

Fluxing of South African chromite ore with colemanite

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Abstract – South African chromite ores are typically smelted together with various SiO₂- and CaO-containing fluxes, normally quartzite and limestone respectively. The purpose of the SiO₂ is to lower the high melting point of the ore, while CaO is added to ensure that the slag that forms on smelting is fluid enough to enable separation of slag and alloy, and tapping from the furnace. Colemanite is a borate mineral, originating primarily from Turkey, and has the nominal, ideal composition of CaB₃O₄(OH)₃·H₂O. B₂O₃ readily fluxes chromite, and low amounts of this compound can yield a similar lowering of melting point as SiO₂ can. In addition, colemanite already contains CaO, which aids in making the resulting smelting slag more fluid.

Laboratory-scale smelting tests were conducted at Mintek over the course of 18 months. The work included the evaluation of a variety of boron-containing materials to replace conventional fluxes. The results of the laboratory tests and modelling work are presented in this paper.

Keywords: chromite, smelting, ferrochromium, colemanite, boron, energy

INTRODUCTION

The BOFLUX project was an initiative launched by Mintek and two other partners (see acknowledgements) in response to the second ERA-MIN joint call in 2014 on sustainable supply of raw materials in Europe. At the time, both chromium and borate minerals were on the 2014 EU critical raw materials list (European Commission, 2014). In this document, it was quoted that South Africa held 80% of the world's chromite resources, while Turkey held 98% of the world's borate minerals.

The project was based on the premise that several process improvements were possible using borate minerals as fluxes during chromite smelting, when compared to conventional fluxes. The possible improvements envisaged were lower impurity levels (higher Cr grade), reduced operating temperatures, reduced flux consumption, reduced slag to metal ratios, and lower energy consumption. Similar work on laboratory and industrial scale has been conducted in, *inter alia*, Kazakhstan in the production of ferrosilicon and ferrosilicochrome (Akberdin, Kim, Ilmaz, & Zhuchkov, 2013). This prompted an investigation into whether similar benefits were possible for South African chromite smelting operations, starting with fundamental and laboratory-scale research, which could be used as a guideline for further work.

In this paper, conventional fluxing of chromite ore in South African operations is discussed, to set the scene, followed by the principles behind fluxing with borates, in this case, specifically colemanite. Results from laboratory-scale tests done at Mintek, where conventional fluxes were tested against borates, then follow.

CONVENTIONAL SMELTING OF CHROMITE IN SOUTH AFRICA

Chromite sources and smelting operations in South Africa

Chromite ores in South Africa (SA) originate mainly from the Bushveld Complex. Broadly, the MG1, MG2, and LG6 seams in the complex are mined to produce feed for chromite smelting, while the UG2 seam is mined as a source of platinum group metals (PGMs). The 'discard' streams from UG2 ore processing have become a valuable raw material for ferrochromium producers, as predicted some 14 years ago (Cramer, Basson, & Nelson, 2004).

The composition of chromite varies substantially, and a comprehensive overview of each ore or concentrate is beyond the scope of this paper. The typical compositions of some South African chromite ores are given in Table I (Geldenhuys, 2013).

Table I: Typical compositions of South African chromites
(major components listed, mass %) (Geldenhuys, 2013)

Origin	Cr ₂ O ₃	FeO	MgO	Al ₂ O ₃	SiO ₂	Cr/Fe
SA LG6	46.6	25.0	10.8	15.1	0.6	1.6
SA UG2	42.6	27.4	9.3	14.9	1.2	1.4
SA MG	42.9	28.5	8.8	15.7	3.0	1.3

It is very important to point out that ores listed in Table I are just a few examples of what is used in industrial practice. Several smelting operations rely on various other chromite sources that vary both in the %Cr₂O₃, Cr/Fe ratio, and amount of gangue minerals.

South African chromite ores and concentrates are blended to obtain a Cr/Fe ratio that is high enough to produce 'charge chrome', a special grade of high-carbon ferrochromium (HCFerCr). Charge chrome contains about 50-53% Cr, 6-8% C, 4-6% Si, with the balance being Fe, with minor impurities such as S and P (Gasik, 2013).

Although the majority of ferrochromium in SA is produced via the submerged arc furnace (SAF) route, some 8-10% of other ferrochromium products (*e.g.*, plasma chrome – a low-carbon FeCr alloy) are produced using DC furnace technology.

The type of furnace, operating temperature, and slag composition are all factors that affect the recovery of Cr from chromite, and the quality of the final product. The Cr/Fe ratio of the ore largely determines the Cr content of the product produced in a particular furnace. Typical figures for chromium recoveries in various furnaces are given in Table II (Gasik, 2013). The energy required for smelting is also given (kWh/t FeCr product).

Table II: Chrome recovery and energy consumption for different furnaces used for FeCr production, partially adapted from (Gasik, 2013) and personal communication with producers

Type of Furnace	Chromium Recovery	SEC* (kWh/t)
Open AC Furnace (without raw material screening)	70–75%	4000–4300
Closed AC Furnace (with pelletized feed and pre-heating)	83–88%	3100–3400
Pre-reduction followed by closed AC Furnace	88–92%	2400**
Closed DC Furnace	88–92%	3850–4200

*SEC: Specific Energy Consumption

** Electrical energy consumed, *i.e.*, excluding energy required from burning fuel in the pre-reduction kiln

The chromite feed material is often pelletized and then subjected to either pre-reduction or sintering before it is charged to a SAF. A broad outline of process operations for ferrochromium production in South Africa is given in Figure 1. Note that it is no longer common for most producers to have lumpy ore as the primary feed material.

