CHAPTER 1
INTRODUCTION

The purpose of this first chapter is to introduce the reader to the work conducted during this project. It also aims to provide the reader with some perspective by describing the industry to which the current work is relevant.

1.1 INDUSTRY BACKGROUND

The ilmenite smelting process that is the focus of this project is a stage in the production routes of the Ti/TiO_2 industry focussed on the upgrading of titanium dioxide containing minerals to either titanium dioxide pigment or titanium metal. No up-to-date quantitative information (capacities, prices, growth rates, etc.) on this industry was available for inclusion in this text. For this reason the industry and the various process stages and materials are only described qualitatively here.

Figure 1 shows the position of the ilmenite smelting process on a map of process routes found in the Ti/TiO_2 industry (Kahn, 1984; Stanaway, 1994). The dotted lines in Figure 1 indicate routes of intermediate products that are uncertain. It is very possible that these routes may be in use, as will be explained later, but this was not verified. The ranges of TiO_2 content of the various minerals and intermediate products are listed in Table 1 (Stanaway, 1994).

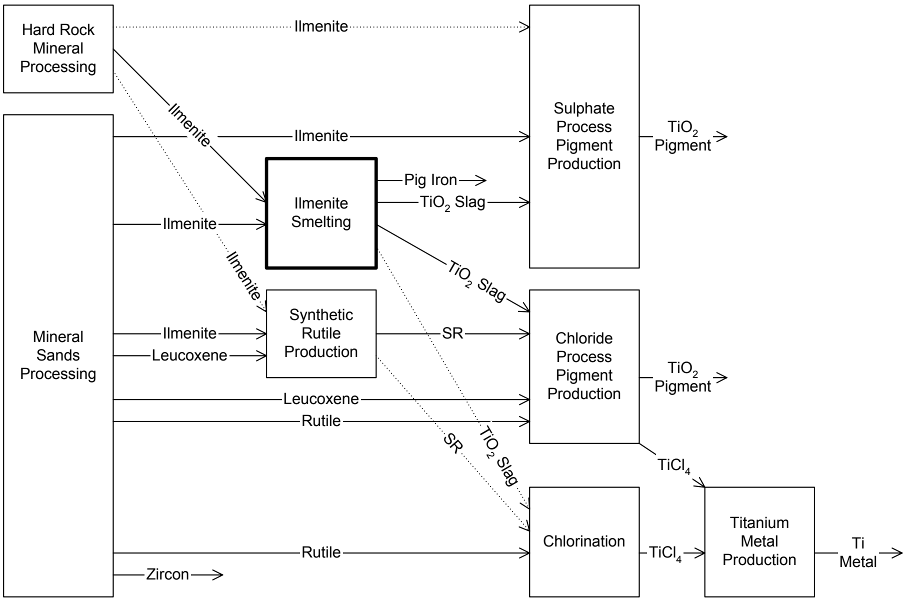

Figure 1 - Process routes in the Ti/TiO_2 industry. (Kahn, 1984; Stanaway 1994)

Material	TiO_2 Content
Ilmenite	37 – 54%
Leucoxene	55 – 65%
Rutile	95%
TiO_2 slag	75 – 85%
Synthetic Rutile (SR)	90 – 93%

Table 1 - TiO_2 feedstock composition. (Stanaway, 1994)

The minerals and process stages indicated on Figure 1 are described in more detail below. These descriptions only serve to introduce the reader to the industrial context of this project, and do not aim to provide complete details of the materials and processes.

1.1.1 Minerals

The minerals indicated on Figure 1 (rutile, leucoxene, ilmenite and zircon) are often found together in sand-type mineral deposits and are collectively referred to as 'heavy minerals'. Ilmenite is also found in hard rock deposits where the other heavy minerals are present to a lesser degree or not at all.

a. Rutile

As indicated by Table 1, rutile (nominally TiO_2) contains the highest level of TiO_2 of all the heavy minerals. It is the feedstock of choice for chloride pigment production (and most probably for titanium metal production via chlorination also) because of its bulk density, low iron content and low impurity content (Stanaway, 1994). The sulphate pigment producers do not use rutile because it is insoluble in sulphuric acid (Stanaway, 1994).

b. Leucoxene

Leucoxene (also referred to as leucoxenised ilmenite) is ilmenite that had been naturally upgraded to a higher TiO_2 content as a result of iron that had been leached out by ground water. It is a feedstock used by the chloride pigment producers, but since there are rutile crystals in the grains, the sulphate pigment producers do not favour it. Leucoxene is also used for synthetic rutile production.

c. Ilmenite

The TiO_2 content of ilmenite (nominally $FeTiO_3$) can vary over a wide range as is indicated in Table 1. Weathering can concentrate TiO_2 in ilmenite in the same way that leucoxene is formed from ilmenite. Significant levels of impurities (MgO, CaO, SiO_2, MnO, etc.) in the mineral can yield ilmenite with TiO_2 content lower than the 52.6% in pure stoichiometric ilmenite.

