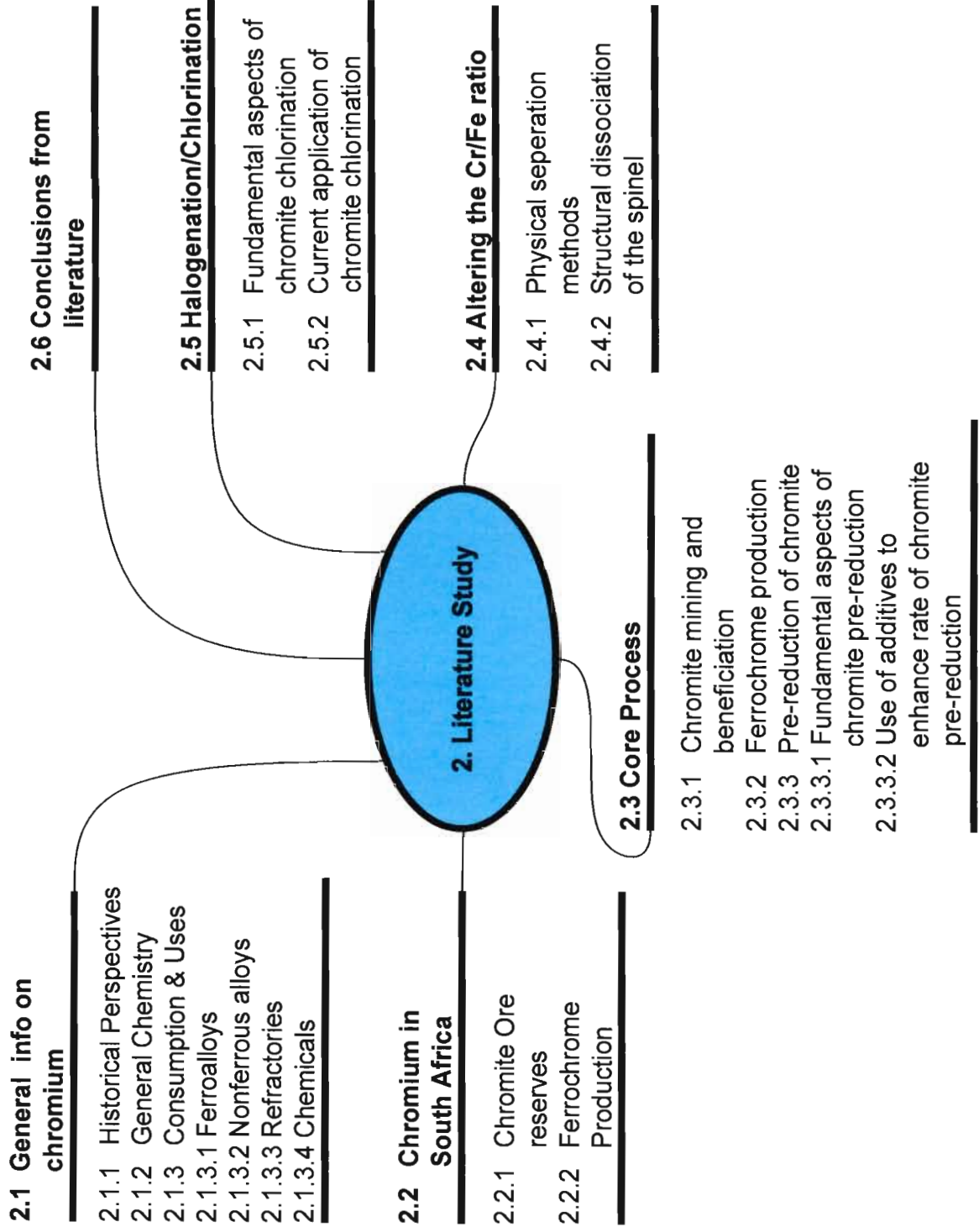
## **1.2 Objectives**

The specific objectives of this study were:

- 1.2.1** The compilation of a thorough literature survey wherein the importance of the chromium industry in South Africa, processes utilised by this industry, the nature of the local chromite ores and past attempts to alter the Cr-to-Fe ratio of chromite ores, with specific reference to chlorination of chromite, are summarised.
- 1.2.2** Attempted chlorination of local chromite ore, to remove iron from the spinel matrix, without the use of chlorine and hydrochloric gasses. The system chosen will be based on technical consideration, but the requirements of a low cost solution will also be considered. Various process controlling factors will be investigated. These include reaction temperature, the atmosphere during chlorination (e.g. reducing or oxidising), and concentration of the chlorinating substance. A number of analytical techniques will be used to evaluate the samples before and after attempted chlorination; these include breaking strength, SEM/EDS (Scanning Electron Microscope integrated with the OXFORD INCA 200 EDS), and chemical analysis.



**1.2.3** Making recommendations with regard to further work in this important research area. Since this is the first investigation of this nature at the North-West University, it might not deliver a final solution, but it should make recommendations pertaining to future research.



## Chapter 2

### Literature study

---

In this chapter, an overview of relevant literature is provided. General information on chromium is provided, which entails the discovery of chromium, uses and applications, as well as general chemistry. An understanding of the importance of chromium-related resources and industry in South Africa is also provided. This chapter also focuses on the core processes utilised during ferrochrome production in South Africa. Finally, past attempts to alter the Cr-to-Fe ratio of chromite, with specific focus on the chlorination, are discussed.

---

### 2.1 General information on chromium

#### 2.1.1 Historical perspective

There is no distinctive evidence that chromium was known to the ancients. It is possible, though, that the Hittites (a kingdom centred in northern Turkey from the 18<sup>th</sup> century BC) used chromium minerals in the making of their weapons of “stainless steel” and that Medieval and Renaissance artists utilised yellow and orange chromium minerals (Niagru, 1988a). Such early uses of chromium would have been accidental, since the attributes of chromium metal and its other forms were unknown at that stage. It is, however, easy to understand why this particular metal made such a late entrance into the industrial world. The only mineral from which chromium is recovered economically (chromite) is uncommon, extremely refractory, unattractive in appearance and has very few desirable properties. It is therefore not surprising that the metal was first isolated not from chromite ore,

but from crocoite, a rare but exceedingly attractive mineral found in a Siberian gold mine (Niagru, 1988a).

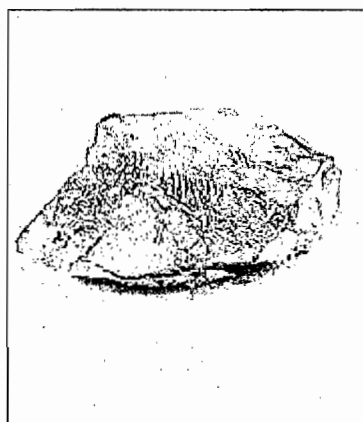
Johan Gotlob Lehmann, a former Russian mining official and then professor of chemistry in St. Petersburg, is credited with the discovery of crocoite in 1766 (Niagru, 1988a) at Beserof (Siberian gold mine). This bright red-orange mineral was subsequently analysed by various chemists, with inconclusive results, and hence remained a matter of curiosity for nearly three decades. In 1797, the French chemist Louis Nicolas Vauquelin succeeded in isolating chromium metal by first producing chromium oxide ( $\text{Cr}_2\text{O}_3$ ), which he subsequently reduced with charcoal in a furnace (Niagru, 1998a, Roza, 2008). Less than 150 years later, this metal had become crucial to the military survival and economic well-being of all the industrialised nations. It is currently the most important alloying metal in modern cast iron, steel and non-ferrous metallurgy, and has played a huge role in most technological developments. The technique that eventually led to the industrial scale production of chromium by means of the aluminothermic process was developed by H. Goldschmidt in 1895 (Niagru, 1988a). This so-called thermite process yields 97-99% pure chromium metal that has a low carbon content, with iron and aluminium as the principal impurities.

In 1821, the French scientist Pierre Berthier found that when chromium was alloyed (mixed) with iron, the new metal could resist corrosion (Roza, 2008). However, it was too brittle to be of any use. During the next fifty years, other scientists experimented with combinations of iron, chromium and other metals. In 1872, two Englishmen, viz. Woods and Clark, filed a patent for a weather-resistant iron alloy that was 30 to 35% chromium and 2% tungsten (Roza, 2008). This alloy was one step closer to the discovery of stainless steel, but it lacked one essential ingredient. French chemist Henri Moissan heated ore that contained chromium and iron in an electric furnace with carbon in 1893. The result was an alloy he called ferrochrome. This metal contained large amounts of chromium and small amounts of carbon that helped to make the metal stronger. Since then, many scientists experimented with various concentrations of carbon, iron and chromium until stainless steel,

as we know it today, was developed. However, it is not really known who created stainless steel for the first time.

### 2.1.2 General chemistry

Chromium can occur in various oxidation states and its compounds have numerous colours. Chromium's name is derived from the Greek word 'chromos', meaning colour. The green colour of emeralds is due to the presence of chromium in the mineral beryl and the colour of ruby is due to the substitution of  $\text{Cr}^{3+}$  ions for  $\text{Al}^{3+}$  ions in the structure of  $\alpha\text{-Al}_2\text{O}_3$ . Chromium (atomic number 24) is the first element in group 6 of the periodic table and lies above molybdenum and tungsten. The ground state outer electronic configuration is  $3d^54s^1$  and, similar to Ti and V, it shows the highest oxidation state corresponding to the loss of all these outer electrons, i.e. +6 (Nicholls, 1987).  $\text{Cr}^{6+}$  is a strong oxidising state, with chromium typically bonded to fluorine or oxygen. Chromium exists in all oxidation states from +6 to -2, but the +3 state is by far the most stable and common (Nicholls, 1987).



**Figure 2.1** A photo of chromium metal, illustrating its light silver colour

Chromium is a light silver grey lustrous metal (Illustrated in **Figure 2.1**) that has considerable inertness to chemical attack. It is therefore widely used to plate other metals to give them a shiny corrosion-resistant coating. Chromium is inert to attack by nitric acid, phosphoric acid, and aqua regia at room

temperature, but does, however, dissolve in non-oxidising acids such as dilute hydrochloric and sulphuric acids. When not in the passive state, chromium readily enters solution in salts of copper, tin, and nickel with precipitation of these metals. At high temperatures, chromium reacts with alkali metal hydroxides, hydrogen halides, water and many non-metals including oxygen and halogens (Nicholls, 1987).

### **2.1.3 Consumption and uses**

Different industrial applications require different forms of chromium, such as chromite, ferrochrome, chromium metal, chromite refractory bricks, chromite foundry sands, chromite acid, and other chromium compounds. The 7.6 million tons of chromite consumed globally each year (ICDA, 2008) is distributed among three principal industrial end-uses, i.e. metallurgical, refractory and chemical applications (Niagru, 1988b). Of these, metallurgical applications are by far the largest, with an estimated 90% of all mined chromite being utilised (ICDA, 2008). Only the principal industrial applications of chromium and its compounds are subsequently discussed.

#### **2.1.3.1 Ferro-alloys**

Chromium-containing steels can be divided into three arbitrary groups based on the chromium content i.e. low-chromium engineering steels with less than 3% chromium, tool steel with 3-12% chromium and stainless steel that contains over 12% chromium (Niagru, 1988b).

Small amounts of chromium (less than 3%) significantly increase the tempering resistance, hardness and strength of steels by delaying the transformation that takes place during the heat treatment, thereby increasing the capacity of steel to harden. These low-chromium steel are extensively used in the manufacturing of automobiles, machinery and agricultural equipment (Niagru, 1988b).

Steels containing 3-12% chromium also show enhanced corrosion and oxidation resistance that increases with the chromium content, but reactivity against corrosion is not generally achieved with less than 12% chromium. Low-carbon steel in this category finds wide application in petroleum and chemical industries. Steel with medium carbon content is used in casting and tools for light services, such as wrenches and pliers. High-carbon steel in this category is used as magnetic steels and for valve manufacturing (Niagru, 1988b).

The most important industrial application for chromium is in the production of stainless steel (over 12% chromium content). Stainless steel is classified into three broad groups on the basis of their microstructures i.e. austenitic, martensitic and ferric. In general, the quality of stainless steel increases with the chromium content. Additionally, changing the carbon content and the heat treatment, the tensile and yield strength, as well as hardness can be increased (Niagru, 1988b).

#### **2.1.3.2 Non-ferrous alloys**

Metallic chromium is used primarily in non-ferrous alloys where the use of less expensive ferrochrome alloys may introduce undesirable amounts of iron into the system. Familiar applications include the super-alloys used in jet engines and the chromium-containing alloys used in nuclear reactors (Niagru, 1988b).

#### **2.1.3.3 Refractory**

Historically, one of the most important uses of chromium ore was for refractory purposes. Such application stems from the fact that chromite has a high melting point (2040°C) and is almost chemically inert, which causes resistance to attack by acids and bases at high temperature (Niagru, 1988b).

### 2.1.3.4 Chemicals

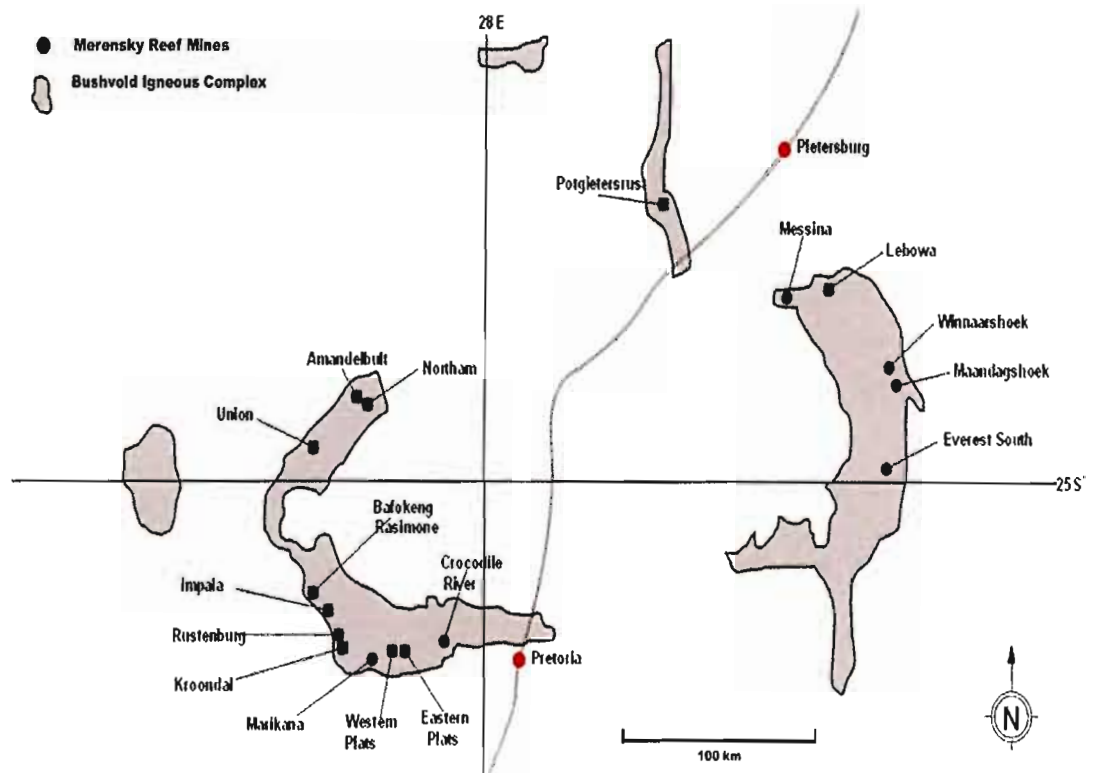
The first commercial application for chromium ore was in the manufacturing of chromium compounds for use as pigments and in mordant dyeing. Today more than 70 chromium compounds are in commercial use. However, only a few of these compounds are produced in large quantities, with notably sodium chromate, potassium chromate, potassium dichromate, ammonium dichromate, chromic acid and the basic chromic sulphate used primarily for the leather tanning process (Niagru, 1988b).

## 2.2 Chromium in South Africa

### 2.2.1 Chromite ore reserves

Chromite is the only commercially recoverable source of chromium. **Figure 2.2** shows the Bushveld Igneous Complex, and the platinum group mines of the Merensky reef. Since the chromite-ore resources in South Africa are associated with platinum group metals (PGM) mineralisation within the Bushveld complex (Xiao and Laplante, 2004; Cramer et al., 2004), this graphical representation also gives a good indication of the distribution of chromite resources in South Africa.





