The candidate's responses (in blue) appear together with the comments from the examiners as supplied via Professor Hurman Eric and the Faculty Office.

New sections have been added to the thesis to include a critical review of the thermodynamic literature around the activity coefficients in the cobalt and iron oxide system, an appraisal of the literature regarding the partitioning of platinum group metals between iron alloys, sulfide mattes, and slags, as well as a detailed section on furnace design showing how the various fundamental relationships developed in the thesis were used in the case of the ConRoast process.

8 December 2014
MEMORANDUM

Date: 28 May 2013
To: Professor R H Eric
    Chemical & Metallurgical Engineering
    University
From: Mrs T Swanson
Re: Examination of Thesis: Mr R T Jones

Enclosed are copies of examiner's reports on the Thesis submitted for examination by Mr Jones. The candidate is to make corrections as required by the examiners. Please liaise with the candidate in this regard.

He is required to make these corrections to the satisfaction of the Supervisor and must re-submit his research for re-examination by external examiner.

He has 3 months to complete the corrections and submit work for re-examination.

A student whose thesis has to be re-examined after revision is required to pay a re-examination fee of R4960.

A34 Revision
Candidates are entitled to appropriate supervision while revising theses in response to examiners' reports. Revision shall be done within a maximum period of six months, unless application for a further extension is supported by the Faculty Graduate Studies Committee. Faculties will not require students to pay additional fees if revision is completed within three months. Beyond that, candidates will be required to pay all fees. Failure to submit at the end of the period allowed for revision may result in termination of candidature.

The candidate has offered for examination a thesis entitled "Fundamental aspects of alloy smelting in a DC arc furnace". The thesis is unusual in that it consists of 5 distinct sections, each of which is essentially self-contained but linked by the theme that all involve DC arc furnaces.

The thesis is obviously a very personal narrative of many years spent in metallurgical research. The candidate is in fact well known and respected in the pyrometallurgical community for his scholarship and professional activities. The very personal nature of the thesis suggests that the candidate is putting up his career achievements at Mintek as evidence that he is worthy of the granting of a PhD. His achievements are impressive, but irrelevant. This thesis alone is required to be the sole ground for award of the degree.

the title of the thesis rather misleading. While three chapters are on fundamental aspects, a large portion of the thesis is an account of the development of DC arc furnace technology and one particular process, the ConRoast process. The candidate justifies the inclusion of a detailed discussion of the ConRoast process by indicating that it illustrates how the material in the three fundamental chapters are used in practical process design. Unfortunately those connections are very limited in scope and greatly lacking in convincing detail.
The thesis is generally very well written although there is frequent use of colloquial and unacceptably vague expressions such as "successful metallurgy", "feed recipes" and "a very nice wide range of data". The frequent use of "in the interests of simplicity" is also irritating. Simplicity is not a virtue in a PhD thesis. The use of the personal pronouns as "I" and "we" is unacceptable and the candidate should have used the accepted style of scientific writing i.e. to write in the third person.

the way the thesis is structured is unsatisfactory. A PhD must involve;
- a critical review of the literature,
- the identification of gaps in the knowledge,
- the framing of research questions or hypotheses,
- the development of a technique to obtain data to answer the research questions,
- a thorough and critical examination of the data, including an analysis of the impact of experimental error,
- a discussion of the results, and how they link with current knowledge, and
- a succinct conclusion.

The candidate has robbed himself of the opportunity to delve into a topic to the depth expected by covering several loosely connected topic areas.

Does this thesis demonstrate that the candidate has acquired the skills required of a PhD researcher?

- There is no literature survey whose intent was to identify gaps in current knowledge, and therefore no carefully framed research questions or hypotheses as a result.
- There is a notable lack of critical analysis, either of the published literature or the candidate's own results.
- There is no evidence of an error analysis of the candidate's results or a consideration of the effects of likely errors on them.

Where a critical theoretical analysis in depth was possible, and this is especially evident in Chapter 3, it was not done. Chapter 4 contains some complex equations but they appear to all be from the literature and are poorly and incompletely discussed in the thesis. There are a set of interesting photographs which must have been very difficult to obtain, but the connection between them and the theory is qualitative and weak. Chapter 5 makes simplifying assumptions which are justified without hard evidence and then develops equations (cleverly, it has to be said) which relate only to the slag in the furnace. Chapter 6 is initially a fascinating account of the problems involved in bringing a process to commercialisation, but then documents the technical development of the ConRoast process in excruciating detail. This chapter is very repetitive and could do with severe editing to ensure a logical and clear flow of information.

this thesis, in its present state, should not be awarded a PhD. the candidate improve and rewrite his work, but rewriting to correct most of the issues below is not enough. The candidate must demonstrate proficiency in the skill of critical analysis of the literature, at the minimum, if he is to deserve the awarding of the PhD degree.
Detailed comments

Introduction

p.2 what is meant by "a DC reactor is used to stabilise the arc"?

A reactor, also called an inductor, and sometimes known as a choke, is a device for introducing inductive reactance into an electrical circuit. All three terms describe a coil of insulated wire – having a low resistance and high inductance. A reactor opposes changes in electric current passing through it, by developing a voltage across it proportional to the rate of change of the current. When the current flowing through an inductor changes, the time-varying magnetic field induces a voltage in the conductor, according to Faraday’s law of electromagnetic induction, which opposes the change in current that created it. In this way, the reactor stabilizes the current.

Inductors are used to block the flow of alternating current (AC) while allowing direct current (DC) to pass; inductors designed for this purpose are called chokes.

Section 1.2 is both repetitive and naïve in the way it discusses smelting. Although this is only an introduction, the technical level of discussion needs to be much deeper than what is written here.

This section has been re-written to remove the repetition. Some further technical detail has been added to this introductory section.

p.4 2nd paragraph: the term "greater efficiencies" is used but only makes sense when referred to some particular specified operational parameter which is to be improved.

An improved understanding of the design and operation of DC arc furnaces should lead to higher productivity and greater efficiency of energy usage.

p.7 the statement that multi-phase multi-component systems are so complex that it is often impossible to "pick out" the most important relationships can be challenged.

I stand by my assertion ‘that it is often difficult to pick out the most important relationships’. I have seen this far too often in international projects where engineers have struggled to grasp the essence of a process.

p.9 the relevance of the paragraph above 1.5.3. It is gracious to acknowledge a colleague, but is the work of this colleague referenced in this thesis i.e. directly relevant and utilised?

The arc modelling work mentioned in this paragraph is a direct outgrowth of the arc photography and electrical modelling presented in this thesis. The reader might well be interested in exploring this work further. It is also important to avoid the impression that all
of the ‘Mintek work on arcs’ can be lumped together. It is better to explain the relationship clearly.

p.10 the comment that the tapping interval and the volume of liquids retained in the furnace between taps significantly effects the residence time distribution is surely self-evident?

One might hope that the general trends might be self-evident, but I have had to re-design the tap-hole spacing of at least one furnace where the owner’s team did not appreciate the significance of this relationship. I have re-worded the statement to highlight the fact that the effects can now be quantified by using the equation.

p.10 it is said that it is sometimes necessary to change the composition of the molten bath - is the candidate referring to slag, or to metal?

