# Thermomechanical analysis of raw materials used in the production of Soderberg electrode paste

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*“Learn from yesterday, live for today, hope for tomorrow.*

*The important thing is not to stop questioning.”*

-Albert Einstein

# Declaration

I, Hannelie Roos, hereby declare that the dissertation entitled: ***“Thermomechanical analysis of raw materials used in the production of Soderberg electrode paste”***, submitted in fulfilment of the requirements for the degree MEng is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution in whole or in part.

Signed at Potchefstroom.

| | |
|---|---|
| Hannelie Roos | Date |

# Acknowledgements

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- All my friends and family for moral support.

# Abstract

Applications of chromium vary widely (refractories, chemicals and metallurgical); however, the greatest benefit of chromium is its ability to improve the corrosion resistance, strength and hardness of steel. South Africa possesses approximately 75% of the viable global chromite reserves and, as a result, dominates the ferrochrome market with production in excess of 5 million mega tonnes per year – making it an industry of extreme importance to the South African economy

Submerged arc ferroalloy production furnaces mainly use Soderberg electrodes – self-baking continuous electrodes that are produced *in situ* during furnace operation. Electrode breakings may affect a furnace in a number of ways depending on the nature and location of the break. Low furnace power input, abnormal charging and tapping conditions, as well as loss of production are among the more common negative implications associated with electrode breaks. The successful operation of Soderberg electrodes is dependent on two main factors: high quality electrode paste and effective electrode management procedures. This study focused on electrode paste quality.

The raw materials utilised in the production of Soderberg electrode paste consists of calcined anthracite mixed with a tar pitch binder. In this study the focus was on the development of an experimental procedure to measure the dimensional changes of electrode paste raw materials as a function of temperature by means of thermomechanical analysis (TMA). Three uncalcined anthracite (Zululand chips, Zululand duff, and Tendele duff) and two tar pitch samples (low and high softening point pitches, i.e. LSP and HSP) were obtained from a local paste producer. Electrode graphite samples were also obtained from a local pre-baked electrode supplier.

The experimental procedure for both the anthracite and tar pitches consisted of two phases: sample preparation and TMA measurements. During the sample preparation procedure for the tar pitches, the two tar pitches were heat treated in order to prevent softening in the TMA (preventing possibly damage the instrument), where after pellets were pressed for TMA measurement. The anthracite samples were

calcined at 1200, 1300 and 1400°C in the anthracite sample preparation phase. TMA sample pellets of calcined and uncalcined anthracite were pressed using only water as a binder.

TMA was performed on pellets produced from the heat-treated tar pitch samples, uncalcined and calcined anthracite samples, as well as core drilled pellets of the pre-baked electrode graphite. The dimensional changes of these pellets were measured, as a function of temperature, through three consecutive heating (room temperature to 1300°C) and cooling (1300°C to approximately 100°C) cycles under a $N_2$ atmosphere.

A significant shrinkage (> 12%) for both the LSP and HSP tar pitches occurred during the first TMA heating cycle. During the second and third heating cycles of the LSP and HSP tar pitches, dimensional changes were approximately 2%. This indicates that substantial structural reordering of the carbonaceous binder takes place during the first heating cycle. TMA results obtained for all three the calcined anthracite samples investigated indicated thermal dimensional changes of less than 1%. The anthracite samples calcined at the highest experimental calcination temperature (1400°C) prior to TMA analysis had the smallest dimensional changes. This confirmed that higher calcination temperatures result in a higher level of structural ordering and dimensional stability. Considering the combined calcined anthracite and tar pitches TMA results, the importance of the initial baking of a Soderberg electrode at temperatures exceeding the baking isotherm temperature (475°C) becomes apparent – the dimensional behaviour of the tar pitch binder and the calcined anthracite differ dramatically, making the newly-formed electrode very susceptible to breakage. Once structural reordering of the pitch had taken place, thermal dimensional behaviours of the materials are much more similar, significantly reducing the risk of thermal shock-induced electrode breakages.

In contrast to the relatively small dimensional changes measured for the calcined anthracite samples, the shrinkages measured for the uncalcined samples during the first TMA heating/cooling cycle were substantial (6-8%). This indicates the importance of the anthracite calcination process, before the electrode paste is formulated. Improperly calcined anthracite present in electrode paste would result in additional dimensional shrinkage that would have to be accommodated in the baking of a new electrode section. Considering the large shrinkage of the tar pitch that already takes place, it is unlikely that a strong enough electrode would be formed if this occurs. From the results, it also became apparent that the

anthracite with the highest fixed carbon and lowest ash contents exhibited the smallest shrinkage during *in situ* TMA calcination. High fixed carbon, low ash type anthracites are therefore less prone to dimensional instabilities in Soderberg electrodes, as a result of poor calcination.

The dimensional changes observed in the calcined anthracites were very similar to those observed for the electrode graphite samples. The expansions/shrinkages observed in the graphite samples were mostly less than 0.5%, whereas the expansions/shrinkages observed in the various calcined anthracites were approximately 0.6 to 0.9%. The difference in the magnitude of the dimensional behaviour between the calcined anthracites and the graphite can be attributed to the fact that the graphite had already undergone maximum structural ordering (having been pre-baked at 3000°C).

***Keywords:*** *electrode management, electrode paste, ferrochrome production, Soderberg electrode(s), thermomechanical analysis*

# Opsomming

Chroom het heelwat verskillende alledaagse toepassings (vuurvaste materiale, chemiese en metallurgiese toepassings). Die grootste industriële voordeel is die vermoë van chroom om metale se weerstand teen korrosie te versterk, asook om metale te versterk en harder te maak. Suid-Afrika beskik tans oor ongeveer 75% van die wêreld se ontginbare chromietreserwes en is ŉ leier in die produksie van ferrochroom in die wêreld met ŉ jaarlikse ferrochroom-produksiesyfer van ongeveer 5 miljoen megaton

Soderberg-elektrodes word meestal in ferroallooi-oonde gebruik en hierdie elektrodes word kontinu binne-in die oond tydens produksie vervaardig. ŉ Elektrodebreuk kan die produksieoond op ŉ aantal maniere affekteer, afhangende van die aard en die posisie waar die breuk plaasvind. Die mees algemene negatiewe impakte wat veroorsaak word deur elektrodebreuke sluit in: lae oondkraginsette, abnormale laai- en dreineringstoestande, sowel as ŉ verlies in produksie. Die suksesvolle bestuur van Soderberg-elektrodes is hoofsaaklik afhanklik van twee faktore, naamlik die gebruik van hoë kwaliteit elektrodepasta en effektiewe elektrodebestuurprosedures. In hierdie studie is die fokus geplaas op die kwaliteit van elektrodepasta.

Soderberg-elektrodepasta word geproduseer deur gekalsineerde antrasiet met ŉ teerbinder te vermeng. In hierdie studie is ŉ eksperimentele metode ontwikkel om die dimensionele veranderinge van die rou materiale wat gebruik word in die vervaardiging van elektrodepasta as ŉ funksie van temperatuur te bepaal deur van termomeganiese analise (TMA) gebruik te maak. Drie ongekalsineerde antrasiet monsters (Zululand antrasietklippies, fyn Zululand en Tendele-antrasiet) en twee teer monsters (lae en hoë sagwordende pikke d.i. LSP en HSP) is verkry vanaf ŉ plaaslike pastaproduseerder. Grafiet elektrodemonsters is ook bekom vanaf ŉ plaaslike verskaffer.

Die eksperimentele metode wat uitgevoer is vir beide die teer- en antrasietmonsters het bestaan uit ŉ voorbereidings- en ŉ TMA-fase. Gedurende die monstervoorbereidingsfase van die teermonsters, is tere aanvanklik behandel deur verhitting om versagting in die TMA te voorkom wat moontlik die instrument kan beskadig. Na hierdie behandeling van die tere, in pilletjies gedruk. Die antrasietmonsters is

gekalsineer by 1200, 1300 en 1400°C tydens die monstervoorbereidingsfase. TMA pilletjies van gekalsineerde en ongekalsineerde antrasiet is gedruk deur slegs van water as bindingsmiddel gebruik te maak.

TMA-analises is uitgevoer op al die gedrukte pilletjies, sowel as die silindriese monsters wat vanuit die grafiet-elektrodes geboor is. Die dimensionele veranderinge in bogenoemde monsters is bepaal as ŉ funksie van temperatuur tydens drie opeenvolgende verhittings- (kamertemperatuur na 1300°C) en verkoelingsiklusse (1300°C na ongeveer 100°C) in ŉ $N_2$-atmosfeer.

Beduidende krimping (>12%) vir beide die LSP en HSP tere is tydens die eerste TMA verhittingssiklus waargeneem. Gedurende die tweede en derde siklusse is dimensionele veranderings van slegs ongeveer 2% waargeneem. Dit dui daarop dat daar aansienlike strukturele herordering van die koolstofmateriaal plaasvind tydens die eerste verhittingssiklus. Die TMA-resultate van al drie die gekalsineerde antrasietmonsters het dimensionele veranderings van minder as 1% getoon. Die antrasiete wat by die hoogste eksperimentele kalsineringstemperatuur (1400°C) gekalsineer is, het die kleinste dimensionele veranderings getoon. Dit bevestig dat hoër kalsineringstemperature ŉ hoër mate van strukturele ordering en dimensionele stabiliteit tot gevolg het. Die gekombineerde TMA-resultate van die gekalsineerde antrasiet en die teerbinders dui op die belangrikheid van die aanvanklike bakproses (by temperature hoër as die 475°C bak-isoterm) van Soderberg-elektrodes. Die dimensionele gedrag van die twee materiale verskil drasties wat die nuut-gevormde elektrode meer vatbaar vir breuke maak. Sodra strukturele herordering in beide materiale plaasgevind het, word die dimensionele gedrag baie meer dieselfde wat die risiko van ŉ elektrode-breuk as gevolg van termiese skokke noemenswaardig verminder.

Die dimensionele verandering wat gemeet is tydens die eerste TMA-siklus vir die ongekalsineerde antrasiet was ongeveer 6-8%, wat beduidend verskil van die gemete waardes vir die gekalsineerde antrasiet. Hierdie beklemtoon die belangrikheid van die kalsineringsproses voor die saamvoeging van die elektrodepasta. Antrasiet wat nie behoorlik gekalsineer is nie, kan lei tot addisionele krimping tydens die bak van ŉ nuwe elektrodeseksie. Indien die aansienlike krimping van die teerbinders in ag geneem word, is dit onwaarskynlik dat die elektrode sterk genoeg sal wees indien hierdie addisionele krimping sou plaasvind. Die resultate dui ook daarop dat die antrasiete met die hoogste vaste-koolstof- en die laagste asinhoud die minste krimping veroorsaak tydens TMA-kalsinering. Hiervan kan afgelei word dat

antrasiet met ʼn hoë koolstof- en lae asinhoud sal lei tot minder dimensionele onstabiliteit in Soderberg-elektrodes, indien onvolledige kalsinering plaasgevind het.

Die dimensionele veranderings waargeneem vir die gekalsineerde antrasiet was soortgelyk aan die waarnemings vir die grafiet monsters. Die krimpings/uitsettings in die grafietmonsters was hoofsaaklik minder as 0.5% vergeleke met die krimpings/uitsettings in die verskeie gekalsineerde antrasiete van ongeveer 0.6-0.9%. Die verskil in die groottes van die dimensionele veranderinge in die twee materiale is toegeskryf aan die feit dat grafiet reeds maksimum strukturele ordering bereik tydens die vervaardigingsproses van die grafiet-elektrodes waar die elektrodes teen 3000°C gebak word.

*Sleutelwoorde: elektrodebestuur, elektrodepasta, ferrochroomproduksie, Soderberg-elektrode(s), termomeganiese analise*

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# List of symbols and abbreviations

| Symbols | | |
|---|---|---|
| **Symbol** | **Meaning** | **Unit** |
| % | | Percentage |
| °C | Temperature | Degrees Celsius |
| °C/min | Heating rate | Degrees Celsius per minute |
| µm | Length | Micrometer |
| bar | Pressure | |
| cm | Length | Centimetre |
| g | Weight | Gram |
| kN | Force | Kilo-Newton |
| l/min | Flow rate | Litre per minute |
| m | Length | Meter |
| mg | Weight | Milligram |
| mm | Length | Millimetre |
| mN | Force | Milli-newton |
| MΩ | Resistivity | Mega-ohm |

| Abbreviations | | |
|---|---|---|
| **Symbol** | **Meaning** | **Unit** |
| BF | Basicity factor | |
| HSP | High softening point | |
| IR | Infra-red | |
| LSP | Low softening point | |
| LVDT | Linear variable displacement transducer | |
| MVA | Power | Megavolt-ampere |
| MWh | Power | Megawatt-hour |
| NWU | North-West University | |
| Par. | Paragraph | |
| SA | South Africa | |
| SANS | South African National Standard | |
| TMA | Thermomechanical analyser | |

# Chapter 1: Introduction

## 1.1. Project motivation

### 1.1.1. Project background

Chromium, as a metal, was first isolated in 1798 but was only put to regular use twenty years later in pigments for wallpaper manufacturing. During the 20th century, chromium became increasingly important as an alloying element with the development of the world steel industry. Applications of chromium can broadly be divided into three areas: Metallurgical applications, chemical applications and refractories. The majority of chromium (approximately 91 %) is, however, applied for metallurgical end-uses (Moisane, 2007).

The greatest benefit of chromium to the metallurgical industry is its ability to improve corrosion resistance, strength and hardness of steel. Chromium is an irreplaceable component in stainless steel and it is therefore the leading end-use for chromium (Moisane, 2007). Almost three quarters of the globally produced chromium is in the form of various grades of ferrochromium. Customer requirements often dictate the production specifications for ferrochromium, which is graded according to carbon and chrome content (Ringdalen, 1999).

Located in the Bushveld complex, South Africa possesses approximately 75% of the global chromite reserves. As a result, South Africa dominates the world ferrochrome market with ferrochrome production, which is close to 5 million mega tonnes per year. The stainless steel production industry consumes approximately 90% of the global ferrochrome produced. South Africa mainly produces charge chrome, which is preferred to high carbon ferrochrome in the production of stainless steel. As a result, more than 40% of the ferrochrome utilised by the global stainless steel industry is South African produced ferrochrome (Ruffini, 2006).

The safe and profitable production of ferrochromium is dependent on five general process aspects: Metallurgical control, charging of the furnace, tapping the furnace, energy input and specific energy consumption, and electrode management. Of the above-mentioned process aspects, electrode management is perhaps the most important process management aspect (Beukes, 2011; Roos, 2010).

The most vital part of any electric reduction furnace is the electrode system. Ferroalloy production furnaces mainly use Soderberg electrodes – a self-baking continuous electrode that is produced *in situ* during furnace operation. Cylindrical casings are filled with electrode paste, which is then baked as the electrode is slipped through the contact shoes (Innvær & Tveit, 1983).

Electrode breaks may affect a furnace in a number of ways depending on the nature and location of the break. Electrode breaks in the vicinity of the furnace roof are particularly dangerous as this is close to the weak, unbaked part of the electrode column. Abnormal furnace power, charging and tapping conditions and loss of production are among the common negative implications on furnace operation associated with electrode breaks. A broken electrode will continue to impact negatively on furnace operation until a new electrode is slipped and baked (Ord *et al.*, 1995).

The successful operation of Soderberg electrodes is dependent on two main factors: High quality electrode paste, and highly effective electrode management procedures (Ray *et al.*, 2007). A variety of aspects are involved in the electrode management procedure. In this study, however, the focus will be on electrode paste quality. An experimental procedure will be developed in order to determine the dimensional behaviour of electrode paste materials under thermal conditions similar to those found during everyday furnace operation. This will be done in order to obtain an accurate impression of the expansion and shrinkage of electrode paste during the baking of a Soderberg electrode. The developed experimental procedures will enable paste producers to perform better quality control on electrode paste by selecting raw materials with similar thermal expansion properties.

### 1.1.2. Previous studies

Numerous studies regarding temperature distribution in Soderberg electrodes and the effect of thermal stresses on Soderberg electrodes have been published in open literature, i.e Calculation of thermal stresses in Soderberg electrodes (Innvær & Olsen, 1980), Operational parameters for Soderberg electrodes from calculations, measurements and plant experience (Innvær *et al.*, 1985*)*. However, as far as the author could establish, research published in open literature regarding dimensional change in the raw materials used to produce Soderberg electrodes is very limited. Innvær *et al.* (1985) mentioned that thermal stresses accumulate inside the baked part of the electrode during the decent into the furnace, but are eventually released – probably due to structural reordering during the graphitisation process. Arnesen *et al.* (1979) briefly mentioned that electrode paste shrinks during baking. The magnitude of the dimensional changes that take place during baking was, however, not quantified.

### 1.1.3. Industrial significance

Successful completion of this project will benefit the ferrochromium industry, as well as other smelting industries using Soderberg electrodes, in a number of ways. The developed experimental procedure could be implemented by paste producers in order to perform better quality control on the raw materials used to produce electrode paste. Measuring the dimensional changes of the raw materials beforehand will enable paste producers to select materials with more compatible thermal dimensional properties, which would reduce the risk of breaking an electrode due to thermal stresses.

The study will also benefit the industry on plant level. As was mentioned previously, electrode management is probably the most important daily focal point at any ferrochrome smelter (Par. 1.1.1). Information on the dimensional behaviour of raw materials (i.e. paste and calcined anthracite) in the electrode columns during the baking of the electrodes will be of significant value in the prevention of electrode breaks due to thermal stresses.

## 1.2. Project objectives

Three main objectives have been identified for this project:

1. The development of an experimental procedure to determine the dimensional changes of electrode paste raw materials by means of thermomechanical analysis.
2. Applying the developed procedure towards determining the dimensional changes in tar and calcined anthracite as a function of temperature.
3. Interpretation of the practical implications of the developed procedure and obtained results on electrode management with particular reference to the ferrochrome industry.

## 1.3. Scope of the investigation

In order to achieve the objectives set for this project, the following was done:

1. Characterisation of the obtained tar pitch and anthracite samples. The anthracite samples were chemically analysed (proximate and ultimate analysis) and additionally, the melting points of the tar pitches were accurately determined.
2. An experimental method was designed in order to determine the thermal dimensional changes of the samples obtained. This included a sample preparation procedure and subsequent thermomechanical analysis (TMA).
3. The thermal dimensional changes of pre-treated tar pitch, calcined and uncalcined anthracite, as well as pre-baked electrode graphite were measured as a function of temperature.
4. The generated data was interpreted and the industrial relevance of the results was investigated.

This dissertation is divided into the following chapters:

1. Chapter 1: A brief introduction to the project, project background and motivation.
2. Chapter 2: An in-depth literature study of the ferrochrome production industry and current technology with particular reference to Soderberg electrode paste production and electrode management.
3. Chapter 3: A detailed discussion of the sample preparation procedures, experimental procedures and raw material characterisation.
4. Chapter 4: Discussion of the generated results and the investigation of the industrial relevance thereof.
5. Chapter 5: Evaluation of the study and recommendations for future research.

# Chapter 2: Literature survey

This chapter is dedicated to an in-depth literature study on the various aspects of ferrochrome production with a particular reference to electrode paste production, *in situ* Soderberg electrode production and electrode management.

## 2.1. Importance of the South African ferrochrome industry

Chromite, the only natural commercially viable source of chromium, is a key raw material in the ferrochromium production process. Chromite is a complex mineral varying widely in composition. The chromite spinel consists of magnesium, aluminium, iron and chromium in various proportions depending on the deposit (Kumar *et al.*, 2010). Chromite is classified according to its end-use, i.e. metallurgical grade, chemical grade or refractory grade (Gu & Willis, 1987). Metallurgical grade chromite, used in ferrochrome production in South Africa, typically contains 43 to 45% $Cr_2O_3$ with a 1.5:1 to 1.6:1 chromium to iron ratio (Cramer *et al.*, 2004).

South Africa holds a key position in the world ferroalloys industry, due to an abundance of natural resources, as well as a history of relatively low electricity costs. The chromite reserves in the Bushveld complex constitute approximately 75% of the global chromite resources, which is mainly used in the production of high carbon or charge ferrochrome (Ruffini, 2006) – a high carbon ferrochrome that is relatively inexpensive and has relatively loose specifications (Ringdalen, 1999).

Ferrochrome is added to steel in order to improve the corrosion and oxidation resistance. The steel industry utilises high carbon or charge ferrochrome for the production of stainless steel and currently consumes approximately 90% of the ferrochrome produced worldwide (Ruffini, 2006). South Africa currently produces approximately 40% of the annual world ferrochrome, making the ferrochrome industry a vital contributor to the South African economy (Kumar *et al.*, 2010). Figure 2-1 shows the annual world ferrochrome production contributions for 2009.