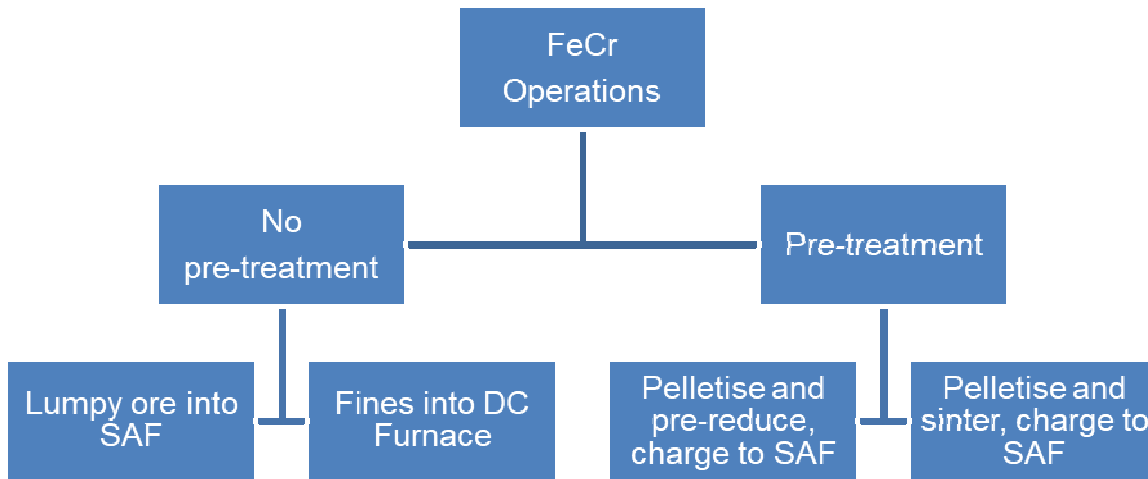


Figure 1: Broad categories of FeCr smelting operations in South Africa

A brief overview of the fundamentals of fluxing in conventional ferrochromium production

Chromite ore contains a mixture of complex spinel minerals and pyroxenes. Most of the chromium and iron in chromite is present as $(\text{Fe,Mg})(\text{Cr,Al})_2\text{O}_4$ spinel. A graphical representation of the spinel structure is given in Figure 2. Once the ore has been processed through a beneficiation plant, one is left with an ore or concentrate that consists of up to 95% spinel.

If one, for example, expresses the composition of the ore as a mixture of ideal spinel minerals, the LG6-type ore composition could be recalculated to be approximately 21.3% MgAl_2O_4 , 23.3% MgCr_2O_4 , 42.2% FeCr_2O_4 , 12.6% Fe_3O_4 , and 0.6% SiO_2 .

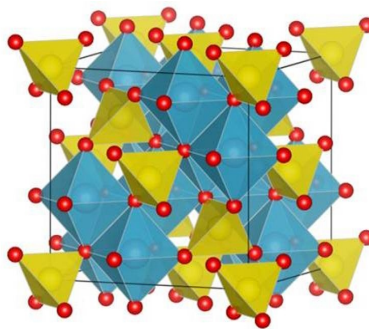
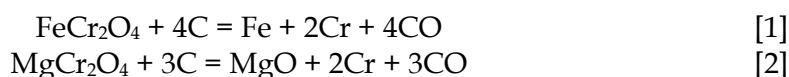


Figure 2: A graphical representation of a complex spinel phase (crystallography365.wordpress.com).
In general, spinel = AB_2O_4 . Yellow tetrahedra = 'A', blue octahedral = 'B', red = oxygen anions.

The purpose of chromite smelting is to reduce most of the Cr_2O_3 in the $MgCr_2O_4$ and $FeCr_2O_4$ spinel phases to Cr, and to separate the metallic phase from a slag phase comprising the main gangue minerals – MgO , Al_2O_3 , and SiO_2 .

Reduction of chrome spinel occurs both directly and indirectly in different parts of the furnace, is complex, and is very well described in the work done by Hayes (2004). Simplified overall reactions for the reduction of chromium and iron oxide in the chrome spinel by carbon are listed below.



As a side reaction, occurring in conjunction with process temperatures between 1700°C and 1750°C, some SiO_2 is reduced to Si which dissolves into the alloy.



Inevitably, reduction of Fe^{2+} and Fe^{3+} in the ore occurs at the typical smelting temperatures of above 1650°C and hence dilutes the final FeCr product with Fe. Further dilution of the product is by reduction of the limited amount of iron oxides in the reductant, as well as reduction of SiO_2 to Si from ore, reductant, and fluxes.

The nature of spinel is such that removal of oxygen from the structure causes a charge imbalance which is restored by migration of cations to vacancies created during reduction. For example: when Cr^{3+} is reduced to Cr^{2+} , ions migrate to the outer parts of an ore particle, and are replaced by Al^{3+} ions. In turn, for example, stable $MgAl_2O_4$ forms in the structure, which needs to be fluxed to facilitate separation between metal and slag. This mechanism is well described by, *inter alia*, Hayes (2004).

To reduce the melting point (liquidus temperature) of the gangue material, SiO_2 is added to the furnace as quartz flux, which dissolves the $MgAl_2O_4$ spinel and dilutes other gangue minerals.

On an isothermal projection of the SiO_2 - MgO - Al_2O_3 phase diagram at 1650°C (Figure 3) it is easy to see that the gangue in typical South African ores is not fully molten. The melting points of the gangue components of MG, LG6, and UG2 ores are around 2000°C, namely, 2014, 1987, and 2008°C respectively. Fluxing with even a limited amount of SiO_2 reduces the melting point significantly to temperatures between 1650 and 1750°C, but the slag then contains 35-40% SiO_2 and is quite viscous at these levels.