A change in composition would take place in both the slag and the metal, especially in those cases where they are in chemical equilibrium with each other. I have clarified in the text that both slag and metal are affected.

p.12 what is the relevance and importance of the statement that the ConRoast process has been studied at a number of South African universities??

I was asked to highlight the significance of the work presented in the thesis, and I thought this information might be relevant. However, I have now removed this statement.
Applications of DC Arc Smelting Furnace Technology

p.13  "the slag, in most cases, floats on top of the metal."  Is there a case where it does not? If yes, it would have helped if the author had stated what it is.

In the case of silicon smelting, which is usually an almost slagless process, it is possible for the slag (especially one that is SiC-rich) to be denser than the silicon metal. This is an unusual set of circumstances, so I didn’t think it was worth mentioning. I have re-worded the statement in an attempt at avoiding unnecessarily raising the curiosity of the reader: “it is usual for the less-dense slag to float on top of a denser metal layer”.

p.14  3rd line from top - the word "resulting" implies a logical connection or conclusion from the previous phrase relating to an open plasma arc. Is the connection between these statements so obvious to the reader?

I have made the logical connection more obvious by saying that “the highly turbulent conditions under the arc promote good mixing and result in a fairly uniform temperature distribution across the molten bath of the furnace”.

p.14  what does the statement "provided that these two dependent variables are correctly balanced according to thermodynamic requirements" actually mean? This statement is far too vague and generic.

The statement was meant to convey that the two variables ‘power’ and ‘feed rate’ depend are mutually interdependent. I have re-written the section as follows:

“the rate of loss of energy from the furnace vessel is primarily dependent upon the temperature of the bulk of the molten contents, and does not vary significantly with either feed flux or power flux (as long as the feed rate and power are correctly balanced, according to thermodynamic requirements, in order to maintain a constant temperature)”

p.14  is the photo of Sir William Siemens really necessary? Reference in caption?

My intention in including the historical photographs was to acknowledge the roles of the people who pioneered the fields of study and innovation that led to the development of the DC arc furnace. This also serves a pedagogical purpose in that information retention (for many readers) is enhanced by the inclusion of pictorial elements in the text. However, I do acknowledge that it might seem strange to include the photographs of people on their own, so I have changed the layout to juxtapose the pictures of the inventors with their inventions. Most of the photographs of historical figures from more than a century ago are now in the public domain (according to copyright law in many jurisdictions, which usually extends copyright to seventy years beyond the life of the photographer), so may be used without permission being required. However, I have obtained permission nevertheless. I have added references to the original images within the captions.

p.15  similarly, of what value is the photo of Paul Heroult? Reference in caption?
Please see comment above.

p.16 There is some historical interest in Figure 2.5, but the photos of Tesla and Westinghouse are quite unnecessary - and they are not referenced in the caption.

I have removed the photographs of Nikolai Tesla and George Westinghouse, as suggested.

p.17 the author to say why the DC arc furnace is so suitable for steel scrap melting.

In order to explain the suitability of DC arc furnaces for steel scrap melting, it is necessary to discuss first the advantages of EAFs, then to distinguish between AC and DC options. I have added a new section “2.2.3 DC arc furnaces for steel scrap melting” where this is covered in some detail.

p.17 the digression commencing "Before continuing with the history ....." is not logically placed here in the text. the term "simplified" when used in a PhD thesis where discussion in depth.

I have moved the section that talks about classification of furnaces according to temperature and particle size closer to the beginning of the chapter. Some discussion of this is necessary before the “chromite fines smelting problem” is discussed. I have removed and re-worded the mention of the “simplified” classification.

p.18 Figure 2.8 is not referenced in the caption - where did it come from. This figure has some use, but it seems dated. What does "slag resistance" mean? Why mention a reverberatory furnace which is now obsolete, while not mentioning, for example, TSL furnaces which are now widely used

This figure is one that I drew myself, based on a classification that has been widely used at Mintek in presenting the areas where DC arc furnaces are applicable. The cut-off points for ‘low’ and ‘high’ temperatures (1500°C) and for ‘fine’ and ‘coarse’ particle sizes (10 mm) are somewhat arbitrary, but quite reasonable.

A “slag resistance” furnace is one where the energy is delivered by means of ohmic or resistive heating of the slag. For example, please see R.H. Eric (2004) Slag properties and design issues pertinent to matte smelting electric furnaces, Journal of the SAIMM, available at http://www.saimm.co.za/Journal/v104n09p499.pdf .

I agree that reverberatory furnaces are fading fast, but I don’t think they are quite extinct yet. The ones in Zambia were closed a few years ago and have been replaced by flash and TSL furnaces. However, as far as I know, there is still a coal-fired reverberatory furnace in operation at Palabora Mining Company (please see their website at http://www.palabora.com/smelter.asp ). I understand that there is also still a reverberatory furnace operating at Onahama in Japan running on mainly recycled copper using shredded tyres as fuel.
I have re-drawn the figure, adding a mention of TSL furnaces, as suggested.

p.18 "One particular advantage in a circular furnace...." Is it not an advantage in a rectangular furnace? What is the significance of "circular"?

I have re-worded this section to make it clear that I am discussing the repulsion of arcs in a three-electrode circular AC furnace. (This does not apply to a rectangular furnace.)

“For example, in a circular three-phase AC furnace with three electrodes, the arcs repel one another, flaring towards the walls, leading to hot spots on the areas of the side-walls in closest proximity to the electrodes, whereas there is no arc repulsion in the case of the single DC arc.”

p.18 "because of the AC skin effect" is contained in a badly structured sentence. As written it implies that the AC skin effect applies to a DC furnace.

I have re-written the sentence, and replaced it with the following wording:

“Large AC furnaces suffer from the so-called ‘skin effect’ where the current is concentrated in the outer periphery of the electrodes. This means that, in large DC furnaces, a higher current can be carried per electrode (or smaller electrodes can be used for the same current) as compared to the AC case.”

p.19 "successful metallurgy" is a vague colloquial term which should not be used. The candidate needs to be specific regarding what was successful.

“These trials were metallurgically successful, in that an alloy of the required composition was produced with a sufficiently high recovery of chromium, …”

p.20 "the metallurgy that was proven" is again unsatisfactorily colloquial.

“the metallurgical process that was proven”

p.20 "Since then we have seen this concept....". The use of "we" is unacceptable in a thesis (as was mentioned earlier - all use of "I" and "we" should be removed).

“Since then, that concept has been applied in a number of areas.”

p.21 The sentence at the foot of the page is far too long and clumsy, clouding the meaning for the reader.

I have split the sentence into two.
“However, it has been shown (Reynolds et al., 2010) that the arc attaches to the electrode in a high intensity spot (~3.5 kA/cm²) that moves rapidly over the relatively large surface of the graphite electrode tip (the cathode) as well as over the surface of the molten slag surface (the anode), to maintain the lowest resistance path. The arc column tends to move away from the relatively cold and high-resistance feed materials.”

p.25 last few lines, do AC arc furnaces depend on slag resistivity?? Why would that be the case?

I have added the following illustrative example.

“Slatter (1995) has pointed out that high CaO slags, with conductivities too high for submerged arc furnace operation, can be used for the production of extra-low-sulfur alloys.”

I have also clarified that the comparison is between an AC submerged-arc furnace and a DC open-arc furnace.

p.27 why can't a submerged arc furnace give good control of slag composition?

