CHAPTER 10
COMPOSITIONAL INVARIANCE OF HIGH-TITANIA SLAG

This chapter is dedicated to the observed compositional invariance of high-titania slag. The compositional invariance as observed by Pistorius (1999) and others is first discussed. This is followed by a review of the possible causes as reported by Pistorius. Finally, a new mechanism is proposed by which the compositional invariance can be explained.

10.1 THE RELATIONSHIP BETWEEN FeO AND Ti_2O_3

Pistorius (1999) identified a relationship between FeO and Ti_2O_3 in industrial high-titania slags. This relationship was subsequently investigated further (Pistorius, 2002; Pistorius and Coetzee, 2003; Pistorius, 2003; Pistorius, 2004). The relationship is illustrated in Figure 158 and Figure 159.
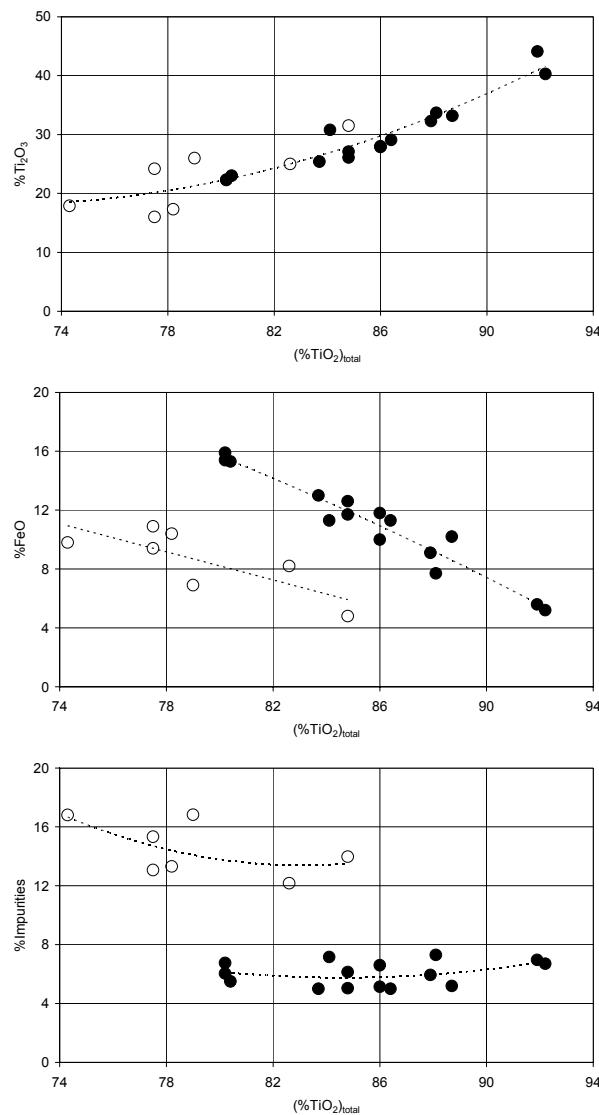

Figure 158 – Compositional relationships in industrial high-titania slags.
Filled circles indicate slags from South African ilmenites and empty circles slags from Canadian ilmenites. The horizontal axis indicates the total Ti content of the slag as TiO_2.
Recreated from Pistorius (2002).

The data presented in Figure 158 serves as background and highlights the difference between slags produced from South African and Canadian ilmenites. The most important difference between these ore types is the significantly higher alkali earth content of Canadian ilmenites (Pistorius, 2002).