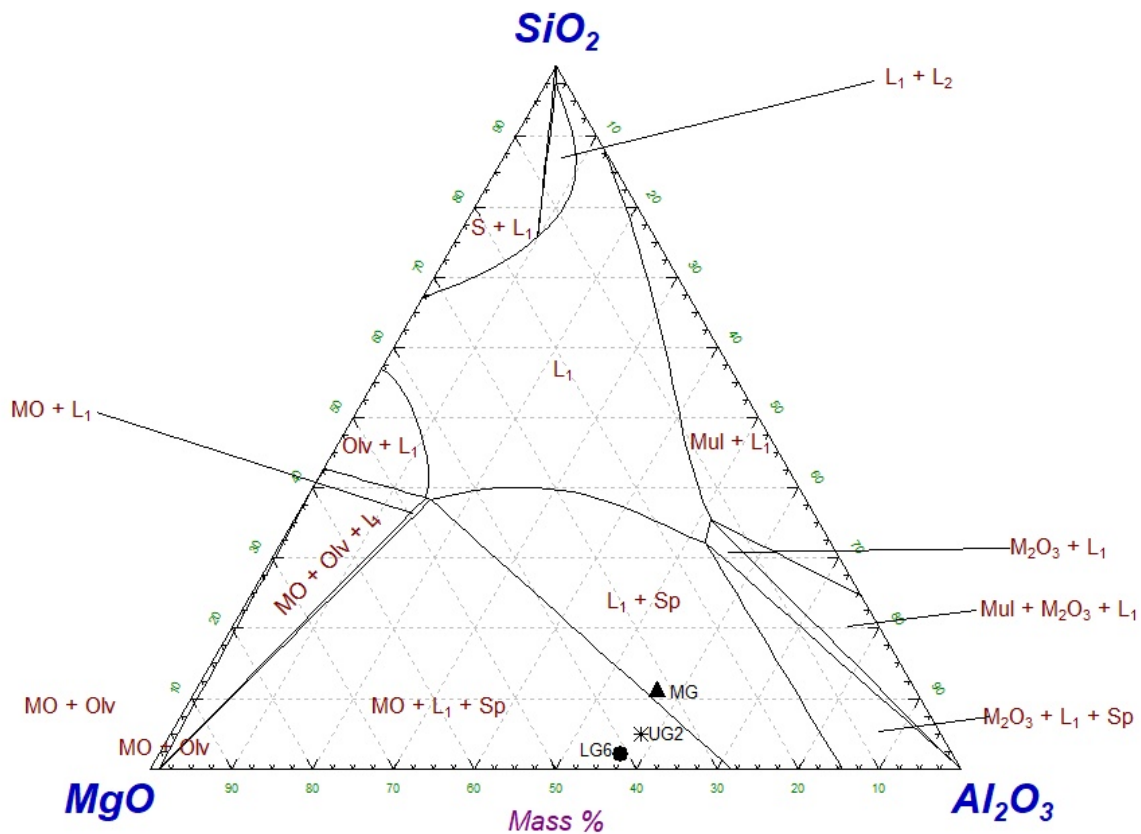


Figure 3: Isothermal projection of the SiO_2 - MgO - Al_2O_3 system at 1650°C
 (Diagram drawn in FactSage 7.1; Sp = Spinel, MO = Monoxide (MgO), S = SiO_2 , M_2O_3 = corundum, L = Liquid, Olv = Olivine)

A basic oxide, CaO , is added to lower the viscosity of the slag. In many operations, the CaO level is maintained between 10 and 15%, to ensure that the slag is sufficiently fluid for tapping.

Aside from tapping, the fluidity of the slag is extremely important, as it determines the rate of settling of alloy droplets through the slag. Aside from physical separation, slags with CaO/SiO_2 ratios are known to yield better recovery of chromium from a slag melt (Holappa & Xiao, 2004). In addition, higher amounts of CaO in the slag do lead to lower activities of SiO_2 , which in turn keeps Si levels in the metal lower compared to low- CaO slags.

Somewhat counter-intuitively, the addition of CaO to the slag does result in a slight increase in liquidus temperature, but the effect of CaO on the viscosity of the slag is larger than the increase in liquidus temperature for South African chromite smelting slags (Jones & Erwee, 2016).

Typical furnace operating temperatures in South African smelters are between 1700°C and 1750°C , which is close to the liquidus temperature of the slag. This is not accidental, and significant effort goes into choosing the correct fluxing regime for a specific ore mixture. The composition of the slag is designed deliberately such that the slag liquidus temperature is 100 – 150°C higher than the liquidus of the alloy (Jones & Erwee, 2016), which melts between 1520 and 1580°C .

Colemanite as a possible flux for ferrochromium production

As an alternative to SiO_2 as flux and CaO as slag modifier, borate minerals have been suggested for chromite smelting. Colemanite can be approximated by the formula

$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Water of crystallization is released from pure colemanite at temperatures above approximately 400°C , leaving behind CaO and B_2O_3 , the combination of which melts at approximately 930°C . Colemanite ores, however, also contain some impurities such as S , SiO_2 , Al_2O_3 , and MgO .

B_2O_3 is a very strong flux for gangue in chromite ores (MgO and Al_2O_3). This is quite evident if one considers Figure 4.