The direct contact between the slag and the electrodes in a submerged arc furnace makes it difficult to control the degree of iron reduction, because the electrode carbon takes part in the reactions as well as does the reductant carbon. In the case of ilmenite smelting, very fine control of the degree of reduction is required to meet the desired composition of both the titania slag and the pig iron.

“The high electrical conductivity of titania slags and the required accurate control of the slag composition effectively rule out the use of conventional submerged-arc technology (where carbon from the electrodes comes into direct contact with the slag) for the smelting of ilmenite.”

p.28 so AC arc furnaces can operate in open-bath mode with open arcs ..... as do DC arc furnaces, why DC arc furnaces are so superior to AC furnaces. Many of the benefits seem to relate to the open-bath open arc-mode.

In the Introduction section, it was made clear that the concept of a ‘DC arc furnace’ includes direct current, open arc, and open bath conditions. The open bath allows the processing of fines. The open arc provides a source of energy that does not depend much on slag composition. The DC operation reduces electrode consumption, and provides a directed arc jet and good mixing. The combination of these attributes makes the DC arc furnace successful. In the case of ilmenite smelting, Anglo American wasn’t able to licence the AC open-arc technology.

p.30 why is a detailed understanding of the electrical behaviour of the arc so important for ilmenite smelting but apparently not for the other examples given?
Nearly all of the resistance in an ilmenite-smelting furnace is in the arc, as the slag is highly conductive (as is the metal). Therefore, in order to understand the dissipation of power in the furnace, a detailed understanding of the electrical behaviour of the arc is required.

p.30 why is Figure 2.19 needed? There is such a cursory reference to it in the text

I have removed this figure from Chapter 2, and have left the detailed discussion of this subject to Chapter 4. The figure was originally included to illustrate the electrical modelling that was required for ilmenite smelting.

p.31 metals can also be recovered from waste slag by other furnace technologies - not only using a DC arc furnace.

In general, a number of furnace types can be used for the recovery of various metals from slags. The next paragraph explained that much of the cobalt in the slag was present in oxide form. Other furnaces were included in the client’s unpublished pre-feasibility study for the Chambishi project. The DC arc furnace was seen as the most suitable for the high-temperature reducing conditions that were required.

I have re-worded the beginning of this paragraph to say that "One very effective method for the recovery of valuable metals, such as cobalt, from non-ferrous smelting slags, involves treating these waste materials with a carbonaceous reducing agent in a DC arc furnace".

p.32 cobalt-bearing alloy containing 5-14 wt% Co... presumably it was an iron alloy??

Yes, this was an iron alloy. I have clarified this in the text.

“approximately 100 tons of cobalt-bearing iron alloy was produced (containing 5 to 14% Co)”

p.35 why is the point that stainless steelmaking dusts pollute the environment made on this page, after it has just been made on p.34?

The second mention of this fact provided some additional detail. However, I have now combined the relevant sentences, so as to avoid the duplication.

p.36 the comments on the bottom of page 36. Nickel laterites are always both dried and pre-reduced in a kiln in current practice.

This introduction was meant to explain the need for drying and pre-reduction. I have made some small changes to the wording. I have tried to keep the discussion fairly general as far as equipment is concerned, as it is no longer true that kilns are always used for the pre-treatment of laterite ores that are to be smelted. Further detail is provided later in the discussion of the Koniambo process.
p.37 lateritic material is fed? Not calcined and pre-reduced feed? 

I have clarified the statement by saying that “calcined lateritic material is fed”.

p.40 the iron-based alloy is "more efficient" at collecting PGMs than a matte? Can a more thermodynamically appropriate explanation for this be given? Are the activity coefficients of various PGMs in both solvents known? 

The siderophilic nature of the platinum group metals is well known. If an iron alloy and a matte are present at the same time, platinum will be preferentially concentrated in the iron alloy. I am not aware of any measured activity coefficients for PGMs in furnace matte or the iron-rich alloys considered here. However, I have added a new section discussing alloy collection versus matte collection of PGMs in the relevant chapter.

Here is the revised wording now used for the introduction: “The distribution coefficients for PGMs in an iron alloy relative to slag are even greater than the distribution coefficients for PGMs in matte relative to slag; as discussed in Section 6.3.1.”

p.40 the last paragraph commences in an unusual way ("It. might seem a little strange...") and then goes on to again explain the principles of the ConRoast process. This repetition is annoying.

I have re-worded this paragraph, and tried to be less repetitive.

p.41 the issue of containment of a matte versus an iron-based alloy is treated very briefly, and unsatisfactorily. It needs elaboration.

I have added further explanation to this section.

“The containment problem is particularly challenging when having to deal with a matte with a very low liquidus temperature, and a slag with a high liquidus temperature in the same furnace vessel. PGM smelting typically operates with very high quantities of slag relative to the matte or alloy, so there is limited opportunity to change the slag composition significantly by adding fluxes. In order to keep the slag molten and sufficiently fluid, the temperature required unfortunately can result in a highly superheated matte that penetrates refractories very easily and is not readily solidified. By changing from matte to an iron-based alloy, this has a similar liquidus temperature to that of the slag, making the problem of containment much easier to manage.”

p.43 why the bracketed comment in the header "not yet commercialised" when the ConRoast process is also not yet commercialised? 

The zinc fuming and magnesium production processes have been taken to an advanced stage of development, but have not yet been adopted by any company. In the case of the ConRoast process, licence agreements are in place and licence fees have been paid to Mintek for a few
years already. This process was also operated on a toll-treatment basis for a number of years at Mintek. I would define this as ‘commercialised’ but still in the early stages of industrial implementation.

p.46 "feed recipes"?? Colloquialisms need to be eliminated in a thesis.

I have removed the mention of “feed recipes”, and have instead spoken of “a wider choice of feed materials and their proportions”.

p.49 what does the term "elegant" mean in the context of the furnace shape?

‘Elegant’ refers to something pleasingly graceful and stylish, but it also has the connotation of unusual effectiveness and simplicity. In the context of furnace shape, the symmetry of the circular cross-section makes it possible to have an even temperature distribution.

p.50 the second last paragraph appears to be out of place.... and highlights my concern with the logical flow of ideas in parts of this chapter.

I don’t understand why the paragraph below is seen as being out of place. The previous paragraph has summarised the various applications of the technology. The paragraph in question explains which types of process are, or are not, suitable for a DC arc furnace. The final paragraph then makes a general concluding statement.

“DC arc furnaces are well suited to reductive smelting processes (e.g., FeCr, TiO2, FeNi), but less so in the case of processes involving a gaseous intermediate such as SiO, or those with a low-melting (super-heated) product.”

Summary: this chapter is an interesting history of the development of DC arc furnace applications and has the clear stamp of the author's personal involvement on it. Many valuable points are made about the virtues of the DC arc furnace, but the several weaknesses are treated very dismissively. The chapter is written very much as a narrative and there is a notable lack of critical analysis.

This chapter was intended to show the variety of smelting applications of DC arc furnaces. I have added some further discussion about the possible drawbacks of cost and thermal efficiency, and how they can be addressed.
Recovery of base metals and PGMs

p.51 the first paragraph makes some very simplistic statements about the relative extents of reduction of metal oxides and the effect of the amount of reductant added. The candidate should have presented this discussion in thermodynamic terms at a level of depth appropriate to a PhD thesis.