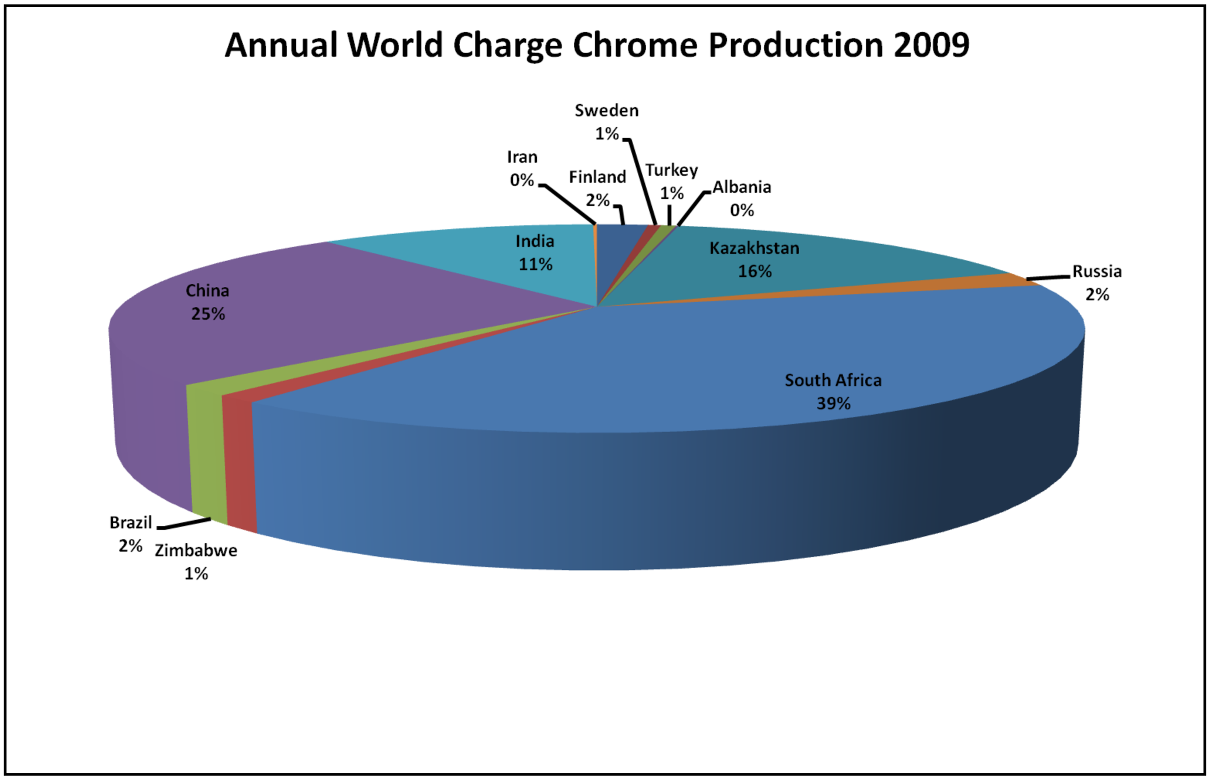

**Figure 2-1:** **Annual world charge chrome production 2009 (ICDA, 2010)**

Combined, the South African ferrochrome producers have a production capacity of almost 5 million tons per year, which is to be increased by expansion projects currently in progress. Table 2-1 shows the production capacities of the various ferrochrome producers in South Africa (Jones, 2011; Beukes *et al.*, 2011).

**Table 2-1:** **Adapted production capacity of SA FeCr producers (Jones, 2011; Beukes *et al.*, 2011)**

| Plant | Locality | Production capacity (ton/year) |
|---|---|---|
| ASA Metals Dilokong | Burgersfort | 360 000# |
| Assmang Chrome | Machadodorp | 300 000 |
| Ferrometals | Witbank | 550 000 |
| Hernic Ferrochrome | Brits | 420 000# |
| 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-MerafeBoshoek | Rustenburg-Sun City | 240 000 |
| Xstrata-Merafe Lion | Steelpoort | 364 000* |
| Xstrata Rustenburg | Rustenburg | 430 000 |
| Xstrata Wonderkop | Rustenburg-Brits | 545 000 |
| TOTAL | | 4 786 000 |

# **Production capacities of these facilities in the original reference** (Jones, 2011) **were updated by *Beukes et al. (2011)*, since it did not consider relatively recent capacity enlargement projects**

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

The fact that South Africa is the largest ferrochrome producer in the world, and the ever-increasing production capacities of the South African ferrochrome producers, clearly emphasises the importance of this particular industry in South Africa.

## 2.2. Ferrochrome production

A generalised process flow diagram, which indicates the most common process steps utilised by the SA ferrochrome producers, is shown in Figure 2-2.

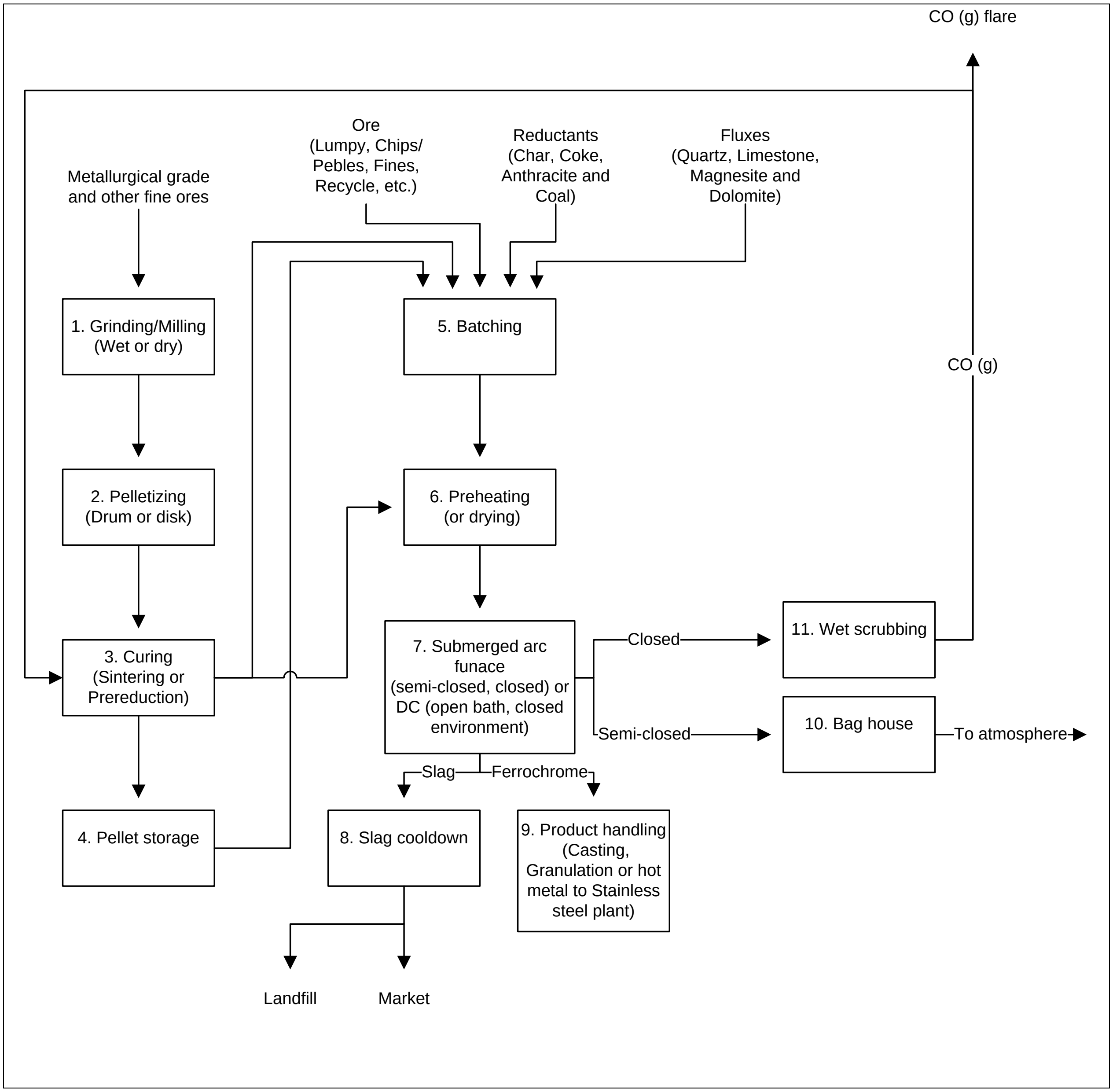

**Figure 2-2: Flow diagram, indicating most common process steps utilized for FeCr production in SA (Beukes *et al.*, 2010; Riekkola-Vanhanen, 1999)**

The South African ferrochrome producers currently use four relatively well-defined process combinations (Beukes *et al.*, 2010).

A. Conventional semi-closed furnace operation. This technology is currently the oldest applied in South Africa, but still accounts for a substantial fraction of the overall production (Gerdiga & Russ, 2007). Coarse (lumpy and chips/pebble ores) and fine ores can be smelted in this type of operation without increasing the sizes of the fine ores by means of an agglomeration process. Even though the direct feeding of fine ores into submerged arc ferrochrome production furnaces is said to cause dangerous blow-outs or bed turnovers (Riekkola-Vanhanen, 1999), a significant amount of fine ores are in fact fed into some South African semi-closed furnaces (Beukes *et al.*, 2010).

With reference to the process flow diagram indicated in Figure 2-2, the process steps followed are 5, 7, 8, 9 and 10. Steps 1-4 would also be included in the case where semi-closed furnaces consume pelletised feed. South African semi-closed furnaces are mostly operated on an acid slag, with a basicity factor (BF) smaller than 1. Equation 2-1 defines the basicity factor (BF):

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

In some cases, semi-closed furnaces may be operated at a BF>1; however, this is less common and usually implemented on a temporary basis in order to compensate for refractory linings that are in poor condition, or if enhanced sulphur removing capacity by the slag is required (Beukes *et al.*, 2010). Higher calcium and magnesium in the feed materials result in the formation of higher concentrations of $CaSO_3$ and $MgSO_3$, which are retained in the slag, hence lowering the presence of sulphur in the ferrochromium metal (Beukes, 2011).

B. Closed furnace operation, usually utilising oxidative sintered pelletised feed (Outotec, 2008), i.e. the Outotec process, as indicated in Figure 2-3. This process was first implemented in Tornio, Finland in 1968 at the Outokumpu ferrochrome plant. The Outotec process is currently the most popular ferrochrome production technology applied in South Africa and is utilised by the majority of green and brown field expansions during the last decade. 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). Presently, this technology is utilised by at least seven ferrochrome smelters in South Africa (Outokumpu, 2004; Outotec, 2008; Beukes *et al.*, 2011).

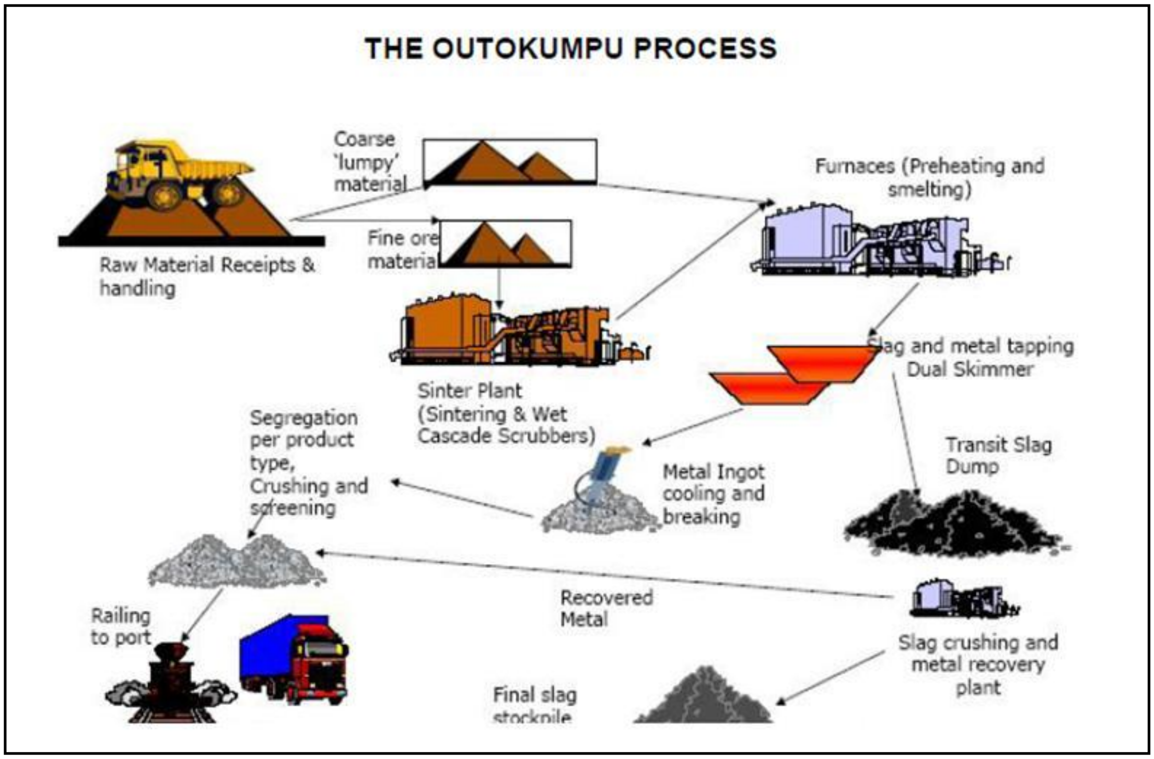

**Figure 2-3:** **Outotec/Outokumpu process flow sheet (Naiker & Riley, 2006)**

C. Premus Technology: This involves closed furnace operation with pre-reduced pelletised feed. The process steps include steps 1, 2, 3, 4, 5, 7, 8, 9, 11 and are graphically represented in Figures 2-4 and 2-5. The Premus technology differs substantially from the Outotec technology due to the fact that the pelletised feed consists of pre-reduced pellets that are mostly fed hot, directly after pre-reduction, into the furnaces (Botha, 2003; Naiker, 2007).

This technology provides high metallic oxide recoveries using low cost reductants and significantly reduces electrical energy consumption (Naiker & Riley, 2008; Roos, 2010). The furnaces are closed and operate on a basic slag (BF>1). At present, two SA FeCr smelter plants use this process (Beukes *et al.*, 2010).

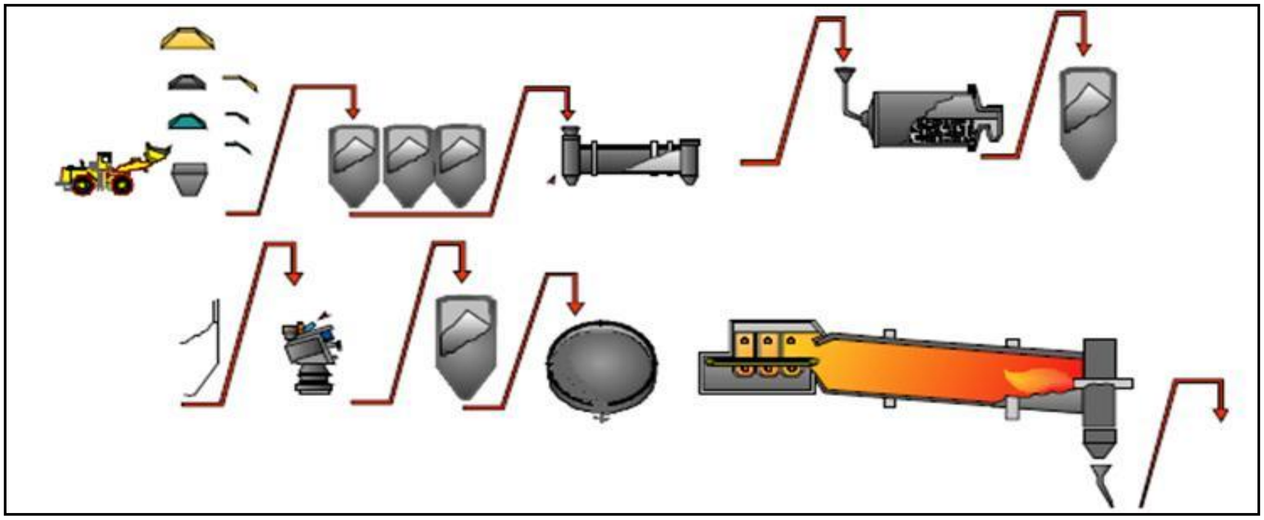

**Figure 2-4: Premus process flow sheet – pelletising and pre-reduction (Naiker & Riley 2006)**

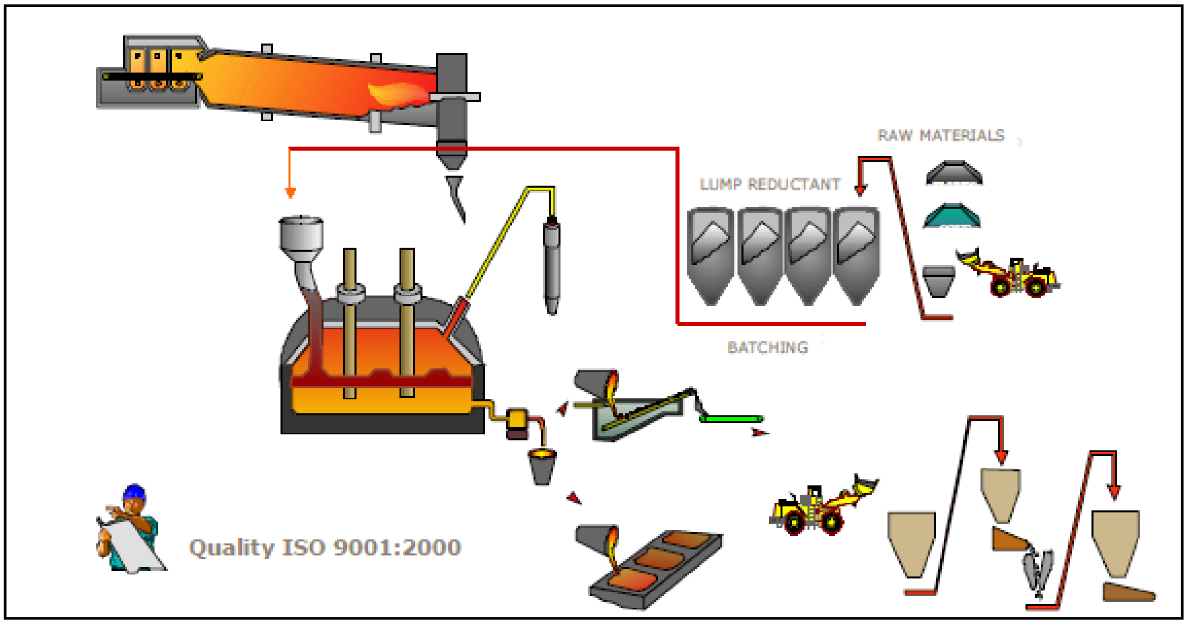

**Figure 2-5:** **Premus process flow sheet – smelting process (Naiker & Riley 2006)**

D. DC arc furnace operation (Curr, 2009; Denton *et al.*, 2004). Feed material for this type of operation can consist exclusively of fine material. Three such furnaces are currently in routine commercial operation for ferrochrome production in South Africa and typically utilise a basic slag regime (BF>1). High specific energy consumption is the biggest disadvantage of this process option, but high chromium recovery is achieved. Process steps include 5, 7 (with a DC, instead of a submerged arc furnace), 8, 9 and 11. Drying (process step 6) might also be included (Beukes *et al.*, 2010).

Traditionally, high carbon ferrochrome is produced by reducing chromite ores with a carbon reductant in large three phase submerged arc furnaces (usually having a capacity of between 10 and 50 MVA). Typically, the furnace diameters are in excess of 10 m (Ringdalen, 1999). During the smelting process, the electrical furnace is charged with chrome ore, a carbon reducing agent, and a flux (usually quartz and/or limestone and magnesite). These materials react with each other and produce two products: slag and liquid ferrochrome (Downing, 1975). Raw materials are fed to the furnace by loading the furnace feed bins, and are transported through feeding chutes by means of gravity to the furnace interior (Beukes, 2011). Figure 2-6 shows a drawing of a submerged arc furnace. Feeding chutes are gold coloured and the electrode columns are silver.

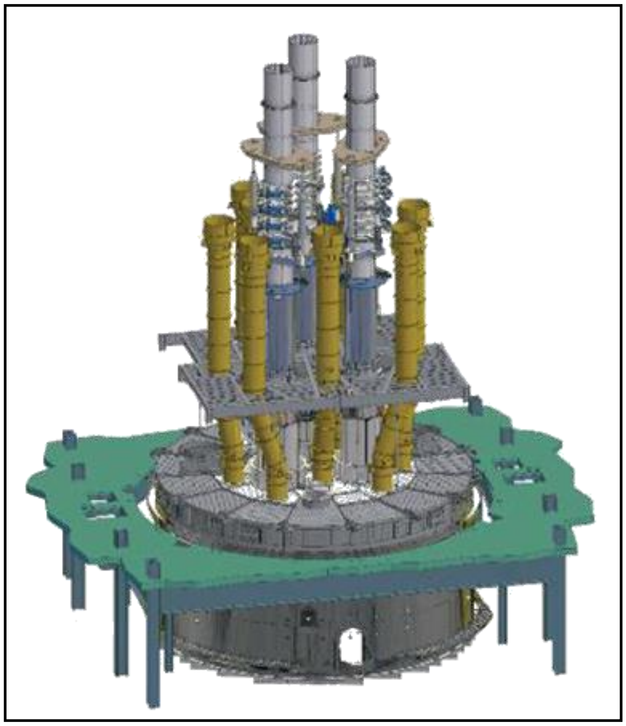

**Figure 2-6: Rendering of a submerged arc furnace (Bateman Engineering, 2011)**

In conventional submerged arc furnaces, current is conducted to the furnace charge by means of three self-baking Soderberg electrodes that heat the furnace burden to temperatures where the slag becomes liquid and ore reduction takes place. Reaction via gas phase reduction of *in situ* generated CO can also take place in the burden, prior to molten zone in the furnace. Liquid slag and metal are periodically tapped from the furnace and CO gas leaves the furnace as off gas (Ringdalen, 1999).