Pistorius (2002) plotted graph (a) of Figure 159 by using the FeO and Ti_2O_3 content as reported in the chemical analyses. He then calculated the Equivalent amounts of FeO and Ti_2O_3 as used in graph (b) by grouping divalent impurities (MgO and MnO) with FeO, and trivalent impurities (V_2O_3, Cr_2O_3 and a portion of Al_2O_3) with Ti_2O_3. This was done because it is known that these impurities also occur in the M_3O_5 solid solution.
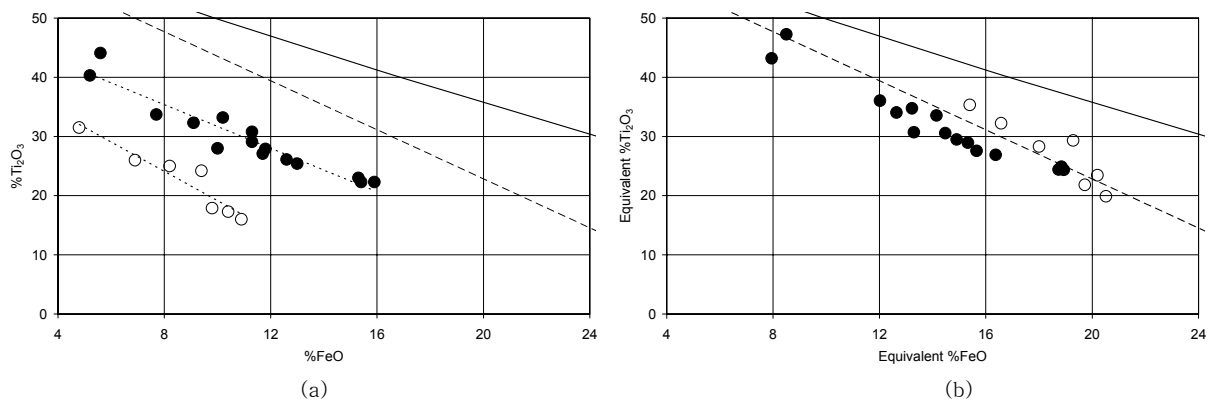
Figure 159 – The relationship between FeO and Ti_2O_3 in industrial high-titania slags.

Filled circles indicate slags from South African ilmenites and empty circles slags from Canadian ilmenites. The dashed line indicates the stoichiometric M_3O_5 composition. The solid line indicates the composition of slag on the slag/(slag + Fe°) boundary shown in Figure 14 and represents equilibrium between slag and iron metal. Recreated from Pistorius (2002).

The recalculated Ti_2O_3 vs. FeO presented in graph (b) of Figure 159 most clearly displays the observed compositional invariance of industrial high-titania slags close to the stoichiometric M_3O_5 composition. What is especially noticeable is that slags from both South African and Canadian ilmenites display this relationship.

The reason for the significance of this relationship is the fact that some pigment manufacturers specify a maximum Ti_2O_3 content in slags from their suppliers. Understanding this relationship could therefore assist slag producers to improve control over slag quality. It is of course this relationship that is one of the key issues of the current study.

Pistorius (2002) has considered possible mechanisms that could cause the observed relationship. He broadly identified possible causes as reaction equilibrium, kinetic effects and phase chemistry. These candidates are reviewed again below.

10.2 REACTION EQUILIBRIUM AS A POSSIBLE MECHANISM

10.2.1 Arguments For

When one considers the observed relationship between FeO and Ti_2O_3 the most prominent explanation that comes to mind is thermodynamic equilibrium. The reasons are the relatively high temperatures (around 1700 °C) in the smelting furnace and the significant stirring in the slag and metal baths.

The high temperatures make it less likely to find chemical reaction rate controlling steps, and the stirring reduces the probability of finding steps controlled by mass or heat transfer. It would therefore seem that the process should be influenced to a large degree by the drive towards thermodynamic equilibrium.

It is of course known that the slag and metal baths in an ilmenite-smelting furnace are not in thermodynamic equilibrium, and that kinetic effects play a significant role in reactions involving reductant particles. Even when these facts are accepted, it is still argued that thermodynamic equilibrium should have a significant influence on the behaviour of the process. Since there are kinetic barriers between phases that prevent the process from reaching a global equilibrium, one then expects that the influence of the drive towards thermodynamic equilibrium should be visible within a single phase.

The content of different species within a phase should therefore all correlate well with the same dominant factor determining equilibrium in the phase. For example, if measurements of the partial oxygen pressure (P_{O2}) in the slag agree well with a calculated P_{O2} based on the FeO-Fe redox couple, it is expected that a P_{O2} calculated based on the TiO_2-Ti_2O_3 redox couple should give the very similar results. (The fact that the opposite was found to be true by Geldenhuis and Pistorius (1999) is deliberately ignored here for the sake of the argument.)

10.2.2 Arguments Against

While the above argument in favour thermodynamic equilibrium as a possible mechanism is based on qualitative statements and intuition, the case against it is far more concrete.