I have added some information about minimizing the Gibbs free energy of the system. A more detailed discussion in thermodynamic terms follows in the subsequent section.

p.51 the paragraph commencing "I" is not appropriate in a PhD thesis. The candidate has already made a declaration that all of the work in this thesis is his own.

This paragraph has been deleted.

p.52 the reason given for expressing recovery of other metals in terms of the recovery of iron is very weak.

Any metal oxide of the form MO could be chosen as the reference. Iron is a sensible choice because of its prevalence. This section has been re-worded.

p.53 the standard states of the species in 3-1, 3-2 and 3-3 should have been indicated, and would not have made the writing unclear or complex. This would have obviated the need for the trivial comments about standard states at the foot of the page.

The reaction between Fe and Co and their oxides was used merely as an example of this kind of reaction (where Ni or Cr could equally have been used). For this reason, I preferred not to introduce the distraction of specifying particular standard states directly within this reaction. However, I have added a comment about an appropriate selection of standard states for this reaction in the temperature range of interest in the present context of reductive smelting in DC arc furnaces.

The section that is now numbered as 3.5 contains a more detailed discussion about the appropriate selection of standard states in the Fe-Co system.

p.54 the lumping together of the activity coefficients, although the comment again about "interests of simplicity" is annoying. This is a PhD thesis and simplicity is not expected or wanted. The effect of composition of the phases on activity coefficients is discussed but not in a satisfactory way. Much stronger evidence could have been provided, together with graphical representations, and the need to resort to a single reference from the geological literature seems strange. It needs to be justified.

I have changed the wording as follows:
"For the purpose of clarity in the development of subsequent equations, we may lump together the ratio of the activity coefficients of these four chemical species in solution."
However, I would respectfully argue that the benefits of 'simplicity' in the resulting equation are real, as long as we are able to select the most important variables and the correct form of the equation. Complicated equations with many unknown variables are likely to remain unused for design purposes, whereas a simple equation that captures the essence of the process is likely to prove to be a very useful tool.

I do believe that simplicity is an important goal to aspire to. Indeed, Occam's razor suggests that the simpler theory with fewer (or less onerous) unproved assumptions is probably the most appropriate one.

I do agree that unwarranted over-simplification is not desirable, so I have expanded on the section that explains that the activity coefficients are composition-dependent. A new section providing considerable detail on these activity coefficients has also been added. The final test remains how well the resulting equation is able to fit measured data and predict the operation of new processes.

p.56 the final equation 3-13 is interesting, although limited to a system with 1:1 stoichiometry, as is acknowledged later. The dismissal of the possibility of using published data for K and the individual activity coefficients in order to further quantify the relationship was very unwise. It is said that this was done because it would have been necessary to assume equilibrium, yet previously the candidate said that conditions in the DC arc furnace very closely approach equilibrium. Obtaining the data from the literature would have demonstrated that the candidate knew how to access such data and would have allowed him to critically assess the data. This is a major missed opportunity.

I have made a few small changes to the wording in the text at this point to show that I have allowed for both possibilities – either using published thermodynamic data, or fitting the $K\gamma$ value to measured experimental data from the system of interest. Both approaches have their place.

A new Section 3.5 examines the thermodynamic data (equilibrium constant and activity coefficients) for the iron and cobalt system, as suggested.

Conditions in a DC arc furnace do indeed often approach equilibrium conditions, not always perfectly. The complex multi-component phases in real industrial systems are often modelled only somewhat simplistically by thermodynamic relationships derived from systems with fewer components.

There is further commentary on thermodynamic data for a couple of specific example systems in later sections.

p.57 "without having to take into account the other materials present"?? The values of activity coefficients do depend on the other materials present and so the relationship is likely to apply well only in a limited region of iron recovery.

It is possible to study the effect of the recovery of Fe on the recovery of another metallic element without explicitly having to take into account the other materials present (except, of course, to acknowledge the effect of the influence of composition on the individual activity
coefficients). The later comparison with experimental results shows the applicability of the equation over a wide compositional range.

p.57 The comments at the foot of this page about more complex stoichiometries are frustrating. The candidate should have given the derivation of at least one of them and shown how the relationship resulting was very complex. How this impacts on the utility of the relationships could then have been discussed on a firmer footing.

I have added a new section (Section 3.4) that provides additional detail on this subject.

p.58 Much of the commentary on this page is trivial. What is a "kind of symmetry"?

Perhaps “type of symmetry” would be a better choice of words than “kind of symmetry”. The usual widely understood four types of plane symmetry are rotational, translational, reflection, and glide reflection. In this case, reflectional symmetry is exhibited.

The wording has been revised to the following:

A pair of curves with reciprocal values of $K\gamma$ exhibit symmetry involving reflection across the ‘$K\gamma = 1$’ line.

p.59 Sense of the last sentence on this page.

The wording has been revised to the following:

The CoO in the slag is associated primarily with Fe$_2$SiO$_4$, although analysis by scanning electron microscopy also showed some Fe$_2$SiO$_4$ particles with no detectable Co or Cu.

p.60 What is the point about the discussion of the standard state of CoO? Provided that the standard state of CoO is taken as solid for both the activity coefficient data and the equilibrium constant then it is irrelevant that CoO is referenced to the solid state and the other oxides to the liquid state.

It is clearly understood that any self-consistent choice of standard states can be used. This paragraph simply outlines the reasons for the particular choice that was made. I have deleted the section that points out that “free energies of formation of solid and liquid phases become equal at the melting point”, as this (although true) is not strictly relevant to the discussion.

p.60 The source of the equilibrium constant value given needs to be stated.

The equilibrium constant was calculated using FactSage 6.2 thermodynamic software (Bale et al., 2002), and the calculation has now been documented in greater detail in the thesis. The free energy of reaction is derived from data from the following sources. CoO(s) data is from the JANAF Thermochemical Tables (Stull & Prophet, 1985). Data for Co(l) for the temperature range 1768-6000 K, and Fe(l) for the temperature ranges 298.15-1811-6000 K, is
from the SGTE Data for Pure Elements (Dinsdale, 1991). FeO(l) data is from École Polytechnique de Montréal (Pelton, 1992). Over the temperature range of interest (between 1500 and 1600°C), K has a value of approximately 20. It is interesting to note that calculations done using an earlier version of this data resulted in a value for $K$ of approximately 30. The more recent value is the one that should be most trusted.

p.60 the second paragraph represents a limited attempt at critical comparison of data from the literature, but it is a poor attempt. The activity coefficient values for all of the species involved should have been collected and listed, compared and criticised. It is puzzling also that earlier the candidate said that only data for CoO(s) was available, but then states in this paragraph that the activity coefficient data was for CoO(l). It is difficult to avoid the conclusion that the candidate is not comfortable or confident in using the published data and performing critical analysis. This issue is becoming a major weakness of this thesis.

A much more detailed section on the activity coefficients has now been added to the thesis.