**Figure 2.2** A graphical representation of the Bushveld Complex and PGM mines of the Merensky reef (Wikipedia, 2009)

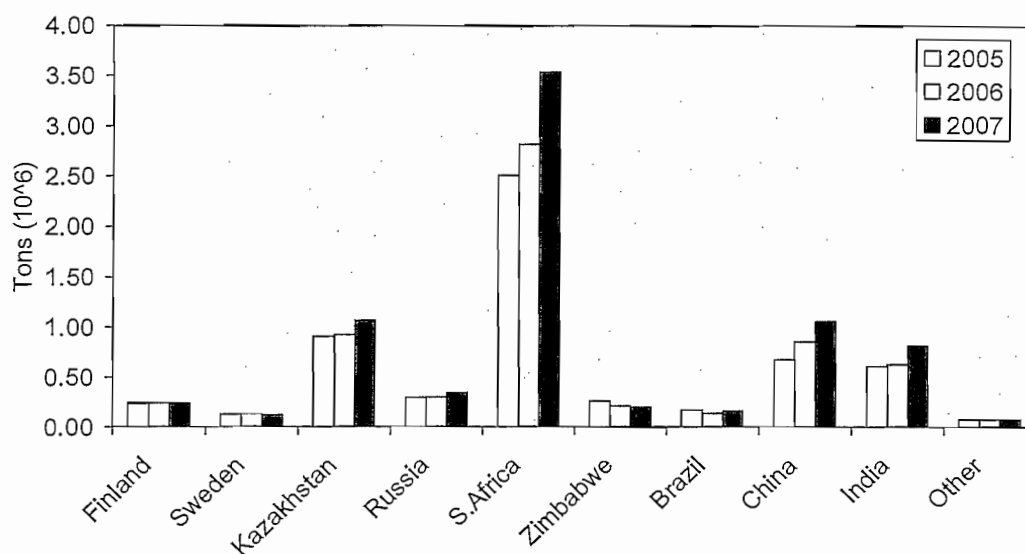
It is generally accepted that South Africa holds between 74% (Cowey, 1994) to 80% (Riekkool-Vanhanen, 1999) of the world's viable chromite ore reserves. These resources are consolidated in the Bushveld Complex. This geological phenomenon, which consists of an enormous saucer-like intrusive igneous mass, extends for about 400km from east to west and roughly the same distance from north to south. It is located in the central and slightly western portion of the South African Highveld (Howat 1994). The complex is highly mineralised and comprises of deposits of fluorspar and tin in the acidic phase, PGMs and chromite in the mafic phase along with some other minerals. The four major areas in which the chromite ore is mined are in the eastern chromite belt, the western chromite belt, the Zeerust district, and the area south of Potgietersrus.

The deposits in the Zeerust and Potgietersrus areas, where resources are limited, have Cr-to-Fe ratios of 2 to 2.9 (Howat, 1994). The major deposits in

the western and eastern Bushveld, with vast deposits, have Cr-to-Fe ratios of 1.5 to 1.6 (Howat, 1994). The annual production of chromite in South Africa was approximately 3.5 million tons for 2007 alone (ICDA, 2008). The local ferrochrome industry also receives significant volumes of UG2 chromite process residue from PGM industry in South Africa (Cramer et al., 2004). This UG2 chromite ores usually have Cr-to-Fe ratios of 1.3 to 1.4 (Cramer et al., 2004). Significant, but smaller, chromite resources are also found in countries such as Zimbabwe and the former USSR states. Those deposits have Cr-to-Fe ratios of 2.6 to 3.5 and 2.8 to 3.0, respectively (Howat, 1994).

## 2.2.2 Ferrochrome production

According to the 2007 production statistics of the International Chromium Development Association (**Figure 2.3**), South Africa produced approximately 46.2% of the world's charge chrome, which is the most common ferrochrome grade (ICDA, 2008).



**Figure 2.3** Global production of charge ferrochrome (2005 to 2007)

All the ferrochrome assets of Xstrata, the world's largest ferrochrome producer, are also within South Africa. There are at least 14 separate ferrochrome production facilities in South Africa (Jones, 2008), with a

combined production capacity of 4 340 000 tons/year. **Table 2.1** gives an overview of the production capacities of these facilities

**Table 2.1** Production capacity of SOUTH AFRICAN ferrochrome producers as in mid-2008 (Jones, 2008)

| Plant                      | Locality            | Production capacity (ton/year) |
|----------------------------|---------------------|--------------------------------|
| ASA Metals Dilokong        | Burgersfort         | 125 000                        |
| Assmang Chrome             | Machadodorp         | 300 000                        |
| 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           | Richardsbay         | 135 000                        |
| Tubatse Ferrochrome        | Steelpoort          | 360 000                        |
| Xstrata Lydenburg          | Lydenburg           | 400 000                        |
| Xstrata-Merafe Boshoeck    | Rustenburg-Sun City | 240 000                        |
| Xstrata-Merafe Lion        | Steelpoort          | 364 000                        |
| Xstrata Rustenburg         | Rustenburg          | 430 000                        |
| Xstrata Wonderkop          | Rustenburg-Brits    | 545 000                        |
| TOTAL                      |                     | 4 340 000                      |

## 2.3 Core process

### 2.3.1 Chromite mining and beneficiation

Although chromite is one of the hardest known minerals, the chromite found in South Africa is relatively friable and easily breaks down to the size of the chromite crystal (Gu and Wills, 1998). Due to this friability, it is common to only recover 10-15% lumpy ore (particle size of 6 to 150mm) and 8-12% chip/pebble ores (particle size 6 to 25mm) during the mining and beneficiation processes employed by South African chromite mines (Glastonbury et al., 2009). The remainder of the ore (73-82%) are in the <6mm fraction, which would typically be milled or crushed to <1mm and upgraded to a >45% Cr<sub>2</sub>O<sub>3</sub> content. This upgraded <1mm ore is generally termed metallurgical grade ore.

South African chromite ore is produced by selective mining. This run-of-mine ore is then beneficiated to suite the requirements of the application. **Table 2.2** gives the typical chemical analysis of the various chromite grades.

**Table 2.2** Typical chemical composition of the different chromite ore grades produced (ICDA, 2007)

|                            | Cr <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | FeO  | CaO | Al <sub>2</sub> O <sub>3</sub> | MgO  | P     | S     | Cr:Fe |
|----------------------------|--------------------------------|------------------|------|-----|--------------------------------|------|-------|-------|-------|
| Run-Of-Mine Ore            | 38-39                          | 9                | 23   | 1.9 | 15.5                           | 11.9 | 0.001 | 0.005 | 1.55  |
| Lumpy & Pebbles            | 39-39                          | 8.4              | 24   | 1.9 | 15.5                           | 11.6 | 0.002 | 0.005 | 1.55  |
| Metallurgical grade: fines | 44-45                          | 2.5              | 24.9 | 1.4 | 15.6                           | 10.6 | 0.002 | 0.005 | 1.55  |
| Chemical grade: fines      | >46                            | <1               | 25.7 | 0.8 | 15.4                           | 10.3 | 0.002 | 0.004 | 1.55  |
| Foundry grade              | >46                            | <1               | 25.7 | 0.8 | 15.4                           | 10.3 | 0.002 | 0.004 | 1.55  |
| Refractory grade           | >46                            | <1               | 25.7 | 0.8 | 15.4                           | 10.3 | 0.002 | 0.004 | 1.55  |

South African run-of-mine chromite ores have to undergo at least rudimentary beneficiation. Several methods are employed, of which the choice of method depends on a considerable degree on the type of product desired. Simple screening and hand-sorting operations may be adequate in some cases, but complex heavy-medium, magnetic, flotation and gravity separation may be necessary in others (Gu & Wills, 1998). Heavy medium and gravity concentration are currently the most commonly-employed chromite beneficiation processes. In some instances, high-intensity magnetic separation may be used, while floatation is used in only a few instances (Gu & Wills, 1988).

Heavy medium separation is the most economic method for treating coarse (10-100mm) particles, while finer particles are often treated by jigs, spirals and shaking tables (Gu & Wills, 1988), with spiral concentration currently preferred. Recovery of chrome via these processes can be up to 80-85% (Gu & Wills, 1988), but there are still limitations on the improvement of the Cr<sub>2</sub>O<sub>3</sub> grade. Improvements of 1-4% have been achieved, hence increasing the Cr<sub>2</sub>O<sub>3</sub> grade from about 40 to 44% (Gu and Wills, 1988).

All chromites are paramagnetic at room temperature, with their susceptibilities depending on the Fe<sup>2+</sup> content. It has been speculated that the distribution of magnetic ions is not uniform in the crystal structure and therefore,

ferromagnetism is created in the more concentrated sections. In a low magnetic field (about 0.1T), chromite can be separated from ferromagnetic minerals as a non-magnetic product (Gu & Wills, 1998).

Although flotation is not a major method of beneficiation for chromite ores, fatty acids, such as oleic acid, have been used where this method has been adopted. One of the major difficulties with flotation is the wide variation in surface properties of chromites from different locations (Gu and Wills, 1988).

### 2.3.2 Ferrochromium production

The production of ferrochrome is an energy-intensive process that mainly utilises electricity and fossil fuels. Factors affecting energy consumption include the quality of raw materials, treatment before smelting, as well as the utilisation of reaction energies and heat contents from the processes (Riekköal-Vanhanen, 1999).

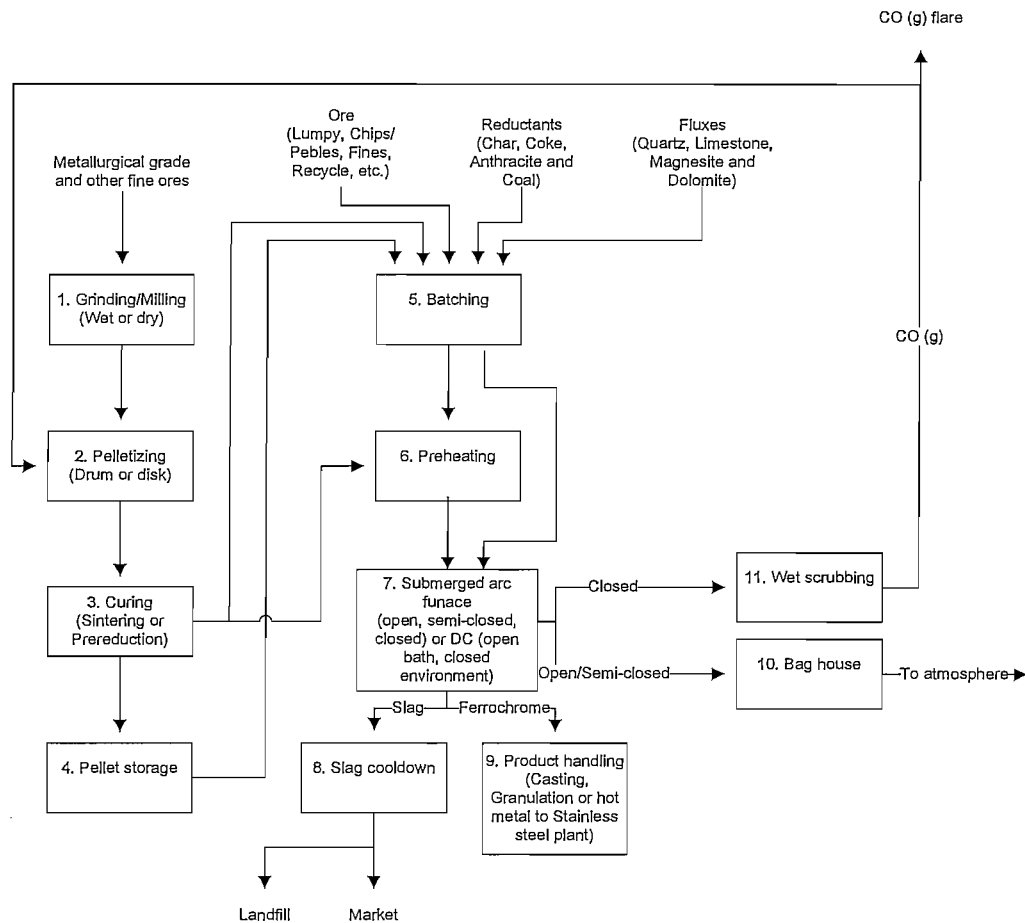
The chromite raw materials utilised for ferrochromium production are lumpy or pebble ores, ore fines and agglomerated fines (Glastonbry et al., 2009). The majority of chrome ore produced in South Africa is fine ore (Glastonbry et al., 2009). In order to prevent furnace instabilities, fine ores are converted to more furnace friendly lumpy material (Riekköal-Vanhanen, 1999). These materials may be sintered directly or agglomerated by briquetting, micropelletising or pelletising.

Ferrochrome is produced pyrometallurgically by carbothermic reduction of chromite (Riekköal-Vanhanen, 1999). The main reactions are:



A generalised process flow diagram, adapted from Riekköal-Vanhanen (1999), is shown in **Figure 2.4**, which indicates the most common combinations of process steps utilised by the South African ferrochrome

producers. However, this process flow diagram does not cover every possible process combination; it is, however, adequate for the discussions in this study.



**Figure 2.4** Generalised flow diagram adapted by Beukes et al., (2009) from Riekkool-Vanhanen (1999), indicating the most common combination of process steps utilised during ferrochrome production in South Africa

In general, four relatively well-defined process combinations are utilised by the South African ferrochrome producers (Beukes et al., 2009):

- A) Conventional semi-closed furnace operation with bag filter off-gas treatment. This is the oldest technology applied in SOUTH AFRICA, and still accounts for a substantial fraction of overall production (Gediga &

Russ, 2007) In this type of operation, coarse (lumpy and chips/pebble ores) and fine ores can be smelted without an agglomeration process undertaken to increase the size of fine ores. Although it has been mentioned (Riekkölä-Vanhanen, 1999) that fine ores cannot be fed directly into a submerged Ferrochrome arc furnace without causing dangerous blow-outs or bed turnovers, a substantial amount of fine ores is in fact fed into some SA semi-closed furnaces. With reference to the process flow diagram indicated in **Figure 2.4**, the process steps followed are 5, 7, 8, 9 and 10. Some semi-closed furnaces do consume pelletised feed, in which case process steps 1-4 would also be included. Most of the SOUTH AFRICAN semi-closed furnaces are operated on an acid slag, with a basicity factor (BF) smaller than 1. This BF can be defined by equation 2.3

$$BF = \frac{\%CaO + \%MgO}{\%SiO_2} \quad (2.3)$$

Some semi-closed furnaces might operate on  $BF > 1$ , but these are less common and such operations are sometimes only temporarily undertaken to compensate for refractory linings being in poor condition, or if enhanced sulphur removing capacity by the slag is required.

- B) Closed furnace operation usually utilises oxidative sintered pelletised feed (Outotec, 2008). This has been the technology most commonly employed in SOUTH AFRICA, with the majority of green and brown field expansions during the last decade making use of this process. Process steps usually include steps 1, 2, 3, 4, 5, 7, 8, 9 and 11, with or without 6. In all green field Ferrochrome developments, the pelletising and sintering (steps 2 and 3) sections were combined with closed furnaces. However, pelletising and sintering sections have also been constructed at plants where the pelletised feed is utilised by conventional semi-closed furnaces. These furnaces are usually operated on an acid slag ( $BF < 1$ ).

- C) Closed furnace operation with pre-reduced pelletised feed (Botha, 2006; Naiker, 2007). The process steps include steps 1, 2, 3, 4, 5, 7, 8, 9, 11. The pelletised feed differs substantially from the oxidative sintered type due to the fact that the pellets are pre-reduced and mostly fed hot, directly after pre-reduction, into the furnaces. The furnaces are closed and operate on a basic slag ( $BF > 1$ ). At present, two SA Ferrochrome smelter plants use this process.
- D) DC arc furnace operation (Curr, 2009; Denton et al., 2004). For this type of operation, the feed can consist exclusively of fine material. Currently three such furnaces are in routine commercial operation for Ferrochrome production in SOUTH AFRICA and typically utilise a basic slag regime. Process steps include 5, 7 (with a DC, instead of a submerged arc furnace), 8, 9 and 11.

### 2.3.3 Pre-reduction of chromite

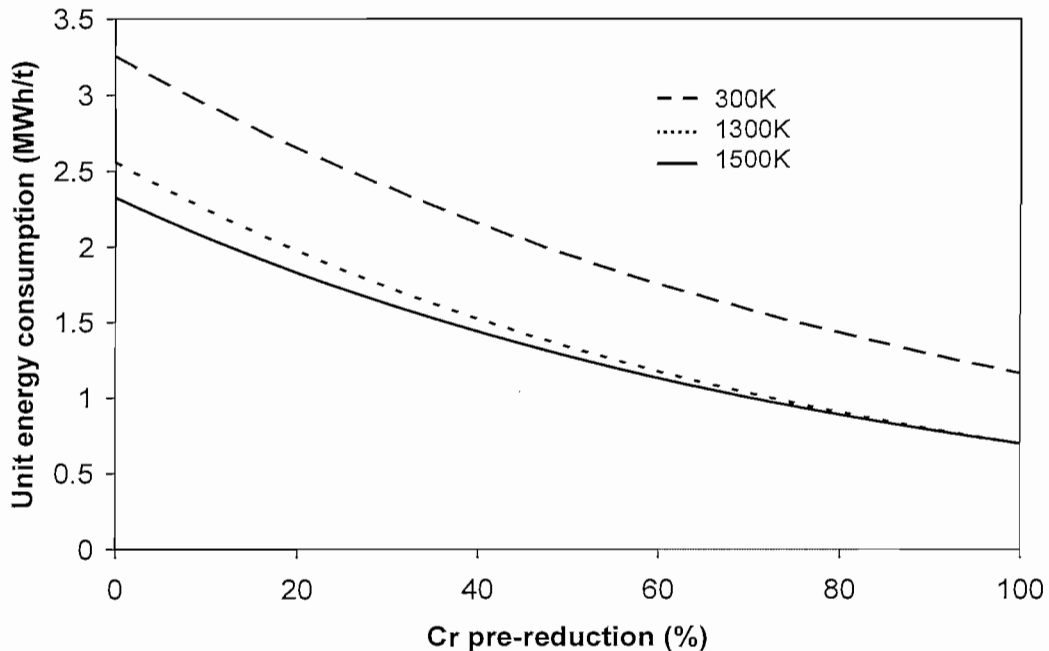
Although various processes are utilised for the production of ferrochrome (Par 2.3.2) there are three reasons why pre-reduction of chromite is important and should be explored further in this literature survey:

- a) At present, high carbon ferrochrome is mainly produced in arc-furnaces. A disadvantage of this process is the amount of electrical energy needed for the reduction of the metal oxides to the metal. In order to improve the cost efficiency, carbothermic pre-reduction of chromite has become an attractive option, since it has the lowest specific energy consumption (MWh/ton ferrochrome) of all ferrochrome production processes. **Figure 2.5** shows the effect of the net energy consumption during ferrochrome production as a function of the degree of pre-reduction (Takano et al, 2007).
- b) Pre-reduction of chromite is already applied on an industrial scale in South Africa and is in fact the second most commonly applied



ferrochrome production process (process combination C, Par 2.3.2). It is therefore not only of academic importance, but also industrially relevant.