The profitable and safe production of ferrochrome is dependent on five general production aspects: i) metallurgical control, ii) furnace charging, iii) tapping the furnace, iv) power input and specific energy consumption, and v) electrode management. The above-mentioned aspects will briefly be discussed in paragraphs 2.2.1 to 2.2.5, with an in-depth discussion on the aspects of electrode management and paste production further in the literature study.

## 2.3. Pillars of ferrochrome production

### 2.3.1. Metallurgical control

The production of ferrochrome is a pyrometallurgical process, during which chromite is carbo-thermically reduced to chromium. The main reaction is:

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$$

The reduction of iron oxides and a small amount of silica also take place simultaneously (Riekkola-Vanhanen, 1999).

The furnace is charged with a mixture of chromite in the form of lumpy ore, pebbles, chip ore, pre-reduced pellets, sintered pellets or metallurgical grade ore, carbon reductants and fluxes (Beukes, 2011). The charge mixture may either be cold, pre-heated or pre-reduced (Riekkola-Vanhanen, 1999). Coke is normally used as a carbothermic reducing agent (Ringdalen, 1999); however, other carbon reducing agents such as char, coal and anthracite may also be used (Beukes, 2011). Fluxing materials include quartzite, bauxite, olivine, dolomite, limestone, magnesite and calcite (Riekkola-Vanhanen, 1999). Figure 2-7 indicates the basic inputs and outputs for a ferrochrome production furnace.

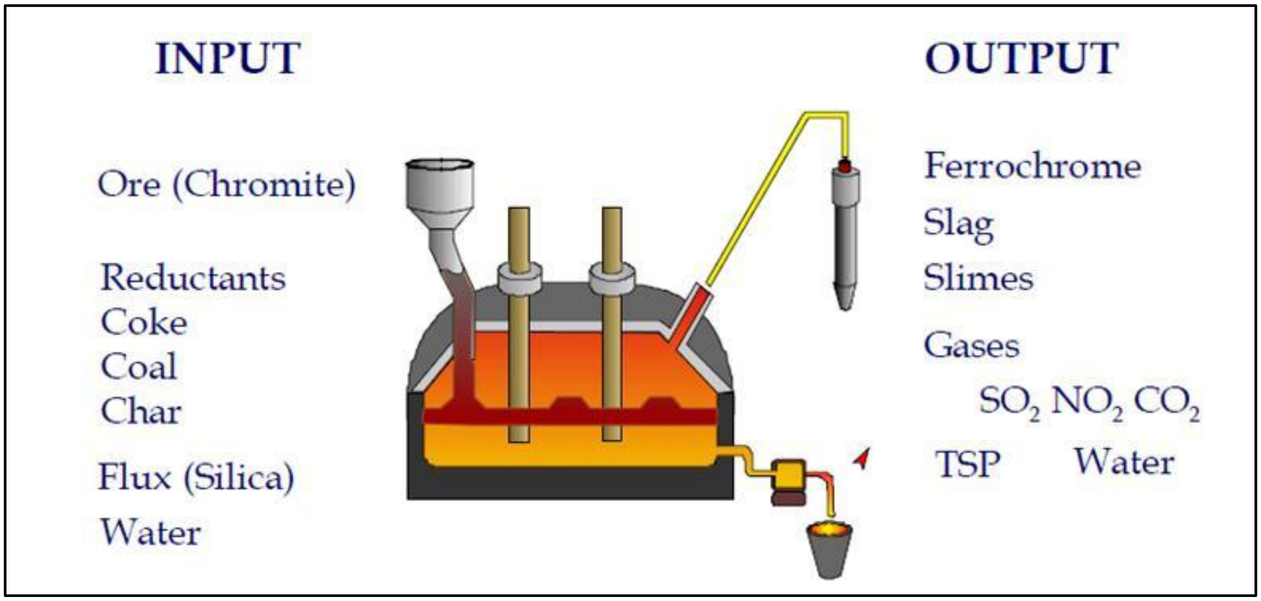

**Figure 2-7: Furnace inputs and outputs (Naiker & Riley, 2006)**

Materials are fed to the furnace according to a metallurgical balance, which is updated on a regular basis with the current feed material analysis. Alterations to the metallurgical balance are made according to current furnace conditions, as well as slag and product (ferrochrome) analysis. The most important variables of the produced ferrochrome are the silicon, chromium and carbon contents (Beukes, 2011; Roos, 2010).

Chrome ores used in the ferrochromium production process contain slag-forming oxides in addition to the reducible chromium and iron oxides. Several slag properties are important in order to obtain the correct metal composition, high chromium recovery and satisfactory furnace operation, e.g. a suitable slag melting point and a viscosity that enables easy tapping and good slag/metal separation (Riekkola-Vanhanen, 1999). The slag melting temperature can be regulated by means of control mechanisms such as the slag basicity and slag viscosity (Beukes, 2011).

Effective metallurgical control is of critical importance for the successful production of high quality ferrochrome. Poor metallurgical control may result in a variety of negative implications on the process such as low quality ferrochrome (high silicon content), large slag volumes, poor reduction of chromite ore (low recovery), difficulty in tapping the furnace due to a high slag viscosity and difficult electrode management (Beukes, 2011; Roos, 2010).

### 2.3.2. Charging the furnace

Open, semi-closed and closed submerged arc furnace configurations are currently used in the ferrochromium production industry (Riekkola-Vanhanen, 1999; Beukes *et al.*, 2010). Raw materials (consisting of chromite ore materials, reductants and fluxes) are usually mixed outside of the furnace, which is then periodically or continuously charged into the furnace. Reduction reactions and metal production proceed continuously even though the charge mix might be added periodically in certain furnace configurations (The EPRI Centre for Materials Production, 1996). Figure 2-8 indicates the cross sectional placement of electrodes and raw material feed chutes in semi-closed (indicated as “open”) and closed submerged ferrochrome smelting furnaces.

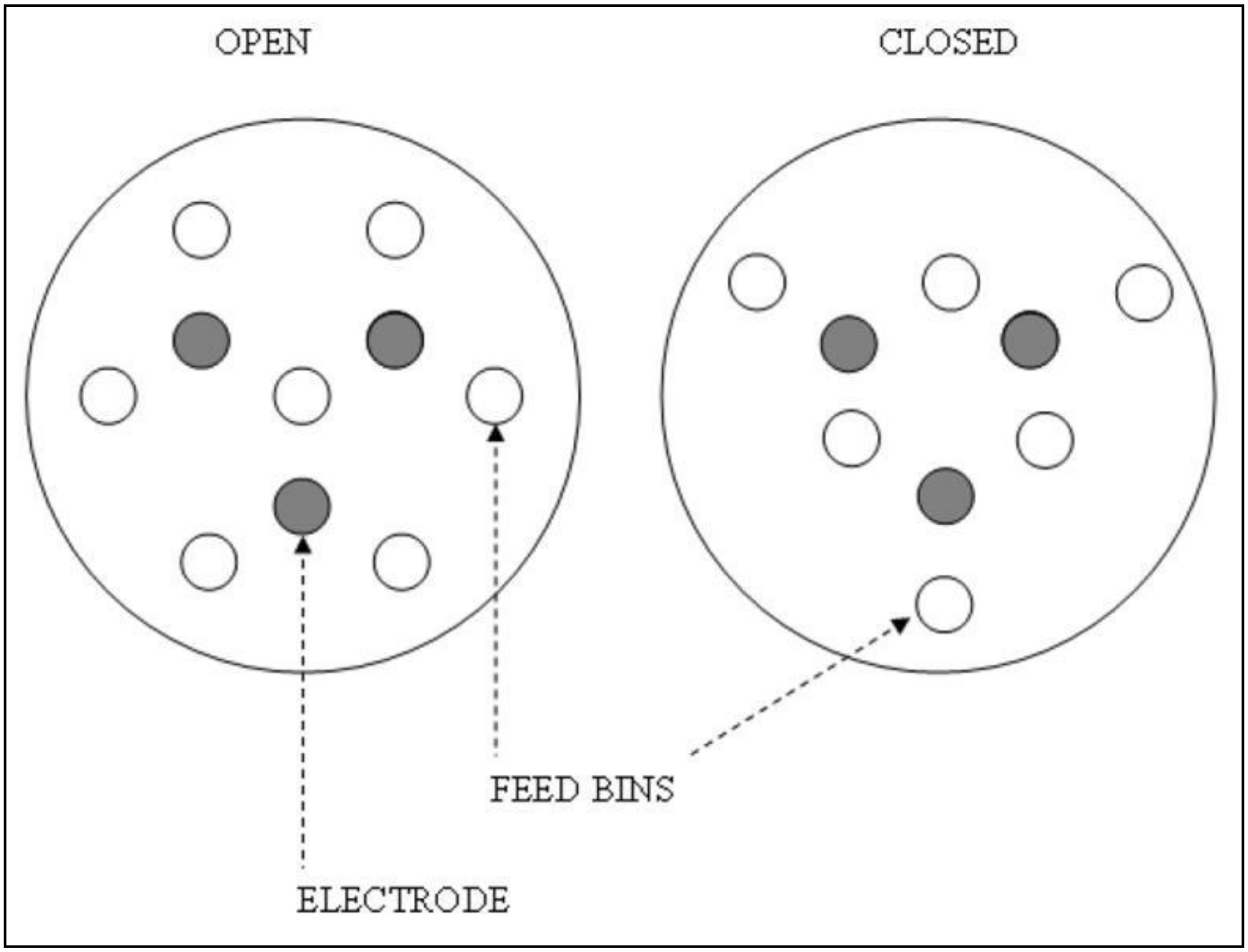

**Figure 2-8: Open and closed submerged arc furnace configuration (Dall, 2008)**

Uneven furnace charging (e.g. loading of certain feed chutes, while other are not fed) may result in lateral mechanical stresses on the electrodes, which could result in electrode break(s). The furnace feed chutes should therefore be charged in an even sequential manner, as failure to do so will result in uneven material distribution inside the furnace (Beukes, 2011; Roos, 2010).

### 2.3.3. Tapping the furnace

Apart from process gases, molten slag and metal are produced by the smelting process. However, these materials cannot build up infinitely in the furnace and the furnace therefore has to be drained, or tapped as the process is commonly referred to. Tapping of a furnace may either occur at fixed time intervals, or when a fixed quantity of electricity consumption has been reached (Riekkola-Vanhanen, 1999).

Slag and metal are removed through a tap hole – a specially designed refractory inset in the furnace side wall with a circular opening. The tap hole is usually opened by means of pneumatic or hydraulic drilling, and/or oxygen lancing (indicated in Figure 2-9), where after the furnace products are channelled from the tap hole to the tapping vessels as indicated in Figure 2-10 (Riekkola-Vanhanen, 1999).

**Figure 2-9: Oxygen lancing prior to tapping of the furnace (Oriel Resources Ltd, 2007)**

**Figure 2-10: Metal tap at SA Chrome (Bateman Engineering, 2011)**

A regular tapping cycle is imperative to the metallurgical health of the furnace. Irregularities in the tapping cycle may result in a number of issues with the operation of the furnace, such as carbon deficiency that may impact negatively on electrode management (Beukes, 2011; Roos, 2010).

### 2.3.4. Power input and specific energy consumption

Ferrochrome production is a very energy intensive process, making energy perhaps the largest cost factor (Riekkola-Vanhanen, 1999; Hearn & Roos, 2004). Electricity and fossil fuels are the main energy sources in modern ferrochrome production processes. The consumption of energy is affected by a number of factors, including the raw material qualities, pre-treatment before smelting, as well as the effective utilisation of reaction energies and latent heat from the processes (Riekkola-Vanhanen, 1999).

The power input of a furnace is the amount of electrical power received from the furnace transformer(s) and directly impacts on the production volume of the furnace (Beukes, 2011; Dall, 2008). Three phase submerged arc furnaces generally have a transformer capacity ranging from 10 to 50 MVA, but furnace capacities of up to 105 MVA are also found (Ringdalen, 1999). The power output of the furnace transformer is controlled by a tap changer. Burden conductivity – a function of the electrode lengths, metallurgical control, tapping and charging of the furnace – can limit the power input to the furnace (Beukes, 2011; Dall, 2008).

The specific energy consumption (MWh/ton) of a ferrochrome production furnace can be defined as the amount of energy consumed by the furnace per ton ferrochrome produced (Beukes, 2011; Dall, 2008). Reaction energy of 2.1 to 2.3 MWh is associated with the reduction of one ton of chrome ore – however, the electrical energy consumed by the furnace will be much higher, depending on the chromite composition, applied furnace technology and general operational conditions of the furnace (Riekkola-Vanhanen, 1999). Practically, specific energy consumptions for ferrochrome furnaces in South Africa range from approximately 2.4 to 4.0 MWh/ton ferrochrome (Beukes, 2011).

### 2.3.5. Electrode management

The most vital part of an electric reduction furnace is considered to be the electrode system. In contrast to the pre-baked electrode alternatives available in the industry, Soderberg electrodes are baked during furnace operation. Electrode paste is added to a cylindrical steel electrode casing, which is then baked as the electrode is slipped through the contact shoes (Innvær & Tveit, 1983). Figure 2-11 shows the electrode system of an open configuration submerged arc furnace (Bateman Engineering, 2011).

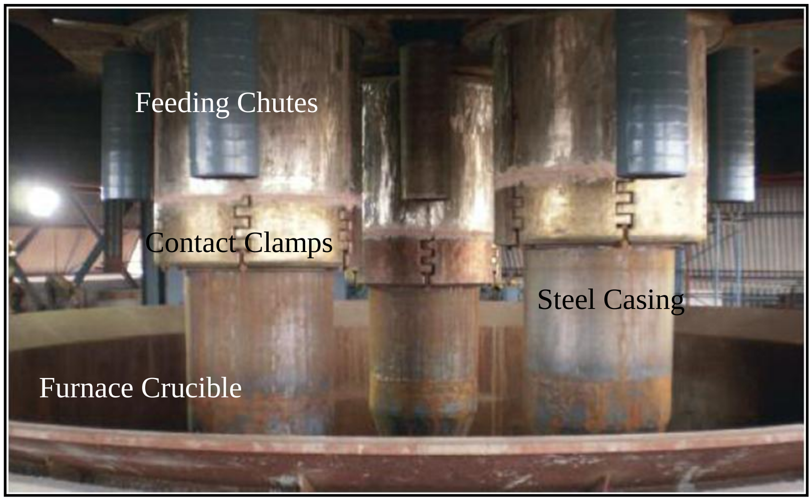

**Figure 2-11: Electrode system of an open configuration submerged arc furnace (Bateman Engineering, 2011)**

Good electrode performance is dependent on the electrode paste quality, reliability of the electrode equipment and correct electrode operation (Innvær & Tveit, 1983). However, the electrodes are periodically exposed to severe conditions inside the furnace including high currents, high temperatures, thermal stresses (due to temperature variations), irregular slipping, as well as chemical and mechanical wear. Inability to withstand the aforementioned conditions will cause problems with the electrodes that potentially may result in an electrode break – affecting the whole furnace operation (Innvær, 1989).

## 2.4. Aspects of electrode management

The electrode system is responsible for the conducting of electrical energy from the furnace transformer to the smelting zone inside the furnace (Asphaug & Innvær, 1997). Two general types of electrodes are used in industrial metal smelting applications, pre-baked electrodes and continuous self-baking electrodes (Soderberg electrodes).

Pre-baked electrodes are mainly used in smelting applications that require particularly high product purity and where the ash content of an amorphous carbon electrode will be too high. Pre-baked electrodes are produced by stamping, pressing or extruding a mixture of calcined anthracite or coke and tar pitch into moulds, which is then subsequently baked at temperatures form 1000 to 3000°C, depending on the application (GrafTech International, 2011). Continuous self-baking electrodes (Soderberg electrodes) are frequented to pre-baked electrodes due to the additional costs involved in the production of pre-baked electrodes (Habashi & Toromanoff, 1989). Utilisation of pre-baked electrodes also implies regular furnace shutdowns to attach additional lengths of pre-baked electrodes, to the ones currently in operation. Continuous self-baking electrodes systems do not require such shutdowns, since electrode extensions are made in operation (Beukes, 2011).

Continuous self-baking electrodes consist of a cylindrical steel casing extending from a platform located above the furnace, down into the furnace interior. The electrode casing serves as a mould for the electrode and is filled with a carbon electrode paste (consisting of tar pitch binder mixed with calcined anthracite or coke). Lower down in the casing, the electrode paste is baked into a solid carbon electrode by heat from the furnace and electrical current passing through the casing (Habashi & Toromanoff, 1989). Figure 2-12 shows a cylindrical steel electrode casing as viewed from the top of the electrode column.

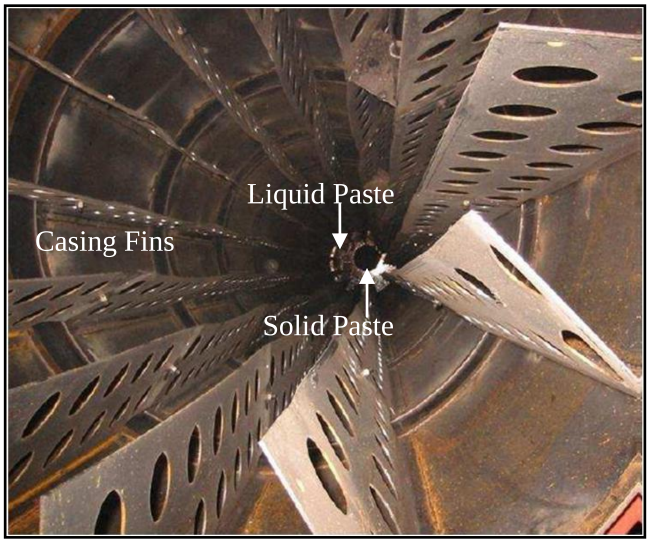

**Figure 2-12:** **Cylindrical steel Soderberg electrode casing (Nelson & Prins, 2004)**

The electrode paste added to the top of the electrode casing starts to soften, and fills out the electrode casing at approximately 50 to 100°C (Arnesen *et al.*, 1979). At a temperature of approximately 400 to 500°C (commonly referred to as the baking zone), the electrode paste is baked into a solid carbon electrode with adequate mechanical strength (Innvær *et al.*, 1985).

The mechanical strength and electrical conductivity of the electrode increase as the baking process progresses. Initially, during the softening of the electrode paste and the early stages of the baking process, electrical energy is conducted by the steel electrode casing and the casing fins. At approximately 900°C the electrode reaches a high mechanical strength, and the almost isolating carbon paste is baked into a carbon electrode able to conduct the full electrical current (Asphaug & Innvær, 1997). Figure 2-13 shows a schematic representation of the electrode column. Relevant electrode temperatures are also indicated.