As indicated by Figure 1, ilmenite is the most widely used natural mineral in the Ti/TiO_2 industry. It can be upgraded to feedstock for pigment production by either smelting or synthetic rutile production. In addition, sulphate pigment producers are able to use ilmenite directly for pigment production. This is however not preferred because of the increased levels of waste material produced.

d. Zircon

Zircon (nominally $ZrSiO_4$) is the only product from mineral sands processing that does not contain titanium. It is used in the ceramic tile industry for the manufacture of coatings, and in the refractory materials industry as a component in refractory bricks.

1.1.2 Hard Rock Mineral Processing

Hard rock mineral processing is used in cases where ilmenite occurs in hard rock deposits and not in the form of mineral sands. This type of processing is used in Canada and Norway to concentrate hard rock ilmenite. In both cases the ilmenite product is smelted to produce pig iron and high-titania slag. The purpose of this mineral processing stage is therefore to provide an ilmenite concentrate that can be upgraded to a suitable feedstock for pigment production.

1.1.3 Mineral Sands Processing

The mineral sands processing stage in Figure 1 is common to most process routes leading from ore to pigment or metal. This stage yields up to four products, depending on the ore body. These products are the four minerals discussed above. The purpose of this stage (within the context of the Ti/TiO_2 industry) is to produce rutile concentrate for direct use in chloride pigment production, to produce leucoxene either for direct use in chloride pigment production or in synthetic rutile production, and to produce ilmenite that can be upgraded to be a suitable feedstock for pigment production (both sulphate and chloride routes).

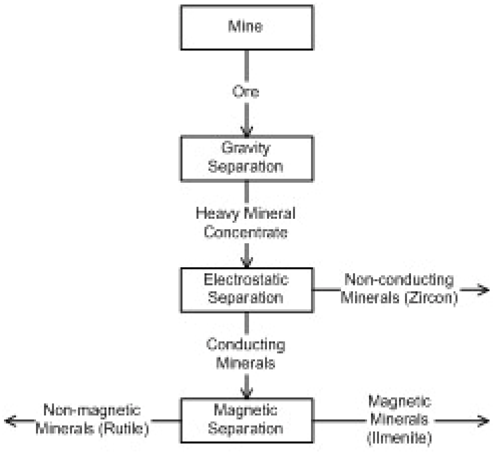

Figure 2 – Main process steps in a mineral sands operation. (Kahn, 1984)

Figure 2 shows a simplified process flow of a mineral sands processing operation. Mining can be done by dredging or hydraulic methods. The ore is then gravity separated by, for example, spirals to yield a heavy mineral concentrate that can be beneficiated further. Electrostatic and magnetic separation are used to extract the valuable minerals from the concentrate.

1.1.4 Ilmenite Smelting

The ilmenite smelting stage shown in Figure 1 and, more specifically, the ilmenite smelting furnace, is the focus of the current work. The stage is outlined briefly here and the ilmenite smelting furnace process is discussed in more detail in CHAPTER 2.

The purpose of this stage is to upgrade ilmenite to a suitable feedstock for sulphate and chloride pigment producers. Figure 3 shows the main steps to be found in various ilmenite smelting operations. Ilmenite can be brought into the furnace via the following three routes:

- Feed ilmenite received from the mineral processing plant directly into the furnace at ambient temperature. Most ilmenite smelters (Richards Bay Minerals, Namakwa Sands, and Ticor South Africa) utilise this route. It is not sure whether the Tinfos operation in Norway is able to feed ilmenite directly into their furnace.