- c) Additionally, chlorination of chromite (in order to alter the Cr-to-Fe ratio) has been achieved on laboratory scale under so called carbochlorinating environments (Par 2.5), which implies chlorinating under CO gaseous environments. If chlorination of chromite is considered as a potential option to alter the Cr-to-Fe ratio of chromite, the potential environment (e.g. oxidising, reducing, CO-rich, etc.) of the application should also be contemplated. Currently, the pre-reduction process is the only commercial process where at least a partially CO-rich gas environment occurs prior to furnace smelting.



**Figure 2.5** Net energy requirements for the production of 1 ton of ferrochrome as a function of the degree of pre-reduction and charging temperature (Takano et al, 2007)

### 2.3.3.1 Fundamental aspects of chromite pre-reduction

Before proceeding, the terms reduction or pre-reduction, as well as metallisation need to be clarified. Barnes et al. (1983) pointed out that these terms were not well defined previously and therefore proposed definitions. Since the removal of oxygen is associated with reduction, the term reduction was defined as (Barnes et al., 1983):

$$\%R = \frac{\text{Mass of oxygen removed}}{\text{Original removable oxygen}} \times 100 \quad (2.4)$$

If solid carbon is used as the reducing agent, CO is the reaction product (as illustrated later in equations 2.7 to 2.9) and therefore reduction can also be defined as (Barnes et al., 1983):

$$\%R = \frac{\text{Mass of CO evolved}}{28/16 \times \text{original removable oxygen}} \times 100 \quad (2.5)$$

The amount of removable oxygen for both the above-mentioned definitions is defined as the oxygen associated with  $\text{Fe}_2\text{O}_3$ , FeO and  $\text{Cr}_2\text{O}_3$ .

Metallisation is defined as (Barnes et al., 1983):

$$\%M = \frac{(\text{Cr}^0 + \text{Fe}^0)}{(\text{Cr}_{\text{tot}} + \text{Fe}_{\text{tot}})} \times 100 \quad (2.6)$$

Although these definitions are not applied as such by all investigators, they provide a good foundation for further discussions. The relationship between metallisation and reduction is not linear since (Barnes et al., 1983):

- In the early stages of reduction  $\text{Fe}_2\text{O}_3$  is reduced to FeO, without metallisation



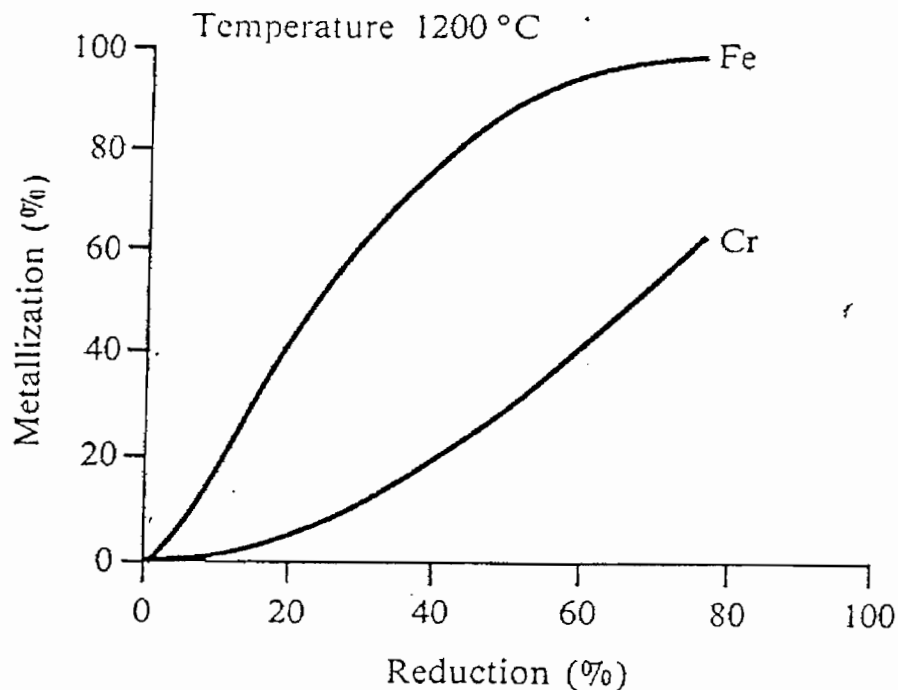
- FeO is reduced to  $\text{Fe}^0$ , producing 1 mole of CO for every mole of  $\text{Fe}^0$  produced



- $\text{Cr}_2\text{O}_3$  is reduced to  $\text{Cr}^0$ , producing 1.5 mole of CO for every mole of  $\text{Cr}^0$  produced



Dawson and Edwards (1986) illustrated the above-mentioned differences between metallisation and reduction, as is shown in **Figure 2.6**.



**Figure 2.6** Graphical illustration of the relationship between reduction and metallisation, based on South African LG-6 chromite (Dawson & Edwards, 1986)

As mentioned earlier, the solid-state reduction of chromite (pre-reduction) prior to arc smelting is a well established practice in the production of ferrochrome (Botha, 2006; Naiker, 2007; Dawson & Edwards, 1986). In the pre-reduction process, chromite ore and finely ground carbon (e.g. coke, char or anthracite) are mixed homogenously and then pelletised. The green pellets (referring to newly formed moist pellets) are then dried in a grate, where after the pellets are then sent through a rotary kiln at temperatures around 1300°C (Dawson and Edwards, 1986).

The extent of pre-reduction achieved on an industrial scale is seldom more than 60% (Dawson and Edwards, 1986). This includes almost complete metallisation of the iron and consequently usually less than 30% metallisation of the chromium (Dawson & Edwards, 1986). The low metallisation of the chromium inhibits potential further energy advantages, as indicated in **Figure 2.6**. The relatively low degree of reduction in current practice is a result of the slow kinetics of reduction of chromite, especially of the  $\text{Cr}_2\text{O}_3$  content. The kinetics is determined by the temperature of operation, which is limited to a maximum of about 1350°C. This limit is imposed by the properties of the chromite ore and the fuel ash if the kiln is fired with pulverised fuel. At temperatures above 1350°C, partial melting of the pellets and the coal ash occurs, that consequently causes dam-ring formation in the kiln and hence poor operation. It is therefore not possible to achieve higher rates of pre-reduction unless substantial changes are made to the current practice. According to Dawson and Edwards (1986), two strategies can be adopted to overcome these limitations:

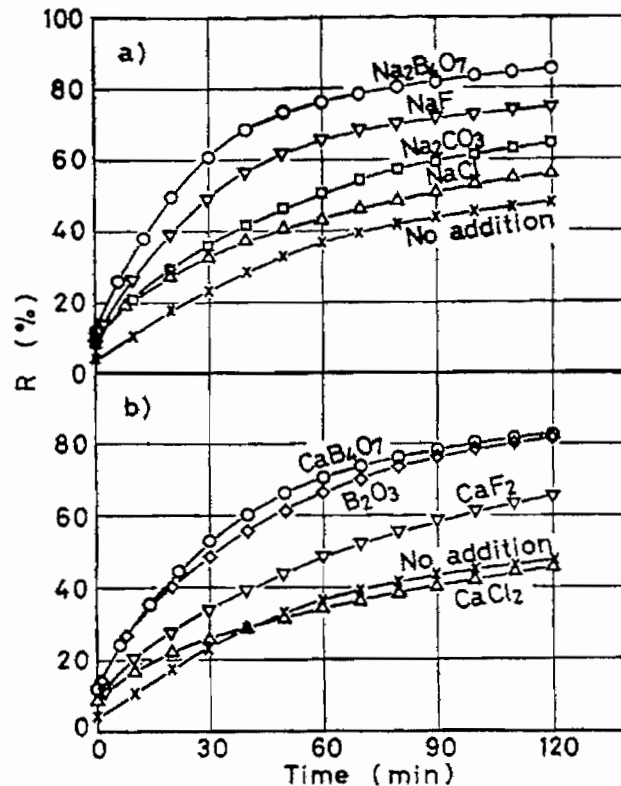
- modification of the process to allow operation at higher temperatures, where the kinetics become more rapid, or
- improve the kinetics of reduction at temperatures compatible with current operational temperature limits.

The first approach has been adopted by Krupp GmbH (Fried, 1984), but the subsequent full-scale industrial application of this approach in South Africa has failed. It is unlikely that the current ferrochrome smelter operations utilising pre-reduction of chromite (Process option C, Par 2.3.2) will be able to operate at higher temperatures. This option is therefore not considered further. The second approach, i.e. to improve the kinetics without increased temperatures, has received much attention and numerous additives have been considered to achieve this. This topic will be discussed in further detail in Par 2.3.3.2.

The exact mechanism for chromite pre-reduction is not considered during this investigation and therefore not discussed.

### 2.3.3.2 Use of additives to enhance rate of chromite pre-reduction

The use of additives to increase the reduction rate of chromite has been investigated extensively. Katayama et al. (1986) proved that the addition of  $\text{Na}_2\text{BO}_7$ ,  $\text{NaF}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{CaB}_4\text{O}_7$ ,  $\text{B}_2\text{O}_3$  and  $\text{CaF}_2$  improved the rate of chromite reduction, while  $\text{CaCl}_2$  inhibited the rate of reduction. This is graphically illustrated in Figure 2.7.



**Figure 2.7** The effect of various additives (1% wt addition) on the reduction rate of Russian chromite (Katayama et al., 1986)

Van Deventer (1988) indicated that  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Fe}^0$ , enhanced the rate of carbothermic reduction of chromite.  $\text{Cr}^0$  as an additive had little influence, while  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  inhibited the reaction. Other attempts to increase the rate of reduction of chromite include:

- Dawson and Edwards (1986) proved that  $\text{CaF}_2$  and eutectic mixtures of  $\text{NaF-CaF}_2$  improved reduction.

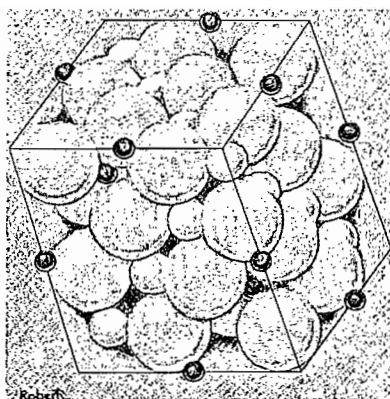
- Ding and Warner (1997) proved that lime catalysed the reduction of chromite.
- Takano et al. (2007) utilised Portland cement, hydrated lime and silica as additives and proved that composite pellets containing these compounds had enhanced reductions of chromite.
- Nunnington and Barcza (1989) investigated the addition of granite and fluorospar.

The above-mentioned references are by no means a comprehensive list, but it certainly indicates the past research activities in this field and signifies the importance.

## 2.4 Altering the Cr-to-Fe ratio

### 2.4.1 Physical separation methods

Conventional methods of beneficiation, such as gravity concentration, magnetic separation and flotation are unlikely to increase the Cr-to-Fe ratio of chromite ore, since both the iron and chromium are part of the same mineral phase, i.e. the spinel (Shao-Bo Shen et al., 2009). This is graphically illustrated in **Figure 2.8**. Obviously, the exception to this generalisation, i.e. that iron cannot be removed from chromite by conventional separation methods, would be ores that also contain iron in a separate mineral phase, i.e. gangue materials. The general formula for chromite is  $(\text{Fe,Mg})\text{O} \cdot (\text{Cr,Al,Fe})_2\text{O}_3$ , with iron in the 2+ and chromium in the 3+ oxidation states (Gu & Wills, 1988).  $\text{Fe}^{2+}$  may partially be replaced by  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$ , while  $\text{Cr}^{3+}$  may partially be replaced by  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$  and  $\text{Ti}^{4+}$  (Gu & Wills, 1988). Geologically, these substitutions take place at the origin/formation of the different chromites deposits.



**Figure 2.8** Graphical representation of chromite spinel (Large sphere representing oxygen, the medium spheres chromium and the smallest spheres iron)

#### **2.4.2 Structural dissociation of the chromite spinel**

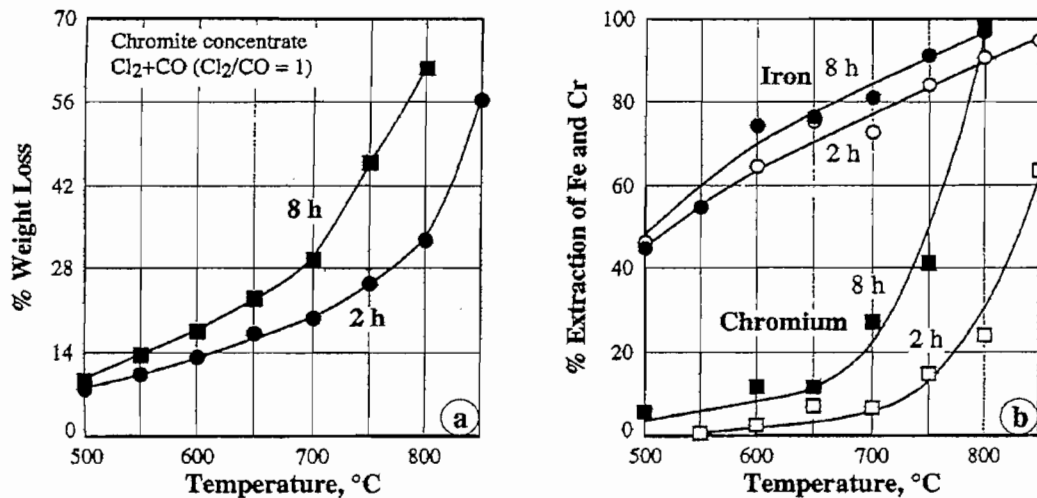
Considering the fact that physical separation methods are not suited for the alteration of the Cr-to-Fe ratios of chromite that do not have appreciable amounts of iron in the gangue materials (Par 2.4.1), iron can only be removed by chemical structural dissociation of the spinel (Shao-Bo Shen et al., 2009). Some chemical techniques such as hydrometallurgical methods, roasting and leaching, as well as chlorination can therefore be considered as potential methods to achieve this. Chlorination of chromite is by far the most commonly applied laboratory scale technique (Shen et al., 2009a; Shen et al., 2009b, Kanari et al., 2001a; Kanari et al., 2001b; Kanari et al., 2000; Kanari et al., 1999). Bergeron and Richer-Lafleche (2006), as well as Robinson et al. (1983) filed patents for the upgrading of chromite via chlorination. It is therefore considered in more detail in the next paragraph.

### **2.5 Chlorination of chromite**

#### **2.5.1 Fundamental aspects of chromite chlorination**

Kanari et al. (1999) studied the carbochlorination of Albanian chromite in the presence of  $\text{Cl}_2$  and CO (without additional additives). In this context, the

term carbochlorination refers to chlorination in the presence of CO. They found that 60% of the iron could be extracted at 600° after two hours, with a chromium extraction of less than 5%. As a result, the Cr-to-Fe ratio doubled. **Figure 2.9** shows the results obtained over the temperature range 500°C to 900°C.



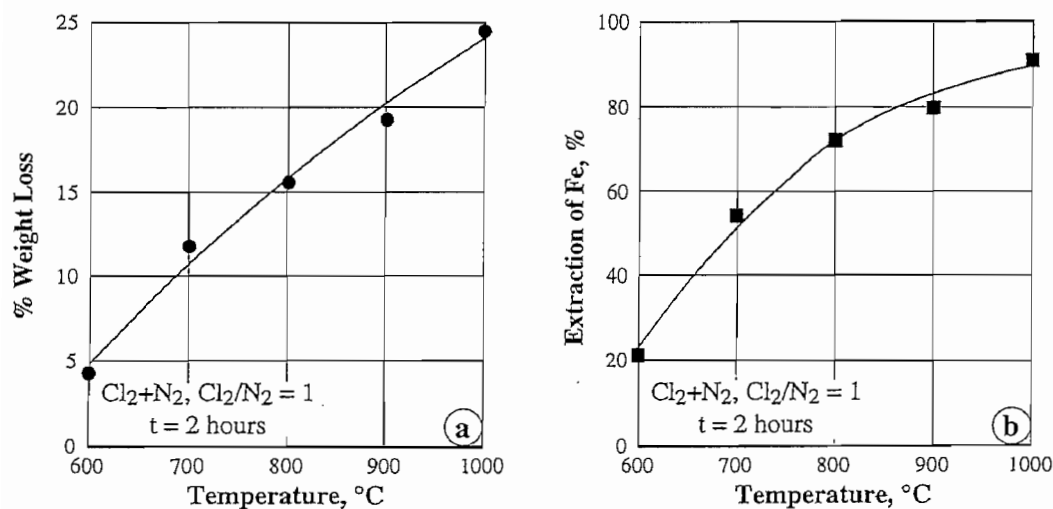
**Figure 2.9** Weight loss and extraction of Fe and Cr versus temperature under carbochlorinating conditions (Kanari et al., 1999)

Kanari et al. (2000) studied the chlorination of Albanian chromite in the presence of three different environments, i.e. i)  $\text{Cl}_2$  and  $\text{N}_2$ , ii)  $\text{Cl}_2$  and  $\text{AlCl}_3$ , and iii)  $\text{AlCl}_3$ , CO and  $\text{N}_2$ . These different environments are discussed separately.