The comment that thermodynamic data was available only for the solid form of CoO applied to the data used for the calculation of the equilibrium constant. It is understood that various authors have chosen either solid or liquid reference states for CoO for their activity determinations.

p.61 it is good to see comments on the accuracy of experimental data, but they are limited in scope. The spread of data on Figure 3.3 is great and the conclusion that a value for $K_\gamma$ of 14 best fits the data is unsound. An examination of the figures on later pages shows that the error in this $K_\gamma$ value will be very large. What impact does this have on the utility of the relationship???

The principal conclusion from this data set is that the model generates a curve of the correct shape to describe the data. (For example, a straight line would not be appropriate.)

The best-fitting $K_\gamma$ value of 14 was found by minimizing the sum of the squared errors.

It needs to be acknowledged that large-scale processes inherently have a great deal of scatter in the data that describes them. However, this should not prevent one from attempting to find a model that provides a sound basis for good predictions to be made. For example, there is much practical utility in a model that allows one to calculate that, for an 80% recovery of cobalt to the alloy to be achieved, the iron recovery needs to be in the region of 25% for this to be the case most of the time.

The significant amount of scatter in this data set prevents much more detailed analysis from being done here, other than to say that there is obviously some uncertainty in the best value of $K_\gamma$ to be used. A range of $K_\gamma$ values from about half to double the chosen value (or say from 6 to 30) would span approximately 70% of the data points. More importantly, the implication of this wide a range of $K_\gamma$ values is that the corresponding uncertainty in Fe recovery would be from 12% to 40% to generate a Co recovery of 80%. The principal value of this example is that it shows that the model has the correct type of shape to fit the results, but a better-controlled data set would be required for greater certainty in the calculated value of $K_\gamma$. Fortunately, the data sets in subsequent examples have much less scatter.
It is also important to take into account the implications of the limitations of commonly available (and cost effective) analytical methods. A targeted 80% recovery of cobalt from a feed material that contains about 1% Co results in slags that often contain less than 0.2% Co, and a 95% recovery would generate a slag containing around 0.05% Co which is at the detection limit for at least one commonly used method of analysis.

p.62 the comments about grade and recovery in ferronickel smelting are obvious. The recovery equation does not directly provide information on the grade of the ferronickel product and so cannot directly illustrate the grade/recovery trade-off.

Once the recoveries of nickel and iron are known, it is a trivial calculation (suitable for a spreadsheet) to calculate the composition (and grade) of the alloy.

p.62 the comments in the last paragraph dismiss the problems with this recovery relationship too easily. These issues of reliability should have been more thoroughly explored and discussed. It is essential for a PhD candidate to critically evaluate his own results and his analysis of them.

The two curves shown in Figure 3.8 do not illustrate a problem with reliability. I have amended the text to make it more clear that the second curve is from an entirely different set of conditions (another campaign using different feed materials). This was intended to show that it would clearly not be appropriate to merely use a value of $K\gamma$ from a previous ferronickel smelting test, but that it would be necessary rather to determine this value experimentally for the particular set of feed materials and operating conditions under consideration. I trust that this has been made sufficiently clear now.

The issue of reliability has already been discussed in my answer to a previous question.

p.63 "a very nice wide range of data" and "data very nicely fitted"? The use of the word "nice" is too vague, colloquial and unacceptable.

I have re-worded these phrases in a less colloquial way.

“In this case, the over-reduced tests produced a very wide range of data for plotting the Cr recovery as a function of Fe recovery. A recovery curve with $K\gamma = 1/35$ provided a good fit to this data.”

p.65 the comments about why the PGMs appear to fit the derived relationship is very important and yet it is covered so briefly. Some work by Morita is referenced but not discussed. This work, and how it possibly explained the candidate's results, should have been discussed thoroughly and critically. Are the PGMs present as oxides? (I doubt it). if not, who would they fit the derived relationship which is based on oxide reduction.

It is not immediately apparent why the PGMs should behave in a similar fashion, as PGMs are often thought of as being extremely unreactive and unlikely to form oxides. However, it
has been found that PGM recovery can also be usefully modelled using the $K\gamma$ recovery equation. The PGMs are grouped together for the purpose of recovery modelling, as the quantities are too small, and the analytical techniques too imprecise at low levels, to meaningfully treat them individually. The existence of PGM oxides in slag can be explained by studying the solubilities of various PGMs under conditions of varying oxygen potential. The valence of the metal ion in the melt may be determined from the experimentally determined slope of the relationship between the log of the concentration of the metal oxide dissolved in the silicate slag and the log of the oxygen fugacity. Examples are provided from the work of Morita et al. (2011), Laurenz et al. (2013), and Borisov et al. (1992, 1994), showing the existence of dissolved oxides of Pt, Pd, Rh, Ru, and Ir.

p.65 last paragraph. Exactly how does the relationship enable the outcomes mentioned to be achieved? Are these outcomes thought to be unable to be achieved without the relationship?? It seems to me that the relationship simply shows the recovery of cobalt, nickel etc. which can be obtained for a given recovery of iron i.e. a given extent of reduction. It provides no means of controlling this relationship.

The $K\gamma$ recovery equation provides a very clear framework for the relationship between Ni, Cr, and Fe to be clearly understood. This provides a rational basis for the selection of an operating point that allows one to recover as much as possible of the valuable metals to the alloy, while minimizing the quantity of iron that is reduced to the metallic form, in addition leaving essentially all chromium dissolved in the slag as CrO.

p.66 why is section 3.7 so brief? Why aren't the results of McCullough given and commented upon?

When I first wrote this section, I wanted merely to point out that the same equation could be applied to converting processes as well as to reduction smelting. I didn’t go into the details of the converting work, because the focus of this thesis is on the applications of reductive smelting. However, as there seems to be some interest in this work, I have expanded this section (Section 3.8) further, and have included some results in graphical form.

p.67 the sentence which commences "Process design calculations can be carried out with confidence....". It implies that this is not possible without the candidate's derived relationship, but this is not true. There are other ways to carry out process design of a smelting process which are theoretically sound.

The reason given that “Process design calculations can be carried out with confidence” is that there is a good theoretical justification for the form of the equation. This makes no comment at all about other valid alternative types of calculations. However, it could be inferred that an arbitrary choice of design basis (e.g., choosing a fixed percentage of a certain component, or a fixed ratio between certain species in alloy and slag) could be criticised for not having a sound basis.

Summary: this chapter derives a novel way of expressing the relationship between the extent of reduction of two different oxides in a smelting system. The candidate's derivation is
variable in terms of its rigour, and the likely error in the obtained value of $K\gamma$ is poorly treated. Theoretical justification of the values using literature data has been treated too casually, and this has robbed the candidate of an essential opportunity to demonstrate his critical analysis skills. The candidate also attributes to this relationship an importance which appears to be over-stated.

I have added further discussion (in Section 3.5.3) about the errors resulting from different values of $K\gamma$. I have also added a new section examining the literature in depth regarding activity coefficients for one example system. Other additional material has also been added to this chapter where requested.
DC arcs and electrical aspects

p.71 "photographs of the arc have been compared to models of its shape"? By whom? Why is there no reference?

This comment has been moved to the next section (4.3) where it is made clear what early work was done by Bowman and colleagues, and how it was applied and extended to more recent work at Mintek.