- Pre-heat ilmenite before feeding it into the furnace. This is an additional route found in newer ilmenite smelters (Namakwa Sands, Ticor South Africa). The chemical energy in the off-gas from the smelting furnace is utilised to reduce the consumption of electrical energy and graphite electrodes.
- Pre-reduce ilmenite before feeding it into the furnace. This route is used by the Tinfos operation in Norway (Rosenqvist, 1992). Ilmenite is first pelletised with bentonite as binder, and then prereduced in a rotary kiln with coal at temperatures of around 1150 °C (Rosenqvist, 1992). The pre-reduction product, with a degree of metallisation (of iron) of around 70%, is then fed into the smelting furnace.

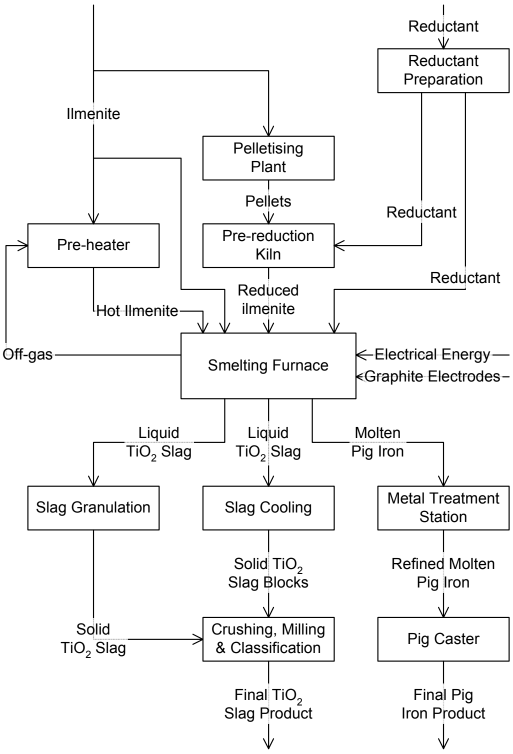

Figure 3 – Main process steps in ilmenite smelting operations.

The smelting furnace itself can be configured in the following ways:

- Rectangular six-in-line AC (alternating current) electric arc furnaces are used by Quebec Iron and Titanium Corporation (QIT) at Sorel in Canada, and by Richards Bay Minerals (RBM) at Richards Bay in South Africa.

  As the name suggests, these furnaces operate with six electrodes. Pre-baked graphite electrodes are used. Ilmenite and reductant are fed into the furnace through a multitude of feed ports in the furnace roof.

- A circular AC electric arc furnace is used by Tinfos at Tyssedal in Norway.

  This furnace has three self-baking Söderberg electrodes and a number of feed ports are also used to feed pre-reduced ilmenite and coal into the furnace.

- Circular DC (direct current) electric arc furnaces are used by Namakwa Sands (NS) at Vredenburg in South Africa, and by Ticor South Africa (TSA) at Empangeni in South Africa.

> These furnaces operate with a single hollow pre-baked graphite electrode. Ilmenite (cold or pre-heated) and reductant are fed into the furnace via the hollow electrode.

The off-gas from the smelting furnaces is usually rich in chemical energy (being mainly CO) and can be used for various heating applications on the site. As stated earlier, the newer smelting plants tend to use this gas to pre-heat the ilmenite and save on their electricity and electrode bills.

After tapping, the metal product from the furnace (typically liquid iron with 2% carbon) is first treated to increase the carbon content and reduce the sulphur content. Some alloy additions may also be done depending on the specification of the particular client. The purified high-carbon metal is then cast into pigs and subsequently shipped.

More than one option is available to handle the slag product tapped from the furnace. The most conventional of these is pouring the slag into pots and letting it cool down in block form. These blocks are then crushed, milled and classified into the desired size fractions required by pigment producer clients. An alternative is to granulate the slag as it exits from the furnace. This option is attractive in that it saves capital cost of crushers, mills and classifiers, and it rules out the need for a block yard for cooling large slag blocks.

1.1.5 Synthetic Rutile Production

The synthetic rutile production stage indicated on Figure 1 has much the same purpose as the ilmenite smelting stage. It aims to upgrade ilmenite and leucoxene to feedstock that is suitable, specifically, for the chloride route of pigment production. The iron in the feed materials is generally not recovered and is turned to waste. This is in contrast with ilmenite smelting that extracts the iron as pig iron that is a valuable by-product for the business and places less strain on the environment.