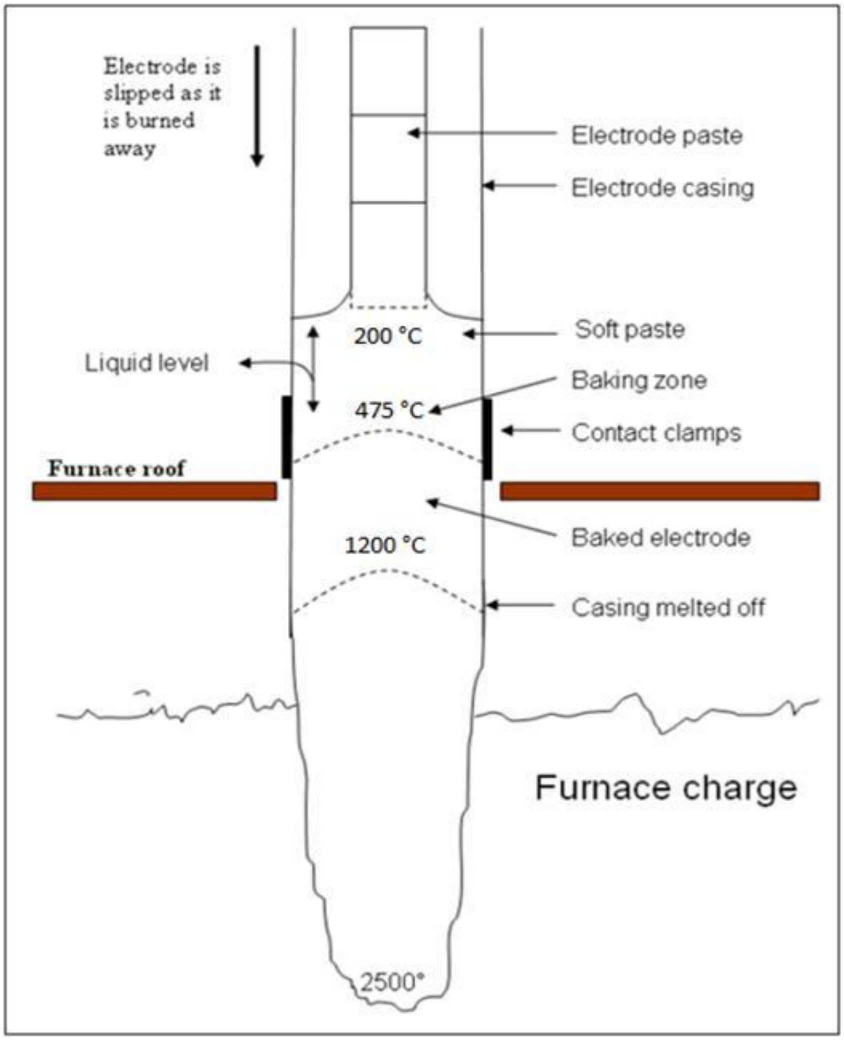

**Figure 2-13:** **Schematic representation of the Soderberg electrode (Dall, 2008)**

### 2.4.1. Qualities of a good electrode

Good electrical conductivity, high mechanical strength and thermal stress resistance are the most important properties of a baked Soderberg electrode. The highest possible degree of electrical conductivity is required of a baked electrode. Immediate conductivity after baking is dependent on the compactness of the electrode (electrical conductivity is reduced by porosity) and the degree of graphitisation the anthracite has obtained during the calcination process. The initial conductivity of the electrode is improved as the temperature increases further down in the electrode, due to the fact that additional graphitisation occurs (Asphaug & Innvær, 1997).

Mechanical strength is of extreme importance in order to avoid and prevent electrode breaks (Asphaug & Innvær, 1997). The mechanical strength of an electrode is temperature dependent (Fidje *et al.*, 1986) and is increased by baking of the electrode (Asphaug & Innvær, 1997). Initially, during the baking process, thermal stresses accumulate inside the electrode, but are largely released further on by structural changes that take place as the baking of the electrode completes at higher temperatures in the lower part of the electrode (Innvær *et al.*, 1985).

The mechanical strength of an electrode is also affected by the elasticity of the electrode. Low binder content along with low calcined anthracite or coke fines content improves the elasticity of the electrode – reducing its mechanical strength. A low elasticity, however, makes the electrode more vulnerable to hard breaks resulting from thermal stresses. The electrode paste quality is therefore critical in order to produce an electrode of high mechanical strength with adequate thermal stress resistance (Asphaug & Innvær, 1997).

### 2.4.2. Electrode breaks

Normally problems with the electrode system of a furnace can be avoided by favourable operating conditions and using suitable electrode equipment and high quality electrode materials. An electrode breakage is the most serious problem that can be encountered with regard to electrode management (Arnesen *et al.*, 1979). Furnace operation may be impacted in a number of ways depending on the nature and location of the electrode break. Electrode breaks can cause abnormal furnace charging, drastically reduced power input, altered tapping cycles and loss of production until the broken electrode is restored (Ord *et al.*, 1995).

Electrode breaks can generally be classified into two main categories: Hard breaks and soft breaks (also referred to as green breaks). A soft breakage is the more serious of the two types, and even though they rarely occur, the effects are usually disastrous. Soft breaks occur when the baking zone (Figure 2-13) moves below the contact clamps. The steel casing of the electrode is unable to conduct the high amount of electrical current and subsequently is partially burned away. This may cause the lower part of the electrode to slip into the furnace – allowing volatiles and electrode paste to catch fire (Innvær, 1992).

This may even result in an explosion, due to the operating temperatures of the furnace and the volatile content of the paste (Beukes, 2011).

Soft electrode breaks can be prevented by a thorough knowledge of the relationship between the slipping rate and the electrode current – the main parameters used to determine the position of the baking zone (Asphaug & Innvær, 1997). Also, the temperature profile in the electrode paste, up to the baking zone, as well as knowledge of the position of the baking zone is critical in avoiding green breaks (Beukes, 2011). A lot of controversy, however, exists about the exact location of the baking zone. Nelson and Prins (2004), and McDougall *et al.* (2004) locate the baking isotherm at 450°C, Innvær*et al.* (1985) and Ord *et al.* (1995) estimate the baking zone to be between 400 and 500°C, and Olsen *et al.* (1972) locate the baking zone at approximately 500°C. Other factors of influence include the slipping increments (a high slipping rate may cause the baking zone to get too low – increasing the risk of a soft break (Asphaug & Innvær, 1997)), electrode casing design and welding, surrounding heat conditions and the softening of the electrode paste (Innvær, 1989).

One of the most common electrode problems encountered in the operation of electric smelting furnaces is hard breakages (Innvær, 1989). Hard breakages occur when a baked part of the electrode breaks loose (Innvær & Olsen, 1980). Thermal stresses on the electrodes are inevitable during unstable furnace operation and shut downs – which can frequently result in a hard break. Effective electrode management procedures, as well as good quality control of electrode paste materials are extremely important in the prevention of hard breaks (Innvær, 1989). Figure 2-14 shows four different electrode hard break surfaces, as well as typical causes. Figure 2-15 shows a hard electrode break during furnace operation (Nelson & Prins, 2004).

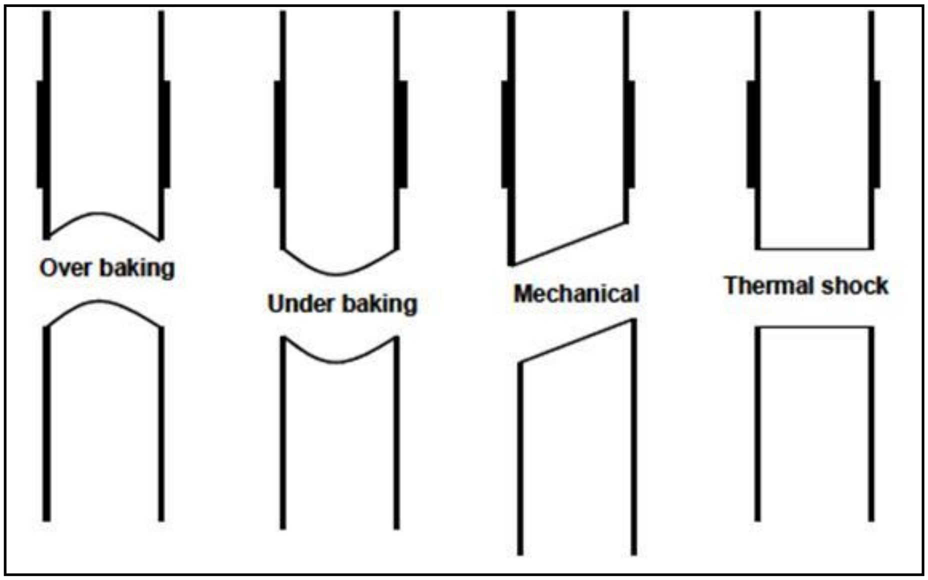

**Figure 2-14:** **Schematic representation of four different hard electrode break surfaces and typical causes of hard electrode breaks (Nelson & Prins, 2004)**

**Figure 2-15:** **A hard electrode break during furnace operation (Nelson & Prins, 2004)**

## 2.5. Electrode paste production

Electrode paste consists of two basic materials – calcined anthracite or coke, mixed with tar pitch binder. Calcined anthracite is most commonly used for the production of Soderberg electrode paste for the ferrochromium industry in South Africa; hence the use of coke is not further discussed. Geologically, anthracite is a coal with a low volatile content. The anthracite is calcined in order to drive off the volatiles and improve the initial conductivity of the electrode paste during the *in situ* formation of the Soderberg electrode (Asphaug & Innvær, 1997). During the calcination process the anthracite is calcined in a shaft furnace at temperatures ranging from about 1200 to 3000°C (Innvær, 1989).

After calcination the anthracite is crushed and screened to an adequate particle size distribution ranging from less than 1mm to a maximum particle size of approximately 15mm. After crushing and screening, the calcined anthracite is mixed with the tar pitch binder and cast into moulds. Paste cylinders (Figure 2-16), with diameters ranging from 0.4m to 1m, are the most commonly produced product; however, briquettes and blocks (Figure 2-17) are also produced (Asphaug & Innvær, 1997).

**Figure 2-16: Electrode paste cylinders (Dall, 2008)**

**Figure 2-17: Electrode paste briquettes (Dall, 2008)**

The paste plasticity is the most important variable regarding the quality of the electrode paste and is defined as the percentage by which the diameter of a small paste cylinder increases when heated under standardised conditions.  Electrode paste with high binder content (30-40%) has a high plasticity that makes the paste flow easily.  On the other hand, a low binder content (15-25%) results in a dry paste with low plasticity (Asphaug & Innvær, 1997).  Figure 2-18 shows the paste plasticity indicated on a paste cylinder.

**Figure 2-18: Paste plasticity indicated on the electrode paste cylinder (Dall, 2008)**

## 2.6. Electrode paste quality

The manipulation of a number of interrelated variables is involved with the manufacturing of Soderberg electrodes (Stanko, 1972). Continuous monitoring of the quality of the electrode paste and the raw materials are crucial in order to produce high quality electrodes. The electrical conductivity of the calcined anthracite can be measured in the laboratory by means of standardised test methods. Slump tests are commonly used in order to determine the plasticity of the electrode paste; however, in development work more sophisticated viscometers will be used. In addition to everyday quality control procedures, the electrical, mechanical and thermal properties of special test electrodes may also be determined (Asphaug & Innvær, 1997).

Similar electrode paste properties seem to be measured by paste producers; however, the methods differ. In addition to measuring electrical conductivity and paste plasticity, other properties such as breaking strength, bending strength, thermal shock absorbance, resistivity, elasticity and liquefying temperature can also be measured (Stanko, 1972; Dall, 2008). In general, however, open access literature regarding tests on electrode paste and raw materials is very limited.

## 2.7. Applications of thermomechanical analysis

Thermomechanical analysis (TMA) is a relatively simple and rapid method by which sample displacement (growth, shrinkage, movement, etc.) is measured as a function of temperature, time and applied force. Thermomechanical analysis is traditionally used for applications such as characterising linear expansion, glass transitions and softening points of materials by applying a constant force to a material sample while varying temperature (Linseis Thermal Systems, 2011).

Figure 2-19 shows a simple schematic representation of a typical TMA instrument. The sample is placed on a support structure inside the furnace. Resting on the sample is a probe that senses changes in the sample length, which is measured by a linear variable displacement transducer (LVDT). The probe and sample support are made from material with a low, reproducible and accurately known thermal expansion coefficient such as quartz or alumina, which also has a low thermal conductivity. The sample temperature is monitored by placing a thermocouple close to the sample. In order to prevent sample oxidation and to assist sample heat transfer, provisions are usually made to establish a gas atmosphere inside the apparatus (Anasys, 2011).

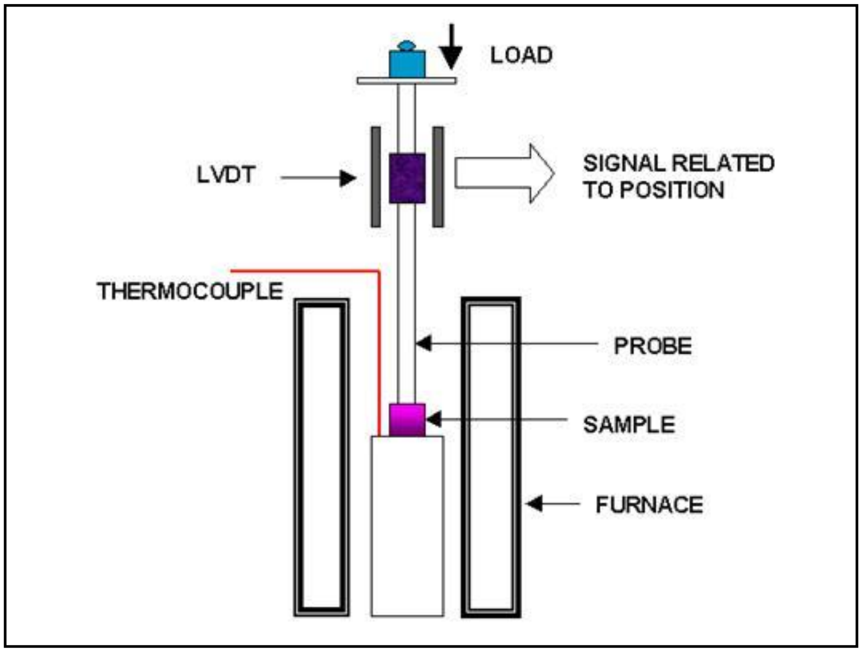

**Figure 2-19: Simple schematic representation of a typical TMA instrument (Anasys, 2011)**

The applications of thermomechanical analysis vary greatly and are by no means restricted to one area of research. Numerous studies that used thermomechanical analysis as part of an experimental procedure are published in open literature – to mention just a few: Ctvrtnickova*et al.* (2010) found TMA to be a suitable technique for observing the physical behaviours of coals that are exposed to high temperatures, fusion, sintering or smelting. Barr and Lewis (1982) used thermomechanical analysis to measure the glass transition of tar pitches. However, as far as the author could establish, there is very little – if any – information available in the open literature with regard to Soderberg electrodes, electrode paste and thermomechanical analysis.

The application of thermomechanical analysis, and the apparatus concerned therewith will be extensively discussed in Chapter 3.

## 2.8. Gaps in literature

Available literature with regard to the ferroalloys industry, smelting technologies and in particular electrode management and electrode paste production is very limited (especially when compared to the amounts of open access literature in research fields such as coal). The literature that is available is relatively old (dating mostly from 1950-1980). This is mainly due to the intellectual property sensitive nature of the ferroalloys and electrode paste industry.

During the literature survey, a number of gaps have been identified in the available literature with regard to the ferroalloys industry. Firstly, very little is published regarding paste production processes and laboratory tests done to determine properties regarding paste quality. During this study, a relatively new technique (TMA) will be applied to test its relevance in addressing some of the gaps in literature with regard to testing of paste properties.

Another gap identified in literature is the seemingly inconsistent statements with regard to the exact temperature of the baking isotherm in Soderberg electrodes. As was discussed in Par. 2.4.2, the location of the baking isotherm is suggested to be in the range 400 to 500°C. This is a too large temperature range, especially if practical and effective electrode management is considered. The exact location of the baking zone is critical in order to implement effective electrode management procedures. Operation without knowledge of the baking isotherm is dangerous as a soft break may result, causing operational hazards such as paste ignition and possibly explosions inside the furnace (Par.2.4.2).

More particularly regarding the topic of this study, very little literature is available in the public domain on the thermomechanical (dimensional) behaviour of electrode paste raw materials (consisting of calcined anthracite and tar pitch binder). Applications of thermomechanical analysis vary widely and are encountered in a large number of study fields. However, no proof of studies similar to the one undertaken in this project could be found in open access literature. This project would therefore address a very specific gap identified in the literature concerning Soderberg electrode paste properties. Information will be generated with particular regard to quality control on electrode paste raw materials and other process aspects such as the baking isotherm and thermal stress properties of Soderberg electrodes.

# Chapter 3: Experimental procedure

## 3.1. Materials

### 3.1.1. Samples received

Soderberg electrode paste raw materials consist of calcined anthracite mixed with a tar pitch binder (Par. 2.5). Since the focus of this study was on electrode paste raw materials, calcined anthracites and tar pitches were the main materials of experimental focus. However, uncalcined anthracite was also investigated, since further insight into the properties of the calcined anthracite could be obtained by also investigation the matching uncalcined materials. The above-mentioned electrode paste is baked *in situ* in a submerged arc furnace during general operation to form electrodes, which gradually change from baked carbon (just below the contact shoe clamps) to graphite (at the tip of the electrode in the arc zone) (Par. 2.4). Since electrode graphite represents the final stage of electrode transformation in a Soderberg electrode system, it was decided to also include pre-baked electrode graphite as a material to be investigated in this study.

Anthracite and tar pitch samples were obtained from Xstrata Chartech (Xstrata Alloys, 2011), one of the largest electrode paste producers in South Africa, while pre-baked electrode graphite samples were obtained from GrafTech (GrafTech, 2011), the only local manufacturer of pre-baked electrodes. Although the tar pitch samples were received from Xstrata Chartech, they originated from ArcelorMittal (ArcelorMittal, 2011), which is currently the only commercial supplier of tar pitch for the manufacturing of electrode paste in South Africa.

Two different tar pitch samples were obtained, low softening point (55-59°C melting point, according to supplier specifications) and high softening point (68-73°C melting point, according to supplier specifications). Already calcined anthracite samples could not be obtained from Chartech due to intellectual property limitations, hence uncalcined samples (Figure 3-1) were obtained that originated from Zululand Anthracite Colliery (Thomaz, 2006) and Tendele Coal Mining (Ikaneng, 2010). These anthracites were calcined as part of the project, which is discussed in Par. 3.3.1.2.

**Figure 3-1:** **Anthracite samples – Zululand chips (left), Zululand duff (middle), Tendele duff (right)**

## 3.1.2. Sample analysis and characterization

### 3.1.2.1. Anthracite characterisation

All characterisation analyses of the anthracite samples were conducted by Advanced Coal Technology analysis laboratory (www.advancedcoaltech.com). In Table 3-1 a summary is given of the standard methods used for characterisation of the anthracite samples. Details of these methods are provided in Appendix A.

**Table 3-1:** **Methods used for anthracite characterization**

| Method | | Ref |
|---|---|---|
| **Proximate analysis** | Moisture content (%) | SANS 5925:2007 |
| | Ash content (%) | SANS 131:2011 |
| | Volatile matter content (%) | SANS 50:2011 |
| | Fixed carbon | By difference |
| Total sulphur via IR spectroscopy (%) | | SANS 19579:2007 |
| Crucible swelling number | | SANS 501:2008 |
| Ultimate analysis | | SANS 12902:2007 |

### 3.1.2.2. Tar pitch analysis

Only melting point determinations were conducted on the tar pitch samples. Another study currently being conducted at the NWU (PhD study of L Shoko) is investigating the linkages between the chemical composition of coal tar pitches and their thermomechanical properties. It was therefore decided not to conduct chemical characterisation of the pitches, to avoid duplication of research results.

The melting points of the two obtained tar pitch samples were determined using a Fisher Johns melting point apparatus (Figure 3-2). A small piece (< 1mg) of tar pitch was placed between two glass plates and heated at a rate of approximately 1°C/min (< 10 on the heating rate adjustment of the apparatus – Figure 3-2). The temperature was indicated by a thermometer connected to the heating platform and the sample was studied through a magnifying glass. A temperature interval was then recorded from where the sample initially seems to soften until the sample is completely softened. These values are to a certain degree dependent on the observational behaviour of the person conducting the test, hence relatively large experimental errors should be assumed.

**Figure 3-2:** **Fisher Johns melting point apparatus**

## 3.2. Experimental apparatus

### 3.2.1. Elite THS 15 tube furnace

An Elite TSH15 single zone horizontal tube furnace (Figure 3-3) was used for the heat treatment procedures, as required for the sample preparations of the tar pitches (Par. 3.3.1.1) and the anthracites (Par.3.3.1.2). This furnace is able to operate up to 1500°C. Air tight heat shields were installed on both ends of the ceramic tube of the furnace. These heat shields housed gas in- and outlets, which enabled the gaseous atmosphere inside the heated chamber to be controlled. The furnace temperature was controlled by a fully programmable electronic unit (Elite Furnaces, 2011).

**Figure 3-3: Elite TSH15 tube furnace**

### 3.2.2. Lloyd LRX Plus material testing machine

A Lloyd LRX Plus material testing machine (Figure 3-4) was used to press the sample pellets (Par.3.3.1.) as required in the sample preparation procedure for TMA experiments. The Lloyd LRX Plus instrument is a single column bench mounted material testing machine ideal for material strength testing applications of up to 5kN (Lloyd Instruments, 2011). Data analysis was done by means of the NEXYGENPlus material test and data analysis software.

**Figure 3-4:** **Lloyd LRX material testing machine**

### 3.2.3. Exstar SS6300 TMA

An Exstar SS6300 thermomechanical analyser (TMA) (Figure 3-5) was used to monitor dimensional changes of the tar pitch, anthracite and electrode graphite samples during heating and cooling. This is a versatile thermo-physical measurement device that can be used to measure expansion coefficient, glass transition, softening, swelling, creep, stress strain characteristics, stress relaxation, dynamic visco-elasticity, etc. The TMA is able to perform a wide variety of measurement modes at temperatures ranging from -150°C to 1500°C with a measurement range of ± 5000µm in displacement with a measurement sensitivity of 0.01µm. Sample length measurement is an automated function and maximum sample dimensions are 10mm diameter and 25mm in height. The sample cylinder in which samples are placed is made of alumina and measurement data is therefore adjusted according to the expansion coefficient of alumina (SII Nano Technology, 2011).