I have also added some further commentary about the arc shape model presented in Equation 4-1. This equation is incorrectly (but differently) printed in the only two places I have found it in the published literature. It is very important to have the correct version published here, as all of the predictions of arc voltage as a function of arc length and current depend on this relationship.

p.71 "this is believed to have a significant effect. .." By whom? Why is there no reference?

I have re-worded this as follows: "This is believed by the author to have a significant effect on the distribution of current and temperature in the molten slag, and the voltage drop across the slag (and is discussed in Sections 4.4 and 4.5)."

p.72 no sense of the comparison between Figs 4.3 and 4.4 on the next page. How does the picture validate the calculated arc shape?

The comparison between the photograph of an arc at Mintek and the shape calculated by Bowman's model is a qualitative one that merely provides some assurance that the model has been correctly applied. The goal here is to have an equation that can be used for design purposes in conjunction with a more complicated model of the molten slag bath. Bowman has already established the principle of the arc model.

p.72 equation 4-2 appears without sufficient explanation or derivation.

The derivation of this equation was done by Bowman (1994), and is shown here to illustrate the type of dependence of voltage on current and other parameters. I have added a small explanation and a reference.

p.74 the integration performed is poorly documented - what are the boundary conditions?

The integration shown in Equation [4-2] is done over the length of the arc. The integration limits are now clearly shown.
more detail should have been provided on the experimental determination of the arc resistivity, why not provide some of the results obtained?

I have added an example graph showing some experimental results and the fitted resistivity value.

"further confirmation"?? that there has been sufficient evidence of the validity of the model (Bowman's model) in the previous paragraph. The comparison between Figs 4.5 and 4.6 is weak validation of the model, but at least a comparison can be seen.

I have re-worded this as follows:
In addition to the verification of the model that was provided by Bowman himself, further confirmation of the validity of the model can be found by noting the good qualitative agreement between the shape of the theoretical curves for voltage versus arc length (as shown in Figures 4.5 and 4.6), and the recently published measured curve for voltage versus arc length obtained from an industrial 60 MW furnace producing ferrochromium, shown in Figure 4.7 (Sager et al., 2010). Publication of this sort of industrial data is extremely rare. Even though the current is not specified, and no scale is given for the arc length (shown by the electrode position), this set of data remains valuable.

what is the arc current for Figure 4.6? Why is there a long black arrow on the figure? What is it pointing to?

This figure is now numbered as Figure 4.7. Unfortunately, the value of the current is not specified, nor is a scale provided for the arc length (probably because these were deemed to be confidential to the company owning the furnace). The long black arrow appeared on the original diagram to point out the region where instability became excessive at a particular (unspecified) value of reactance. This is not relevant to present purposes, so I have edited it out of the image.

it is claimed that Figures 4.7 to 4.10 allow an estimate of the diameter/depth ratio of the cavity formed - how because it is not apparent to me, or demonstrated by the candidate. Any visual estimate must be very unreliable.

Visual assessment and measurements from numerous still and video images such as Figure 4.7 allow one to make a quantitative estimate (albeit a somewhat subjective one) of the typical diameter to depth ratio of the arc depression. At least this allows upper and lower bounds to be placed on this ratio, and 6:1 is judged to be the most representative value.

relate Fig.4.12 to what is said in the text - what is the figure supposed to show?

Video images I was able to take of the high-current arc in an industrial steelmaking furnace at Charter Steel in Wisconsin showed very similar behaviour (in terms of the type of movement of the arc, the spread of the arc from the tip of the electrode, and the formation of a
depression in the slag) to the pilot-scale arcs previously photographed. The figure now numbered as Figure 4.13 shows some sample images from the video clip.

p.81 what are $d_{AAZ}$ and $h_{AAZ}$? If they are diameter and height (depth?) of the depression then $d_{AAZ}/h_{AAZ} = \psi$ and so both equations 4-8 and 4-9 are strange. This is very poorly explained in the text. How can the results in Figure 4.13 be validated? In the text the comparison is very qualitative and seems based on "our assessment".

The variable ($d_{AAZ}$) represents the diameter, and ($h_{AAZ}$) represents the depth of the arc attachment zone (the depression in the slag caused by the thrust of the arc).

If we introduce the variable $\psi$ to represent the diameter to depth ratio, and re-arrange Equation [4-7], the formulae for the diameter ($d_{AAZ}$) and depth ($h_{AAZ}$) follow directly.

The results in what is now numbered as Figure 4.14 serve to show, across a range of diameter: depth ratios, that it is unlikely for the arc to penetrate all the way through the slag to the underlying metal. Actual arc depressions have been photographed (and were not seen to penetrate all the way through the slag), and this mathematical analysis served to provide the explanation for this phenomenon. This is not a case of an abstract theory needing validation, but rather of observations that required analysis and explanation.

p.84 "A large body of experimental evidence and theoretical work exists …? Why is it not referenced? Why is a critical assessment of the literature not performed?

I had originally intended to reference this statement as coming from Cheslak et al. (1969). The reference was included in the list of references, but I had unintentionally omitted it in the text. I have now corrected this omission. As can be seen from the date of the reference, this is an area that has been well studied in the field of fluid mechanics for a very long time, and is generally considered to be well understood.

New wording:
According to Cheslak et al. (1969), the large body of experimental and theoretical work that exists in the field of gas jets impinging on liquid surfaces suggests that a ratio less than 1:1 for the depression shape would be unsustainable.

p.84 "a simple analysis of the sensitivity of the mode!... ..." Where is this a simple analysis? It ought to be shown and discussed. What makes it simple? What assumptions were needed?

The analysis is 'simple' in that it is illustrated by one representative example showing the sensitivity of the assumed diameter / depth ratio on the calculated bath voltage. The text already refers to the results shown in what was Figure 4.15 and is now re-numbered as Figure 4.16. All of the assumptions made in the calculation have been discussed in the sections above.
what Figure 4.15 is meant to show Looking back on this section that the candidate has not actually made any use of the Laplace equation - or has he? If he has, where is the description of how he used it, what assumptions he made and what the analysis shows? The slag depth must be a variable in slag resistance, and it is mentioned on Figure 4.15, but no equation appears containing the slag depth ... why not?? This work is obviously incompletely discussed

Please see the answer immediately above this one regarding what was Figure 4.15 and is now re-numbered as Figure 4.16.

As already explained in the text, the Laplace equation was solved numerically to generate the voltage distribution in the slag bath. The bath voltage is the result of this calculation, and depends on the geometry (including the slag depth, and to a lesser extent the diameter) and the specified current. The result is directly proportional to the slag resistivity (which is assumed to be a constant value).

I have expanded on the section that describes the boundary conditions, and have written them out explicitly in the form of Equations [4-11a] to [4-11e], instead of having only a verbal description in the text. I have also referenced the standard numerical method that was programmed for the solution of the Laplace equation.

As the Laplace equation, with this complicated set of boundary conditions, has to be solved numerically, there is no explicit equation that describes the bath voltage. It clearly does depend on the slag depth. I have added a further two figures to this section. The first graphically shows the resulting current distribution through the slag bath. The second shows a series of voltage-current curves for various bath depths.

I have also added a new Section 4.8 (Design Equations for Arc and Bath Voltages) that includes accurately fitted equations (which I generated from the numerical results, using quintic regression) for the voltage-current relationships at various slag depths.

the descriptions of the photographic work are of interest and show a high level of technical competency on the part of the candidate. It is a pity that the work of Reynolds was not described more fully.