A large number of synthetic rutile production processes exist (Columbia Southern, Murso, Laporte, Benelite, Kerr-McGee, Ishihara, and Becher) (Kahn, 1984). These processes can be classified as involving either partial reduction of iron or total reduction of iron. One partial reduction and one total reduction example are discussed below.

a. Kerr-McGee process

The Kerr-McGee process is shown in Figure 4. It involves partial reduction of ilmenite in a rotary kiln. The kiln is operated under oxygen deficient conditions. The iron in the ilmenite is reduced to the ferrous (2+) state. The reduced ilmenite is batch leached in digesters with an 18 to 20% hydrochloric solution. During leaching the iron is dissolved as ferrous chloride ($FeCl_2$) while the TiO_2 remains as porous solid particles according to the following chemical reaction (Kahn, 1984):

$$FeO.TiO_2 + 2HCl \rightarrow FeCl_2 + TiO_2 + H_2O$$

The spent leach liquor and solid particles are separated and the liquid sent to an acid regeneration plant. The acid regeneration proceeds as follows (Kahn, 1984):

$$4FeCl_2 + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8HCl$$

The separated solids are washed to clean it from chlorides and acid, and then calcined to produce the final synthetic rutile product. (Kahn, 1984)

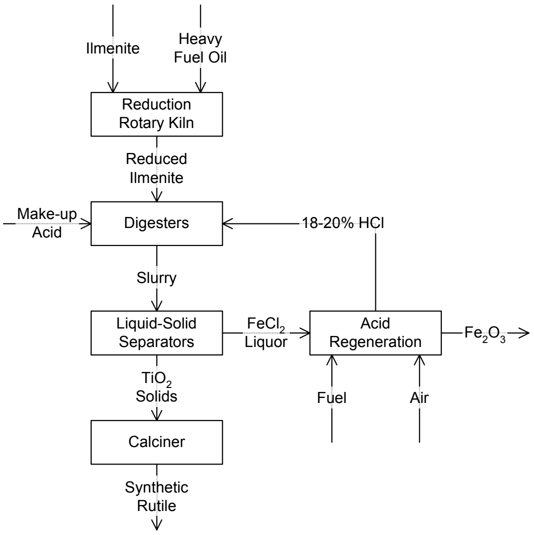

Figure 4 - The Kerr-McGee synthetic rutile process (Kahn, 1984).

b. Becher process

The Becher process utilises complete reduction of iron in ilmenite to produce synthetic rutile. This process is shown in Figure 5.

In the first step of the process, ilmenite is oxidised at around 1000 °C to transform the ilmenite phase to a combination of rutile and pseudobrookite as follows (Kahn, 1984):

$$2FeTiO_3 + \tfrac{1}{2}O_2 \rightarrow Fe_2TiO_5 + TiO_2$$

The oxidation causes cracking and lattice expansion that are beneficial to the overall kinetics in the following reduction step. In the reduction step coal is added to the oxidised ilmenite at around 1200 °C to convert all iron to the metallic state. The excess coal char exiting from the reduction kiln is separated from the reduced ilmenite by magnetic separation after cooling.

The reduced ilmenite is fed into an aerator together with water, some ammonium chloride as catalyst, and large volumes of air. The main reaction taking place in the aerator is as follows (Kahn, 1984):

$$3Fe^{\circ} + 3TiO_2 + 2O_2 \rightarrow Fe_3O_4 + 3TiO_2$$

The iron oxide precipitates as a slime that is separated from the TiO_2 particles by using hydro cyclones. The solids are calcined to produce the final synthetic rutile product. (Kahn, 1984)

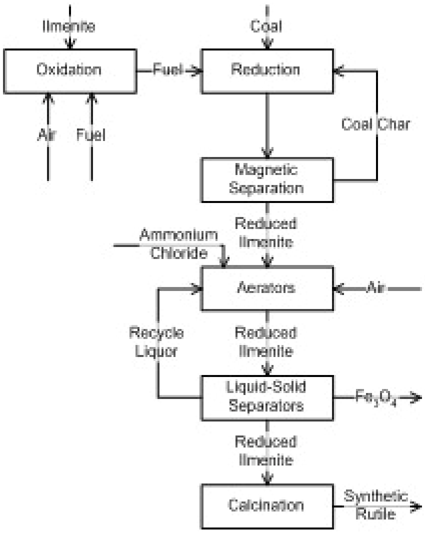

Figure 5 - The Becher synthetic rutile process (Kahn, 1984).