The data presented in Figure 159 clearly shows an offset between actual slag compositions and slag compositions in equilibrium with pure iron metal. It is also well known that the slag bath is not in equilibrium with the carbon dissolved in the metal bath. Geldenhuis and Pistorius (1999) further reported a significant difference between the P_{O2} measured and calculated based on the FeO-Fe redox couple, and the P_{O2} calculated based on the TiO_2-Ti_2O_3 redox couple.

These observations seem to negate virtually all arguments in favour of thermodynamic equilibrium contributing to the FeO-Ti_2O_3 relationship.

10.3 KINETIC EFFECTS AS A POSSIBLE MECHANISM

10.3.1 Arguments For

When Pistorius (1999) identified the FeO-Ti_2O_3 relationship, he suggested that the relative reaction kinetics of the reduction of FeO to Fe and TiO_2 to Ti_2O_3 may govern the extent to which the slag compositions deviate from equilibrium.

Very little is known about the kinetics of reduction reactions taking place in an ilmenite-smelting furnace. This results in reaction kinetics remaining a possible mechanism when other options such as thermochemistry that are understood more clearly cannot explain the observed phenomena.

10.3.2 Arguments Against

Pistorius (2002) presented three arguments against kinetic effects as a possible mechanism. Firstly he observed that the $FeO-Ti_2O_3$ relationship remained remarkably consistent for furnaces with significantly different sizes and stirring patterns. Secondly, the fact that TiO_2 occurs in much higher concentration in the slag compared with FeO, makes it unlikely that mass transfer effects would cause slower reduction rates of TiO_2. Finally, it is difficult to explain, on the basis of kinetics, why Canadian ilmenites show a consistently lower Ti_2O_3 content at a specific FeO content.

In general it must be cited again that the high temperatures and strong mixing in the furnace reduce the likelihood of kinetic effects being responsible for the $FeO-Ti_2O_3$ relationship.

10.4 EUTECTIC GROOVE PHASE EQUILIBRIUM AS A POSSIBLE MECHANISM

10.4.1 Arguments For

Pistorius (2002) stated that the $FeO-Ti_2O_3$ relationship may be determined by the tendency of the slag to solidify as virtually a single phase (M_3O_5). This possibility was further explored and elaborated upon (Pistorius and Coetzee, 2003). The authors argued that the presence of a freeze lining and the resulting influence of the solidification equilibrium between the liquid slag bath and the solid slag of the freeze lining may be the cause of the $FeO-Ti_2O_3$ relationship. This was supported by the observation that this relationship was not evident in cases where a freeze lining was absent (Ban and Krüger, 1988).

It was further argued that the eutectic groove that is close to the M_3O_5 stoichiometric line could serve to constrain the slag composition close to the M_3O_5 composition. For this to be possible, the liquid slag composition had to be between the eutectic groove and the M_3O_5 line on the ternary diagram. This has been shown to be true specifically for South African ilmenites (Pistorius, 2002). The argument was strengthened further by the fact that rutile is present in the solidified slag, as would be expected for a slag composition between the M_3O_5 composition and the eutectic groove. The actual rutile content of the slags was however smaller that what was predicted based on this theory.

10.4.2 Arguments Against

The proposed mechanism causing the $FeO-Ti_2O_3$ relationship (Pistorius and Coetzee, 2003) was tested by using a simple heat transfer model (Pistorius, 2004). The conclusion from this work was that the phase equilibrium between the freeze lining and liquid slag cannot serve to constrain the liquid slag composition to the eutectic groove.

What would the reason be for this mechanism not being able to produce the observed $FeO-Ti_2O_3$ relationship? The most basic explanation is that solidification of slag with a composition between the stoichiometric M_3O_5 line and the eutectic groove is not able to make a lasting change to the composition of the liquid slag.

The reason is that any change in the composition of the slag bath caused by solidification when the original slag bath composition is situated between the stoichiometric M_3O_5 line and the eutectic groove is only temporary. If such solidification had pushed the composition of the slag bath into the eutectic groove, this means that a significant amount of solid slag must have been produced. If the freeze lining thickness is to remain constant, this solid slag must be melted into the slag bath again. This will cause the exact opposite of the initial compositional change into the eutectic groove. The only way in which such solidification can constrain the slag bath composition close to or on the eutectic groove would be for the solid slag product to be removed from the furnace continuously. This is off course not what happens in reality.