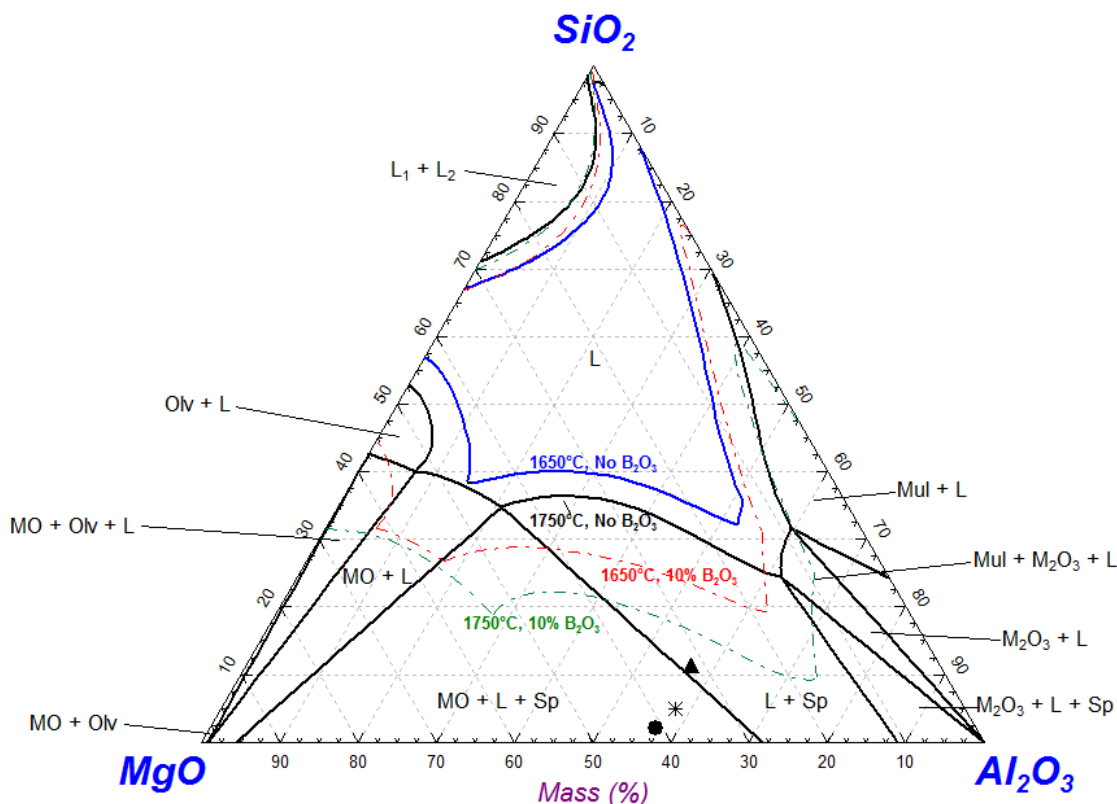


Figure 4: Polythermal projections of the SiO_2 - MgO - Al_2O_3 - B_2O_3 system at 1650°C and 1750°C (Diagram drawn using FactSage 7.1, symbols have the same meaning as in Figure 3)

Figure 4 was calculated using FactSage 7.1, using the FTOxid database for molten oxides. The thick black line is the isothermal projection at 1750°C for the chromite ore and gangue mixture without any B_2O_3 added. Compared to the liquidus region of 1650°C (blue line), it is easy to see that significantly less SiO_2 is required to reduce the melting point of the gangue for typical furnace operating temperatures. Aside from the lower SiO_2 content, a slag at 1750°C would be significantly less viscous (typically 1.5 poise) than a slag at 1650°C .

However, what is also evident in Figure 4 is that only 10% B_2O_3 present in the SiO_2 - MgO - Al_2O_3 system leads to significantly larger liquidus regions at 1650°C and 1750°C , as indicated by the dotted lines in the diagram. In fact, at levels as low as 10% B_2O_3 , the liquidus region at 1650°C is even larger than the liquidus region at 1750°C where no B_2O_3 is present.

As a simplified example, consider the composition of the gangue mixture for a typical LG6 ore (see Table I). The calculated effect of adding either pure CaO , SiO_2 , B_2O_3 , or pure colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) to this gangue mixture is shown in Figure 5.

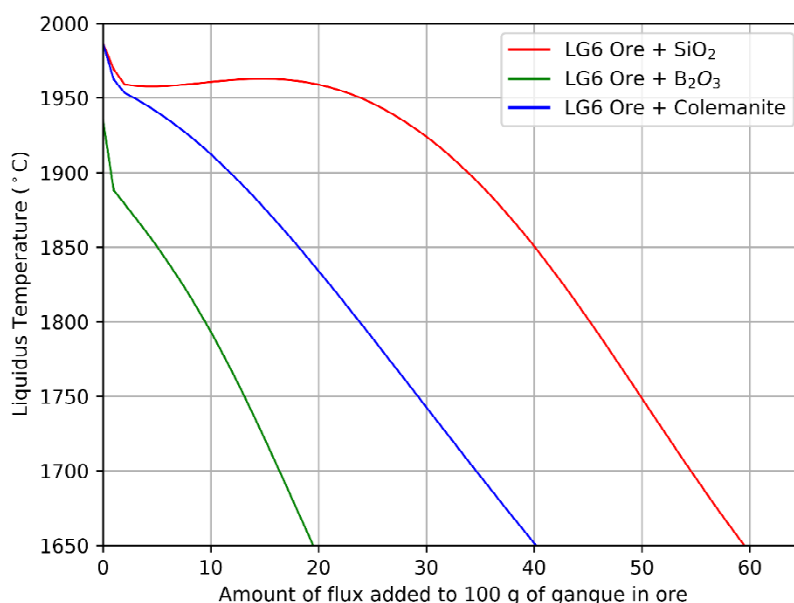


Figure 5: Effect of fluxes on melting point of an ore gangue mixture of initial composition: 57% Al₂O₃, 41% MgO and 2% SiO₂

From Figure 5, it is clear that, to reach a liquidus temperature of about 1650°C, the required amount of B₂O₃ is almost a third of the amount of SiO₂ that would be required. Interestingly, but not surprisingly, the amount of colemanite required is between that of pure SiO₂ and B₂O₃. The reason for this is that colemanite contains CaO as well, which raises the melting point of an MgO-Al₂O₃-SiO₂ mixture. However, the CaO component aids in reducing the viscosity of the resulting slag (see Figure 6).