1.1.6 Sulphate Process Pigment Production

As indicated on Figure 1, TiO_2 pigment and titanium metal are the final products. The sulphate process of pigment production is one process that can be used to convert TiO_2 feedstock to pigment. The preferred raw materials for the sulphate process are high-titania slag and some ilmenites. Leucoxene, rutile and synthetic rutile are not used because of TiO_2 being present in the form of a rutile phase that is insoluble in sulphuric acid (Stanaway, 1994). Even slags with very high TiO_2 content can cause problems because the fraction of TiO_2 present as rutile increases with total TiO_2 content.

The slag or ilmenite is dissolved in sulphuric acid according to the following reaction (Stanaway, 1994):

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

Iron sulphate is removed as solid copperas along with other undissolved solids. Following this, the titanyl sulphate is hydrolysed to hydrated TiO_2 from which TiO_2 is precipitated as either rutile or anatase. The final pigment product is produced after purifying, filtering, calcining and milling of the precipitate. (Stanaway, 1994)

1.1.7 Chloride Process Pigment Production

The chloride process for pigment production is the newer alternative to the sulphate process. A major advantage of the chloride process is the reduced amount of waste generated and therefore smaller environmental impact. The main steps of this process are shown in Figure 6.

The feed material (rutile, synthetic rutile, high-titania slag) is fed into the fluid bed chlorinator together with chlorine and petroleum coke. The following reactions take place in the chlorinator at its operating temperature of around 900 °C (Stanaway, 1994):

$$2C + O_2 \rightarrow 2CO$$

$$TiO_2 + 2Cl_2 + 2CO \rightarrow TiCl_4 + 2CO_2$$

The product gas from the chlorinator contains excess Cl_2, $TiCl_4$, CO, CO_2 and other chlorides. The impurity chlorides ($AlCl_3$, $SiCl_4$, $COCl_2$, $SnCl_4$, $VOCl_3$, etc.) are removed from the $TiCl_4$ by selective distillation (Kahn, 1984). The final purified $TiCl_4$ is converted to TiO_2 by the following reaction (Stanaway, 1994):

$$TiCl_4 + O_2 \rightarrow TiO_2 + Cl_2$$

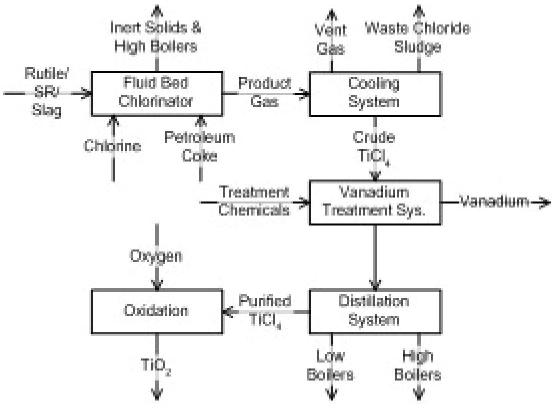

Figure 6 - Main steps in the chloride process for pigment production (Kahn, 1984).

Of specific relevance to ilmenite smelting and this project is the "Inert Solids & High Boilers" output stream from the fluid bed chlorinator indicated in Figure 6. This stream includes high-boiling-point chlorides such as $CaCl_2$ and $MgCl_2$ that exist as liquids at chlorinator operating conditions. These species tend to build up in the bed, making it necessary to purge it before the bed is defluidised (Kahn 1984). Such purging actions are a cost penalty to the operation both because of the waste generated and because of the production loss (Stanaway, 1994).

Poor control over freeze lining thickness in an ilmenite smelting furnace can result in refractory wear and increased levels of MgO in the slag. This directly contributes to the amount of high-boiling-point species in the chlorinator.

1.1.8 Titanium Metal Production

The process of titanium metal production is closely related to the chloride process of pigment production. The reason is that the final stage of titanium metal production also makes use of $TiCl_4$ for conversion to the sponge metal product. (Kahn, 1984)

Due to this significant similarity, some titanium metal producers simply buy $TiCl_4$ from chloride process pigment producers. This is indicated on Figure 1. If a titanium metal producer chooses not to do this, he has to use his own $TiCl_4$ production facility that would look identical to the one shown in Figure 6. The only difference is then the conversion of $TiCl_4$ to titanium metal rather than to TiO_2. A simplified closed-loop titanium sponge production flow sheet is shown in Figure 7. The details of $TiCl_4$ production have been omitted here.