10.5 A NEW MECHANISM PROPOSED

This section describes the details of a new mechanism that is suggested to contribute to the observed $FeO-Ti_2O_3$ relationship.

10.5.1 Requirements

When formulating the mechanism, a clear list of requirements was compiled. These requirements had to be met by the mechanism for it to be considered a feasible explanation of the observed phenomenon, in this case the $FeO-Ti_2O_3$ relationship. The following requirements were listed:

- The mechanism must be able to have a sustained influence on the composition of the slag bath.
- The mechanism must be able to adjust the composition of the slag bath towards the stoichiometric M_3O_5 line.

10.5.2 Background Information

Available information about all of the most important phenomena relevant to the system and the observed phenomenon was consolidated to serve as background for the formulation of the mechanism. These aspects are summarised below.

a. Chemical reaction equilibrium

As has been explained before, the high temperatures and significant stirring in the slag and metal baths create conditions that would favour the drive towards thermodynamic equilibrium. It is therefore expected that the reduction reactions taking place in the furnace would be influenced significantly by such equilibrium. Proof has been provided in Figure 159 that the actual slag compositions do not correspond with the extent of reduction reactions at equilibrium. This is however ignored for the moment to demonstrate the influence of the drive towards equilibrium in isolation.

This influence is shown in Figure 160. This figure was constructed by adding progressively more carbon and adjusting the temperature of the system up to the point where all slag is present in the liquid state. The presence of iron as a reduction product results in the slag composition following the slag/(slag+Fe°) phase boundary.
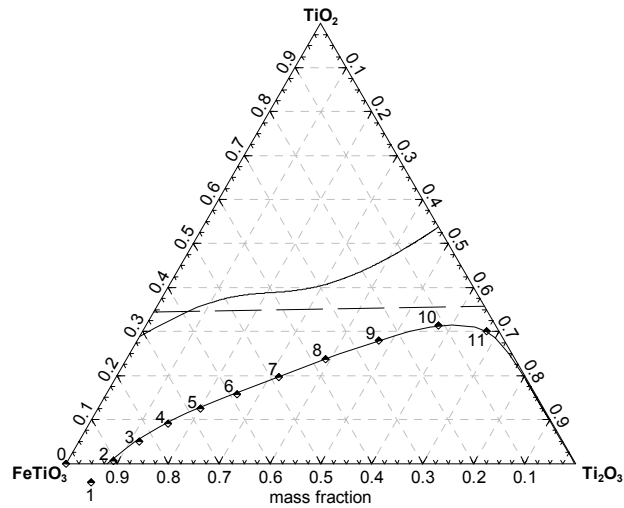
Figure 160 – Slag composition according to reduction reactions
at equilibrium.

Numbers next to the symbols indicate the amount of carbon
added in kg carbon/100 kg ilmenite.

b. Solidification behaviour

The solidification behaviour of the $FeTiO_3$–TiO_2–Ti_2O_3 system was discussed and illustrated in paragraph 2.6.2. Liquidus diagrams were provided in Figure 10 and Figure 11, and liquid slag composition trajectories were demonstrated in Figure 14.

Something that can be concluded from the binaries provided in Figure 9, but that is not evident from the liquidus diagrams and the liquid slag composition trajectory diagram, is the influence of solidification on slag composition. For this reason, Figure 161 was constructed.
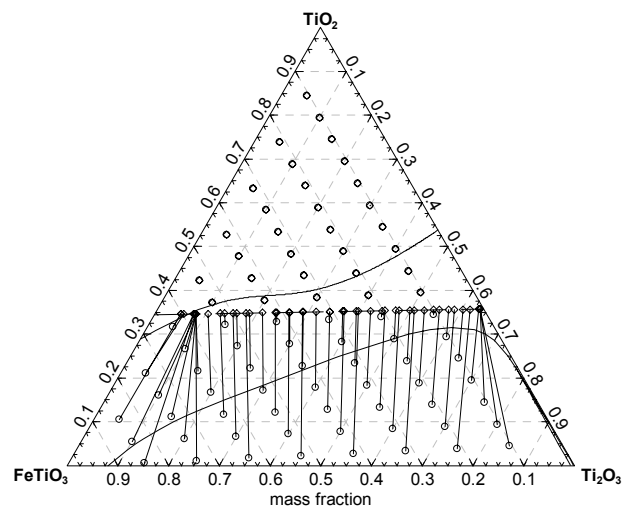