In contrast to their earlier promising results with carbochlorination (Kanari et al., 1999), 60% iron and less than 5% chromium extraction were reported after two hours at 600°, it seemed as if the chlorination process only started at about 600°C in the  $\text{Cl}_2$  and  $\text{N}_2$  environment (Kanari et al., 2000). **Figure 2.10a** indicates the percentage weight loss as a function of temperature. From this graph it is evident that only ~4% weight loss had occurred at 600°C in this environment. Iron extraction as a function of temperature is given in **Figure 2.10b**. Unfortunately, these authors did not quantify the loss of chromium in this environment as a function of temperature. Chromium extraction quantification was only done at 1000°C,



where 13 to 50% of the chromium was extracted, depending on the duration of exposure. Based on the above results, Kanari et al. (2000) recommended that that 800°C could be the most appropriate temperature, but this was not supported by data collected at that temperature.

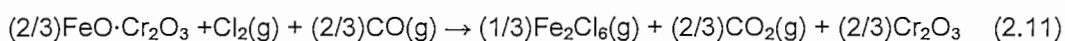
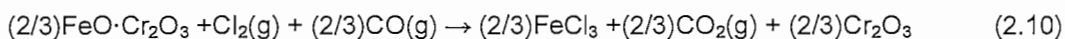


**Figure 2.10** (a) Weight loss of chromite versus temperature in  $\text{Cl}_2$  and  $\text{N}_2$  atmosphere (b) Extraction of Fe% versus temperature in the same atmosphere (Kanari et al., 2000)

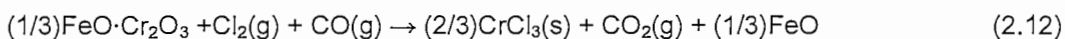
The  $\text{Cl}_2$  and  $\text{AlCl}_3$  chlorinating environment investigated by Kanari et al. (2000) revealed that the addition of  $\text{AlCl}_3$  had no beneficial advantages over pure chlorine chlorination. Better results were obtained by  $\text{AlCl}_3$ ,  $\text{CO}$  and  $\text{N}_2$  chlorination, specifically at 800°C. Although the most iron was extracted under these conditions, 40% of the chromium was also extracted.

The paper by Shen et al. (2009) gave an excellent account on the carbochlorination of chromite of Canadian origin in the presence of  $\text{NaCl}$ . These authors gave some of the general reactions expected to take place:

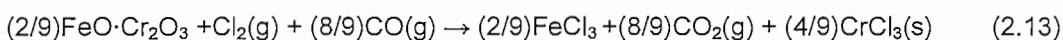
(a) carbochlorination of FeO



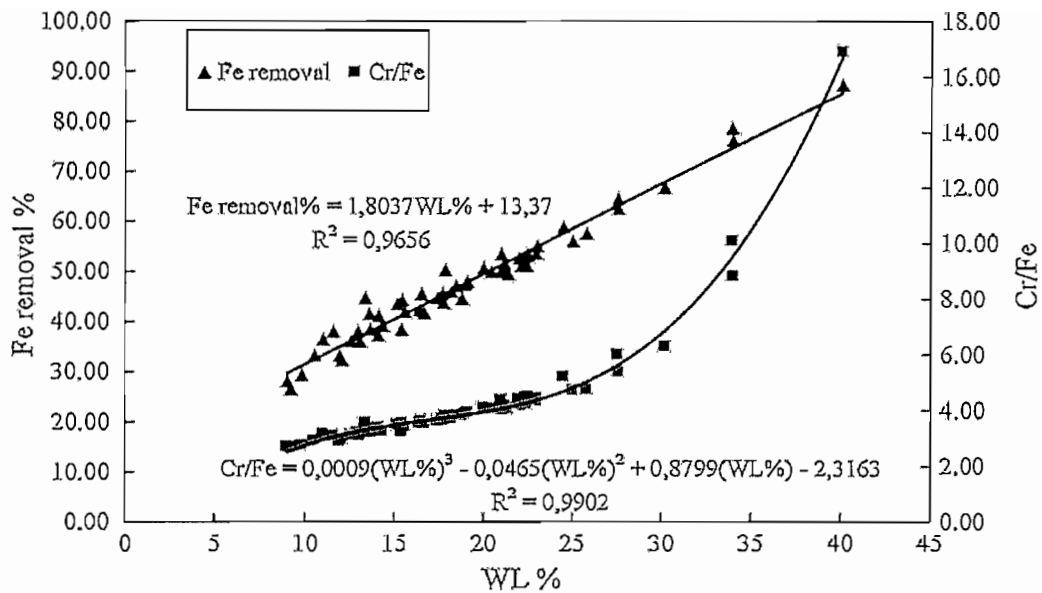
(b) carbochlorination of  $\text{Cr}_2\text{O}_3$



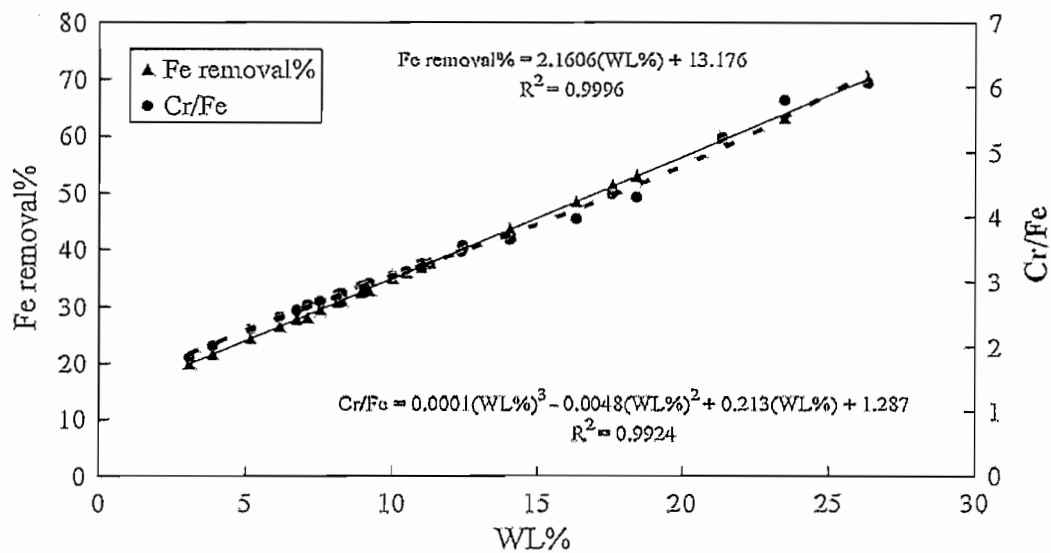
(c) carbochlorination of FeO and  $\text{Cr}_2\text{O}_3$



Based on thermodynamic calculations done with the HSC Chemistry for Windows software package (Outotec, 2009), Shen et al. (2009) concluded that all the above-mentioned reactions (reactions 9 to 12) have Gibbs free energies of less than -50kJ/mol between 25 and 1000°C. This implies that all these reactions are likely to take place. However, due to the fact that the Gibbs free energies of these reactions were so similar, it was impossible to state with certainty which reaction(s) would take place preferentially based on thermodynamic calculations alone. Experimental results obtained by Shen et al. (2009), at temperatures between 606°C and 720°C, are shown in **Figure 2.11**. As can be seen, up to 80% iron extraction was obtained with very high corresponding Cr-to-Fe ratios. These authors claimed that no significant chromium extraction took place up to 720°C, since the percentage iron removal had a linear relationship with the total weight loss (as seen in **Figure 2.12**).



**Figure 2.11** Experimental results by Shen et al. (2009) for carbochlorination of chromite in the presence of NaCl between 606°C and 720°C



**Figure 2.12** Linear representation of Fe removal and weight loss% during carbochlorination of chromite in the presence of NaCl between 606°C and 720°C (Shen et al., 2009)

Shen et al. (2009) also found that chlorination of powdered material was much more effective than chlorination of pelletised material. For example, at 660°C after two hours of exposure under carbochlorinating conditions with 5% NaCl

(by weight) added, the pelletised material had a Cr-to-Fe ratio of approximately 20% below that of powdered material.

In conclusion, Shen et al. (2009) found that the presence of NaCl significantly enhanced the selective removal of iron in chromite by carbochlorination. Although the mechanisms involved in this phenomenon are not clear, these authors made some postulations:

- The added NaCl(s) reacted with the chlorinated product FeCl<sub>3</sub>(s) to form liquid eutectic films on the top and inner surfaces of the chromite particles due to the formation of the low melting point compound NaFeCl<sub>4</sub>. The formation of the liquid eutectic films increased the fluidity of the solid product FeCl<sub>3</sub>(s). Moreover, part of the formed FeCl<sub>3</sub> was probably volatilised in the form of NaFeCl<sub>4</sub> vapour. The formation of the liquid and the gaseous eutectic compound NaFeCl<sub>4</sub> reduced the pore blockage and increased the mass transfer rates of Cl<sub>2</sub>(g), CO(g), FeCl<sub>3</sub>(s), etc. at the deeper cores of the chlorinated chromite particles.
- NaCl–FeCl<sub>3</sub> eutectic is a good solid solvent for FeCl<sub>2</sub>(s), which is formed from the dissociation of FeCl<sub>3</sub>. Cl<sub>2</sub>(g) reacted with the FeCl<sub>2</sub> dissolved in the liquid eutectic films more rapidly than with solid FeCl<sub>2</sub> and thus increased the adsorption rate of chlorine.

In summary, Shen et al. (2009) concluded that NaCl indirectly increased the diffusion rate of Cl<sub>2</sub>(g), CO(g), FeCl<sub>3</sub>(s) and FeCl<sub>2</sub>(s) inside the pore channels of chromite particles and reduced their diffusion activation energies. It is noteworthy that an 80 kJ/mol difference in activation energies between studies in the presence of and without NaCl was observed. This suggests that NaCl probably acted as a catalyst for carbochlorination of iron oxides from chromites.

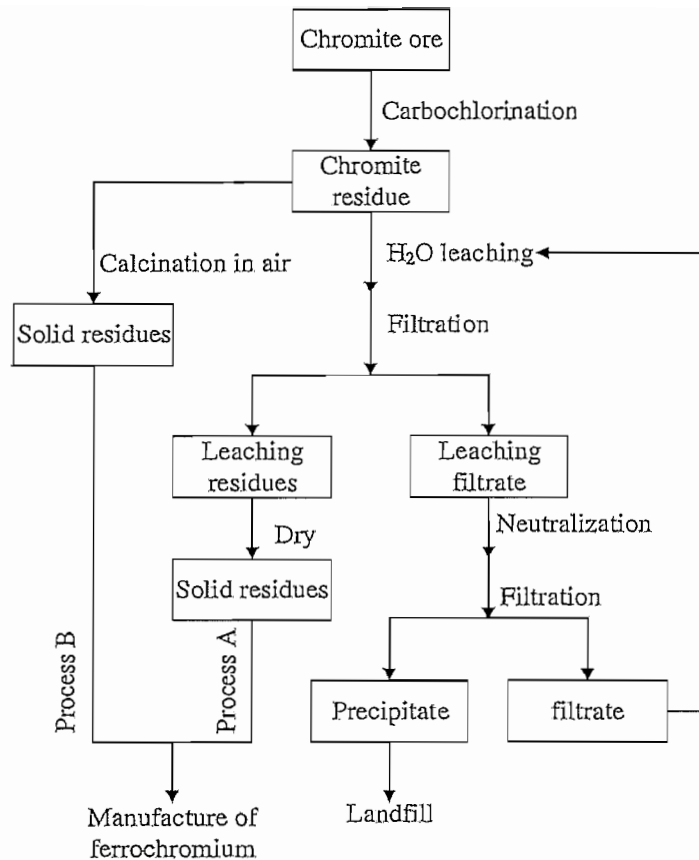
The oxychlorination of chromite has also been reported (Kanari et al, 2001a and Kanari et al., 2001b); this, however, falls outside the scope of this study and is therefore not discussed further.

## 2.5.2 Current application of chromite chlorination

According to the patent by Bergeron and Richer-Lafleche (2006), a possible carbochlorination process would consist of three steps:

- production of chlorine by electrolysis of NaCl solution.
- carbochlorination of chromite ores by using  $\text{Cl}_2$  (g) and  $\text{CO}$ (g) in the presence of NaCl and
- treatment of the unreacted chlorine, as well as the by-products  $\text{FeCl}_3$  and  $\text{CO}$ .

Shen et al. (2009b) also postulated two possible process options (Process A and B **Figure 2.12**) for the beneficiation of chromite by carbochlorination in the presence of NaCl. Of these two options, Process A is probably a more economically feasible option, since it does not require additional leaching, filtration, neutralisation, precipitation and land-filling. However, Shen et al., (2009b) did not mention in their process flow diagram that the carbochlorination was conducted with milled chromite (63 – 75  $\mu\text{m}$ ). Materials handling of such fines always increase the capital and operational costs.



**Figure 2.13** Process options for beneficiation of chromite by carbochlorination in the presence of NaCl (Shen et al., 2009b)

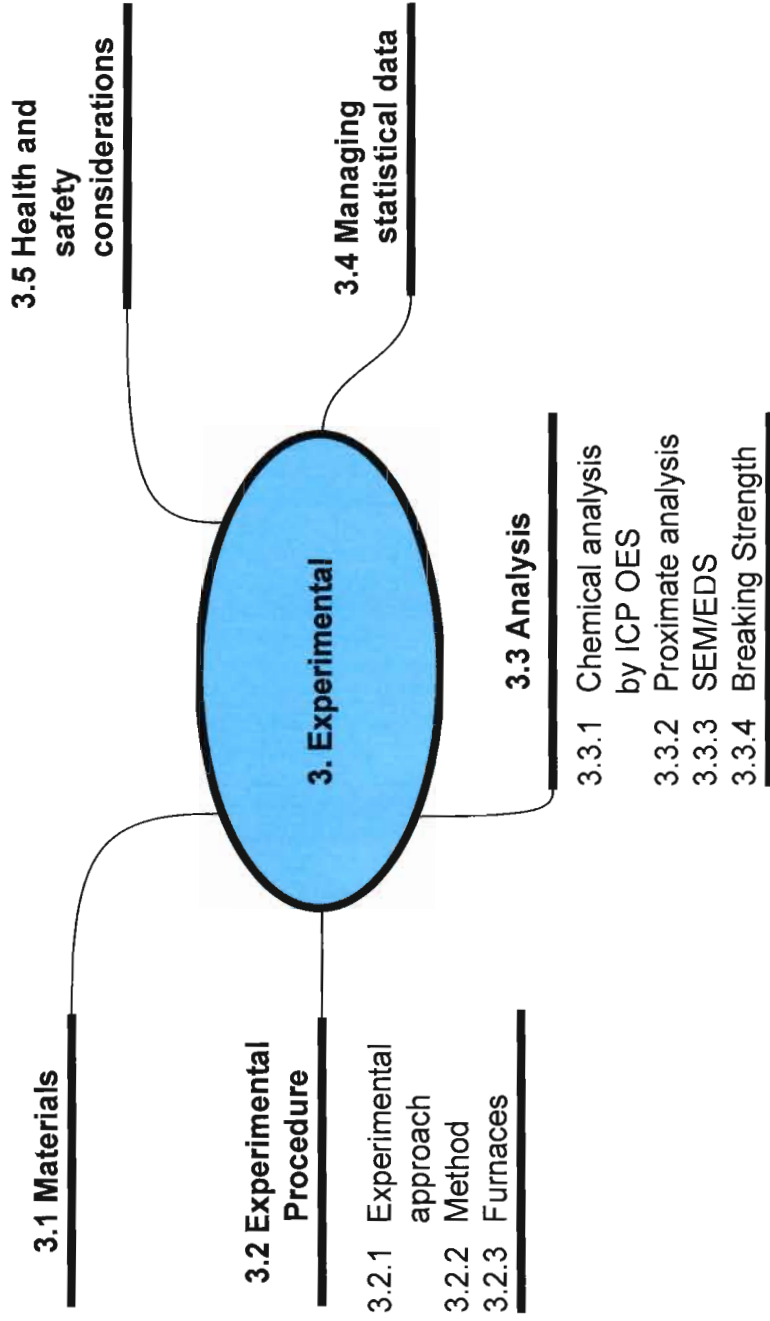
It is the opinion of the author that both the above-mentioned processes (Bergeron & Richer-Lafleche, 2006; Shen et al., 2009b) are currently not economically viable for the upgrading of chromite prior to ferrochrome production. Ferrochrome is a relatively large volume, low profit commodity and the additional costs associated with carbochlorination would not make it a viable option. The author is also not aware of any current application of such processes for ferrochrome production.

Apart from the above-mentioned obvious economical considerations,  $\text{Cl}_2$ , as well as  $\text{CO}$ , are both considered as toxic.  $\text{CO}$  concentrations as low as 667ppm may cause up to 50% of the body's haemoglobin to convert to carboxyhemoglobin (Cosink, 1983). Exposure to 30 ppm  $\text{Cl}_2$  may result in coughing and vomiting, while lung damage can occur at 60 ppm (Holten et al.,

2004)).  $\text{Cl}_2$  is also an extremely strong oxidising agent and thus very corrosive. These health and environmental aspects will also have additional negative capital and operational impacts, making the application of this type of technology even less likely.