This seems to be a very attractive process route because chlorine and magnesium are recycled. The conversion of $TiCl_4$ to titanium metal occurs according to the following chemical reaction (Kahn, 1984):

$$TiCl_4 + 2Mg^{\circ} \rightarrow Ti^{\circ} + 2MgCl_2$$

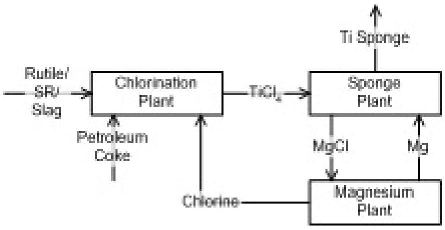

Figure 7 - Simplified process flow of closed-loop titanium sponge production (Kahn, 1984).

The magnesium plant regenerates magnesium and chlorine as follows (Kahn, 1984):

$$MgCl_2 \rightarrow Mg^{\circ} + Cl_2$$

1.1.9 Importance of Ilmenite Smelting

To conclude this overview of the Ti/TiO_2 industry, the focus is drawn back to ilmenite smelting. The important role of ilmenite smelting is illustrated by the volumes of feedstock that it provides to pigment producers. In 1994, high-titania slag represented just over 50% of the mass of feedstock provided to pigment producers (Stanaway, 1994). Stanaway's text only refers to the ilmenite smelters operated by QIT, RBM and Tinfos. Today another two smelters, those of Namakwa Sands and Ticor South Africa, are in operation and another is being planned for the Southern African region. It is therefore likely that the fraction of total pigment feedstock provided by ilmenite smelters may have increased in the past nine years. This is however not confirmed.

The importance of ilmenite smelting in the Ti/TiO_2 industry can therefore not be ignored. It also appears likely that this route of upgrading minerals to suitable feedstock for the pigment industry will grow relative to synthetic rutile production due to the impact that waste materials from synthetic rutile processes have on the environment.

1.2 OVERVIEW OF CURRENT WORK

Before discussing the current work, an introduction to the ilmenite smelting furnace process is in order. Such an introduction is provided in CHAPTER 2. If the reader is unfamiliar with the process, it is suggested that this chapter is read before continuing here.

1.2.1 Objectives

The main objective of this project is to study the dynamic interactions between the freeze lining and slag bath of ilmenite smelting furnaces. The objectives are set out more specifically as follows:

- Study and characterise the time dependent change in
  - freeze lining thickness,

  - freeze lining temperature distribution, and
  - freeze lining composition distribution

  in response to

  - changes in net power input into the slag bath,
  - changes in slag bath composition, and
  - changes in operating set points such as specific energy and reductant inputs.

- Study and characterise the time dependent change in
  - slag bath temperature, and
  - slag bath composition

  in response to

  - changes in net power input into the slag bath,
  - changes in freeze lining thickness, and
  - changes in operating set points such as specific energy and reductant inputs.
- Study and characterise the influence of slag solidification and melting in the furnace on the composition of liquid slag in the slag bath.

The following influences on the freeze lining are considered of secondary importance within the context of this study and are either treated in very simplified ways, or ignored completely:

- The amounts of liquid metal and liquid slag in the furnace,
- the influence of metal and slag taps, and
- the influence of furnace down-time.

1.2.2 Impetus for Study

A number of factors make the freeze lining in an ilmenite smelting furnace particularly important. Firstly, no known refractory material can withstand the chemical attack of highly corrosive liquid titania slag. Secondly, the cost involved in replacing a furnace lining (including cost of the refractory material, labour associated with installation, and lost production time) is expensive (Elstad et. al., 2003) and ilmenite smelting businesses are reliant on furnace linings lasting for up to 10 years.

Poor control of the furnace freeze lining can result in rapid deterioration of the furnace refractory lining. This could ultimately lead to the furnace burning through, and more certainly to early replacement of the refractory lining.

The state of the freeze lining cannot be determined by any direct means, except when the furnace had been switched off and emptied. Even in these circumstances much of the freeze lining would have decrepitated and fallen off the wall by the time the furnace is cold enough to examine. The freeze lining state parameter of primary importance to furnace operation and control is thickness. Also of interest are the distribution of chemical and phase composition, and the distribution of temperature through the lining.

Because no direct measures are available, indirect means are used to infer the state of the freeze lining. Thermocouples installed in the furnace refractory lining on the level of the freeze lining are used to infer thickness. These thermocouples are usually installed a significant distance away from the refractory lining hot face due to the apparent risks of installing thermocouples deep into the lining. The distance of the thermocouple away from the refractory lining hot face and the thickness of the freeze lining add to the total distance between the thermocouple and the point of interest, the interface between the freeze lining and the liquid slag bath.