Figure 161 – The influence of solidification on slag
composition.
A circle indicates an initial liquid slag composition and a
diamond the resulting composition of the slag once it had
completely solidified. Paired circles and diamonds are
connected with solid lines. In most cases slags were cooled to
1400 °C. Only the three compositions at approximately 85%
$FeTiO_3$ were cooled to 1300 °C.

From Figure 161 it is interesting to note that all liquid slag compositions above the stoichiometric M_3O_5 line remain unchanged after solidification. In contrast, all liquid slags with composition below this line are altered to a composition exactly on the M_3O_5 line upon complete solidification.

The reason for the contrast in solidification behaviour is that, in the case of compositions above the M_3O_5 line, solidification products only include oxide phases that are collectively view as slag. The entire mass of liquid slag therefore reports as solid slag once solidification is complete. This is not the case for liquid slag with composition below the M_3O_5 line. For these slags, iron metal becomes stable during solidification. Iron is, off course, not seen as slag. The mass of material that is viewed as slag reports to the pseudobrookite (or M_3O_5) phase. The change in slag (oxide) composition for slags with original compositions below the M_3O_5 join is caused by the disproportionation reaction ($Ti_2O_3 + FeO \rightarrow 2TiO_2 + Fe$) that occurs during cooling. This reaction hence enriches the slag in TiO_2, and depletes it of FeO – giving the composition trajectories that are shown in Figure 161.

c. Kinetic effects

Kinetic effects were discussed in 10.3. It is therefore adequate to state that contributions of mass transfer controlled and heat transfer controlled steps to the compositional invariance are improbable due to the significant stirring in both the slag and metal baths. The relatively small size of reductant particles (less than 10 mm diameter) further contributes to high reaction rates. Something that is not known, is the absolute and relative rates at which reduction reactions occur between slag and reductant particles, and between slag and high-carbon metal. One might speculate that the rate at which TiO_2 is reduced to Ti_2O_3, may differ from the rate at which FeO is reduced to Fe.

d. Industrial data

The last piece of background information is the knowledge of actual compositions of industrial slags. Compositions of a number of industrial slags have been presented in paragraph 10.1. These same compositions are displayed on the TiO_2–$FeTiO_3$–Ti_2O_3 ternary diagram in Figure 162. The actual slag FeO and Ti_2O_3 contents were converted to equivalent contents with the procedure used by Pistorius (2002). It is clear that the compositions of these slags are grouped around the M_3O_5 line. Slags from South African ilmenites tend to have compositions above the M_3O_5 line and slags from Canadian ilmenites below the line.
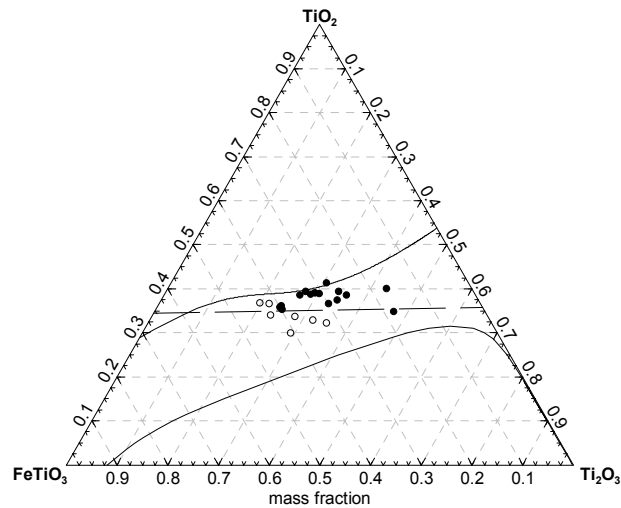
Figure 162 – Ternary view on compositions of industrial slags.

Filled circles represent slag produced from South African
ilmenites and empty circles slags from Canadian ilmenites.