## 2.6 Conclusions from literature

From the relevant literature, it is evident that the chromium-related industry is of great importance for South Africa. Unfortunately, the chromite resources have low Cr-to-Fe ratios and it is therefore of strategic importance to investigate upgrading the Cr-to-Fe ratios, in order to improve the local industry's profitability. It has been established that physical separation methods are unlikely to bring about an improvement in Cr-to-Fe ratios due to the fact that both the iron and chromium are part of the spinel structure. Structural dissociation of the chromite therefore seems to be the only viable option. Chlorination of chromite using  $\text{Cl}_2$ ,  $\text{HCl}$  (g) and other compounds that release  $\text{Cl}_2$  have been investigated on laboratory scale. However, it is unlikely that these practices will be applied on an industrial scale, since the process conditions are aggressive, dangerous and probably not economically viable. Thus, an alternative low cost and safe method of chlorination should be investigated.  $\text{NaCl}$  seems to be a key component in enhancing the chlorination of chromite and its role in this process needs to be better understood.





## Chapter 3

### Experimental

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In this chapter, the materials, experimental procedures and analytical techniques utilised in this study are discussed.

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#### 3.1 Materials

The chromite used in this investigation was received from Xstrata (Lion plant), which utilises the pre-reduction ferrochrome production process (see Par 2.3.3). The material was received in the form of a milled material, ready to be pelletised (see Par 2.3.2 for the process description). This milled material did not only consist of chromite, but also contained carbon (in the form of anthracite) and attapulgite clay. The reason why this industrial mixture was chosen is three-fold:

- This milled material is not a theoretical mixture, but actual material that is utilised on an industrial plant. This enhances the relevance of this study.
- The pre-reduction process is the second most commonly employed ferrochrome production process in South Africa.
- The pre-reduction process is the only commercial ferrochrome production process where at least a partial CO gas rich atmosphere is present during material treatment prior to furnace smelting. Most of the previous attempts at chlorinating chromite were done under carbochlorinating conditions, which implies a CO-rich atmosphere (Shao-Bo Shen et al., 2009; Kanari et al., 2000; Kanari et al., 1995; Bergeron and Richer-Lafleche, 2006; Robinson et al., 2008).

The attapulgite that is present in the above-mentioned mixture is required as a binding material, while the anthracite supplies the carbon required for the reduction.

NaCl was previously used as an additive during chlorination of chromite with Cl<sub>2</sub> and/or HCl gas (Shao-Bo Shen et al., 2009). During this study, it was therefore decided to test the possible chlorination of chromite by NaCl alone, without the afore-mentioned aggressive gasses (Cl<sub>2</sub> and HCl) being present. The NaCl used was received from Set Point Instruments and was of AAR quality (analysed analytical reagent).

## **3.2 Experimental procedures**

### **3.2.1 Experimental approach**

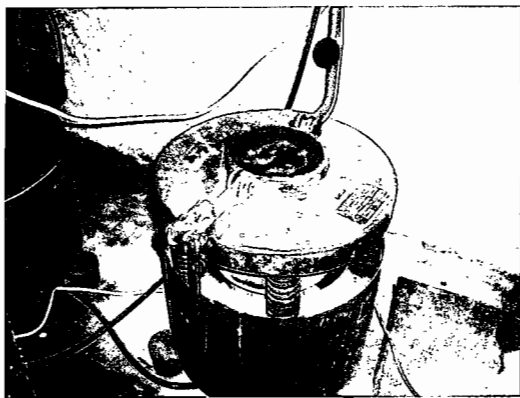
This investigation was based on a mono-variance procedure, wherein the influence of three different parameters i.e. temperature, time and concentration that were investigated were varied one at a time during experimentation. At first the maximum temperature to which the material was exposed was varied, while both the concentration of NaCl and the exposure times were kept constant. Secondly, the NaCl concentration was varied, while the temperature and exposure times were kept constant. Lastly, the exposure time was varied, while the other two variables were kept constant. After each alteration of the afore-mentioned variables, the Cr-to-Fe ratios were measured, as well as other parameters. Different analytical techniques were used, which will be discussed in more detail later.

### **3.2.2 Method**

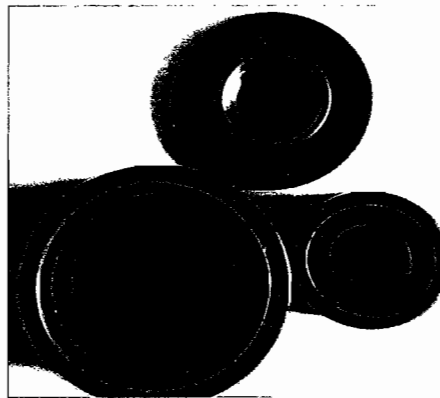
The precise amount necessary to ensure a specific weight percent (wt%) NaCl was weighed and added to a pre-weighed amount of milled chromite/anthracite/bentonite mixture. These two components (NaCl and milled material mixture) were then mixed by hand and subsequently the entire

mixture was pulverized for 30s to ensure that the two components were well mixed.

The pulveriser used in this investigation was a Sibtechnik pulveriser (**Figure 3.1a and b**), commonly used to pulverise solid samples prior to chemical analysis. All parts of the pulveriser, which made contact with the actual sample, were made of tungsten carbide. This prevented possible iron contamination of the pulverised samples. After a specific grind was completed, the contents of the pulveriser were collected in a sample bag for later use. The pulveriser was then cleaned before the next grind commenced.



**Figure 3.1a** Sibtechnik pulveriser



**Figure 3.1b** Tungsten carbide mixing bowl

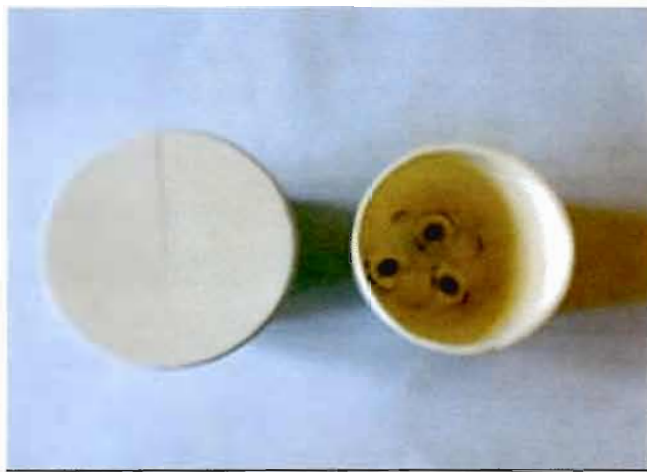
The milled material mixture was then placed into a 13mm die set (Specac PT. No. 3000) and pressed with a force of 1ton, forming a cylindrical pellet of 13mm x 10mm (diameter x height). **Figures 3.2a and b** show the press (Specac 15 ton Hydraulic press), as well as the die set that was used. These pellets were then placed in a crucible (**Figure 3.3**) in a furnace and treated according to a specific high temperature programme. This high temperature programme incorporated a list of parameters that had to be set, according to variables as illustrated in **Figure 3.4**. Once a specific high temperature experiment was completed (step 5 in **Figure 3.4**), the pellets were cooled down in an inert atmosphere. This was done to prevent atmospheric oxidation of the pellets, as the pellets were very hot. Ten pellets were treated at a time in this manner. After cooling, the pellets were analysed as discussed later.



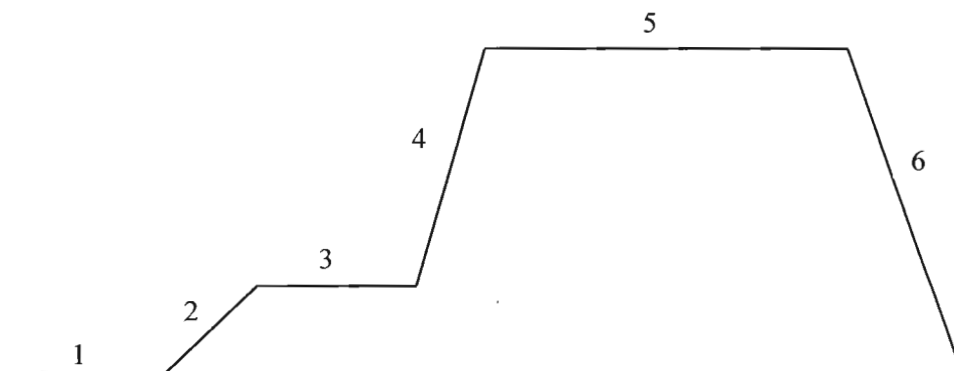
**Figure 3.2a** Press used in pelletising of mixture



**Figure 3.2b** Die set used in pelletising of mixture



**Figure 3.3** Crucibles containing pellets, with and without lid



**Figure 3.4** Temperature programme used in experiment

1. Preheating at 80°C for 30min to ensure release of most moisture.
2. Ramp at 4°C/min.
3. Hold at 200°C for 30min to drive off volatiles and crystalline water.
4. Ramp at 10°C/min
5. Kept at X °C for 2 hours  
X = 500, 600, 700, 800, 900,1000,1100,1200
6. Cool down to room temperature in inert atmosphere.

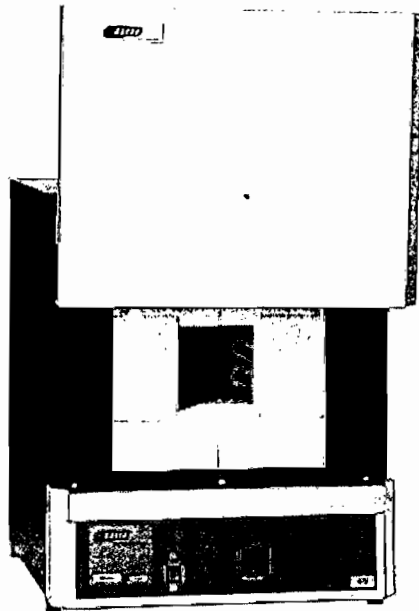
This temperature programme was utilised since it had some relevance to the pre-reduction process utilised in industry. During the industrial process, the green pellets (wet pellets) that are round and not cylindrical as in this study, travel through three heated cambers each having a higher temperature than the previous one, with the intention of driving off the moisture and pre-heating the pellets, prior to the pellets entering the rotary kiln. In the rotary kiln, temperatures as high as 1480°C are encountered (Beukes et al., 2009). The duration that the pellets spend in the grate chambers and kilns during the industrial process is approximately three and a half to four hours, which resembles the time that the pellets were exposed to in steps 3 to 5 (vary between three to four hours and ten minutes, depending on the temperature (X) in **Figure 3.4**).

The effect of an oxidising or partially reducing atmosphere was also investigated. This was done by either removing the lid of the crucible, or leaving it on during the respective high temperature treatment. By leaving the lid of the crucible on, presumably a build up of CO and CO<sub>2</sub> gases took place inside the crucible, due to the high temperature exposure of the carbon present in the pellets. Consequently, a partially reducing atmosphere, or at least a less oxidative environment, was created. In contrast, removing the lid of the crucible exposed the pellets to a higher concentration of oxygen and therefore created an oxidising atmosphere.

### 3.2.3 Furnaces

An Elite BRF15/5 furnace (**Figure 3.5**) was utilised during the high temperature experiments, as discussed in Paragraph 3.2.2. The heating elements of this furnace are made of high-grade silicon carbide. **Table 3.1** gives some standard dimensional and temperature range specifications of this furnace. Other characteristics include:

- Vertical lifting door protects operator from heat when the door is opened.
- Positive break door safety switch isolates chamber from power supply when door is open.
- Double skin case construction ensures that external case surfaces meet safety standards.
- Rapid heating rates ( $1^{\circ}\text{C}/\text{min}$  to  $10^{\circ}\text{C}/\text{min}$ )
- Thermal efficiency, due to effective isolation



**Figure 3.5** Elite BFR15/5 furnace

**Table 3.1** Specification of Elite BFR15/5 furnace utilised during this investigation

| Model   | Max temp (°C) | Chamber dimensions (mm) HxWxD | Chamber capacity (litres) | Max power (KW) |
|---------|---------------|-------------------------------|---------------------------|----------------|
| BRF15/5 | 1500          | 150 x 140 x 250               | 5                         | 4.5            |

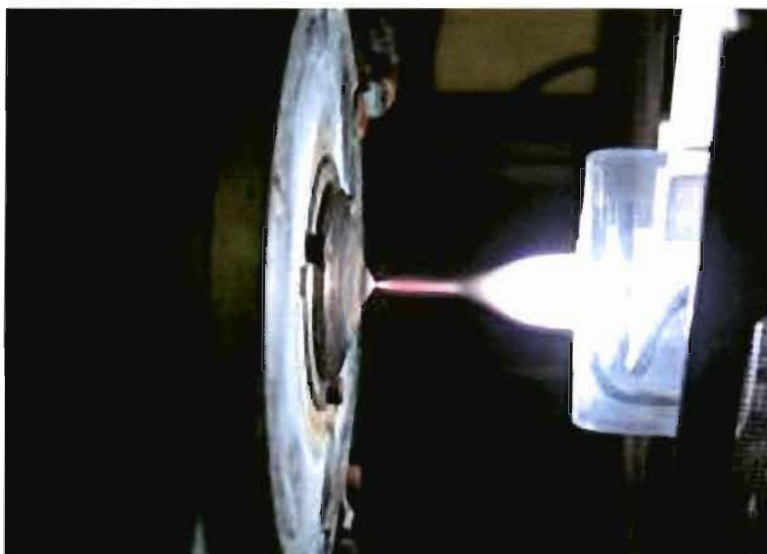
### 3.3 Analysis

#### 3.3.1 Chemical analysis by ICP-OES

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an analytical technique that is used for the detection of trace metals. The ICP-OES is composed of two parts: the ICP (inductively coupled plasma) and the optical emission spectrometer. The ICP produces excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

A peristaltic pump delivers an aqueous or organic sample into a nebuliser where it is atomised and introduced directly inside the plasma flame. The sample immediately collides with the electrons and other charged ions in the plasma and is broken down into charged ions. The various molecules break up into their respective atoms, which then lose electrons and recombine repeatedly in the plasma, giving off the characteristic wavelengths of the elements involved.

Transfer lenses (as seen in **Figure 3.6**) are used to focus the emitted light on a diffraction grating where it is separated into its component radiation in the optical spectrometer. The light intensity is then measured with a photomultiplier tube at the specific wavelength for each element line involved. The intensity of each line is then compared to previous measured intensities of known concentrations of the element and its concentration is then computed by extrapolation along the calibration line.



**Figure 3.6** Electrostatic lens of ICP

In practice, the samples were first milled using a steel bowl, after which 0.2g of a sample was weighed in a Zr crucible.  $\text{Na}_2\text{O}_2$  and carbonate were added as a flux and mixed well using a spatula. The mixture was fused on an automatic fusion apparatus until a complete melt was achieved. The mixture was then cooled and leached in a beaker containing 50ml distilled water. When the reaction stopped, 20ml HCl was added. The crucible was then removed with a rod and washed well with distilled water. After this, five drops of hydrogen peroxide was added and the mixture was then heated on a hot plate until the solution was clear. This solution was transferred into 200ml flask containing HCl and an internal standard. The flask was then made up to volume, again with distilled water and mixed. Finally, the solution was analysed by the ICP-OES (Varian Visto Pro, operated in radial mode).

### **3.3.2 Proximate analysis**

Proximate analysis is a test that is usually performed on coal, coke or other carbonaceous samples. It includes the determination of moisture, ash, volatiles and fixed carbon.



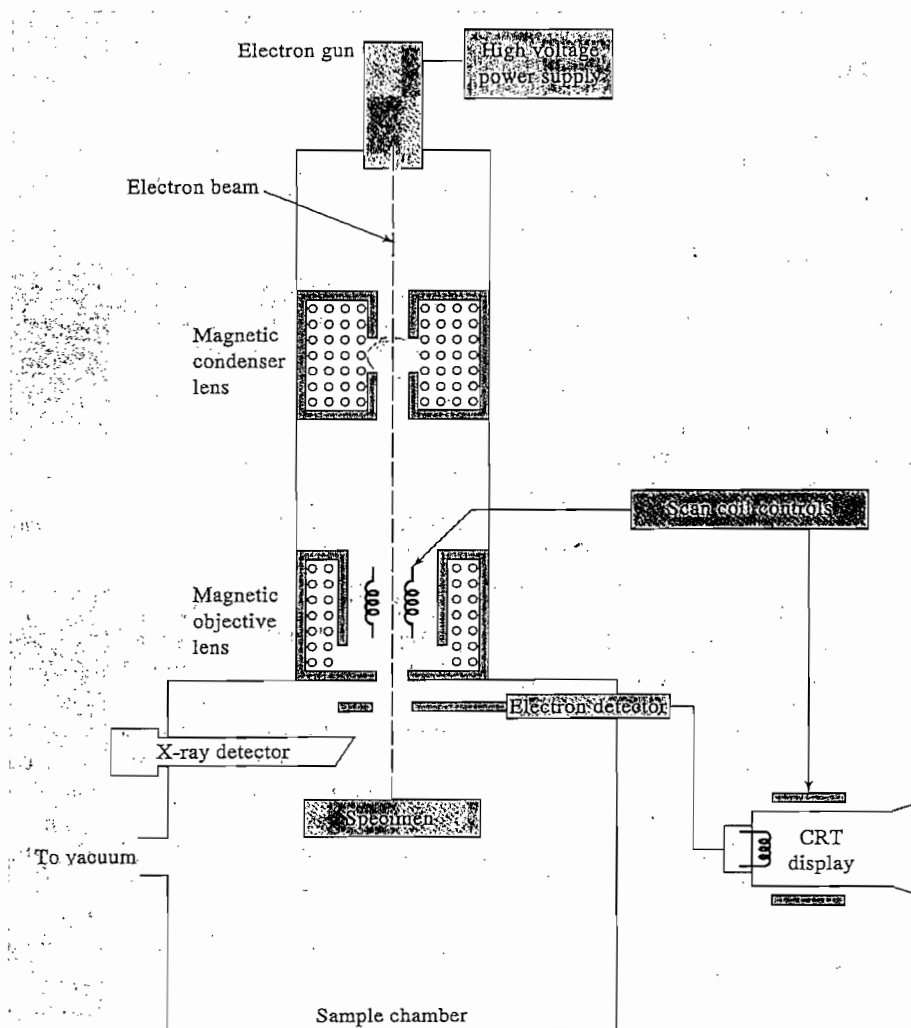
The moisture was determined by heating the sample (with known mass) at 105°C, and weighing it afterwards, to determine the mass water decrease, and hence moisture loss. The volatiles were determined by heating the sample also with known mass of at 900°C for seven minutes in inert atmosphere, and measuring the mass loss. The ash was determined by heating the sample at 950°C for several hours, until a stable mass was obtained. The remaining solid was the ash. The fixed carbon was then determined using the following formula: 100% - (sum of moisture, ash and volatiles).