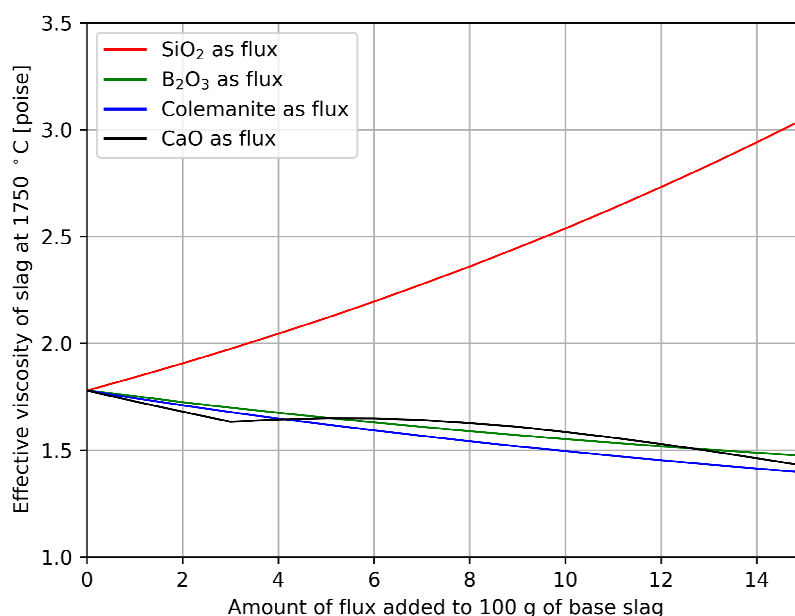


Figure 6: Effect of various fluxes on the viscosity of a chromite smelting slag based on LG6 gangue minerals (calculated using FactSage 7.1)

There is, however, a caveat to using colemanite as a flux for chromite smelting. Unlike SiO₂, which is thermodynamically more difficult to reduce with carbon when compared to Cr₂O₃ and FeO_x during smelting, B₂O₃ is almost as easy to reduce as Cr₂O₃ and CrO in slag, as seen on a modified Ellingham-Richardson type diagram (Figure 7). Solid lines represent the reaction $M + O_2 = MO_2$ for all compounds at unit activity,

while corresponding dashed lines represent the same reactions but at non-standard activity. Ranges for activity values are based on thermodynamic simulations described later in this paper ($M = \text{Cr, Si, B, and C}$). It is important to also mention that the effect of B_2O_3 reduction to volatile B_2O_2 gas is also possible at higher temperatures, which is not present on this diagram, nor are any reactions involving borides, carbides, or carbo-borides. However, in a simple way, what should be apparent from the diagram is that CrO , Cr_2O_3 , SiO_2 , and B_2O_3 all compete for carbon (FeO_x not included).

Aside from contaminating the final product, B_2O_3 reduction will consume excess reductant and also remove B_2O_3 from the slag, making its fluxing effect less effective.

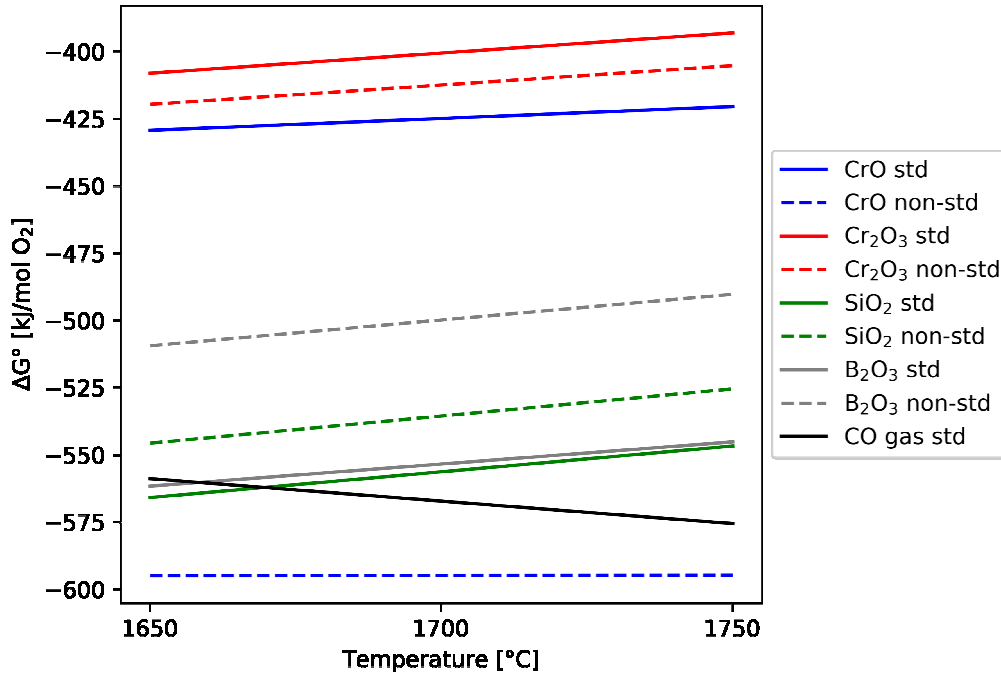


Figure 7: Free energy change of reactions between various compounds with 1 mole of O_2

The potential impact of colemanite as flux

The use of colemanite flux was anticipated to lower the energy requirement for smelting, as it would reduce the smelting temperature to 1650°C , decrease the amount of Si in the alloy which is typically between 4-6%, which in turn would lead to a higher grade of Cr, and lower slag volumes, which could lead to increased furnace throughput. In addition, it was anticipated that lower losses of alloy entrained in the slag would occur as a result of a potentially lower slag viscosity. However, the potential benefits of using colemanite as a flux must always be offset against the cost of doing so.