10.5.3 A Step-by-Step Batch Experiment

The above knowledge about the process was used as the foundation on which the new mechanism was built. The first way of demonstrating the proposed mechanism is by describing a hypothetical step-by-step batch experiment using three of the background information items listed above. These items are knowledge about chemical reaction equilibrium, solidification behaviour and the actual compositions of industrial slags. Because of the uncertainty surrounding kinetic effects, these were not incorporated. All calculations described below were done with FactSage 5.2 and the results of the various steps are shown in Figure 163. The system was allowed to reach equilibrium during each of the steps.
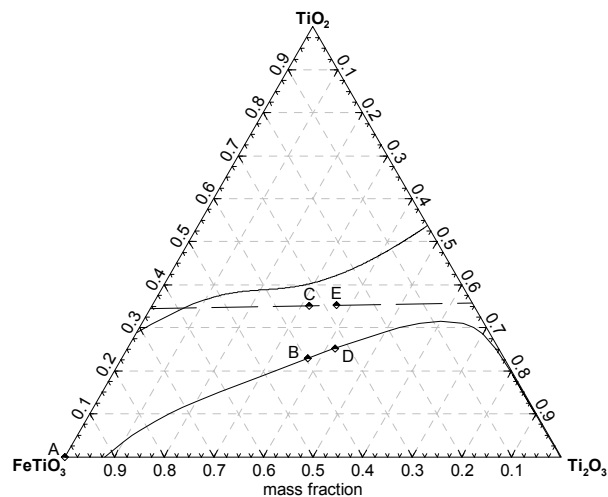

Figure 163 – Composition points resulting from the
hypothetical step-by-step batch experiment.

- Step 1:

  Heat 100 g of stoichiometrically pure ilmenite up to its liquidus temperature (1397 °C according to FactSage 5.2). The composition of the system is indicated by point **A** in Figure 163.

- Step 2:

  Add 7.8 g of pure graphite and heat the system to the liquidus temperature of the slag (1582 °C). This produces 61.6 g of slag with a composition indicated by point **B** in Figure 163. This step also produces 27.9 g of liquid iron with a carbon content of 0.11%.

- Step 3:

  Cool the system to the solidus temperature of the slag (1548 °C). The resulting solid slag has a mass of 60.0 g and consists of only pseudobrookite as indicated by point **C** in Figure 163. An additional 1.6 g of metal is produced during solidification.

- Step 4:

  Remove all metal and heat the system to the liquidus temperature of the slag (1587 °C). The slag composition and mass remains unchanged at point **C** in Figure 163 and 60.0 g respectively.

- Step 5:

  Add 0.48 g of carbon and adjust the system temperature to the liquidus temperature of the slag (1598 °C). The slag composition moves to point **D** in Figure 163 and the mass of slag decreases to 59.3 g.

  It is interesting to note that a line connecting points **C** and **D** on Figure 163 is parallel to the TiO_2–Ti_2O_3 axis of the diagram. This means that only one reduction reaction, the conversion of TiO_2 to Ti_2O_3, occurs between these two points. The FeO to Fe reaction only starts occurring again when the composition of the slag has reached the slag/(slag+ Fe°) phase boundary at point **D**.

- Step 6:

  Cool the system down to the solidus temperature of the slag (1562 °C). The slag's composition moves to point **E** in Figure 163 and its mass decreases to 58.0 g. Roughly 1.3 g of metal is produced.

- Step 7:

  Remove all metal and heat the system again to the liquidus temperature of the slag (1600 °C). The slag's composition and mass remain unchanged.

The above description serves to illustrate that a combination of the drive towards chemical reaction equilibrium, slag solidification and slag melting can contribute to constrain the composition of the slag to the stoichiometric M_3O_5 line. It does not, however, explain how these phenomena occur and combine in the actual process.