**Figure 3-5: Exstar SS6300 TMA**

The TMA measures the dimensional changes of the sample by means of a small probe, which exerted a constant pressure of 50mN on the top of the sample cylinder. Dimensional changes are then recorded as the probe is moved up and down due to expansion and shrinkage of the sample and can be expressed as a function of temperature. The TMA furnace unit, probe and thermocouple are shown in Figures 3-6 and 3-7.

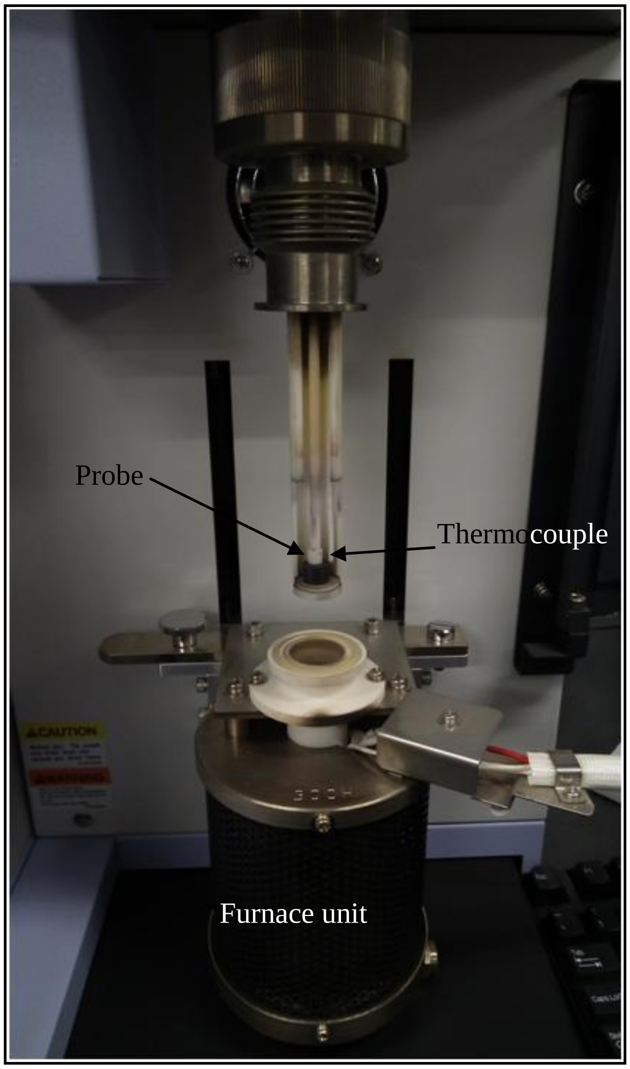

**Figure 3-6:** **TMA probe and furnace unit**

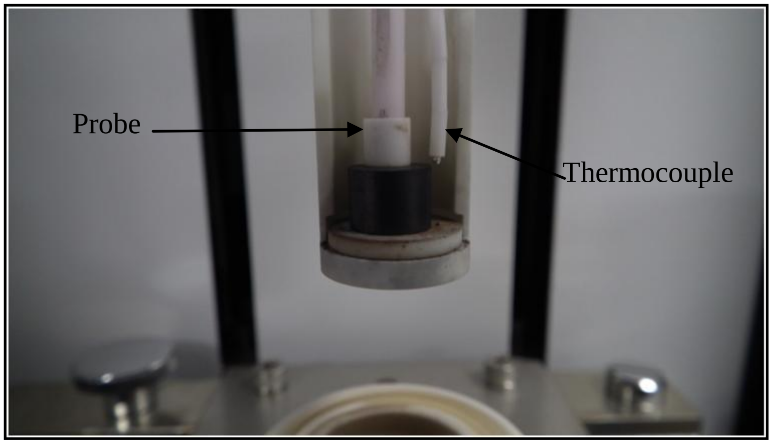

**Figure 3-7:** **TMA probe and thermocouple**

## 3.3. Experimental procedure

### 3.3.1. Sample preparation

As was discussed in Par.3.2.3, the required sample dimensions for the TMA is 10mm diameter, and therefore each material investigated needed to be processed into sample cylinders of the specified dimensions. The height of the sample cylinders was not that critical, as all results were indicated as a percentage deviation from the initial dimensions. The height of the sample pellets could therefore differ; however, a cylinder height of approximately 8-10mm was aimed for. Figure 3-8 shows two typical sample pellets.

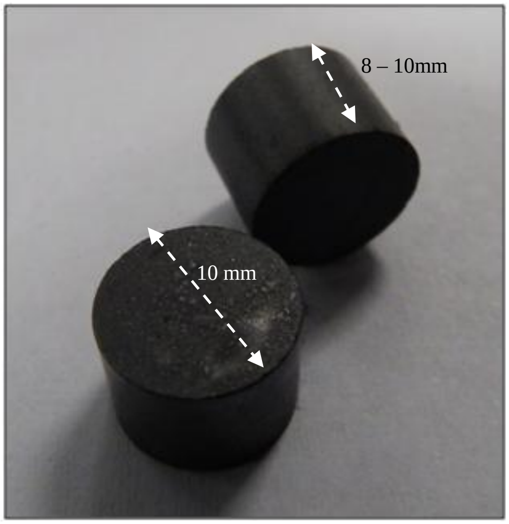

**Figure 3-8: Sample pellets**

#### 3.3.1.1. Tar pitch sample preparation

The tar pitch sample preparation consisted of two steps:

1. Heat treatment of the tar pitch
2. Sample pellet production for TMA testing

Tar pitches have relatively low melting points of 50-80°C, depending on its chemical composition. After melting, a pitch remains a viscous liquid until carbonisation takes place. In order to prevent the tar pitch samples from softening in the TMA (possibly causing damage to the instrument), where the dimensional behaviours of materials were investigated at temperatures of up to 1300°C, the tar pitches were heat treated at a variety of temperatures prior to pellet production. The lowest heat treatment temperature that produced a pellet that did not soften in the TMA was determined by heating the different tar pitch batches form 450 to 500°C (in steps of 25°C) under inert atmosphere for a fixed time period.

Boat crucibles were filled up approximately two thirds with tar pitch (Figure 3-9) and then heated to the desired heat treatment temperature for one hour and kept at that temperature for another two hours. This was done in an Elite TSH15 Tube Furnace (See Par 3.2.1) with a nitrogen flow rate of 1.2 l/min (ambient conditions). After the heating programme was completed, the furnace was switched off and allowed to cool under an inert atmosphere. The material was then subsequently pulverised and sample pellets were pressed from each batch. Pellets were pressed by means of a Lloyd LRX material testing machine (Par 3.2.2), at a pressure of 2kN for 20 seconds in Specac 10mm cylindrical die (shown in Figure 3-10).

**Figure 3-9: Boat crucible used for the heat treatment of the tar pitch**

**Figure 3-10:** **Lloyd LRX material testing machine (left) and cylindrical die (middle) used for pressing pellets, as shown (right)**

Thermomechanical analyses, to determine the lowest temperature at which softening of the past did not occur, were then attempted on the sample pellets under a nitrogen atmosphere (flow rate of 1.7 l/min) to avoid oxidation. For this purpose, a sample pellet from each heat treatment batch was heated and analysed up to 1000°C in the TMA.

#### 3.3.1.2. Anthracite sample preparation

The sample preparation of the anthracite samples consisted of two steps:

1. Calcining of the anthracite
2. Sample pellet production for TMA testing (uncalcined samples and calcined samples)

The three obtained anthracite samples were calcined at 1200, 1300, and 1400°C in a similar manner to the heat treatment of the tar pitch samples. Boat crucibles (Figure 3-9) were filled with approximately 25g of anthracite, which were then calcined in the Elite TSH15 Tube Furnace (Par.3.2.1) at the above-mentioned temperatures. The furnace was heated to the specific temperature in an hour and then kept at that temperature for another two hours. Calcining was done under an inert atmosphere obtained by a nitrogen flow rate of 1.2 l/min through the furnace. After the calcination process, the anthracite was allowed to completely cool under a nitrogen atmosphere inside the furnace in order to prevent oxidation.

Calcined and uncalcined anthracite were then pulverised (using a Siebtechnik vibrational pulverizer) to a fine powder (approximately 75% < -75 µm) in order to press the required 10mm diameter sample pellets. 0.8g of the pulverised material was poured into the cylindrical die (Figure 3-10) and a sample pellet of the anthracite pressed by means of the Lloyd LRX material testing machine (Par. 3.2.2). The pellet was pressed at maximum pressure (5kN) for 60 seconds. This unfortunately failed to produce a pellet with sufficient mechanical strength as the calcined and uncalcined anthracite had very little binding ability. Two droplets of milliQ water (resistivity 18.2 MΩ cm) were then added to the calcined and uncalcined anthracite as a binder, where after and sample pellets for both calcined and uncalcined anthracite could be pressed successfully at 4.5kN for 60 seconds.

#### 3.3.1.3. Graphite sample preparation

Pre-baked electrode graphite sample cylinders of roughly 20cm diameter were obtained from GrafTech. The cylinders were firstly sliced into discs that were approximately 10mm in thickness, using a band saw. The discs were then sliced in half as indicated in Figure 3-11.

**Figure 3-11: Graphite sample cylinders, being cut with a band saw**

The graphite semi-circles were then sliced into long rectangular blocks of fixed width of approximately 15mm by means of a fixed circular saw (indicated in Figure 3-12).

**Figure 3-12: Rectangular graphite blocks**

Graphite sample cylinders with a 9mm diameter were then drilled from the rectangular blocks by means of a core drill. The fixed thickness of the rectangular blocks ensured each sample cylinder had roughly the same height (~10mm). Figure 3-13 shows this process as well as the final sample cylinders.

**Figure 3-13: Core drill and final graphite sample cylinders**

### 3.3.2. Thermomechanical analysis

The dimensional changes of the tar pitch, anthracite and electrode graphite sample cylinders were monitored with an Exstar SS6300 TMA (Par 3.2) during three heating and cooling cycles under an inert atmosphere. During a heating cycle, the sample cylinder was heated to 1300°C at a heating rate of 10°C/min. The sample was then allowed to cool to approximately 100°C before the next heating cycle commenced. A constant nitrogen flow rate of 1.7 l/min (ambient conditions) was used through the TMA instrument during heating and cooling cycles to prevent oxidation, which could impact of the dimensional behaviours. A nitrogen rotameter (Krohne, maximum pressure 15 bar, maximum temperature 100°C, 1.0mm valve opening) was used to control the nitrogen flow rate.

# Chapter 4: Results and discussion

In this chapter, the characteristics of the materials utilised are briefly discussed, followed by the results related to the experimental development of the TMA investigation. The interpretation of the data is also discussed within context of the ferrochromium industry in order to explore possible practical applications with regard to electrode management.

## 4.1. Materials characterisation

### 4.1.1. Anthracite analysis

The results obtained from the various material characterisation analyses conducted on the anthracite samples are summarised below.

**Table 4-1: Proximate analysis of the anthracite samples**

| Sample identification | Zululand chips | Tendele duff | Zululand duff |
|---|---|---|---|
| % Inherent moisture content (air dried) | 2.2 | 3.2 | 1.3 |
| % Ash content (air dried) | 8.1 | 18.6 | 16.2 |
| % Volatile matter (air dried) | 4.9 | 9.5 | 5.2 |
| % Fixed carbon (by difference) | 84.8 | 68.7 | 77.3 |

From the results in Table 4-1, the Zululand chips could be classified as a low ash coal, while the Tendele and Zululand duffs could both be described as medium to high ash coals. When comparing these coals with similar coals from the KwaZulu-Natal region (see Table 4-2), it can be seen that the results obtained from the proximate analyses compare well to other South African anthracites. With an increase in ash, the mineral matter content of the coal increases. This can cause the internal structure of the coal to be weaker than that of pure graphitised anthracite (Spears, 2000). The difference in ash contents of the Zululand samples can be attributed to the duff sample coming from a different float beneficiation fraction than the chips. Inherent moisture is considered to be an indication of the porosity of the coal samples. Increased porosity might be an indication of a coal that will bind better (Takarada *et al.*, 1985).

**Table 4-2: KwaZulu-Natal Anthracites**

| Colliery | Product | Air dry basis | | | |
|---|---|---|---|---|---|
| | | Moisture % | Ash % | Volatile matter % | Fixed carbon % (by difference) |
| CBR Mining | Small nut | 2.5 | 19.0 | 8.3 | 70.2 |
| | Duff | 2.3 | 22.5 | 8.4 | 66.8 |
| Springlake | Small nut | 1.7 | 12.2 | 10.6 | 75.5 |
| | Duff | 1.7 | 14.2 | 11.7 | 72.4 |

Ultimate analysis were also performed on the obtained anthracite samples. The results are shown in Table 4-3.

**Table 4-3: Ultimate analysis of the anthracite samples**

| Sample identification | Zululand chips | Tendele duff | Zululand duff |
|---|---|---|---|
| % Total sulphur (air dried) | 1.13 | 0.69 | 1.2 |
| % Carbon content (air dried) | 83.16 | 71.62 | 75.03 |
| % Hydrogen content (air dried) | 2.55 | 3.09 | 2.25 |
| % Nitrogen content (air dried) | 1.91 | 1.62 | 1.53 |
| % Oxygen content (by difference) | 0.95 | 1.18 | 2.49 |

Using the results obtained from the ultimate analyses it was possible to calculate the atomic oxygen/carbon (O/C) ratio in order to verify the rank of the coal. These ratios are given in Table 4-4. Since all the atomic O/C ratios were below 0.4, all the selected coals can be ranked as anthracites (Bunt, 2010). For comparison, atomic O/C ratios for other anthracites form the KwaZulu-Natal area are also given in Table 4-5.

Table 4-4: Atomic O/C ratios for the selected anthracites

| | Atomic O/C |
|---|---|
| **Zululand chips** | 0.011 |
| **Tendele duff** | 0.016 |
| **Zululand duff** | 0.033 |

Table 4-5: Comparative atomic O/C ratios

| Comparison | Atomic O/C |
|---|---|
| **CBR Mining** | 0.038 |
| **Springlake** | 0.017 |

### 4.1.2. Tar pitch analysis

As discussed in Par. 3.1.2.2, only melting point analyses were conducted on the tar pitch samples. The melting points of the LSP and HSP tar pitches were determined to be between 56-59°C and 70-73°C, respectively. This correlated relatively well with the supplier specification of 55-59°C (LSP) and 68-73°C (HSP).

## 4.2. Results from the sample preparation procedure, prior to TMA analysis

As was discussed in Chapter 3, the thermomechanical analyser can only handle sample cylinders of 10mm diameter. The first phase in the development of the experimental procedure was therefore the development of the sample preparation procedure.

### 4.2.1. Tar pitch sample preparation

The tar pitch samples were prepared according to the procedure discussed in Par. 3.3.1.1. As discussed in Par.4.1.2, both tar pitches have relatively low melting points and therefore it was necessary to heat treat the tars prior to TMA analysis in order to prevent damage to the instrument (Par.3.2.3). The practical (industrial) implication of this is that the results obtained from the TMA experimental procedure would only supply information regarding the dimensional changes of the tar pitch from the baking isotherm further down into the electrode.

Both the low softening point (LSP) and high softening point (HSP) pitches were heat treated at 450°C, 475°C and 500°C in an inert atmosphere (Par. 3.3.1.1). In order to determine the suitability for thermomechanical analysis of the heat treated tar pitches, a preliminary sample pellet was produced from each batch and analysed in the TMA. The preliminary thermomechanical analysis procedure included heating the sample up to 1000°C under an inert nitrogen atmosphere and monitoring whether softening took place (Par. 3.3.1.1). A sudden dimensional change of relatively large proportion would indicate pellet softening. The results obtained from the preliminary thermomechanical analysis done on the pellets made of pre-treated LSP tar pitch are indicated in Figure 4-1. In this figure the percentage dimensional change (indicated on the primary y-axis) as a function of temperature (indicated with red line on the secondary y-axis) is shown.

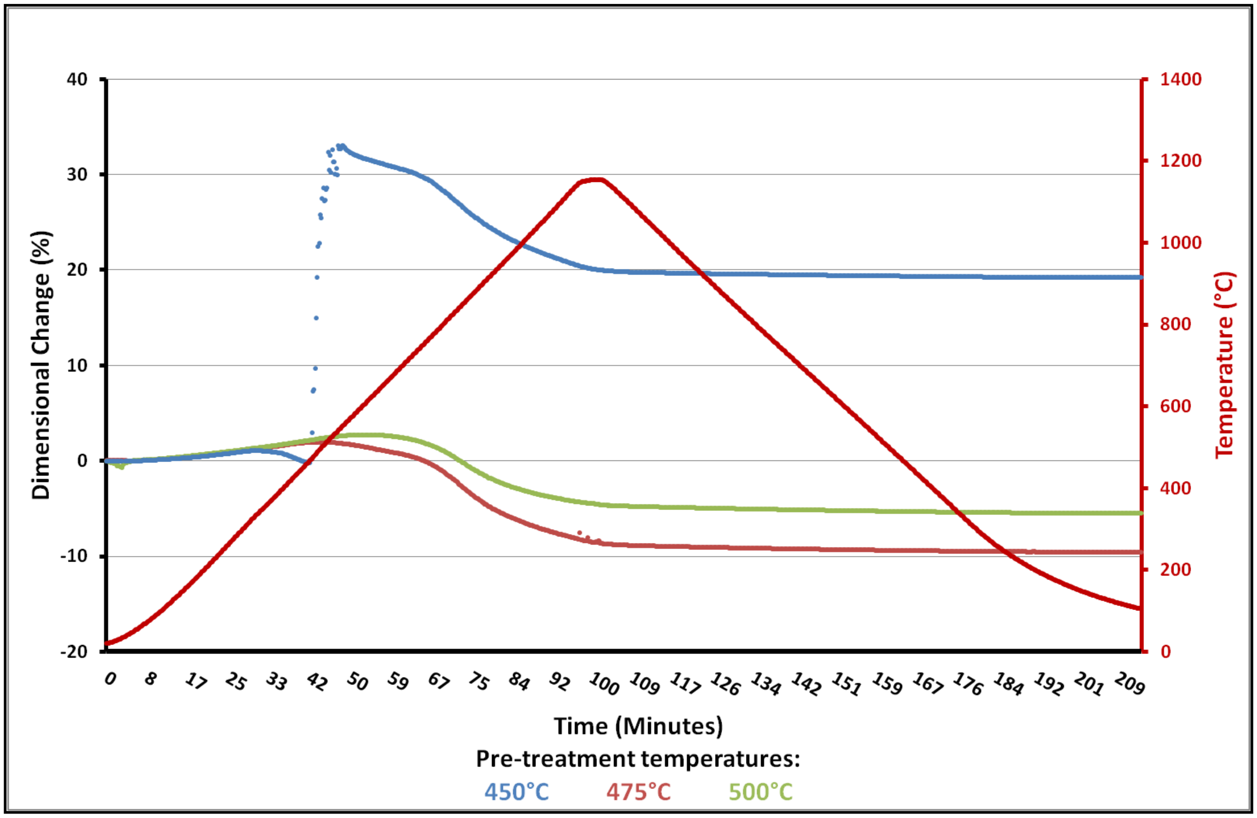

**Figure 4-1:** **Preliminary thermomechanical analysis of pre-treated LSP tar pitch, to determine the minimum pre-treatment temperature resulting in the formation of solid carbonaceous material**

For both the LSP pellets made from tar pitch batches that were pre-treated at 475°C and 500° prior to the TMA analysis, the measured dimensional changes were gradual with no drastic expansions or shrinkages. However, in the case of the pellet made from the LSP tar pitch batch that was heat treated at 450°C prior to the TMA analysis, a significantly large expansion occurred at a temperature of approximately 475°C. Upon investigation it was discovered that pellet softening had taken place at this temperature and that the increase in sample height was due to the inside of the pellet, which started sagging out at the base of the pellet. This pellet is shown in Figure 4-2.

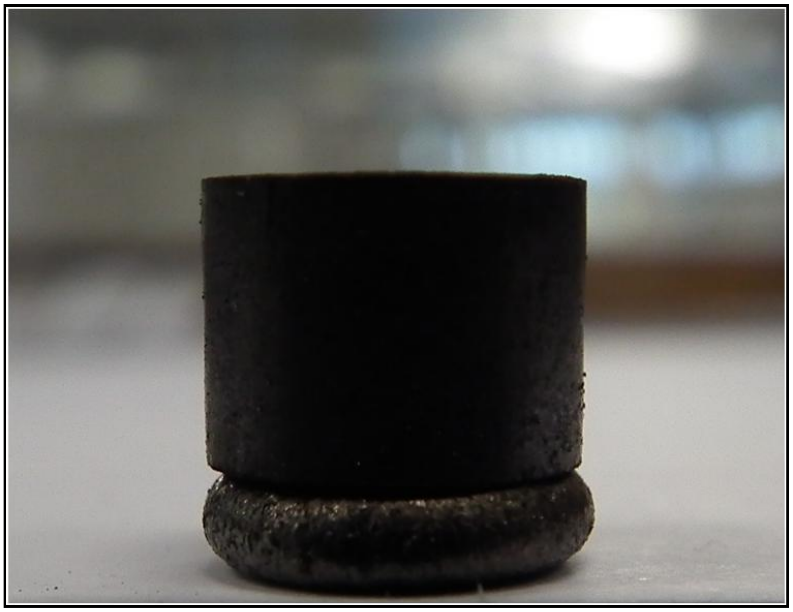

**Figure 4-2: Pellet softening in the 450°C pre-treated LSP tar pitch sample during preliminary TMA analysis**

The results obtained from the preliminary thermomechanical analysis done on pre-treated LSP tar pitch indicated that the minimum heat treatment temperature that yielded a pellet that could safely be analysed in the TMA without risking instrument damage due to pellet sagging/melting was 475°C.