Energy consumption, and cost of production for chromite smelting

Whereas other countries, such as India, Kazakhstan, Finland, China, and Turkey, have increased their production of FeCr over the past three years, the production of FeCr in South Africa has declined from approximately 3.774 million tonnes per annum in 2014 to 3.596 million tonnes in 2017. Amongst the most significant reasons cited for this decline is the high cost of electricity in South Africa. The electricity price in South Africa has almost quadrupled over the last decade (Pariser, 2017).

The direct cash production cost of FeCr in South Africa comprises three main elements: electricity, chromite ore, and reductants. All other costs (labour, maintenance, electrode paste, fluxes, etc.) make up a relatively smaller portion (15%) of this cost.

Table III: Cost of production of FeCr in South Africa in 2016 (Pariser, 2017)

		Percent of total (%)
Exchange rate, ZAR/USD	14.71	
%Cr in FeCr	49.6	
Variable costs	Cost (US cents / lb Cr)	
Raw materials		
Chromite ore	13.87	29.1
Reductants	7.31	15.3
Others (Ex-works) (fluxes, electrode paste)	1.46	3.1
Energy	18.15	38.1
Operating costs	1.69	3.5
Semi-fixed costs		
Labour	3.51	7.4
G&A, Maintenance	1.71	3.5
Total direct cash production cost	47.69	

It is clear that the largest operating cost in the FeCr production process is electricity in South Africa – in 2016 it was a staggering 38.1% of the total production cost. The cost of fluxes and electrode paste is a mere 3.1%. However, fluxes can play an important role in lowering the energy requirement for smelting.

An extensive review of a FeCr furnace energy balance was done by Ringdalen (2015). In this work (and in similar calculations at Mintek), it has been established that the majority (~75% of the total) of the energy consumed in a furnace relates to temperatures above 1200°C, where reduction of chromite and melting of both gangue and metal occurs inside the coke bed.

Of particular importance is the effect of different parameters on the overall energy requirement of the furnace. A selected few are shown in Table IV.

Table IV: Energy savings for a SAF producing FeCr (adapted from Ringdalen, 2015)

Parameter	Saving in energy requirement for smelting
Lower slag temperature by 100°C	~60 kWh/t
Pre-heat raw material by 100°C	~76 kWh/t
Lower %undissolved chromite in slag (5% reduction in %Cr ₂ O ₃)	~122 kWh/t
Drying wet material from 5 to 2% moisture	~81 kWh/t
Decrease %Si in alloy by 2%	~72 kWh/t

With the overall energy requirement for smelting between 3.5 and 4.0 MWh/t, the savings might seem marginal, but if a combination of them can be achieved, important savings can be realised.

THERMODYNAMIC MODELLING AND PARAMETER SPACE SEARCH

Thermodynamic modelling was done to help guide testwork for this project. The modelling was done using FactSage™ 7.1 (Bale, 2016). Databases used were FTOxid (for oxide solutions, including slag), SGTE (for the resulting alloy phase) and FactPS

(for gases, pure oxides, and pure elements). Models were implemented using ChemApp v6.4.5 via the ChemAppForPy API (version 0.1.4). ChemApp is a free-energy minimization module and is also the backbone to the 'Equilib' module of FactSage, hence the two are used interchangeably, as they yield the same result. Free-energy minimization is a method which is used to determine the equilibrium composition of a combination of multiple species under specific conditions (in this case temperature and pressure) where the total Gibbs free energy of the system is minimized. Several thousand permutations were considered using the thermodynamic model.

The optimal level of flux would be such that:

- The smelting temperature can be lowered to 1650°C or less
- All of the gangue (mainly MgAl_2O_4 spinel) is dissolved
- The metal product is not contaminated (at least not more than usual)
- The viscosity of the slag is as low as possible
- The energy requirement for smelting is as low as possible

All of the simulations are done at different smelting temperatures, with the amounts of reductant and flux as variables. One subset of the results of the modelling is shown here as an example. The case presented in this section of the paper is for a metallurgical-grade chromite ore with high-grade colemanite flux and anthracite. The specific temperature used in the simulation was 1650°C. More specific detail on the actual composition of the ore is given in the experimental section of the paper.

Note that the energy requirement was calculated on the basis that slag, alloy, and gas are all at the same temperature. This is not strictly true for operational furnaces, but allows for a relative and consistent comparison between the different cases considered.

Each bar in the three-dimensional plots represents one discrete simulation. First, the energy requirement for smelting is presented in Figure 8(a). As expected, the energy requirement for smelting increases as more flux is used. Note that later in the paper a comparison is made with conventional smelting cases.

In Figure 8(b), the amount of undissolved spinel is shown. As expected, higher levels of colemanite result in lower levels of undissolved spinel at low reductant levels. The lowest reductant level is the stoichiometric amount of carbon required for full reduction of all chromium and iron oxide in the ore; the maximum is 50% more than the stoichiometric amount on a mass basis. Notice that at lower levels of colemanite, the amount of undissolved spinel decreases initially with the amount of reductant, but then increases again. This is due to the reduction of B_2O_3 by carbon that makes the flux ineffective for spinel dissolution. Further evidence of this is in the %Cr and %B recovery to metal (see Figures 8(d) and (f)).

Therefore, a careful balance between the amount of reductant, flux, and temperature is required. This is common for normal fluxes (SiO_2 and CaO), but requires even more attention when borate minerals are used.