10.5.4 Description

In the case of the real process, a mass of pure ilmenite is not an appropriate starting point for a line of reasoning since this may only be representative of conditions when the furnace is first started up. A more

representative starting point is an established slag bath with a composition in the vicinity of the M_3O_5 line as shown in Figure 162. This starting point is indicated by area **A** in Figure 164.
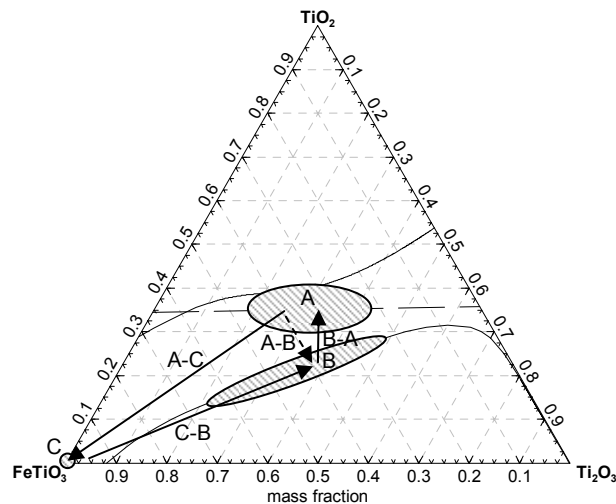

Figure 164 – Illustration of mechanism proposed to cause the
observed compositional invariance.

The proposed mechanism explains the observed compositional invariance close to the stoichiometric M_3O_5 line as follows;

- Ilmenite is continuously added to the process. Because of its low melting point (around 1397 °C according to FactSage 5.2), ilmenite is likely to melt quickly and subsequently absorbed into the slag bath. The influence of ilmenite addition on slag bath composition is indicated by composition vector **A-C** in Figure 164.

- Reductant is also fed continuously to the process. Reaction between reductant and liquid slag causes the slag composition to be drawn towards area **B**. This is indicated by composition vector **C-B** in Figure 164. Because vector **A-C** is unlikely to move the slag bath composition to area **C**, vector **C-B** could have been drawn more realistically from a more intermediate point on vector **A-C**.

- The uncertainties associated with vectors **A-C** and **C-B** in terms of extent and direction can be avoided by focusing on the resultant vector **A-B**. This vector shows the combined influence of ilmenite and reductant fed into the furnace on the composition of the slag bath.

- The impinging arc and entering feed material transfer momentum into the slag bath and thereby causes stirring of the slag bath. This stirring continuously causes slag to be circulated to and from the interface between the slag and metal baths.

  It is well known and it has been reported (Geldenhuis and Pistorius, 1999) that the slag and metal baths exist at significantly different temperatures. This difference has been reported to be between 38 and 86 °C (Geldenhuis and Pistorius, 1999). Subsequent to this work, Pistorius (1999) even used an assumption that the temperature of the metal bath is 150 °C lower than that of the slag bath.

The fact that such a significant temperature difference exists between the slag and metal baths implies that a temperature gradient must exist at the interface between the two baths. This presents a question: Does the transition from the high temperature of the slag bath to the lower temperature of the metal bath occur in a thermal boundary layer in the slag bath, in a thermal boundary in the metal bath, or in thermal boundary layers on both sides of the interface?

Table 25 shows a comparison of a series of physical properties of molten iron and molten slag. A detailed analysis of these properties and the flow conditions in the furnace is required to provide a final answer to the boundary layer question. However, because the thermal conductivity of slag is estimated to be up to one order of magnitude lower than that of metal, it is proposed that all or most of the temperature transition is located in a liquid slag boundary layer.

SYMBOL	DESCRIPTION	UNITS	MOLTEN IRON	MOLTEN SLAG
Pr	Prandtl number	none	1.646×10^{-1}	2.974×10^{1}
μ	Dynamic viscosity	kg/(m.s)	7.000×10^{-3} (Guthrie, 1992)	3.000×10^{-2} (Pistorius and Coetzee, 2003)
c_p	Heat capacity	J/(kg.K)	7.170×10^{2} (Guthrie, 1992)	9.914×10^{2} (FactSage 5.2)
k	Thermal conductivity	W/(m.K)	3.050×10^{1} (Guthrie, 1992)	1.000×10^{0} (Pistorius, 2004)
ρ	Density	kg/m^3	7.030×10^{3} (Guthrie, 1992)	3.800×10^{3}
ν	Kinematic viscosity	m^2/s	9.957×10^{-7}	7.895×10^{-6}
α	Thermal diffusivity	m^2/s	6.051×10^{-6}	2.654×10^{-7}

Table 25 – Physical properties of molten iron and molten high-titania slag.