### **3.3.3 Scanning Electron Microscope**

The Scanning Electron Microscope (SEM) permits the observation of materials in macro- and submicron ranges. The instrument is capable of generating three-dimensional images for the analysis of topographic features. SEM generates high energy electrons and focuses them on a specimen. The electron beam is scanned over the surface of the specimen in a motion similar to a television camera to produce a digital image. Electrons are speeded up in a vacuum until the wavelength is extremely short, only one hundred-thousandth that of white light. Beams of these fast-moving electrons are focused on a sample and are absorbed or scattered by the specimen and electronically processed into an image. Most electron microscopes used to study materials can image down to approximately 10 angstroms (0.001 microns).

When SEM is used in conjunction with energy-dispersive X-ray spectroscopy (EDS), the analyst can perform elemental analysis on microscopic sections of the material or contaminants that may be present. EDS is an analytical technique that utilises x-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental composition of the specimen. X-rays are generated as a result of the ejection of an inner level electron (low energy) from the sample, by an energetic electron from an electron column. The ejected electron is replaced by an electron from a higher energy shell. The energy lost, as it moves from a high energy shell to

a low energy shell, is released in the form of X-rays. Each element has many energy levels and therefore many potential vacancy-filling mechanisms. Consequently, even pure elements emit X-rays at a variety of energies. Because the atomic structure of each element is different, it follows that each element will emit a different pattern of X-rays. A graphical representation of a typical SEM-EDS instrument is shown in **Figure 3.7**.

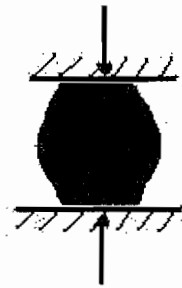


**Figure 3.7** Schematic drawing of a SEM instrumentation, with an EDS detector

The FEI QUANTA 200 ESEM, integrated with the OXFORD INCA 200 EDS system was used for the SEM-EDS analysis during this study. It was operated under a high vacuum, with a voltage of 15 kV, and a working distance of 10 mm.

### 3.3.4 Breaking /compressive strength

By definition, the compressive strength of a material is that value of uni-axial compressive stress reached when the material fails completely. The stress on the material at the time of rupture is known as the breaking strength. The compressive strength is usually obtained experimentally by means of a compressive test. During the period when stress is applied on the sample (which was cylindrical in this case) it is shortened, as well as spread laterally. A graphical representation of this is shown in **Figure 3.8**.



**Figure 3.8** Graphical representation of compressive test

Brittle materials such as concrete and carbon fibre do not have a yield point (yield strength or yield point of a material is defined as the stress at which a material begins to deform plastically), and do not strain-harden, which means that the ultimate strength and breaking strength are the same.

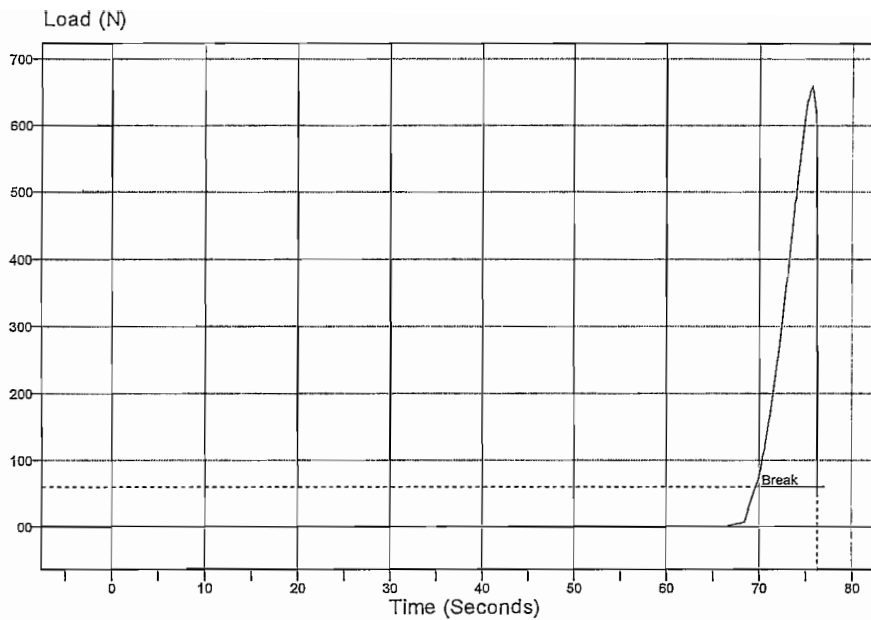
The compressive strength method is based on measurements of the mechanical strength that develops in the pellets as sintering takes place. This is the most common technique to determine the sintering temperature in coal ash (Al-Otoom et al., 2000). The compacted pellets were heat treated and cooled as discussed in Par 3.2.2. The cooled pellets were then crushed using an LRX Plus strength-testing device, by Lloyd instruments (**Figure 3.9**).



**Figure 3.9** LRX Plus, used in breaking strength tests

The compression strength is usually calculated as the maximum force where the pellet breaks, divided by the top area of the pellet (measured as  $\text{N}/\text{mm}^2$  or  $\text{N}/\text{m}^2$ ), or it is given as the pressure applied when the pellet breaks. The latter technique was adopted in this investigation, since the dimensions of the pellets were kept constant throughout the entire study. The compression strength was then plotted against maximum temperature reached during heat treatment.

An average of the breaking strengths of eight pellets exposed to each combination of parameters investigated was measured and the respective graphs were plotted. An example of a typical breaking strength test is illustrated below in **Figure 3.10**. As can be seen from this graph, the maximum strength prior to breaking was very evident and the failures were well defined.



**Figure 3.10** An example of typical force vs. time graph

The instrument's parameters were set to the following values:

- Preload stress → 0.0056kN
- Preload speed → 22mm/min
- Normal speed → 10mm/min

The above-mentioned settings were kept constant for all breaking strength tests, in order to obtain results which could be compared.

### 3.4 Managing statistical data

Numerous analyses were performed for most experiments. In order to make sure that outliers did not influence statistical calculated values, such as averages and standard deviations, the Q-test as recommended by Skoog et al. (2004) was used to identify and eliminate outliers. The absolute value of the difference between the questionable result ( $x_q$ ) and its nearest value ( $x_n$ ) is divided by the spread ( $w$ ) of the entire dataset to give the estimated Q-value:

$$Q = \frac{|x_q - x_n|}{w} \quad (3.1)$$

This Q-value is then compared to a critical  $Q_{crit}$  found in Table 3.2 (Skoog et al., 2004). If the value of Q was greater than  $Q_{crit}$ , the questionable value was rejected from statistical calculations. During this study, 95% confidence levels, as indicated in **Table 3.2**, were used.

**Table 3.2** Critical values for the rejection of quotient Q (Skoog et al., 2004)

| Number of observations | 90% Confidence | 95% Confidence | 99% Confidence |
|------------------------|----------------|----------------|----------------|
| 3                      | 0.941          | 0.970          | 0.994          |
| 4                      | 0.765          | 0.829          | 0.926          |
| 5                      | 0.642          | 0.710          | 0.821          |
| 6                      | 0.560          | 0.625          | 0.740          |
| 7                      | 0.507          | 0.568          | 0.680          |
| 8                      | 0.468          | 0.526          | 0.634          |
| 9                      | 0.437          | 0.493          | 0.598          |
| 10                     | 0.412          | 0.466          | 0.568          |

### 3.5 Health and safety considerations

Additionally to the general health and safety specification of the NWU, extra measures were taken when high temperature experiments were conducted.

This included the wearing of experiment-specific personal protective equipment (PPE), which included the wearing of:

- A face shield
- A leather apron
- Heat resistant gloves

The laboratory in which the furnace was housed was also locked to prevent unauthorised access.

**4.1 Effect of NaCl on Pellet cured breaking strength**

**4. Results & Discussion**

**4.2 Effect of NaCl on Cr-to-Fe ratio of chromite**

- 4.2.1 Possible iron extraction from chromite
- 4.2.2 Quantification of iron extraction and Cr-to-Fe ratios
- 4.2.3 Derived mechanistic information

**4.3 Effect of NaCl on the chromite pre-reduction**



## Chapter 4

### Results and discussions

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In this chapter, the results obtained are discussed. The breaking strength of the cured pellets with NaCl added was determined first. Thereafter the influence of the addition of NaCl on the Cr-to-Fe ratio was studied and finally the effect of NaCl addition on chromite pre-reduction is discussed.

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#### 4.1 Effect of NaCl on pellet cured breaking strength

Although this investigation did not focus on the breaking/crushing strength of the cured pellets, it did pose an opportunity to investigate it. This was due to the fact that the cured pellets (see Par 3.2.2 for curing process) had to be broken for SEM analysis (see Par 3.3.3 for detail). Instead of breaking the pellets by hand for SEM analysis, they were broken on a crushing strength instrument (see Par 3.3.4 for detail) that was used to obtain quantitative information about the strength of the pellets.

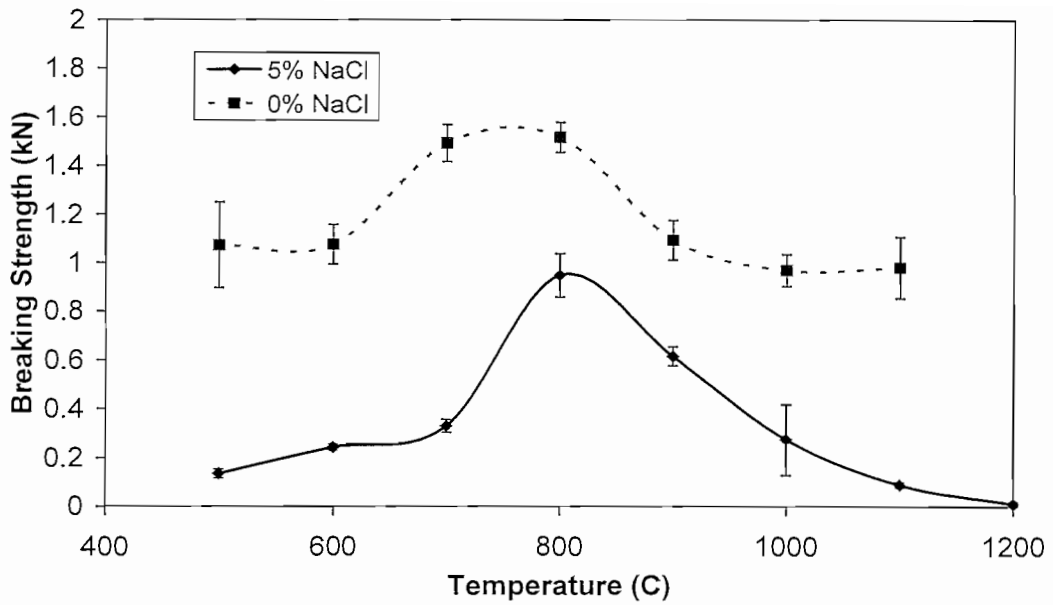
In an industrial ferrochrome production environment it is not preferred to feed fine ores directly into a submerged ferrochrome arc furnace, since it makes the furnace material more impermeable and traps the gases generated during the reduction process. This could result in bed turnovers and blowing of the furnace. These terms describe the instability of the surface layer of the furnace bed material. Bed turnover and blowing can vary from minimal disruption of the bed material, to catastrophic turnovers of a substantial amount of bed material. Apart from the obvious safety risks associated with such instability, bed material instability also results in more feed material fines being suspended into the furnace off gas (Beukes et al., 2009). Thus, one of

the objectives of pelletisation in an industrial context is to convert fine ores into larger agglomerates. It is therefore very important to know the cured strength of pellets, since this determines how much fine material will be formed during the transport, handling and loading of the pellets. Cured strength of agglomerates is usually determined by measuring the:

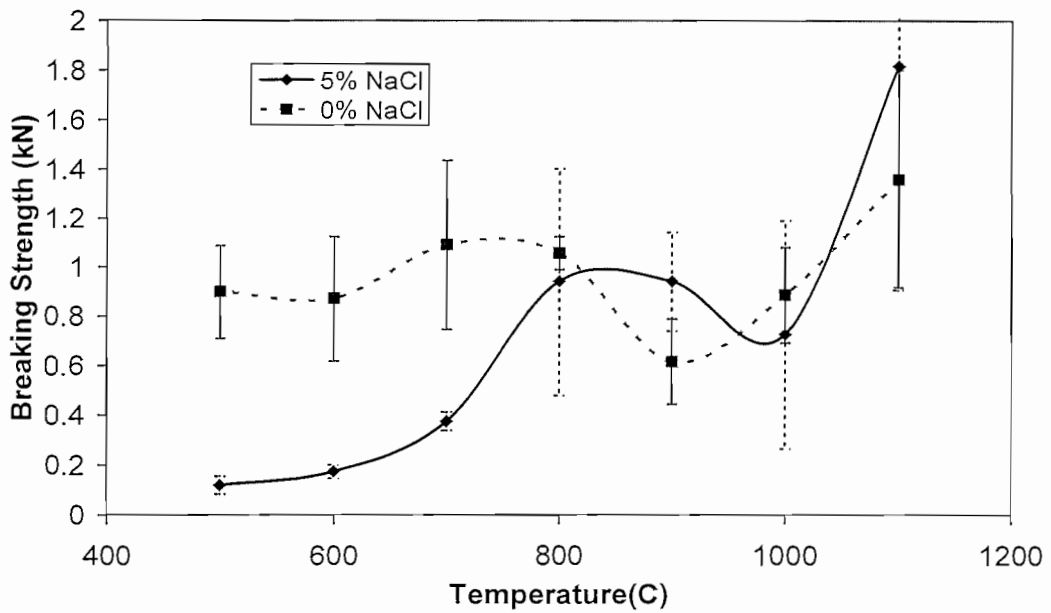
- abrasion strength
- breaking or crushing strength

Abrasion strength is usually measured by determining the amount of fine material generated during the tumbling of agglomerates in a rotating drum, under standard conditions (e.g. design of drum, rotating speed, rotations per time unit and total rotations). Breaking strength is an indication of the potential fines formation of the pellets under load. A practical example of this would be pellets at the bottom of a furnace feed bin, which would have to carry the load of several meters of furnace feed material above it. The abrasion strength of the cured pellets was not measured during this investigation, but the breaking strength was.

The breaking strength of the pellets versus the maximum curing temperature for both mixtures containing 0% and 5% NaCl that were treated in a partially reducing atmosphere (see Par 3.2.2 for detail) is shown in **Figure 4.1**. Similarly, the breaking strength of the pellets that contained 0% and 5% NaCl that were treated in an oxidising atmosphere (see Par 3.2.2 for detail) is shown in **Figure 4.2**.



**Figure 4.1** Effect of NaCl addition on the pellet cured breaking strength in a partially reducing atmosphere



**Figure 4.2** Effect of NaCl addition on the pellet cured breaking strength in an oxidizing atmosphere

From the data shown in **Figure 4.1** it is clear that the NaCl-containing pellets cured in a partially reducing atmosphere were substantially weaker than the pellets without NaCl. This is in agreement with the results obtained by Nel (2009), who indicated that the cured breaking strength of coal ash pellets were substantially lowered by the addition of NaCl if high temperature curing took place in an inert atmosphere (N<sub>2</sub> atmosphere). The exact reason why NaCl would reduce the cured breaking could not be established, but Nel (2009) proposed a few possible explanations. Nel (2009) proposed that volatilisation of NaCl would increase the porosity of the pellets, therefore reducing the breaking strength. This argument is, however, unlikely to be applicable to the current results, since NaCl only melts at 801°C (Weast, 1970) and would therefore not be volatilised at the lower temperatures where lower breaking strengths were already observed (**Figure 4.1**). Nel (2009) also proposed that sodium could be incorporated into the aluminosilicates of the clay, resulting in the formation of brittle glass phases that would decrease the breaking strength in pellets. This argument might hold some relevance to these results, although it would require the formation of some sort of eutectic mixture(s) that includes NaCl, to lower the melting point and thus enable an effect on the breaking strength below the melting point of NaCl (801°C).