Considerable effort went into the capturing of still and video images of arcs and their interaction with molten slags. This photographic study led to a much greater understanding of this system.

The dynamic arc modelling carried out by Quinn Reynolds for his PhD (which grew out of the work described here) has been comprehensively documented in his thesis and in a number of publications (as referenced). A brief description of this work was provided here, as it is peripherally relevant to the work currently under discussion.
In this chapter equations have been developed. Perhaps, but it is not clear that they have been developed by the candidate as opposed to those whose work he has referenced. Far too little detail of the equations and their solution has been presented to give confidence that they are the original work of the candidate.

Clearly, the work of others has been built on (and appropriately referenced) and then extended and integrated by myself to create an overall model that can be used for design purposes.

A corrected version of Bowman's model of arc shape was used in the integration of his equation that describes the arc voltage as a function of current, arc length, and arc resistivity. Measurement procedures were set up, and measurements were made at Mintek of arc voltage as a function of arc length, from which the arc resistivity could be calculated. The resulting arc model can now be used for scale-up and design purposes.

Maecker's equation for arc thrust was used together with my own equations for the description of the cavity in the molten slag caused by the thrust of the arc. The diameter: depth ratio that is used in the model was determined from my photographic work.

My assumption of the current distribution on the slag surface was used together with a standard numerical solution of the Laplace equation to describe the voltage across the slag bath. Quintic equations were numerically fitted by myself to the calculated results to make them more accessible for design work.

Equations have been generated for the electrical design of DC arc furnaces.

**Summary:** this chapter discusses important issues in relation to the operation of DC arc furnaces, but the modelling work presented appears to be mostly the work of others and it is poorly described. There are figures that are difficult to interpret. The acquisition of photographs of the arc is certainly original but they are not well used to support any theoretical modelling. The chapter is very disappointing in that again it shows little critical analysis of the literature or of the candidate's own work.

I have added a number of new graphs and equations to more clearly highlight my own contribution in formulating a set of design curves and equations by means of which the electrical design of DC arc furnaces can be carried out. Additional clarification of various sections has been provided.
**Residence Time**

p.99  It is interesting that previous assertions have been made that, in the DC arc furnace, the slag and metal closely approach equilibrium. This was the basis of the "K\gamma" approach in the previous chapter. Now it is said that studies have been made of the effect of retention time on the degree of cobalt recovery from a slag. If retention time does affect cobalt recovery then clearly the slag and metal were not in equilibrium - unless the study found no effect (the candidate does not summarise the results of that study) - but if that is the case then this chapter is not needed.

Chemical equilibrium between the slag and metal, and the need for retention time in the furnace are not mutually exclusive. It is quite reasonable that some time might need to pass before the attainment of chemical equilibrium; as long as sufficient time has been spent inside the furnace, the products leaving the furnace might well be at, or close to, the equilibrium composition. An alternative situation might occur where chemical equilibrium is rapidly attained at the slag-metal interface, but some settling time is required for the minuscule metal droplets to coalesce and disengage from the slag.

I have added a brief clarification to this effect in the opening paragraph of this chapter.

p.100  The paragraph immediately above 5. It makes good points.

Thank you.

p.100  Simplifying assumptions again. This is OK if they are well justified and do not unreasonably limit the utility of the results. Figure 2.1 shows two tapholes, so the assumption that all tapping is from a single hole - and involves a single phase - is clearly contrary to industrial practice. The candidate recognises this and gives reasons for making the assumption. He says that the assumption is reasonable ("not a bad one") but this would have been much more believable had he given data from several operations to validate his assumptions. He comments that if the assumption is not made then the equations are more complex - but they would also be of a wider applicability.

The simplification of talking about a single phase was to simplify the discussion and derivation of equations. Please see the new text below:

In real furnaces, the feed material is separated into two streams (such as slag and metal) that may be tapped separately. However, in this chapter, for the purpose of keeping the argument simple and clear, we will be talking of the molten material in the furnace as though it was a single phase. This does not diminish the applicability of the resulting equations in any way. In fact, the equations that are developed apply equally to the molten slag or to the molten metal, and can be applied to each of these phases individually.

There are also some circumstances when the equations can be applied to the overall furnace contents as a whole, such as if the metal and slag are tapped at similar times in similar ratios. Alternatively, if the amount of metal produced is very small, it may be possible to ignore it and apply the equations to the slag on its own.
The candidate further assumes that slag is less dense than metal- is there a case where it is not???. He also says that this "doesn't really affect the main argument at all" (what does "really" mean in this context?). Well, of course not - because the candidate has assumed that only one phase is being tapped. There are no slag and metal layers in his analysis.

In the case of silicon smelting, which is usually an almost slagless process, it is possible for the slag (especially one that is SiC-rich) to be denser than the silicon metal. This is an unusual set of circumstances, so I didn’t think it was worth mentioning here. I have reworded the statement below, and have left out the superfluous "really".

Old version: " We are also assuming, for clarity of discussion, that the slag is less dense than the metal, so that the slag floats on top of the metal, but this doesn’t really affect the main argument at all."

New version: " We are also assuming, for clarity of discussion, that we have the usual situation in the furnace where there is a less-dense slag floating on top of a denser metal layer, but this doesn’t affect the main argument at all."

I have addressed the issue of separate slag and metal layers in the previous section.

It is assumed that slag and metal are perfectly mixed - but why make this assumption? Again the candidate has stated that he is assuming only one phase is being tapped. missing the point here???

The assumption of perfect mixing within each phase is the same as that made for the textbook description of a continuously stirred tank reactor (CSTR). Some assumption of the distribution is required (for example, perfect mixing, or, alternatively, plug flow), and perfect mixing is a reasonable assumption that has wide utility. Without this assumption, one cannot further assume that the mean residence time of material exiting the furnace is the same as the material remaining inside.

I have addressed the issue of separate slag and metal layers in a previous comment.

"the effects of the first few tapping cycle are rather transient"? They are either transient, or they are not. Also, if the slag is perfectly mixed then the candidate's analysis applies equally to early tapping cycles and late tapping cycles.

I have replaced "rather transient" with "transient". The early tapping cycles (where the furnace is first filled) have a slightly different residence time distribution to the steady-state distribution which is achieved after a few cycles.

The candidate specifically refers to the importance of the slag taphole position and says that this determines the fraction of molten material removed during tapping now that the candidate is in fact discussing the removal of slag only from the furnace and that the statement that the molten material is a single phase simply means that it is slag. This could have been made explicit on page 100. It also means that further analysis relating
the time it takes to change composition in the furnace refers to the slag composition only. Surely the change in the alloy composition is as important, if not more so???

I have addressed the issue of separate slag and metal layers in a previous comment.

I have also added the following clarification here, with respect to the comments about the positioning of the slag tap-hole: (This applies particularly to cases where the metal level in the furnace does not change very much.) I have also clarified the discussion about tapping through separate slag and metal tap-holes.

There are many cases where the slag behaviour and properties (viscosity, electrical conductivity, freezing behaviour, and aggressiveness towards refractories) are more important to the process design than the metal composition is.

The analysis of residence times applies equally to both the slag and the metal.

p.109 "If one wants to achieve a constant mean residence time" of what? It must be slag, based on the candidate's assumptions.