The results obtained from the preliminary thermomechanical analysis done on the pre-treated HSP tar pitch were similar to that of the LSP tar pitch. Again it was found that the dimensional changes measured for the pellets made of HSP tar pitch pre-treated at 475°C and 500°C prior to the TMA analysis were gradual, but the pellet made from the 450°C pre-treated HSP material softened. The results obtained from the preliminary thermomechanical analysis of the HSP tar pitch were similar to those obtained from the LSP tar and are shown in Figure 4-3.

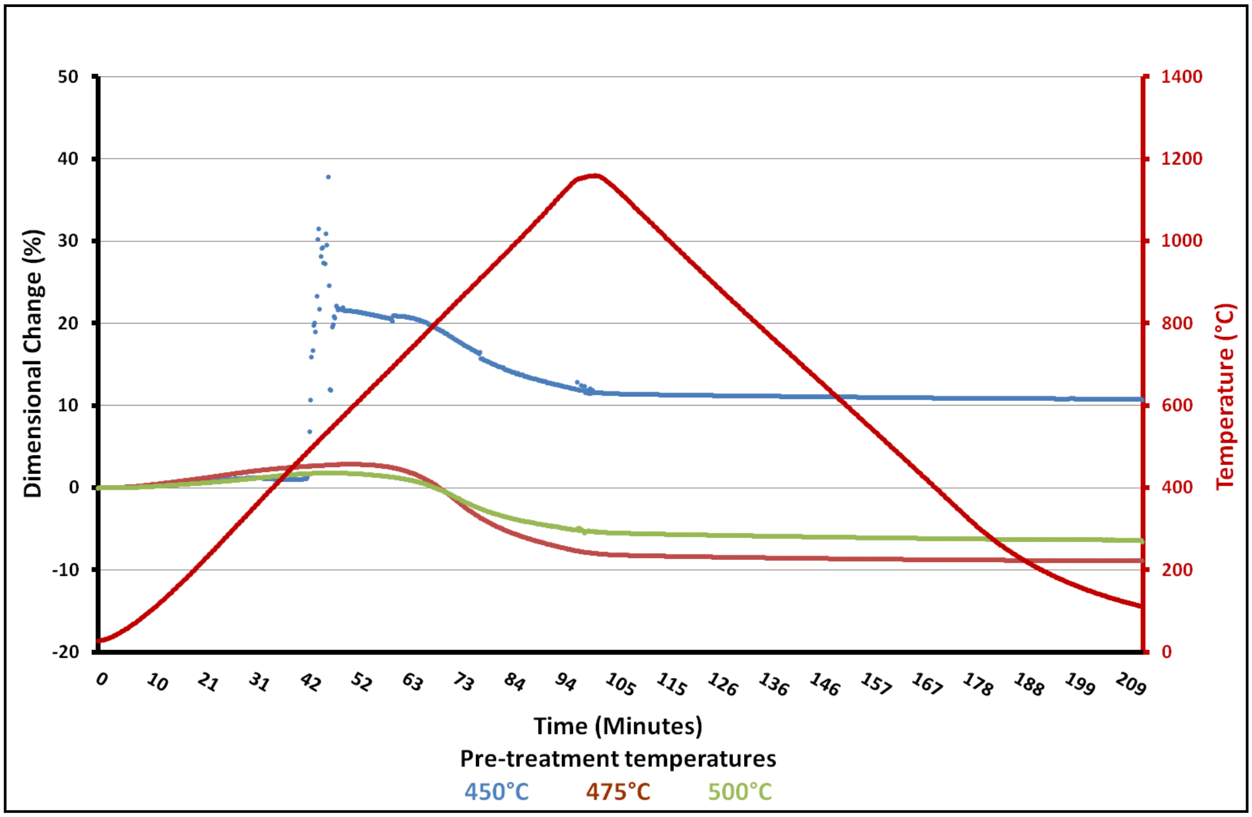

**Figure 4-3:** **Results for preliminary thermomechanical analysis – HSP tar pitch**

The results obtained from the preliminary thermomechanical analysis done on both the LSP and HSP tar pitches indicated that 475°C is the minimum pre-treatment temperature prior TMA analysis, which yielded pellets that did not soften (melt) during TMA analysis. Therefore, all the remaining thermomechanical analyses done on both the tar pitches (LSP and HSP) were done on pellets made from sample material pre-treated at 475°C under $N_2$ prior to TMA analysis.

Apart from being an important experimental procedural development step, the above-mentioned determination of the minimum temperature at which both the LSP and HSP tar pitches did not soften after pre-treatment, this result also has significant industrial relevance. The baking zone isotherm (Par. 2.4) is a very important parameter for practical Soderberg electrode management. It indicates the minimum temperature at which an electrode can support itself, since the tar pitch binder has transformed for a molten liquid to a solid carbonaceous material. Currently, literature (Innvær *et al.*, 1985; Mc Dougall *et al.*, 2004; Nelson & Prins, 2004; Olsen *et al.*, 1972; Ord *et al.*, 1995) indicates this baking zone isotherm temperature to be somewhere between 400 and 500°C. However, this temperature range is too wide to serve as a practical guide for electrode management. Also, as far as the author could assess, there is no public domain literature available that mentions the baking zone isotherm temperature of South African produced tar pitches. The fact that the minimum pre-treatment temperature in an inert atmosphere required to obtain solid (non-melting/softening) carbonaceous material from both LSP and HSP tar pitches was 475°C, indicates that this temperature can be used as a practical baking zone isotherm temperature for South African produced electrode pastes.

### 4.2.2. Anthracite sample preparation

Raw materials used in the production of electrode paste for Soderberg electrodes consist of calcined anthracite mixed with a tar pitch binder (Par. 2.5). Due to intellectual property limitations, samples of calcined anthracites being utilised by paste producers in South Africa could not be obtained. Therefore, the sample preparation procedure for the anthracite samples consisted of two phases, calcination of the raw anthracites and anthracite sample pellet production.

According to literature, higher anthracite calcinations temperatures result in greater reordering of the carbon structure, leading to increased electrical conductivity. Calcining of the anthracite should be done at a temperature of at least 1200°C (Stanko, 1972; Sem, 1954); however, in practice, anthracites can be calcined at temperatures of up to 3000°C (Asphaug & Innvær, 1997). Better anthracite electrical conductivity is beneficial, since it implies that a newly-formed section of a Soderberg electrode would perform its primary objective, i.e. conducting electricity into the burden material, better (Asphaug & Innvær, 1997; Stanko, 1972).

However, due to the unavailability of a laboratory furnace with a very high maximum temperature it was decided to calcine the three obtained anthracites at 1200, 1300, and 1400°C. Sample pellets from each batch of calcined anthracite (3 different samples X 3 different temperatures = nine batches in total) were then pelletised (Par 3.3.1.2) and analysed in the TMA. In the interest of studying the effect of calcination on the dimensional behaviour of anthracite, uncalcined samples were also prepared for thermomechanical analysis according to the method discussed in Par. 3.3.1.2.

### 4.2.3. Pre-baked electrode graphite sample preparation

Due to the above-mentioned limitation (Par 4.2.2) with regard to the availability of a very high temperature laboratory furnace for the calcinations of the anthracite samples, it was decided to also conduct thermomechanical analysis on pre-baked electrode graphite samples. The inclusion of this pre-baked graphite effectively meant that the results obtained from the thermomechanical analysis of the tar pitches, as well as the laboratory calcined anthracites could be compared with the results obtained from the electrode graphite. This was a significant addition to the scope of the study, since electrode graphite is ultimately formed in Soderberg electrode systems. In contrast to the sample preparation procedures of the tar pitch and anthracite samples where pellets were pressed (Par. 3.3.1.1 and Par. 3.3.1.2), cylindrical pellets were core drilled out of the solid electrode graphite material (Par. 3.3.1.3).

## 4.3. Thermomechanical analysis

After the successful completion of designing a sample preparation procedure for the tar pitch, anthracite and electrode graphite sample materials, the dimensional changes of the sample materials as a function of temperature were investigated.

### 4.3.1. Tar pitch

Thermomechanical analysis was performed on the tar pitch samples according to the procedure discussed in Par. 3.3.2. The dimensional change of each sample was measured as a function of temperature through three heating and cooling cycles in which the samples were heated to 1300°C and allowed to cool down to approximately 100°C under an inert $N_2$ atmosphere. A minimum of three separate experiments were performed on each tar pitch (LSP and HSP) to ensure repeatability of the results. Since each experimental run was not always initiated on exactly the same starting temperature (e.g. differences in room temperature and the TMA furnace starting temperature) each dataset was interpolated to fit on the same temperature profile in order to effectively compare the results. Linear interpolation was used, which was deemed accurate enough since a very large amount of measurements were taken (approximately 1027 data points per experimental repetition).

#### 4.3.1.1. LSP tar pitch

The results obtained from the thermomechanical analysis performed on the LSP tar pitch samples are shown in Figure 4-4.

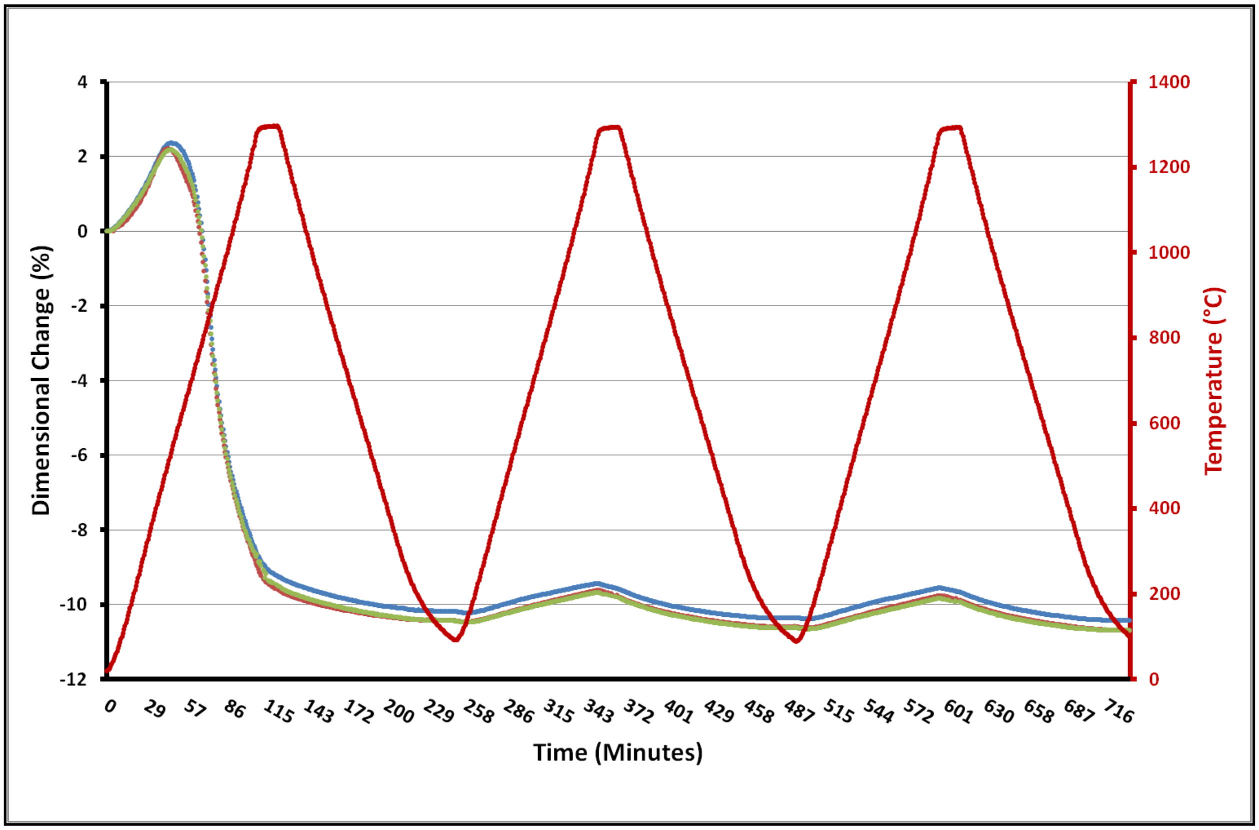

**Figure 4-4: Thermomechanical analysis results of the LSP tar pitch**

Similar to previous results, the percentage dimensional change is indicated on the primary y-axis (black) and temperature is indicated on the secondary y-axis (red). Additionally, the heating and cooling cycles are indicated by the red line. During the initial heating cycle, a small expansion occurs up until approximately 500°C. This initial expansion is due to thermal expansion that occurs, since the tar pitch was already heat treated up to 475°C in an inert atmosphere prior to the TMA analysis (Par.3.3.1.1.). The data up to this temperature can therefore not be used, since thermal dimensional changes could not be measured of the pitches in its softening range (0-475 °C). At temperatures above 500°C, the LSP material started to shrink and reached a maximum shrinkage at the maximum indicated temperature (1300°C). The total shrinkage is in excess of 12% after the initial thermal expansion of the pellet. However, in the following two heating cycles, the thermal expansion and shrinkage were much less in comparison to the first cycle with thermal expansion and shrinkage in excess of 2%. The difference in the magnitude of the dimensional changes between the first heating cycles and the second/third heating cycles can be attributed to structural reordering of the carbonaceous material that took place during the first heating cycle in the TMA (Feng *et al.*, 2002). During the first cycle, the tar pitch is heated to a temperature of 1300°C for the first time, since it was prepared only at 475°C.

The repeatability of the thermomechanical analysis was relatively good as all three repetitions (blue, maroon and green lines in Figure 4-4) followed the same trend with minor deviations occurring. With such small experimental deviations and the large amount of measurements taken (approximately 1027 data points per run) it was difficult to indicate experimental error. It was therefore decided to indicate the minimum and maximum expansions/shrinkages of the TMA analysis of the LSP pitch repetitions on a graph in order to establish a range of expansion/shrinkage. The minimum and maximum expansion/shrinkage range for the LSP tar pitch is shown in Figure 4-5.

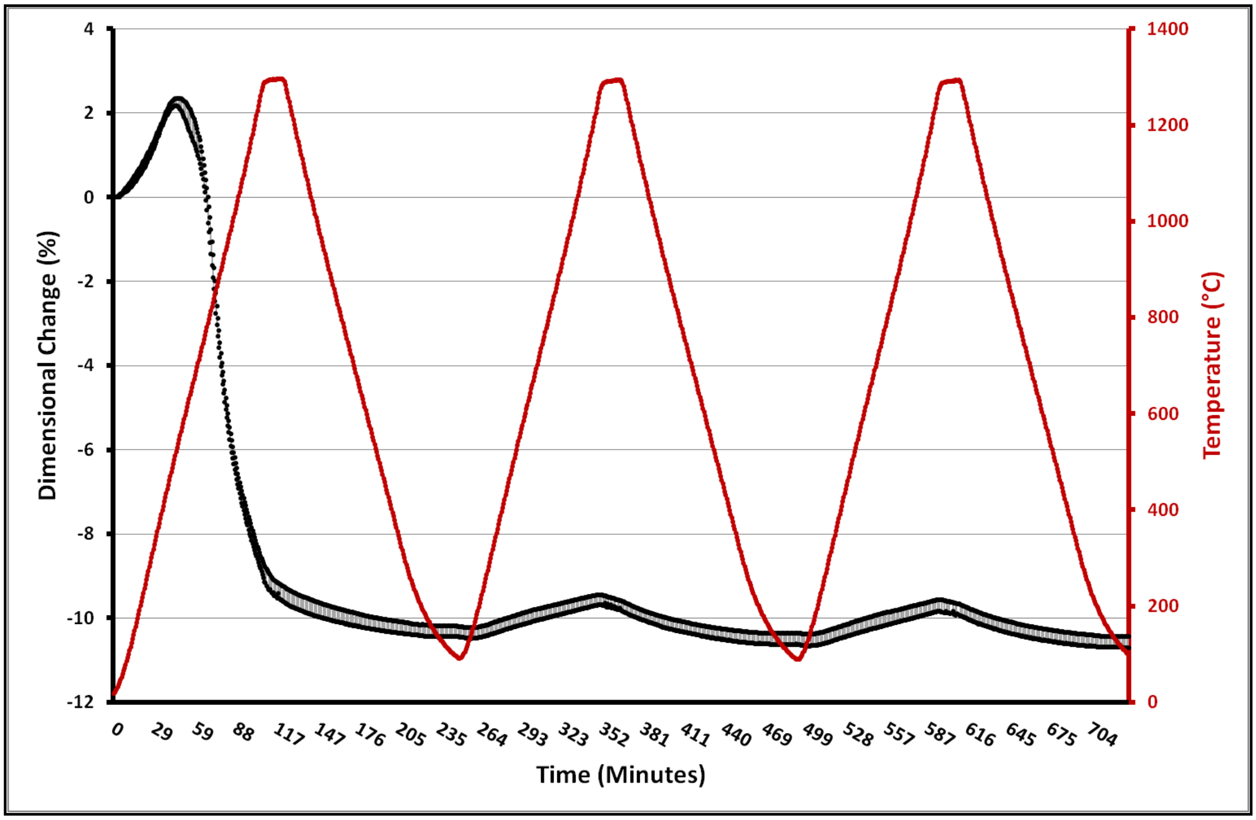

**Figure 4-5:** **Minimum and maximum thermal expansion/shrinkage range for the LSP tar pitch**

In the graph shown in Figure 4-5, the percentage dimensional change is again indicated on the primary y-axis (black), temperature on the secondary y-axis (red) and the temperature cycles indicated by the red line. The minimum and maximum thermal expansion/shrinkage is indicated by the top and bottom black lines respectively and the range of thermal expansions/shrinkages are indicated by the grey area between the black lines. The difference between the minimum expansion/shrinkage line and the maximum expansion/shrinkage line is relatively small – amounting to approximately 0.5%.

#### 4.3.1.2. HSP tar pitch

The results obtained from thermomechanical analysis on the HSP tar pitch is shown in Figure 4-6.

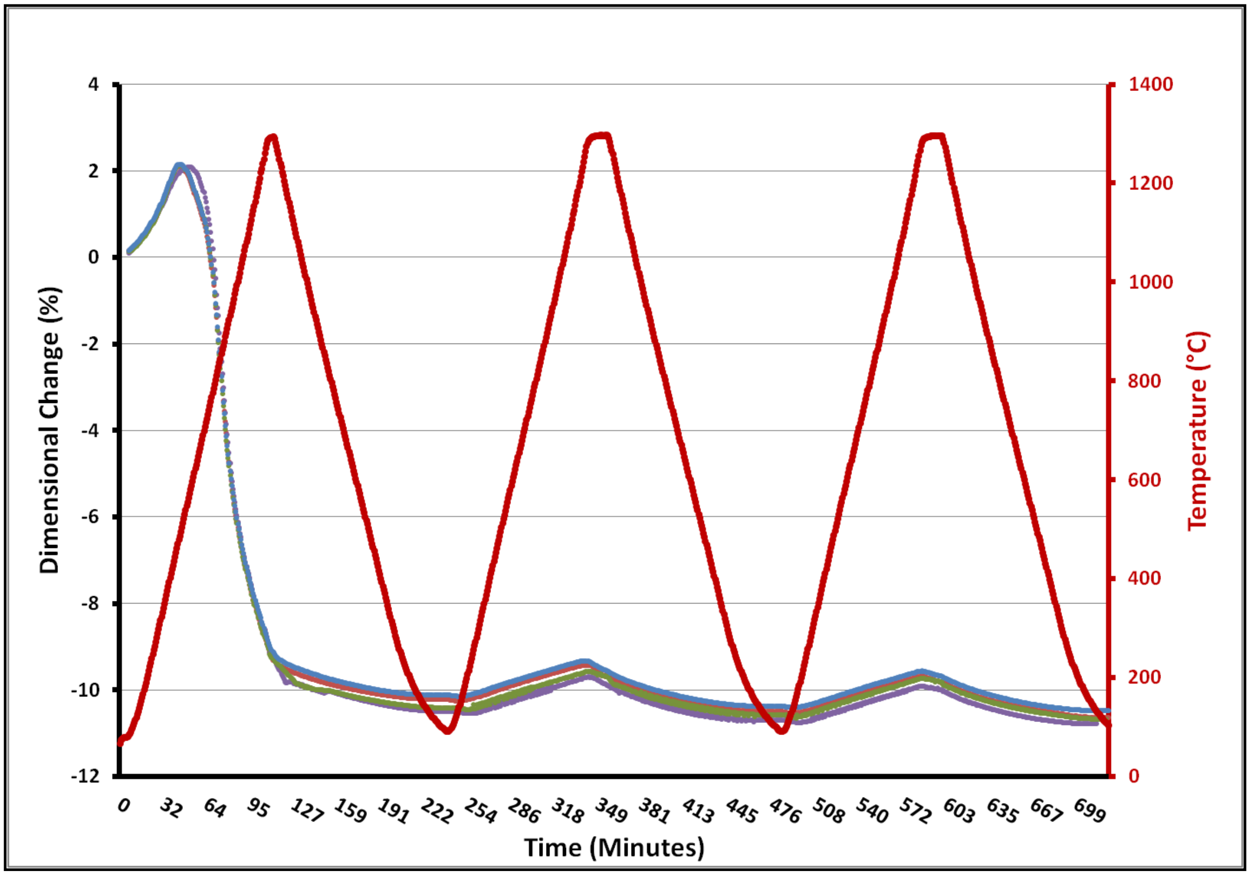

**Figure 4-6:** **Thermomechanical analysis results of the HSP tar pitch**

The results obtained for the HSP tar pitch are very similar to those obtained for the LSP tar pitch. The initial expansion of approximately 2% up to 500°C is not considered further, as previously discussed. The sample then undergoes shrinkage in excess of 12% up until the maximum temperature of the heating cycle is reached. During the following two heating/cooling cycles, dimensional changes of approximately 2% occur. As with the LSP tar pitch, the difference in the magnitude of the dimensional changes between the first heating cycle and the second and third cycles can be attributed to structural reordering of the carbonaceous material.