Because of the existence of this boundary layer in the slag, the liquid slag circulated to the interface between the slag and metal baths will be cooled. This cooling causes solidification of slag as pseudobrookite and also precipitation of iron metal. The majority of the precipitated metal is taken up into the metal bath. The solidified slag and the remainder of the metal are circulated back into the hotter bulk slag mass. Under the conditions prevalent in the bulk slag, the solidified slag melts and the iron becomes thermodynamically unstable and acts as a reductant converting TiO_2 to Ti_2O_3 and FeO.

The solidification and melting behaviour described above is presented by composition vector **B-A** on Figure 164.

Now it must be confirmed whether the proposed mechanism satisfies the requirements stated earlier. Firstly, it can be said that through this mechanism a sustained influence is exerted on the composition of the slag bath. This is a result of the circulation of slag to and from the interface between the slag and metal baths, and because of the effectively irreversible nature of the action by which iron is removed from the slag phase. It is seen as irreversible because most of the metal is taken up into the metal bath.

Secondly, the mechanism clearly provides a means of adjusting the composition of the slag bath towards the stoichiometric M_3O_5 line.

10.6 A REFLECTION ON REDUCTION MECHANISMS

From the above proposed mechanism it is possible to gain some important insight into the mechanisms of reduction reactions in the furnace.

10.6.1 Reactions in the Bulk Slag and on the Slag Bath Surface

Firstly consider contact between a reductant particle and slag having a composition in area **A** of Figure 164. Such slag may be found on the surface of the slag bath or in the 'body' of the slag bath away from the turbulent zone underneath the electrode. Initially reduction will only involve the conversion of TiO_2 to Ti_2O_3. The reason for this is that iron metal is not stable under the initial conditions. The composition of the slag in close proximity of the reductant particle must first be changed towards area **B** and the slag/(slag+$Fe°$) phase boundary were iron metal is able to form. Depending on the rate at which the liquid slag close to the reaction interface with the shrinking reductant particle is being renewed via diffusion and convective mass transfer, the liquid slag in the small system may reach a point of iron metal stability or it may not.

If metal is indeed formed, the produced droplet or droplets must somehow find its way to the metal bath. It is likely that, during this travel, it will come into contact with liquid slag that is representative of the bulk conditions (composition in area **A** and temperature close to the bulk slag temperature) in the slag bath. According to the available thermodynamic data, the carbon in the metal droplet will first react with TiO_2 to form Ti_2O_3 and CO gas. This leaves a virtually pure iron droplet. Under the bulk slag conditions iron is also not stable. It will react with TiO_2 and Ti_2O_3 and FeO will be produced.

It therefore seems that iron produced by reduction reactions between liquid slag and reductant that has to travel through the bulk slag to reach the metal bath, is unlikely to eventually be taken up into the metal bath.

10.6.2 Reactions at the Interface between the Slag and Metal Baths

For the portion of the interface area between the slag and metal baths where metal is precipitated as a result of cooling, the tendency of the high-carbon metal to reduce slag will be inhibited for two reasons.

Firstly, the metal at the interface will be enriched in Fe because of the newly precipitated metal and, as a consequence, the carbon content will be lower as a result of the dilution effect. In this way a mass transfer barrier is created that will tend to decrease the rate at which carbon is removed from the metal bath.

Secondly, the slag at the interface will be at least partly solidified. The rate of reaction between liquid metal and solid slag is likely to be lower than reaction between liquid metal and liquid slag.

10.6.3 Reactions in the Turbulent Zone underneath the Electrode

The zone underneath the electrode is likely the most uncertain part of the process in terms of prevalent conditions and reaction mechanisms. A number of observations can however be made.

The local slag composition in this zone is likely to be drawn relatively far towards zone **C** in Figure 164 because of the ilmenite entering through the electrode. It is likely that at least some reduction takes place in this zone due to the high temperatures and the presence of reductant particles. It is also likely that,

because of the slag composition, a significant amount of iron metal is formed as a result of the reduction reactions.

Finally, it is likely that, because of the significant presence of both metal droplets and reductant particles and because of the high temperatures, much of the carbon reaching the metal bath is dissolved into metal droplets in this zone.