This distance together with the thermal conductivity and heat capacity of the freeze lining and refractory lining materials has an important influence on the thermocouple signal. It determines the lag between the time when a change in conditions at the freeze lining hot face takes place, and the time when the influence of the changed conditions is detected in the thermocouple signal. This lag is typically in the order of hours. Because the thermocouple signal is used to control the freeze lining thickness, this lag results in dead time in the control problem, making it a much more difficult problem to solve. These signals are also used for monitoring the state of the refractory lining over periods of months and years. Having reliable and interpretable signals for this purpose is another important issue to consider when deciding on the positions at which the thermocouples are installed.

A better understanding of the dynamic response of the freeze lining to changing conditions in the slag bath can contribute in a number of ways to the improved operation and control of an ilmenite smelting furnace:

1. The influence of thermocouple position relative to the refractory lining hot face on the controllability of freeze lining thickness can be quantified. In this way modification of existing thermocouple installations or new installations can be justified responsibly. Modified and new installations can contribute directly to improved freeze lining control and refractory lining monitoring.
2. Knowledge of the dynamic behaviour of the freeze lining can be used directly in the design and development of controllers that can possibly be used for closed-loop control of freeze lining thickness. Implementation of such a controller can result in higher furnace throughput and extended life of the refractory lining. Throughput can be increased by running safely with a thinner freeze lining and by controlling the furnace energy balance in such a way that slag foaming is avoided.
3. Knowledge of the influence of solidification and melting at the freeze lining hot face on the slag bath can be used in the design and development of a more complete slag chemistry control strategy that takes this influence into account. Implementation of such a strategy can result in tighter control over slag chemistry and improved overall process efficiency. Efficiency will improve when slag chemistry is tightly controlled around the set point because excessively high TiO_2 content in the slag and associated high temperature conditions, resulting in increased heat losses and increased probability of slag foaming, will be avoided.

In addition to the direct contributions to furnace operation and control, the results of this study will contribute to the already existing and growing body of knowledge about ilmenite smelting. It will perhaps contribute a small piece to the puzzle regarding the compositional invariance of ilmenite smelting slag close to the M_3O_5 composition. It will also add to the current understanding of freeze lining behaviour, and possibly provide new options for improving furnace control and operation. The added knowledge can be used in future work to improve the process and, perhaps to a lesser degree, to better understand and improve other similar processes.

1.2.3 Approach

The approach of this project is purely one of mathematical modelling. The regions of interest in the ilmenite smelting furnace are modelled to such a degree of detail as is required to achieve the objectives of the study. Because of this, numerous assumptions and simplifications are made to arrive at manageable modelling problems that can serve a purpose in the current work.

As a combination of heat transfer and chemical reactions determine the behaviour of the freeze lining and of the furnace as a whole, the modelling technique applied focuses on these aspects. Because it is believed that a detailed description of momentum transfer and therefore fluid flow in the furnace will not add significantly to the value of the models at this stage, momentum transfer is not incorporated into the models except for some simplifications and assumptions in this regard.

1.3 ORGANISATION OF CURRENT TEXT

The remainder of the current text is organised as follows:

- CHAPTER 2 is dedicated to describing the ilmenite smelting process and relevant prior work done on the process.
- CHAPTER 3 describes the details of a one-dimensional heat transfer and chemical reaction model of the freeze lining and furnace wall that is used for modelling the dynamic behaviour of the freeze lining.
- CHAPTER 4 describes the details of a mathematical model similar to the one in CHAPTER 3 that is used for modelling formation and melting of the crust on top of the slag bath.
- CHAPTER 5 describes the details of a mathematical model of the entire ilmenite smelting furnace process. This model incorporates the models described in CHAPTER 3 and CHAPTER 4 into a formulation describing the slag bath, metal bath, furnace atmosphere and all relevant chemical reactions.
- CHAPTER 6, CHAPTER 7, CHAPTER 8 and CHAPTER 9 provide details and results of experiments focussed on studying the dynamic behaviour of the freeze lining and slag bath in response to various influences. The work described in these chapters is the main focus of this project.
- CHAPTER 10 provides a focussed discussion of the observed compositional invariance of high-titania slags close to the stoichiometric M_3O_5 composition. A mechanism by which this invariance can be explained is presented here.
- CHAPTER 11 is the concluding chapter that contains summarising statements about the work and results obtained.