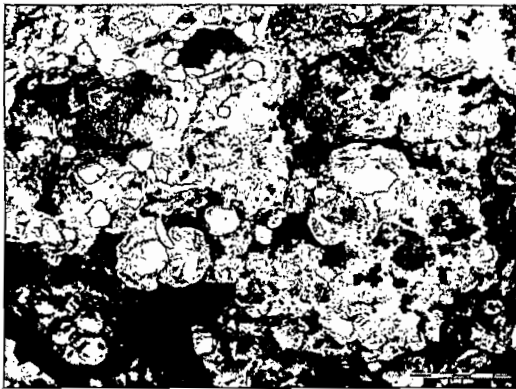
Considering the results shown in **Figure 4.1** further, it is also clear that the breaking strength of both the NaCl containing and the pellet mixtures without NaCl cured in a partially reducing atmosphere followed the same trends i.e. an increase in breaking strength from 500°C to 800°C, where after the breaking strength of both pellet mixtures decreased substantially. The maxima in breaking strength at 800°C correlated well with the melting point of NaCl at 801°C (Weast, 1970). Thus, it seems as if the melting of the NaCl weakened the pellets cured in a partially reducing atmosphere. The previously mentioned proposals by Nel (2009) could have relevance at temperatures above the melting point of NaCl and are therefore put forward as possible explanations for the decrease in breaking strength of the cured pellets above 800°C as seen in **Figure 4.1**: These explanations are:

- Volatilisation of NaCl above its melting point would increase the porosity of the pellets, hence reduce breaking strength. Proof of NaCl volatilisation under experimental conditions was found later and is given in Par. 4.2.
- After melting of NaCl, sodium could be incorporated into the aluminosilicates of the clay, resulting in the formation of brittle glass phases that would decrease the breaking strength.

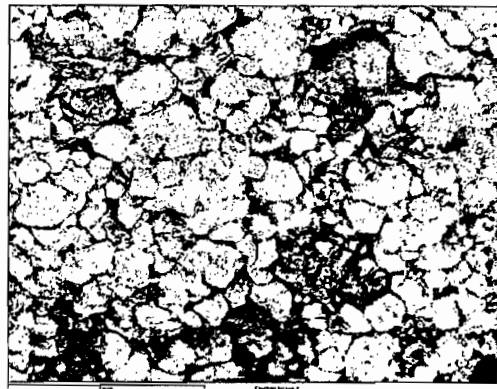
The breaking strength of the pellets cured in an oxidising environment (**Figure 4.2**) had similar trends to those cured in a partially reducing atmosphere, with strength increasing up to approximately 800°C, where after strength decreased. This again indicated that melting of the NaCl had an effect, as explained previously. However, in contrast to the pellets cured in a partially reducing atmosphere, the strength of both types of pellets (with and without NaCl addition) cured in an oxidising environment increased above ~900°C. Additionally, the breaking strength of the pellets with NaCl was at least equal to the strength of the pellets without NaCl, cured above ~1000°C. The increase in pellet strength above 900°C in an oxidising environment can be attributed to the formation of a thin oxidised layer on the outside of the pellets. SEM-EDS (see Par 3.3.3 for description of technique) analysis of this outer layer of pellets cured at 1200°C in an oxidising environment showed that it was totally depleted in carbon, thus indicating that oxidation of the outer layer took place. It further seemed that the pellet strength obtained from this oxidised layer was not negatively influenced by the presence of NaCl.

To further illustrate the effect of the above-mentioned oxidised layer on the breaking strength of the pellets, an additional experiment was conducted. Un-milled metallurgical grade chromite (mostly < 1mm in size) was pelletised (see Par 3.2.2 for procedure) with powdered anthracite and attapulgite clay. The mixing ratios of these materials were kept exactly the same as the pulverised materials used previously (see Par 3.1), except that the chromite was not milled fine. Using un-milled chromite made it even more difficult to bind the particles through high temperature curing, but enabled the possible

identification of the binding mechanism between particles. These mixtures were treated separately in an oxidising and partially reducing atmosphere. A micrograph of the outer layer of a pellet made from this mixture cured at 1200°C in an oxidising environment is shown in **Figure 4.3a**. The inside of a pellet made from this mixture that was cured in a partially reducing atmosphere is shown in **Figure 4.3b**. Comparison of these two images indicates clearly that sintered bridges formed between particles that were fully oxidised, i.e. total carbon burn-off (**Figure 4.3a**), while these sintered bridges were not evident between particles where carbon was still present, obtained from the partially reducing atmosphere (**Figure 4.3a**). This clearly indicates why the oxidised layer discussed earlier imparted such an increase in breaking strength on the pellets cured in an oxidizing atmosphere.



**Figure 4.3a** A micrograph of the oxidised outer-layer



**Figure 4.3b** Micrograph of layer that experienced partially reducing atmosphere

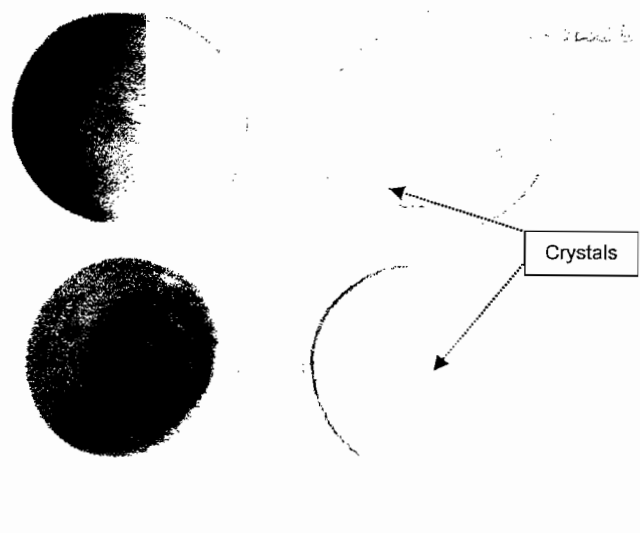
## 4.2 Effect of NaCl on Cr-to-Fe ratio of chromite

### 4.2.1 Possible iron extraction from chromite

After heat treatment of the pellets in the furnace at high temperatures (Par 3.2.2), fine metallic like crystals were noticed inside and on the lids of some of the crucibles that contained pellets during curing. It was evident that these crystals only formed if:

- the pellets contained NaCl and
- if the curing temperature was 900°C.

No crystals were observed for any other conditions investigated. **Figure 4.4** shows images of typical crucibles with their matching lids in which pellets were heat treated at the same temperatures. The crucible on the left contained pellets without NaCl and shows no evidence of any fine crystal formation in the crucible or on its lid. In contrast, the crucible on the right, which contained pellets with NaCl, clearly had crystal formation on the surface inside the crucible and on the lid



**Figure 4.4** Two identical crucibles exposed to the same atmosphere (reducing). Crystals formed on and around the lid of the crucible containing 5% NaCl at 900°C

The crystals that formed were subsequently analysed by means of SEM and SEM-EDS analysis. **Figure 4.5** show a SEM micrograph of the crystals found on the lid of a crucible wherein the sample material containing NaCl was placed in and cured up to 900°C in a partially reducing atmosphere. SEM-EDS surface analyses of the area where the crystals occurred, as well as the crystals themselves, are given in **Table 4.1**.





**Figure 4.5** Micrograph of crystals on lid of crucible, in which a chromite/carbon/attapulgite mixture containing 5% NaCl was treated at 900°C in a partially reducing atmosphere

**Table 4.1** SEM-EDS weight percentage (wt %) analysis of total area, as well as the specific crystalline material itself (area 1)

| Spectrum   | Na    | Mg   | Al   | Si   | S    | Cl    | Ca   | Fe    | O     | Total |
|------------|-------|------|------|------|------|-------|------|-------|-------|-------|
| Total area | 13.63 | 1.19 | 2.26 | 6.38 | 1.62 | 13.99 | 3.65 | 30    | 27.28 | 100   |
| Area 1     |       |      |      |      |      |       |      | 77.73 | 22.27 | 100   |

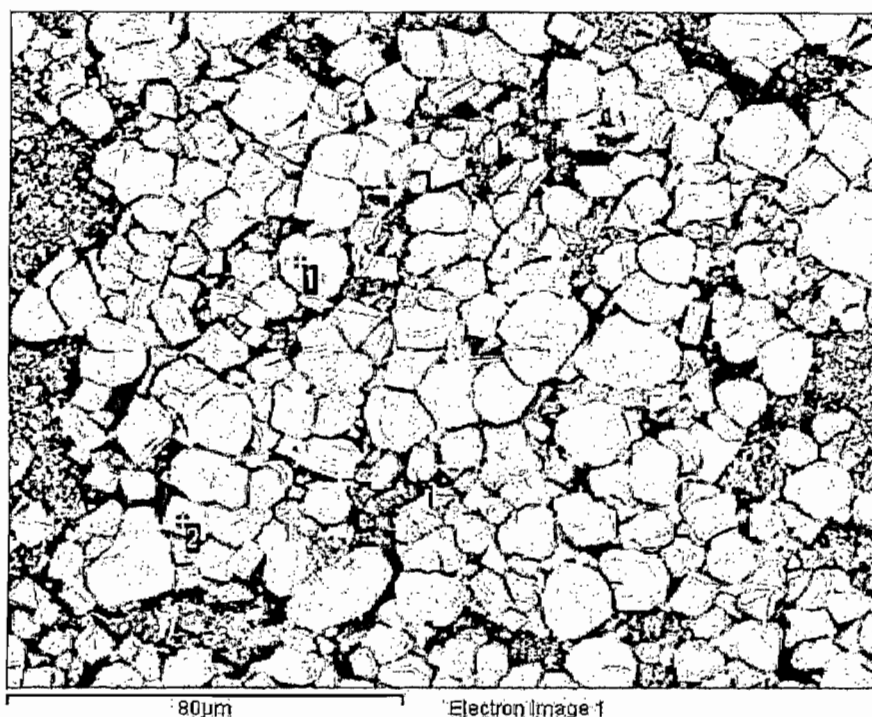
The SEM-EDS analysis (indicated as "Area 1" in **Table 4.1** and as "1" in **Figure 4.5**) revealed that the crystals contained 77.73 wt% Fe and 22.27 wt% O. The ratio of Fe/O ratio for these crystals was therefore 3.4903457. This value corresponds well with the theoretical weight ratio of Fe/O in pure FeO:

$$\frac{\text{Molecular mass Fe}}{\text{Molecular mass O}} = \frac{55.847}{15.9994} = 3.490568 \quad (4.1)$$

It can therefore be concluded with a very high degree of confidence that FeO crystals formed inside the crucibles and on the lids, if material mixtures

containing NaCl were treated at 900°C, or higher. Additionally, it was interesting to note the occurrence of Na and Cl as part of these crystalline areas (as part of “Total area” in **Table 4.1**). This indicated that some NaCl had indeed vaporised out of the material’s mixture, which supported the theory proposed earlier in Par 4.1 – that the breaking strength could be negatively influenced by the vaporisation of NaCl at temperatures above its melting point.

Another example (at 1000°C curing temperature) of the formation of FeO crystals inside a crucible is shown in **Figure 4.6** and **Table 4.2**. The ratio of Fe-to-O for these crystals was again the same as that of theoretically pure FeO, thus again suggesting it to be FeO.



**Figure 4.6** Micrograph of crystals on lid of crucible, in which a chromite/carbon/attapulgite mixture containing 5% NaCl was treated at 1000°C in partially reducing atmosphere

**Table 4.2** SEM-EDS weight percentage (wt %) analysis of area 1 and 2 found on lid of crucible, as indicated in Figure 4.6

| Spectrum | Fe    | O     | Na    | Cl    |  |  | Total |
|----------|-------|-------|-------|-------|--|--|-------|
| Area 1   | 77.73 | 22.27 |       |       |  |  | 100   |
| Area 2   |       |       | 37.07 | 50.03 |  |  | 100   |

The observation that FeO was isolated outside the chromite mixture after high temperature curing at or above 900°C in the presence of NaCl, was of great interest. If iron could be extracted from chromite in this fashion, it could have substantial benefits for the ferrochrome industry, as explained previously (Par 2.2 and 2.4). It was therefore important to try and quantify the extraction of iron, which is discussed in Par 4.2.2 below.

## 4.2.2 Quantification of iron extraction and Cr-to-Fe ratios

Although the isolation of FeO from the chromite mixtures (Par 4.2.1) was interesting and of academic importance (see paragraph 4.2.3), the exact amount of iron that was extracted by the different experimental procedures had to be quantified. For this purpose ICP-OES analyses (Par 3.3.1) were done on the cured pellets to determine Cr and Fe contents. The results obtained are shown in **Table 4.3**.

**Table 4.3** Chemical analyses of pellets cured at different temperatures, with 0 or 5 wt% NaCl, in oxidising or reducing atmospheres

| Temp / °C | % NaCl | Oxidizing atmosphere |      |       | Partially reducing atmosphere |      |       |
|-----------|--------|----------------------|------|-------|-------------------------------|------|-------|
|           |        | Cr%                  | Fe%  | Cr/Fe | Cr%                           | Fe%  | Cr/Fe |
| BASE      | 0      | 22.6                 | 16.8 | 1.369 | 22.6                          | 16.8 | 1.369 |
| 500       | 0      | 23.7                 | 17.2 | 1.378 | 23                            | 16.9 | 1.36  |
| 500       | 5      | 22.2                 | 16.1 | 1.379 | 23.4                          | 17.1 | 1.368 |
| 600       | 0      | 24.8                 | 17.9 | 1.385 | 23.4                          | 17   | 1.376 |
| 600       | 5      | 23.3                 | 17   | 1.371 | 22.3                          | 16.6 | 1.343 |
| 700       | 0      | 24.6                 | 18.3 | 1.344 | 23.9                          | 17.5 | 1.366 |
| 700       | 5      | 23.3                 | 17.3 | 1.347 | 22.8                          | 17   | 1.341 |
| 800       | 0      | 23.7                 | 17.6 | 1.347 | 23.8                          | 17.8 | 1.337 |
| 800       | 5      | 22.9                 | 16.9 | 1.355 | 22.8                          | 16.6 | 1.373 |
| 900       | 0      | 24                   | 17.7 | 1.356 | 23.7                          | 17.6 | 1.347 |
| 900       | 5      | 23.1                 | 16.8 | 1.375 | 22.9                          | 16.9 | 1.355 |
| 1000      | 0      | 24.9                 | 18.4 | 1.353 | 24                            | 17.7 | 1.356 |
| 1000      | 5      | 24.2                 | 17.7 | 1.367 | 23.1                          | 16.8 | 1.375 |
| 1100      | 0      | 25.8                 | 19.1 | 1.351 | 24.9                          | 18.4 | 1.353 |
| 1100      | 5      | 25.9                 | 18.8 | 1.378 | 24.2                          | 17.7 | 1.367 |
| 1200      | 0      | 25.4                 | 18.8 | 1.351 | 25                            | 18.7 | 1.337 |
| 1200      | 5      | 25.3                 | 18.8 | 1.346 | 27.6                          | 20.3 | 1.360 |

From the above data, it is clear that the Cr-to-Fe ratio did not really change under any of the experimental conditions, in comparison with the base mixture that was untreated and contained no NaCl.

The results given in **Table 4.3**, however, caused some concern, as the Cr-to-Fe ratios were lower than expected, i.e. smaller than 1.4. This could have been due to a systematic error (Skoog et al, 2004) during the analytical procedure or the leaching processes prior to analysis. However, this possible systematic error could not be identified and it was therefore decided to prepare another set of pellets cured under the similar conditions. These were then analysed at the laboratory of a local ferrochrome producer. Additionally, 10% and 15% NaCl containing mixtures were also prepared. These results are summarised in **Table 4.4**.

**Table 4.4** Chemical analyses of pellets cured at different temperatures, with either 0, 5, 10 or 15 wt% NaCl, in oxidising or reducing atmosphere respectively

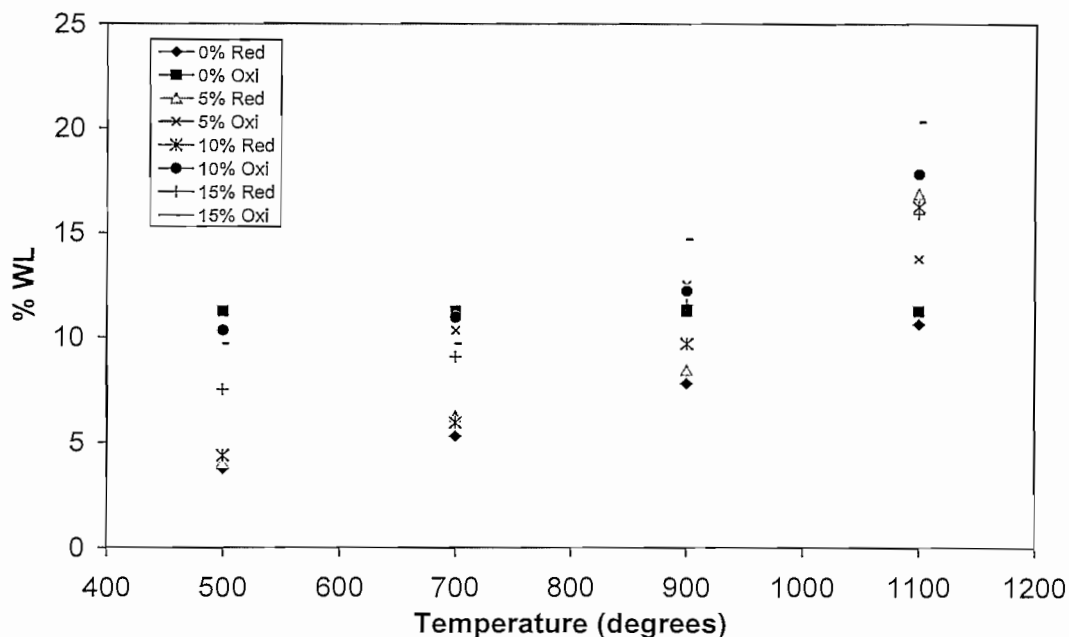
| Temp / °C | % NaCl | Oxidizing atmosphere |       |       | Partially reducing atmosphere |       |       |
|-----------|--------|----------------------|-------|-------|-------------------------------|-------|-------|
|           |        | Cr%                  | Fe%   | Cr/Fe | Cr%                           | Fe%   | Cr/Fe |
| BASE      | 0      | 24.17                | 17.01 | 1.42  | 24.17                         | 17.01 | 1.42  |
| 500       | 0      | 27.14                | 18.66 | 1.45  | 25.25                         | 17.54 | 1.44  |
| 500       | 5      | 25.65                | 17.84 | 1.44  | 23.70                         | 16.72 | 1.42  |
| 500       | 10     | 24.55                | 17.15 | 1.43  | 22.84                         | 16.16 | 1.41  |
| 500       | 15     | 23.52                | 16.42 | 1.43  | 22.28                         | 15.98 | 1.39  |
| 700       | 0      | 27.22                | 18.76 | 1.45  | 25.25                         | 17.67 | 1.43  |
| 700       | 5      | 25.76                | 17.85 | 1.44  | 24.33                         | 17.03 | 1.43  |
| 700       | 10     | 24.55                | 17.30 | 1.42  | 22.74                         | 15.95 | 1.43  |
| 700       | 15     | 23.58                | 16.39 | 1.44  | 23.27                         | 16.50 | 1.41  |
| 900       | 0      | 26.97                | 18.79 | 1.44  | 25.79                         | 18.09 | 1.43  |
| 900       | 5      | 24.65                | 17.41 | 1.42  | 25.10                         | 17.56 | 1.43  |
| 900       | 10     | 24.87                | 17.29 | 1.44  | 24.23                         | 17.22 | 1.41  |
| 900       | 15     | 27.04                | 18.64 | 1.45  | 23.56                         | 16.70 | 1.41  |
| 1100      | 0      | 26.31                | 17.93 | 1.47  | 26.94                         | 18.82 | 1.43  |
| 1100      | 5      | 26.35                | 18.36 | 1.44  | 25.91                         | 17.71 | 1.46  |
| 1100      | 10     | 26.03                | 18.45 | 1.41  | 24.27                         | 16.90 | 1.44  |

The data in **Table 4.4** confirmed the earlier results (**Table 4.3**) that the addition of NaCl did not have any effect on the Cr-to-Fe ratios, irrespective of curing temperature and atmosphere. All that happened was that the

concentration of Cr and Fe increased as the volatile matter was released, as pre-reduction took place and as the carbon burnt off. This implied that the iron extracted from the chromite was negligible. Thus, the FeO that formed on the walls and lids of the crucibles, used to cure the pellets that contained NaCl at or above 900°C (Par 4.2.1), was insignificant in the overall Cr-to-Fe ratio.