The range of experimental deviation (Figure 4-7) for the HSP tar pitch, indicated by the grey area, was again found to be in the order of 0.5%.

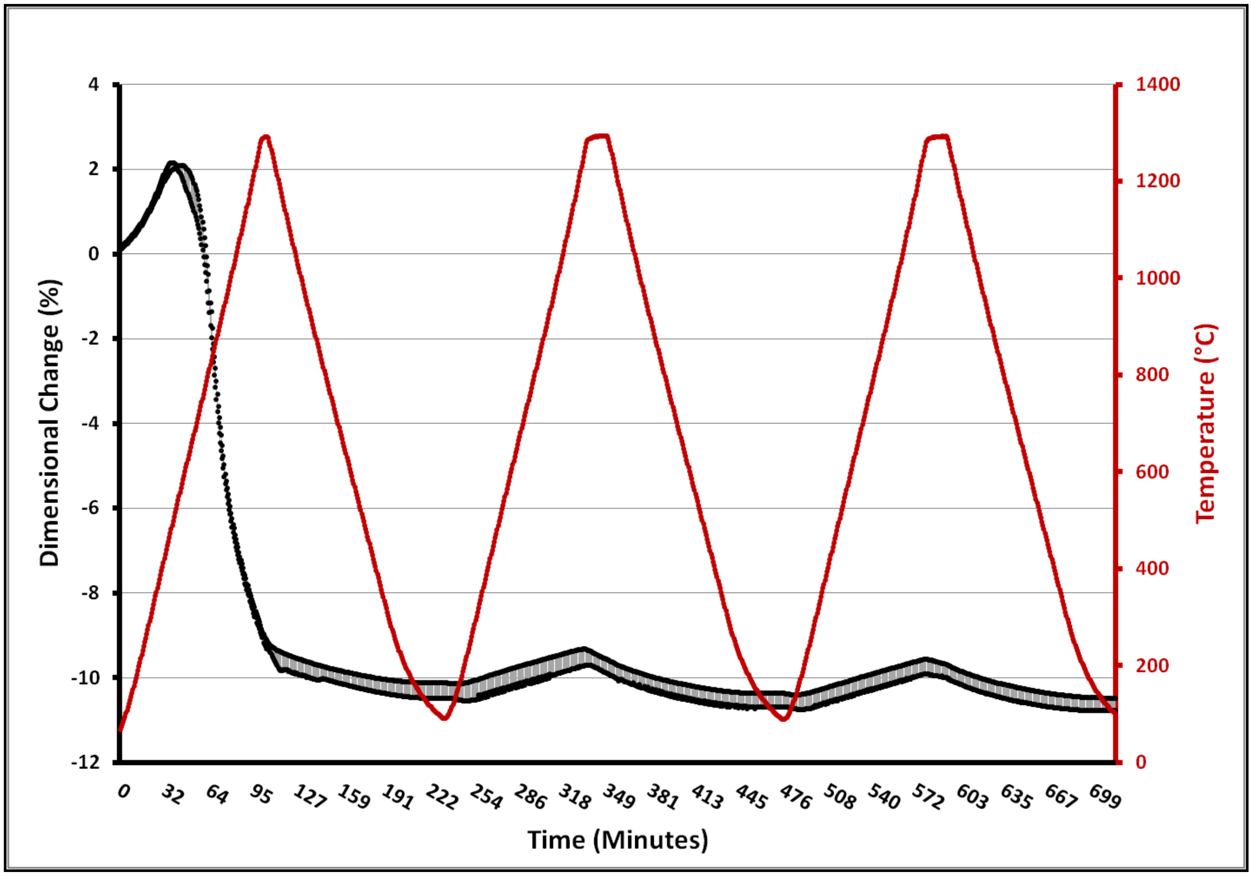

**Figure 4-7:** **Minimum and maximum thermal expansion/shrinkage range for HSP tar pitch**

### 4.3.1.3. Industrial significance of TMA tar pitch results

The data generated by the thermal mechanical analyses done on the tar pitch binders provide valuable information with regard to electrode management, particularly to the area just below the contact shoes, i.e. from the baking zone isotherm further down into the electrode. Repeated heating cycles were used to simulate plant conditions such as furnace shutdowns, which directly impact the electrode system and electrode management. The large shrinkage (in excess of 12% for both the LSP and HSP tar pitch binders), which occurred during the first heating cycle, indicates that the electrode is most vulnerable to failure during the initial baking process. During the baking process the electrode becomes reasonably stable with regard to dimensional change as structural reordering of the carbonaceous binder takes place. At high temperatures (up to 1300°C tested), the structural reordering that took place significantly reduces the risk for a breakage occurring. This was confirmed by the second and third heating cycles of the LSP and HSP tar pitches, during which the dimensional changes that occurred were approximately 2%. Alternatively, it can be stated that the dimensional change of the tar pitch binder in a Soderberg electrode, baked for the first time above temperatures exceeding the baking isotherm, is approximately 600% higher than the dimensional changes occurring in subsequent heating/cooling cycles.

## 4.3.2. Anthracite

Thermomechanical analysis was performed on the calcined and uncalcined anthracite samples according to the procedure discussed in Par. 3.3.2. The dimensional change of each anthracite sample was measured as a function of temperature through three heating and cooling cycles in which the samples were heated to 1300°C and allowed to cool to approximately 100°C under an inert $N_2$ atmosphere. A minimum of three runs were performed on each batch to ensure repeatability of the results

### 4.3.2.1. Calcined anthracite

#### 4.3.2.1.1. Zululand anthracite chips

Three samples of each calcination temperature (1200, 1300, and 1400°C) were analysed in the TMA. The average dimensional change of the three runs was then calculated for each data point. The results for the average expansion at the three different calcination temperatures are shown in Figure 4-8.

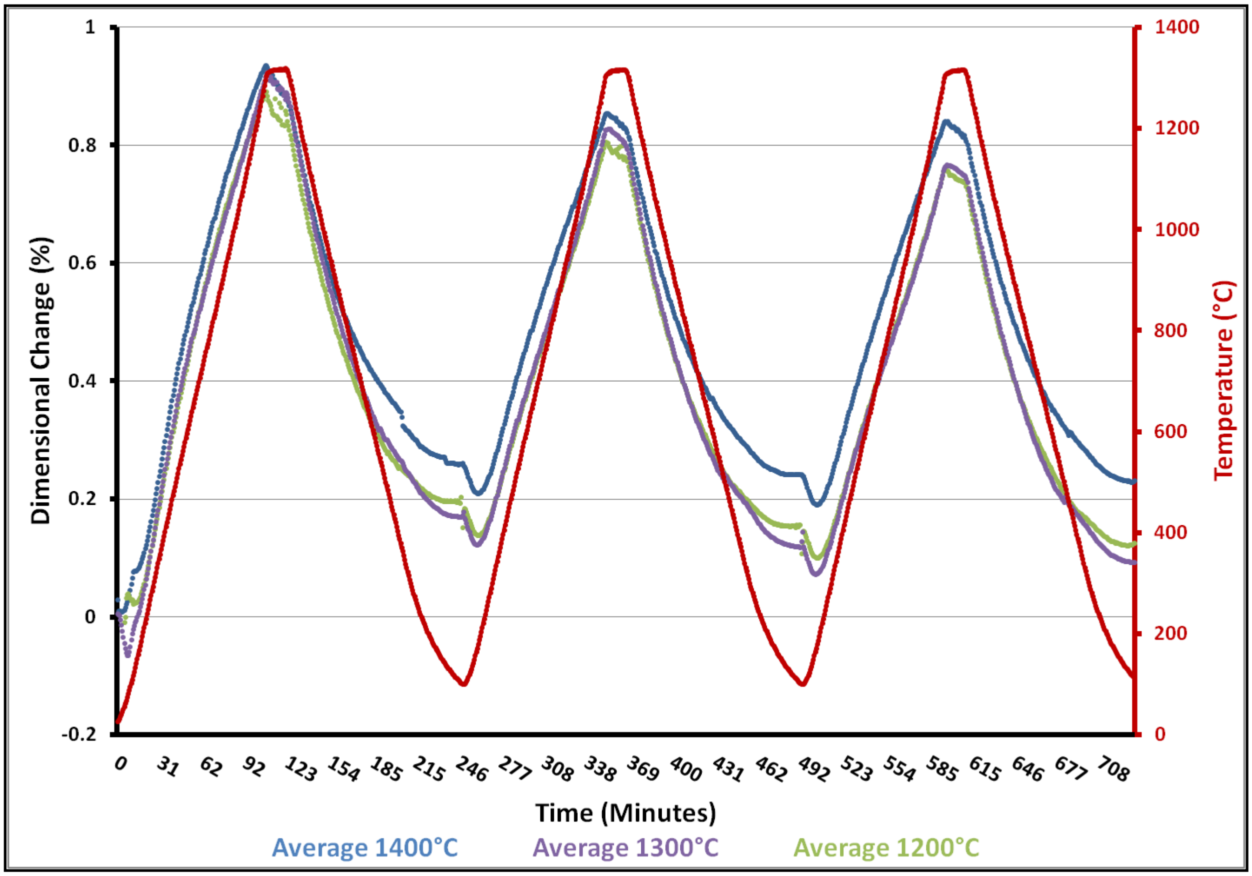

**Figure 4-8:** **Average TMA analysis for the calcined Zululand anthracite chips**

The initial expansion during the first heating cycle was approximately 0.9% for all three the anthracites previously calcined at the three different temperatures. The expansion/shrinkage during the following two cycles were slightly less – amounting to about 0.7%. As can be seen from Figure 4-8, the average expansion of the 1400°C calcined anthracite is slightly less than that of the 1200 and 1300°C calcined anthracite – it is especially visible during the first cycle. This is due to structural reordering that had taken place during the calcining process, prior to the TMA analysis. The TMA runs were performed up to 1300°C and because this specific anthracite sample had previously been calcined at a higher temperature (1400°C), the structural reordering that had taken place was at a more complete stage than that of the 1200 and 1300°C calcined anthracites, hence slightly less thermal dimensional changes were observed for it.

Slight deviations occur in the dimensional changes of the anthracite samples calcined previously at 1200 and 1300°C during the first cycle; however, the dimensional behaviour becomes much more similar during the second and third cycle. During the first cycle, the 1200°C calcined anthracite sample was heated to 1300°C for the first time, hence a bit of structural reordering took place, but during the next cycle the 1200°C calcined sample behaved very similar to the 1300°C calcined anthracite.

#### 4.3.2.1.2. Zululand anthracite duff

The Zululand anthracite duff was calcined at 1200, 1300, 1400°C and analysed in the TMA. The average dimensional changes for each batch were calculated and are shown in Figure 4-9.

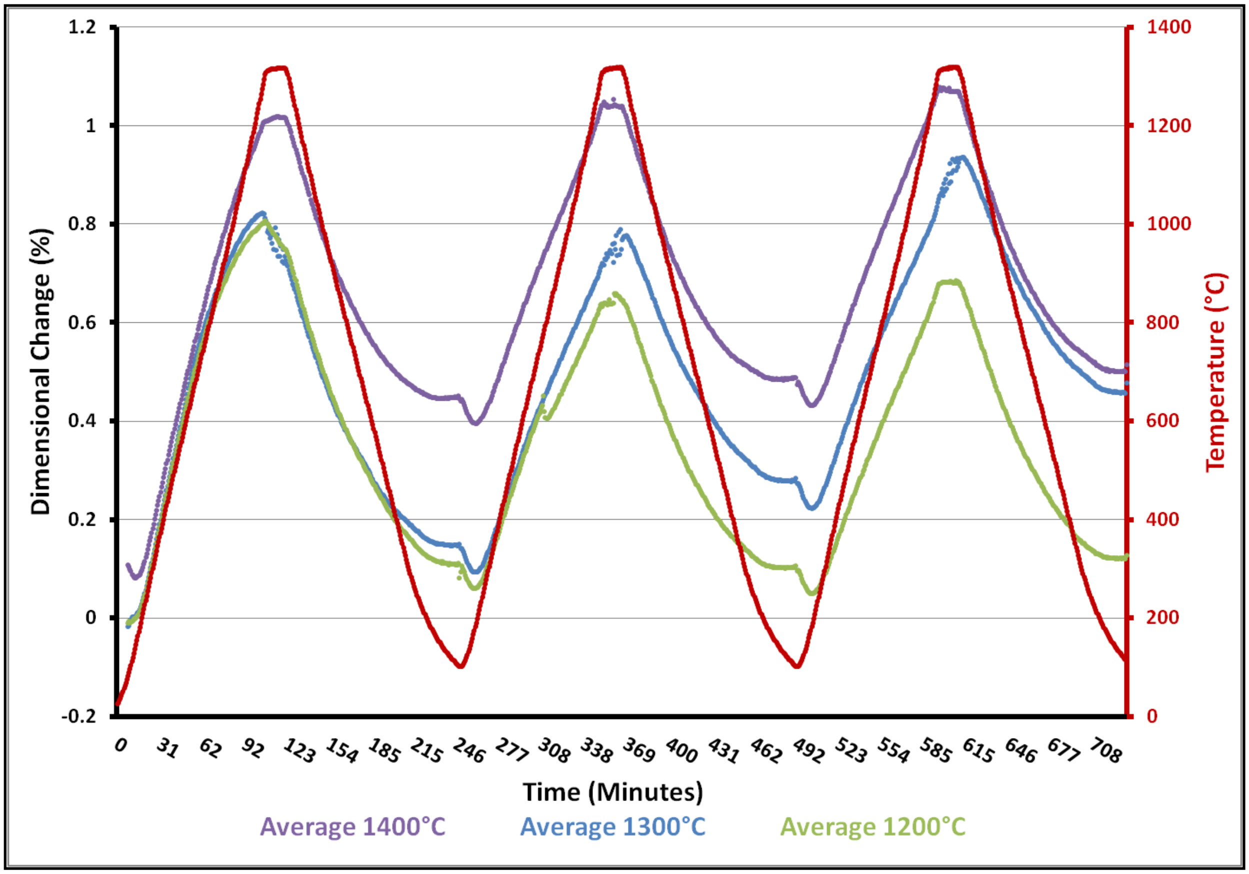

**Figure 4-9:** **Average TMA analysis for the calcined Zululand anthracite duff**

During the first heating cycle, the 1200 and 1300°C calcined anthracite had a differential shrinkage (about 0.7 %), which was slightly larger than that of the 1400°C calcined anthracite (about 0.6 %). The anthracite, calcined at 1400°C, has a higher level of structural ordering than that of the 1200 and 1300°C calcined anthracite because it was previously heat treated at a higher temperature. During the second and third heating cycles, the expansions/shrinkages that took place were very similar in size for the 1200 and 1300°C calcined anthracite, with the anthracite calcined at 1400°C showing expansions/shrinkages slightly less than the 1200 and 1300°C calcined anthracites.

#### 4.3.2.1.3. Tendele anthracite duff

Tendele anthracite duff was calcined at three different temperatures – 1200, 1300, and 1400°C and three samples from each calcined batch were analysed in the TMA. The average of the obtained results for each calcined batch is shown in Figure 4-10.

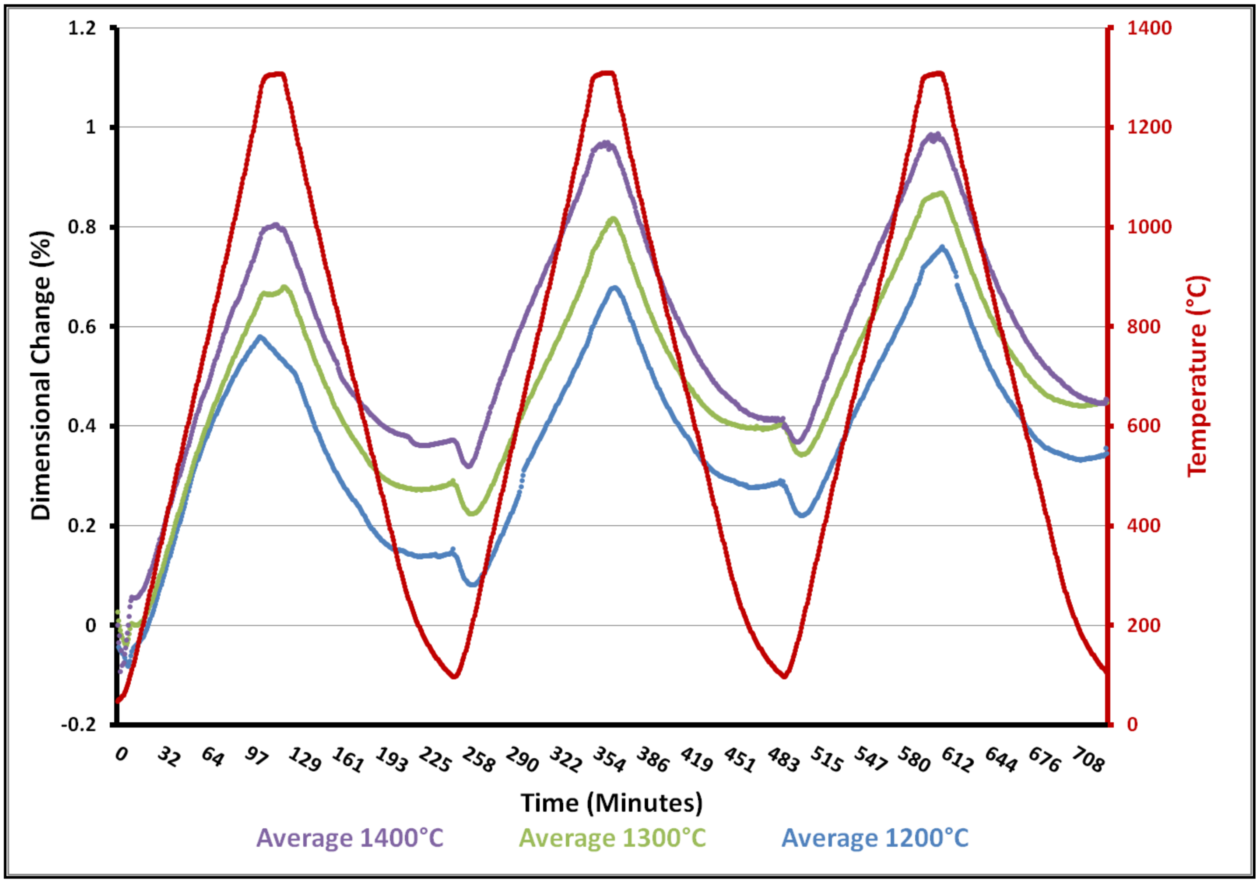

**Figure 4-10: Average TMA analysis for the calcined Tendele anthracite duff**

The Tendele duff anthracite, similar to the Zululand chips and duff, also showed smaller delta shrinkage for the anthracite previously calcined at 1400°C during the first heating cycle than the anthracite previously calcined at 1200 and 1300°C.

#### 4.3.2.2. Uncalcined anthracite

According to literature, one of the reasons for calcining anthracite prior to Soderberg electrode paste production is to stabilise the anthracite dimensionally (Stanko, 1972) – in other words, to have structural ordering of the anthracite take place prior to paste production. Uncalcined sample pellets of each of the three obtained anthracites were produced according to the method discussed in Par. 3.3.1.2. Thermal mechanical analysis was performed on the uncalcined anthracite samples, during which the sample pellet was heated from room temperature to 1300°C and allowed to cool to approximately 100°C for three consecutive heating/cooling cycles (Par. 3.3.2.). The average dimensional changes, for the three runs performed on each anthracite, were then calculated and are shown in Figure 4-11.