Aside from boron contamination of the product, losses due to entrainment can also occur if there is no clear balance between carbon and flux addition. In this case, however, all is not lost (see Figure 8(h)). Despite lower levels of B_2O_3 in the slag, CaO that enters the furnace with colemanite aids in lowering the slag viscosity in almost all cases.

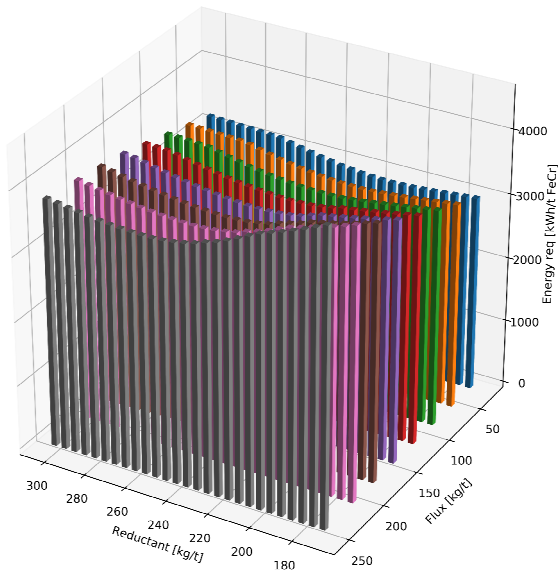


Figure 8(a): Energy requirement

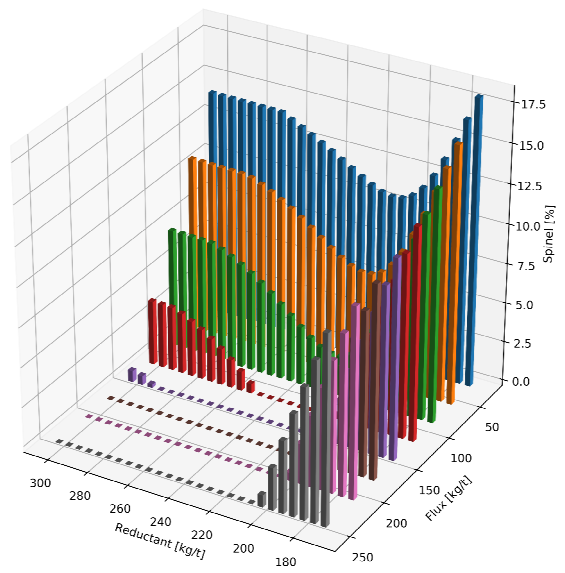


Figure 8(b): Undissolved spinel

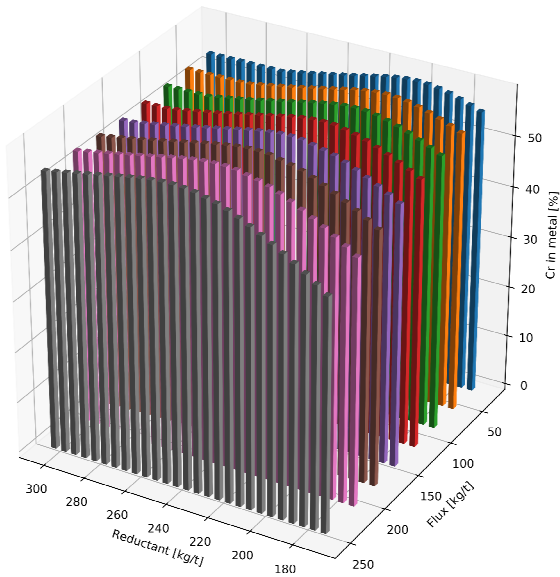


Figure 8(c): %Cr in metal

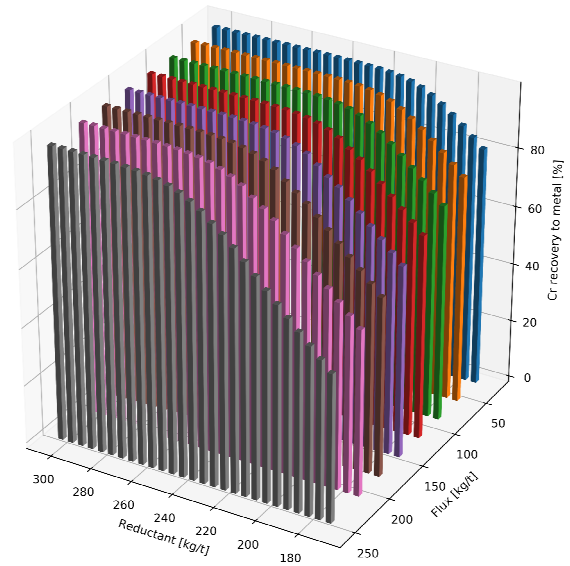


Figure 8(d): %Cr recovery to metal

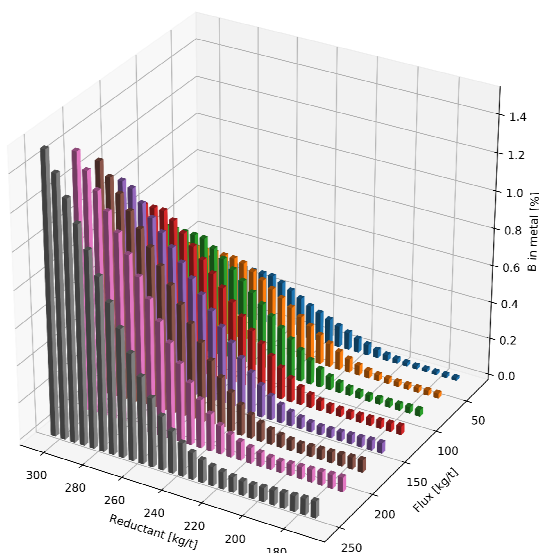


Figure 8(e): %B in metal

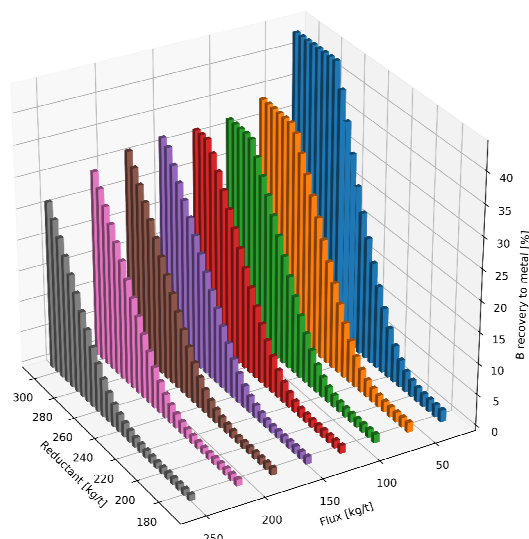


Figure 8(f): %B recovery to metal

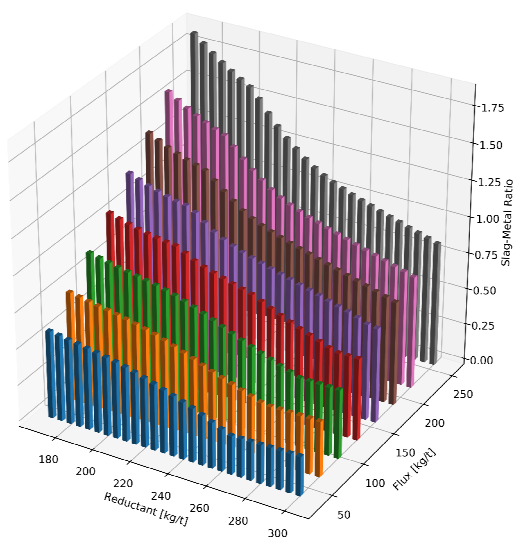


Figure 8(g): Slag/Metal ratio

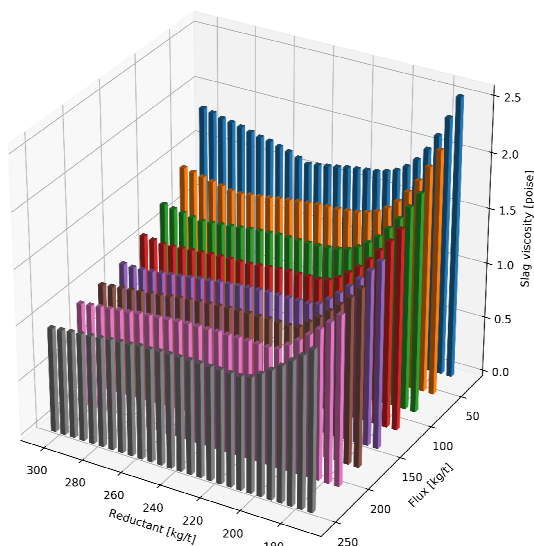


Figure 8 (h): Effective slag viscosity

From all of the modelling results, taking into account all of the factors, such as energy consumption, slag viscosity, and possible contamination of the product with boron (with subsequent loss of boron from the slag), testwork was planned. The amount of flux added depended on the grade of both ore and colemanite sources. Only a small subset of the results is presented in this paper.

EXPERIMENTAL METHODS

Overall, laboratory-scale crucible tests were conducted for about 18 months. Various grades of chromite ores, as well as different types of borate minerals, were tested. These included pure B_2O_3 , various grades of ulexite ($NaCaB_5O_6(OH)_6 \cdot 5H_2O$) as well as various grades of colemanite. In this paper, only a subset of all of the results is given; in this case, that of two grades of both chromite and colemanite. The tests with colemanite were benchmarked against tests with SiO_2 only, B_2O_3 only, and then also conventional smelting regimes.