A constant mean residence time can apply to either the slag, the metal, or both.

p.110 This is interesting, but the candidate needs to justify the need for the analysis i.e. under what circumstances would one care about the time taken to change the slag from one composition to another??

For example, a product grade might need to change, or a faulty batch of feed material might need to be worked out of the system.

p.111 What does this mean "The graphical depiction I developed "???? Did the graph come from the first principles derivation or the other way around?

The novel graphical depiction of residence time that I developed allowed me to derive the residence-time equation from first principles. Of course, the subsequent graphs emanated from these equations.

Summary: again this chapter has interest, and it also has utility.

These objections have been addressed above. The equations that were developed apply equally to the molten slag or to the molten metal, and can be applied to each of these phases individually.
The ConRoast process

p.113 The products of PGM mining "look" very different?? They have changed colour? The candidate should have stated in what respect they are different - presumably in composition?

The wording has been changed to say "the products of PGM mining today differ significantly in composition from those of forty years ago". I have also added some further detail on the various PGM-containing reefs.

p.114 The complete ConRoast process flowsheet has been described in detail elsewhere? Why not describe it here where the reader needs it?

All of the pyrometallurgical operations have been described in this thesis. As this is a pyrometallurgical study, I believe it is sufficient to know that there exists a viable hydrometallurgical process for the refining of the resulting iron alloy. In fact, there are a number of alternative process routes for the refining of the alloy, and not all of these have been disclosed in the open and patent literature (for commercial reasons).

p.115 what does "efficiently controlled by the addition of small amount of carbon" mean? What would inefficient control be?

I initially thought of clarifying the intended meaning by changing 'efficiently' to 'cost-efficiently'. By this, I mean the expenditure of minimum resources (materials and energy, represented by cost) to achieve the desired result. An example of inefficient control would be to add additional non-PGM-containing sulfidic material (as a collector) and to operate at a higher temperature. However, it is perhaps cleaner to simply omit the word 'efficiently' altogether from this sentence.

p.116 "simplicity and efficiency"? "Efficiency" is a word that should only be used in conjunction with a statement as to what parameter of the process is being referred to.

I have substituted 'efficiency' with 'cost-effectiveness'.

p.118 no idea what a "black-empowered smelter/refiner" is.

One of the intentions of the Mineral and Petroleum Resources Development Act (MPRDA) was to empower the previously marginalized black African sector of South African society. The terminology 'black-empowered' is well established in the South African mining industry and in the general political discourse within the country. A 'black-empowered' company is one that has significant ownership and management by black people. I have added a few words of explanation to this effect.
the fact that the iron alloy collects PGMs better than a matte should have been explored further by doing a search on the activity coefficients of PGMs in both solvent systems and discussing the basis for this observation. This is an opportunity to show critical thinking and analysis that has been missed.

As long as alloys collect PGMs at least as well as mattes do, this is not central to the main argument in favour of the ConRoast process. Nevertheless, I have added a new section on the partitioning of PGMs between alloys, mattes, and slags.

The main features of the ConRoast process (i.e. that it is based on an iron alloy rather than a matte) has been repeated several times - and here it is repeated yet again. The impression is that the candidate has brought together material from different publications relating to the ConRoast process, but then not sufficiently edited the whole chapter to eliminate redundant text. This all makes for irritating reading.

I have deleted this repetition, and have re-edited this chapter to remove duplication as far as possible.

Table 6.1 - what is "good metallurgical operation"?? "Good" is an inappropriate word, but in any case, what was "good" about the operations?

'Good operation' was intended to convey steady operation of the process without interruption of anomalous conditions. I have re-worded this.

"Note that. ..... " has been used quite often in the text in previous sections. Very irritating phrase, and unnecessary. The phrase becomes "Please note"!!

I agree that this is a redundant expression, and have removed it from most places where it was used.

The comments about the Kγ relationship here are trivial. The comment is also made that the recovery of the PGMs is a function of the extent of reduction in the furnace. This would be true if the PGMs were present as oxides - but are they? If they are present as elements dissolved in some of the minerals in the feed then why would the degree of reduction have any effect on their recovery? This issue was alluded to in the earlier chapter, but no useful discussion was forthcoming there. It is not at all apparent that the Kγ relationship played a role in the design of the ConRoast process - it seems that it simply provided some data which could be modelled using that relationship.

The recovery of PGMs being a function of the extent of reduction in the furnace is an observable fact. There is perhaps still an argument about whether this is because of the possible oxide nature of some of the PGMs (as proposed by some authors, and discussed in Chapter 3) or because of the increased quantity of the alloy collector.

The Kγ relationship plays an important role in the setting of process parameters for the treatment of new feed materials.
p.162 Why is roasting discussed in detail here, after a detailed discussion of the smelting operations? The logical structure of this chapter.

The main focus of this thesis is on processing involving DC arc furnaces. This remains the central focus of this chapter too. However, it is important to show the impact of upstream and downstream operations, and this is done after covering the smelting aspects. (In fact, the experimental testwork largely followed this chronology too.)

p.166 a "liquid state oxygen-converting process"?? Are there solid state converting processes using something other than oxygen??

Strictly speaking, the term 'converting process' is also used in industries other than metallurgy. For example, in the printing industry, it refers to printing on large rolls of paper, and transforming these into cut sheets. The term 'converting' can also be used to describe the processes of coating and laminating. In the fuel industry, a converting process is used that involves plasma gasification of solid carbonaceous material and Fischer-Tropsch synthesis. However, I have re-worded the present description for greater clarity. It now talks of "a laboratory-scale converting process, in which oxygen was bubbled through the liquid alloy".

p.170 the candidate has not demonstrated that the $K \gamma$ relationship was relied upon in the development of the process.

Further detail has been added to Sections 6.8.3 (page 219, just before Figure 6.3) and 6.9.3 (page 229, just before Table 6.16) to show how the $K \gamma$ relationship was used in the operation of the ConRoast process. The $K \gamma$ relationship plays an important role in the setting of process parameters for the treatment of new feed materials.

p.171 Is this the only discussion of the way in which the electrical relationships developed in the previous chapter contributed to the design of the DC arc furnace used in the ConRoast process?? If so, this is a very poor connection between that chapter and this chapter.

A new section '6.11 Furnace Equipment Design Specifications' has been added to the thesis. Design calculations were included for four sizes of furnace ranging from 1.25 MW to 10 MW, as worked examples.

p.171 the same comments as above apply to the residence time comments. The connections between the previous chapter and this chapter read more as an afterthought.

The new section '6.11 Furnace Equipment Design Specifications' includes a discussion of residence time and the spacing of tap-holes.

**Summary:** The discussion of the move from a laboratory scale to an almost-commercial scale process is a very good case study in the business factors that influence such a change.
However, the great amount of detail given for all of the various campaigns became tedious. There was also frequent repetition of points in the text. It was stated in the Introduction that the ConRoast process was discussed as an illustration of how the work in the previous chapters could be used in the design of a process - but the comments about this were limited to a few very short and poorly described paragraphs.

This chapter has been edited to remove some of the repetition. A new section on furnace design shows more clearly how the various fundamental relationships developed in the earlier chapters were used in the case of the ConRoast process.