The Cr-to-Fe ratios in Table 4.4 were, however, slightly higher than those listed in **Table 4.3** confirming the presumption that a systematic error in the analytical or extraction techniques employed earlier occurred. However, in contrast to a random or gross error, a systematic error does not alter the conclusions that can be drawn from a data trend (Skoog et al., 2004). It is therefore not surprising that the conclusions drawn from the data in **Table 4.4** were the same as those drawn from the data in **Table 4.3**.

In previous papers on the chlorination of chromite, the mass loss of the cured percentage material was correlated to the percentage iron and chromium removed (Shen et al., 2009a; Shen et al., 2009b, Kanari et al., 2001a; Kanari et al., 2001b; Kanari et al., 2000; Kanari et al., 1999). Mass losses were also measured during this investigation (shown in **Figures 4.7**). However, it is not important to discuss these results in any detail, since no significant iron and chromium losses were observed. The observed mass losses could be ascribed to the loss of volatiles, pre-reduction taking place and burn-off of the carbon.



**Figure 4.7** % Weight loss of pellets with different wt% NaCl, cured in oxidizing (Oxi) or partially reducing (Red) atmospheres

#### 4.2.3 Derived mechanistic information

As briefly discussed in Par 2.5.1, Shen et al (2009) found that NaCl significantly enhanced the selective removal of iron from chromite during carbochlorination, i.e. chlorination by chlorine gas and carbon monoxide. Shen et al. (2009) also made some mechanistic deductions for the contribution of NaCl during this process. Essentially, these authors proposed that the added NaCl(s) reacted with the chlorinated product  $\text{FeCl}_3(\text{s})$  to form liquid eutectic films on the top and inner surfaces of the chromite particles due to the formation of the low melting point of the new compound  $\text{NaFeCl}_4$ . The formation of this new compound increased the fluidity of the solid product  $\text{FeCl}_3(\text{s})$ . It was also mentioned that part of the formed  $\text{FeCl}_3$  was probably volatilised in the form of  $\text{NaFeCl}_4$  vapour. This new compound reduced the pore blockage and increased the availability of gas to the cores of the chlorinated chromite particles.

Although this current study was not conducted under carbochlorinating conditions, some relevant mechanistic deductions can be made. The original selection of the material utilised in this study was based on the assumption that the solid reductant present in the materials mixture would produce CO gas inside the pellets when exposed to temperatures that are high enough. This CO formation would generate a partial positive pressure of CO and therefore prevent oxygen from entering the pellets. This assumption was found to be true, since pellets treated in the partially reducing atmosphere had a thin oxidised outer layer (carbon completely burned off) and a core still rich in carbon (indicating that oxidation did not take place). This phenomenon is also observed in the industrial pre-reduction process, where the outer layer of the pellets is oxidised and the inner layer reduced. Thus, the chromite grains inside the pellets utilised in this study were exposed to a similar atmosphere (CO rich) to the chromite investigated by Shen et al. (2009), except that no chlorine gas was present. This enabled us to evaluate the effect of NaCl only, and make some additional mechanistic proposals on the possible contribution of NaCl during carbochlorination.

According to the results obtained in this study, NaCl alone cannot alter the Cr-to-Fe ratio of chromite (Par 4.2.2). However, the addition of NaCl did at least initiate the removal of iron from the chromite (although insignificant in the overall context), as was proven in Par 4.2.1. FeO crystals were observed on the inside walls and lids of crucibles in which chromite mixtures were cured at or above 900°C in the presence of NaCl. This phenomenon was attributed to the fact that NaCl melted at 801°C, where after it seemed able to initiate some iron extraction from the chromite. This indicated that it is not only the possible formation of low melting point species such as those proposed by Shen et al. (2009), but also molten NaCl, that promotes the chlorination and extraction of iron from chromite during carbochlorination. According to the knowledge of the author, this is the first report of this nature, indicating that NaCl on its own can have some sort of initiating effect on the removal of Fe from chromite.

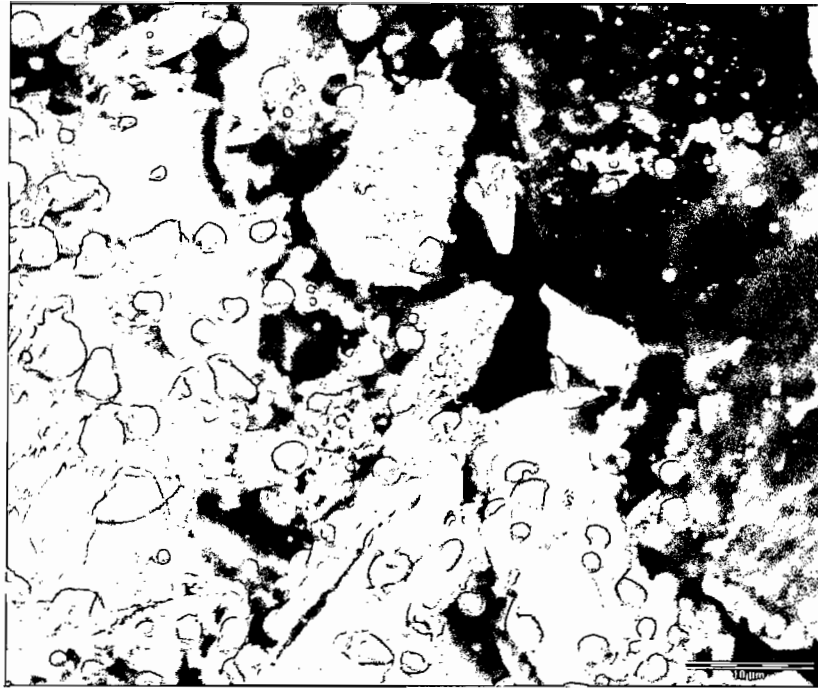


### 4.3 Effect of NaCl on chromite pre-reduction

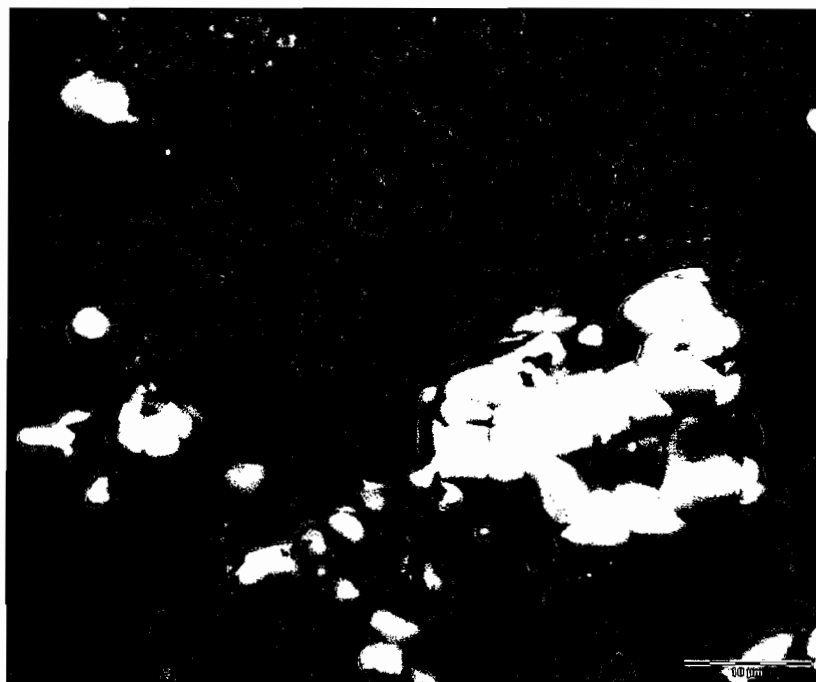
Pre-reduction of chromite is becoming more important due to the potential saving energy that is made possible by utilising it on an industrial scale during the production of ferrochrome (Par 2.3.3). The main objectives of this study were not directly linked to investigating the pre-reduction of chromite. However, certain observations made during the SEM-EDS analyses prompted at least some discussion on the effect of NaCl on the pre-reduction of chromite.

The SEM analyses conducted visually indicated that the addition of NaCl to the chromite/carbon/clay mixtures enhanced the rate of chromite pre-reduction. As an example, backscatter images of two samples cured under exactly the same conditions (1200°C, in a partially reducing atmosphere) are shown in **Figure 4.8** and **Figure 4.9**. The sample shown in **Figure 4.8** did not contain any NaCl, while the sample shown in **Figure 4.9** contained 5% NaCl. From these images, it is evident that globule-like metal particles (combination of Fe and Cr) in the mixture that contained NaCl as an additive were substantially larger than those in the mixture not containing NaCl. Thus, it seemed as if the addition of NaCl enhanced the rate of formation of pre-reduced metal.

As discussed in Par 2.3.2.2, numerous authors have reported that certain additives can enhance the rate of chromite pre-reduction. Katayama et al. (1986) reported that NaCl could be beneficial to the rate of chromite reduction. The experimental observations and deductions made in this investigation therefore seem reasonable and support the findings by Katayama et al. (1986).



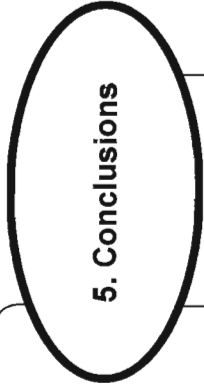
**Figure 4.8** 4000x magnification of a pellet with 0 wt% NaCl, cured at 1200°C in a partially reducing atmosphere



**Figure 4.9** 4000x magnification of a pellet with 5 wt% NaCl, cured at 1200°C in an oxidizing atmosphere

It would have been useful to quantify the effect of NaCl addition on the pre-reduction of the type of material mixture utilised during this investigation by chemical analysis, but since it was beyond the scope of this project it was not pursued. It is suggested that in future such an investigation should be undertaken during which more additives might be added. Additives such as lime (as CaCO or CaO), quartz (SiO<sub>2</sub>) and magnesite (MgCO<sub>3</sub>), which are already utilised as fluxes during the smelting process, could be considered.

**5.1 Project Evaluation**



**5.2 Future perspectives**

**5.3 Conclusions**

# Chapter 5

## Conclusion

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In this chapter the successes and shortcomings of this study are discussed, by evaluating the achievements against the objectives set in the Chapter 1. Based on the results and literature survey, recommendations with regard to future work related to this research are made. This is followed by final conclusions and a self-evaluation of the study in relation to the general requirements of an MSc study.

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### 5.1 Project evaluation

The project evaluation is structured around the objectives set in the first chapter. The points listed below therefore correlate with the objectives set in Par 1.2:

- i) An in-depth literature survey was conducted (Chapter 2). It highlighted the importance of the chromium industry within the South African context (Par 2.2). The low Cr-to-Fe ratios of the local ores, combined with the fact that ferrochrome producers are only paid for Cr-units emphasised the need for research to improve the Cr-to-Fe ratios of the local ores (Par 2.2). The spinel structure of chromite makes any significant iron extraction via physical separation techniques unlikely (Par 2.4). Structural dissociation of chromite therefore seems to be the only viable option. Reasonable successes have been achieved on laboratory scale at improving the Cr-to-Fe ratios of chromite by carbochlorination and addition of NaCl (Par 2.5). Several patents have also been filed, based on these methods. However, none of the processes have been implemented on an industrial scale for ferrochrome production, due

mainly to cost, but also health, safety and environmental considerations (Par 2.5).

- ii) Due to the past successes discussed, it was decided to investigate the effect of NaCl on the Cr-to-Fe ratio of local chromite during high temperature curing, without chlorine or hydrochloric gases being present. For this purpose, cylindrical pellets having a similar composition (chromite/anthracite/attapulgitite) to pellets produced in the pre-reduction ferrochrome process, were prepared. Surface SEM-EDS analyses indicated that some iron could be removed from the chromite matrix if NaCl was added to the mixture and curing temperatures were  $\geq 900^{\circ}\text{C}$ . However, chemical analysis proved that the removal of iron was insignificant and that the Cr-to-Fe ratios did not change under any of the experimental conditions. The earlier SEM-EDS analyses combined with breaking strength analyses results, however, provided some interesting mechanistic information on the contribution of NaCl during carbochlorination. Although not of industrial importance, this information is of significant academic interest. Additionally, SEM-EDS results also indicated that the addition of NaCl to the chromite mixture enhanced the rate of chromite pre-reduction. It could thus be concluded that NaCl on its own cannot alter the Cr-to-Fe ratio during high temperature treatment, but that it does influence other factors, such as cured breaking strength, and pre-reduction rate. Therefore, although the investigation did not succeed in identifying a simple method to alter the Cr-to-Fe ratio, it did make a significant contribution to current knowledge and understanding of the process.
- iii) The final objective concerning recommendations related to further work is discussed in Paragraph 5.2 below.

## 5.2 Future perspectives

From the results and literature survey three recommendations can be made with regard to further work related to this research area.

- i) From the literature survey it seems as if carbochlorination with NaCl as an additive can alter the Cr-to-Fe ration significantly. However, it is unlikely that such a process will be economically viable. It would also pose additional health and safety risks. The results of this study indicated that the addition of NaCl alone cannot serve as a simple additive to improve the Cr-to-Fe ratio during high temperature treatment. However, from literature, it seems as if  $\text{AlCl}_3$  might be a technically-viable option, although the economical viability is questionable, i.e.  $\text{AlCl}_3$  being relatively expensive. It is therefore proposed that an in-depth study be conducted to consider all aspects (including economical) of  $\text{AlCl}_3$  addition.
- ii) Although it was not the initial intention of the study to investigate the effect of additives on chromite pre-reduction, SEM-EDS analyses clearly indicated that its addition did increase the rate of pre-reduction. The literature survey also indicated that numerous additives might have positive effects on the rate of pre-reduction. It is therefore recommended that the effect on the rate of chromite pre-reduction by some additives, which are of direct industrial relevance such as  $\text{CaO}/\text{CaCO}_3$ ,  $\text{MgO}_3$  and  $\text{SiO}_2$ , must be considered in more detail.
- iii) The above-mentioned recommendations also lead to the idea that it might be useful to investigate the effect of different clays (e.g. attapulgite, bentonite, etc.) on the rate of chromite pre-reduction. Currently, only the cost of the clays, and their effect on the green and cured strengths of the industrially-produced pellets are utilised as criteria for selection of binders. However, the composition of these binders might actually have an effect on the rate of chromite pre-reduction.

### 5.3 Conclusions

Although this study did not succeed in proposing a simple process to alter the Cr-to-Fe ratio of local chromite, it did make a contribution to current knowledge. It also facilitated the identification of future projects, which might be more meaningful for the local ferrochrome industry.

In conclusion, the author (the candidate) would also like to do a self-evaluation on the outcomes of this MSc thesis. In general, an MSc thesis should comply with the following:

- i) Identification and description of a relevant problem
- ii) Setting objectives
- iii) Compiling a literature survey and critical assessment of literature where applicable
- iv) Setting up and conducting relevant experiments
- v) Obtaining results and discussion of these results in context of the study and the relevant literature
- vi) Making conclusion based on the results

In light of these requirements, it can be concluded that this study was successful. Additionally, a meaningful scientific contribution was made to understanding the mechanism of NaCl as an additive during carbochlorination. The candidate intends on publishing some of these results obtained. Since it is not required at MSc level to make a significant new scientific contribution, the above-mentioned contribution can therefore be regarded as sufficient proof that the study surpassed the requirements of an MSc study.



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