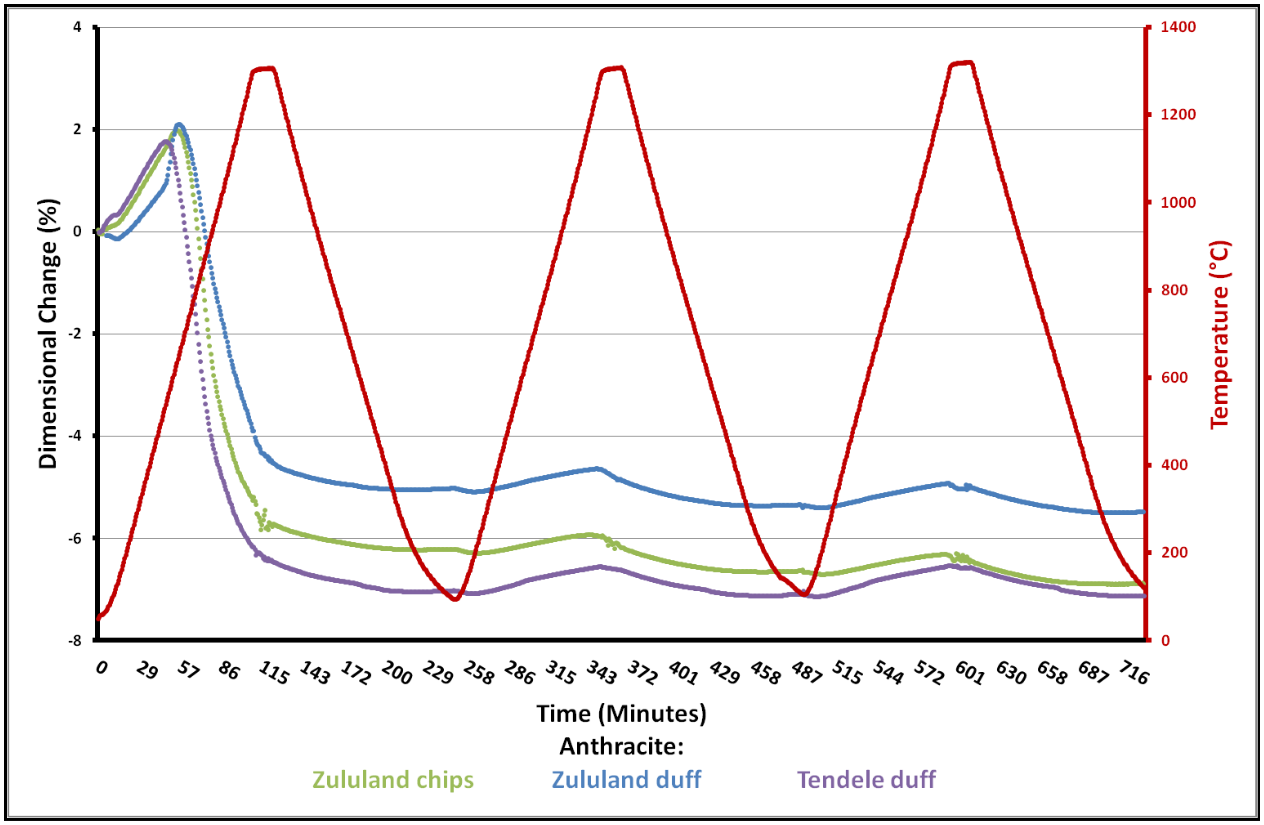

**Figure 4-11: Average dimensional change measured for uncalcined anthracite**

As can be seen from Figure 4-11, the dimensional changes measured during the first heating/cooling cycle are significantly larger than that measured during the following heating/cooling cycles. On average, a shrinkage of 6-8% was measured for each of the anthracites during the first heating cycle, which is very large in comparison to the dimensional changes of approximately 1% measured during the following cycles. During the second and third heating/cooling cycles, the dimensional changes measured were very similar in size to that which was measured with the calcined anthracite. The anthracite sample with the highest fixed carbon and lowest ash content, the Zululand chips (Table 4-1), had the smallest dimensional change, while the anthracite sample with the lowest fixed carbon content and highest ash content, i.e. Tendeleduff (Table 4-1), had the largest dimensional change.

### 4.3.2.3. Industrial significance of TMA anthracite results

During the initial baking of a Soderberg electrode, the conductivity is largely dependent on the steel casing and fins as the unbaked electrode paste has very little conductivity. The anthracite that is part of the electrode paste is calcined prior to paste production in order to improve the initial conductivity of the paste. The conductivity of carbon increases as the structure approaches the structure of graphite (Asphaug & Innvær, 1997). Another motivation for calcining the anthracite prior to electrode paste production is to drive off volatiles and to stabilise the anthracite dimensionally (Stanko, 1972).

Results obtained for all three the calcined anthracite samples investigated indicated thermal dimensional changes of less than 1%. The anthracite samples calcined at the higher experimental calcination temperatures (1400°C) prior to TMA analysis, had the smallest dimensional changes. This proved that higher calcining temperatures indeed result in a higher level of structural ordering and dimensional stability. In contrast to the relatively small dimensional changes measured in the calcined anthracite samples, the shrinkages measured in the uncalcined samples during the first heating/cooling cycle were significantly larger, ranging from 6-8%. The efficiency of the calcination process of the anthracite prior to Soderberg electrode production is therefore extremely important in order to produce dimensionally stable electrodes. It also became apparent that the anthracite sample with the highest fixed carbon content was the least affected by dimensional change during *in situ* calcinations in the TMA instrument. It is expected that this trend will continue beyond the temperature range experimentally tested (1300°C) in the TMA instrument.

Considering the calcined anthracite TMA results within the context of the TMA results obtained for the tar pitches, the importance of the initial baking of a Soderberg electrode at temperatures exceeding the baking isotherm temperature (475°C) is again stressed. During this process, the dimensional behaviour of the tar pitch binder and the calcined anthracite differ dramatically – the tar pitch binder undergoes shrinkage of more than 12%, while the calcined anthracite expands (thus opposite motion) approximately 0.9%.

### 4.3.3. Graphite

In order to establish a benchmark for comparing the dimensional changes of the anthracite and tar pitch binders, thermomechanical analysis was also performed on pre-baked electrode graphite samples. Due to the fact that graphite was pre-heated to approximately 3000°C, it will have the highest level of structural ordering and will therefore be most stable dimensionally. The results for the thermomechanical analysis done on the electrode graphite samples are shown in Figure 4-12.

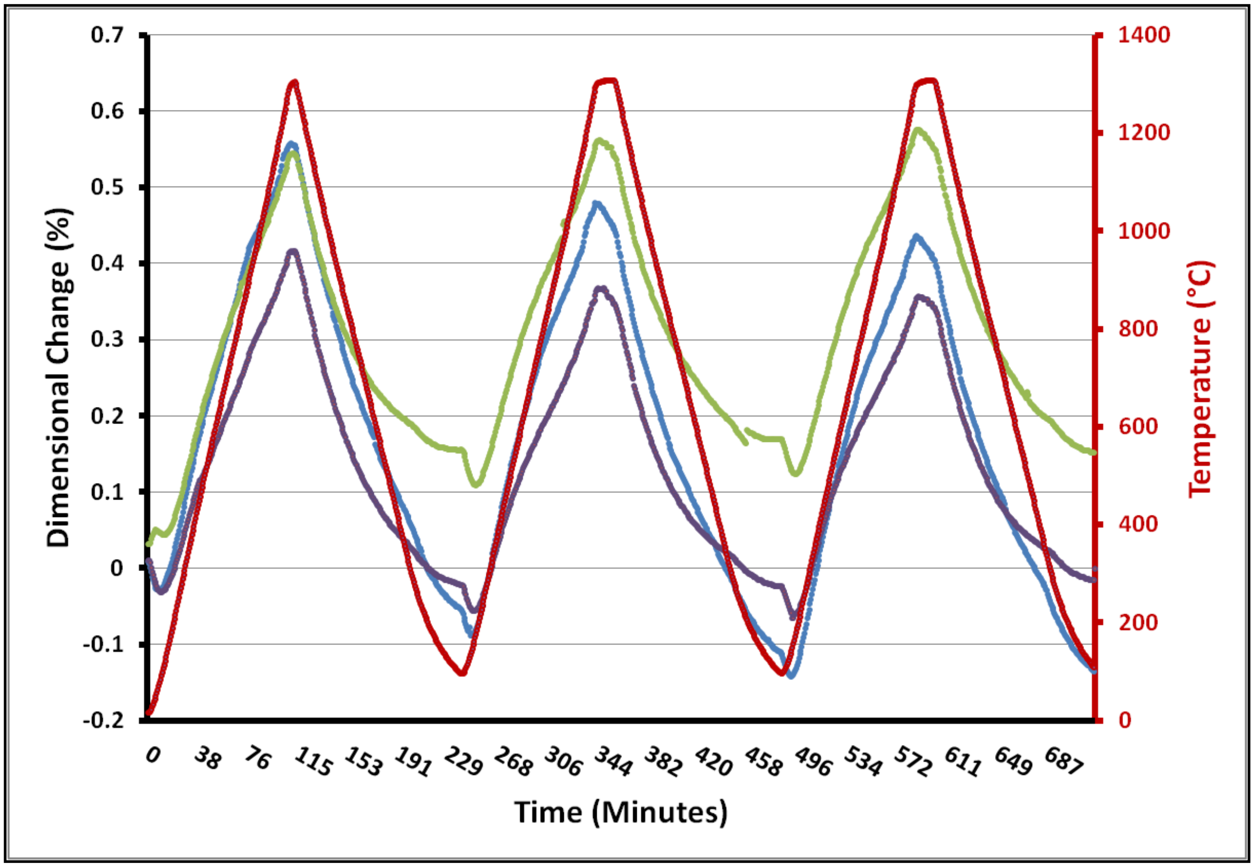

Figure 4-12: Thermal expansion of three core drilled graphite samples

As can be seen from Figure 4-12, the dimensional changes of the electrode graphite samples are relatively small (~0.5%). The repeated heating and cooling cycles result in similar expansion/shrinkage graphs. Since these samples were taken from actual electrodes that were pre-baked at 3000°C, it can be stated with confidence that the carbon structure of these samples has been converted to maximum structural ordering (i.e. graphite). It is therefore expected that the heating and cooling cycles will result in similar expansion/shrinkage graphs. Minor differences in the graphs can be attributed to the heterogeneity, i.e. containing air pockets, of the core drilled graphite samples. Figure 4-13 shows the heterogeneity of one such a sample.

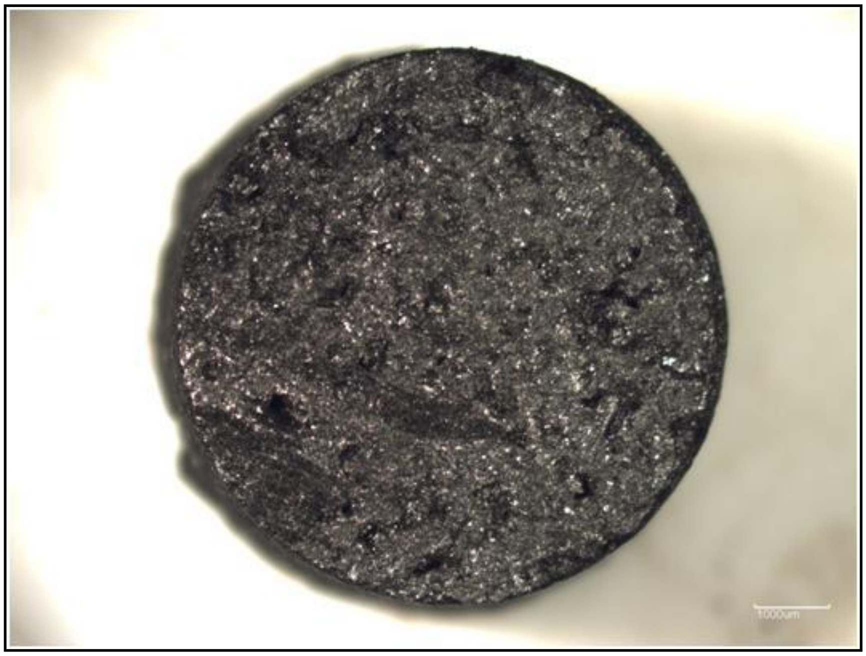

**Figure 4-13:** **Air pockets within a core drilled graphite sample pellet**

## 4.4. Comparison of dimensional behaviour and industrial significance

The dimensional changes observed in the calcined anthracites are very similar to those observed in the graphite samples. The expansions/shrinkages observed in the graphite samples were mostly less than 0.5%, whereas the expansions/shrinkages observed in the various calcined anthracites were approximately 0.6 to 0.9%. The difference in the magnitude of the dimensional behaviour between the calcined anthracites and the graphite can be attributed to the fact that the graphite has already reached maximum structural ordering (having been pre-baked at 3000°C), whereas this is not the case with the calcined anthracite.

However, the dimensional changes measured in the uncalcined anthracites during the first heating/cooling cycle were much larger than that measured in the graphite and calcined anthracite samples – having a shrinkage of approximately 6-8%. During the second and third heating cycles, the dimensional behaviour of the uncalcined anthracite samples was the same as that of the calcined anthracite.

During the initial heating, both the tar pitch binders showed a shrinkage of approximately 12%, which is a very large dimensional change – especially when compared to the dimensional changes observed in the calcined anthracites. During the following heating cycles the tar pitches follow the same trend in dimensional behaviour as the calcined anthracites; however, the expansions/shrinkages of approximately 2% are still larger than that of the calcined anthracites.

This information indicates two very important factors in producing high quality Soderberg electrode paste – the efficiency of the calcination process, and the quality of the tar pitch binder. An inefficient calcination process will result in significant dimensional change in the electrode paste during the initial baking of the electrode. The approximately 6-8% shrinkage of uncalcined (or poorly calcined) anthracite, combined with the approximately 12% shrinkage of the tar pitch binder will have disastrous consequences for the electrode. The calcination process should therefore be done at the highest possible temperatures in order to ensure maximum dimensional stability. Anthracite with the highest possible fixed carbon content should also be selected, since it was apparent that such samples are less prone to dimensional change.

The dimensional behaviour of Soderberg electrodes is also largely affected by the dimensional behaviour of the tar pitch binders. It is therefore imperative that tar pitch binders of a high quality with the correct thermal expansion properties are selected for the production of Soderberg electrode paste. The anthracites used in the production of Soderberg electrode paste are dimensionally stabilised during the calcining process prior to paste production. This is, however, not the case with the tar pitch binders – which receive no pre-treatment in order to improve the properties of the tar pitch prior to paste production. Operational personnel should be made aware of the differences in dimensional behaviour of pitches and calcined anthracite, in order to sensitise them for the baking of a new electrode section for the first time above the baking isotherm temperature.

# Chapter 5: Project evaluation

## 5.1. Project evaluation

The success of a project is mostly determined by the number of objectives successfully achieved. The three main objectives identified were: i) the development of an experimental procedure to determine the dimensional changes in electrode paste raw materials by means of thermomechanical analysis (TMA), ii) the practical application of this experimental method in order to determine the dimensional behaviour of various anthracite and tar pitch samples utilised by local electrode paste producers, iii) and the interpretation of the results with possible practical implications in electrode management with particular regard to the ferrochromium industry. The achievement of these objectives is subsequently evaluated separately.

*Objective (i): The development of an experimental procedure to determine the dimensional changes in electrode paste raw materials by means of thermomechanical analysis (TMA).*

Due to the specific requirements for the TMA samples (non-softening material; cylinders of 10mm diameter and approximately 10mm height), the experimental method consisted of two phases: sample preparation and TMA measurement. Different sample preparation procedures had to be developed for each material investigated (tar pitch, anthracite and electrode graphite) in order to address specific properties of each material.

The tar pitch samples needed to be heat treated in an inert atmosphere prior to TMA in order to obtain a solid carbonaceous material that could be pelletised (by compression in a die set). The minimum pre-treatment temperature prior to TMA that yielded pellets that did not soften in the TMA was determined to be 475°C. Calcined anthracite samples could not be obtained due to intellectual property limitations, therefore the anthracite samples needed to be calcined prior to pellets being pressed for TMA. The samples were calcined at 1200°C (the minimum calcining temperature specified in literature), 1300 and 1400°C. Uncalcined anthracite was also pressed into pellets that could be analysed with the TMA. The electrode graphite material had to be core drilled in order to obtain pellets of the appropriate diameter for

TMA measurements. Therefore, the sample preparation procedure for all materials investigated was successfully completed. Thereafter, TMA measurement could be undertaken (objective ii).

A limitation of the study was that anthracite calcination was only performed up to 1400°C, while calcination up to 1800°C is commonly applied in the paste production industry. This shortcoming was unavoidable, since operational problems were experienced with the laboratory furnace at the NWU that is able to achieve 1800°C, thus another laboratory furnace with a lower maximum temperature had to be used.

*Objective (ii): Practical application of this experimental method in order to determine the dimensional behaviour of various anthracite and tar pitch samples utilised by local electrode paste producers.*

The dimensional behaviours as a function of temperature up to 1300 C of all the materials considered could be undertaken, by means of TMA analysis. During the first heating/cooling cycle of the TMA, both the tar pitches (pre-treated at 475°C) shrank in excess of 12%. During subsequent heating/cooling cycles, the tar pitches had dimensional deviations of only ~2%. The expansions/shrinkages observed for the calcined anthracites were approximately 0.6 to 0.9%, while the uncalcined anthracites shrank 6-8% during the first TMA heating cycle and ~1% during subsequent heating/cooling cycles. The expansions/shrinkages observed in the graphite samples were mostly less than 0.5%.

*Objective (iii): Interpretation of the results with possible practical implications in electrode management with particular regard to the ferrochromium industry.*

From the tar pitch sample preparation procedure, the baking isotherm temperature for South African produced Soderberg electrode paste was derived at 475°C. Literature specifies the baking isotherm to be between 400°C and 500°C, which is too wide a range for practical electrode management. Knowing the actual baking isotherm temperature for South African produced Soderberg electrode paste will definitely assist local ferrochromium producers in practical electrode management.

Considering the combined calcined anthracite and tar pitches TMA results, the importance of the initial baking of a Soderberg electrode at temperatures exceeding the baking isotherm temperature (475°C) becomes apparent. The dimensional behaviour of the tar pitch binder and the calcined anthracite differ dramatically, i.e. shrinking >12% and expanding 0.6-0.9% respectively, making the newly-formed electrode very susceptible to breakage. Once structural reordering of the pitch had taken place, thermal dimensional behaviours of the materials are much more similar, significantly reducing thermal shock-induced electrode breakages (e.g. during shutdowns and subsequent warm-up procedures).

In contrast to the relatively small dimensional changes measured for the calcined anthracite samples, the shrinkages measured for the uncalcined samples during the first TMA heating/cooling cycle were substantial (6-8%). This indicates the importance of the anthracite calcination process, before the electrode paste is formulated. Improperly calcined anthracite present in electrode paste would result in additional dimensional shrinkage that would have to be accommodated in the baking of a new electrode section. Considering the large shrinkage of the tar pitch that already takes place, it is unlikely that a strong enough electrode would be formed if this occurs. From the results it also became apparent that the anthracite with the highest fixed carbon and lowest ash contents exhibited the smallest shrinkage during *in situ* TMA calcination. High fixed carbon, low ash type anthracites are therefore less prone to dimensional instabilities in Soderberg electrodes, as a result of poor calcination.

Lastly, it can be stated that the overall experimental procedure developed in this study (incorporating sample preparation and TMA analysis) could be implemented by Soderberg electrode paste producers for in-house quality control checks of raw materials. Very limited information on test procedures related to Soderberg electrode paste production is currently available in the public domain literature. The techniques developed can certainly assist in improving the quality of paste that is produced, which will ultimately lead to improved electrode management at ferrochrome smelters.

## 5.2. Future perspectives

Even though all three the objectives were successfully achieved, some recommendations with regard to further research in this research field can be made:

i) It is recommended that similar research must be done on composite mixtures of the tar pitches and the calcined anthracites, in order to identify matrix effects that might occur if these components are mixed to form electrode paste.

ii) The results presented in this study indicated that there was no real difference in thermal dimensional behaviour of the LSP and HSP tar pitches. This could just be accidental and it is therefore recommended that pitches from various other sources also be considered in a similar manner, to determine if the chemical composition of a pitch will influence its thermo-dimensional behaviour above the baking isotherm temperature. Performing chemical analysis on the tar pitches would be vital for such a study.

iii) A procedure should be developed to characterise the thermo-dimensional properties of electrode paste, prior to reaching the baking isotherm temperature. The results presented in this work were limited to investigating the tar pitches at temperatures exceeding the aforementioned temperature.

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# Appendix

## A. Description of standard methods used for characterisation

| | |
|---|---|
| **SANS 5925:2007** | Moisture content of coal samples intended for general analysis (air-oven method). |
| **SANS 131:2011** | Determination of ash. |
| **SANS 50:2011** | Determination of volatile matter. |
| **SANS 19579:2007** | Determination of total sulphur through IR spectroscopy. |
| **SANS 501:2008** | Determination of the crucible swelling number. |
| **SANS 12902:2007** | Determination of total carbon, hydrogen and nitrogen – instrumental methods. |