It is imperative to state that crucible-based testwork for smelting has inherent limitations and that larger, pilot-scale testing would be required to assess all of the possible benefits, if any, of one flux over the other. However, crucible-based testwork is of great value to assess the relative performance of one smelting regime to another, as many of the variables can be fixed, and other parameters changed systematically, to observe the effect they have on smelting performance.

Raw materials

Two chromite ores were tested: one with a high Cr/Fe ratio typical for charge chrome production, and the other an ore with a low Cr/Fe ratio. Only the results for tests using the chromite ore with a high Cr/Fe ratio are presented in this paper, as the other results will be published separately in future. Flux materials were reagent grade SiO_2 , CaO , and B_2O_3 , and two grades of colemanite, referred to as high-grade colemanite (HGC) and low-grade colemanite (LGC) in this paper. The reductant in all cases was anthracite, sourced locally, often used in chromite smelting operations. The composition of each material is given in Tables V to VII.

Table V(a): Normalised, average composition of the ore tested (mass %), as determined by ICP-OES (accredited method developed by Mintek)

Ore	Cr_2O_3	Al_2O_3	CaO	FeO	SiO_2	MgO	MnO	TiO_2	Cr/Fe
High Cr/Fe ore	44.12	12.61	0.81	22.77	6.61	12.30	0.22	0.56	1.71

Table V(b): Normalised average composition of the borate minerals (mass %)

Flux	CaO	FeO	SiO_2	MgO	LOI*	B_2O_3	Na_2O
High-grade colemanite	27.0	0.04	4.0	3.0	25.46	40	0.5
Low-grade colemanite	26.0	-	13.0	-	34	27.0	-

* Crystal water, moisture, and any volatile matter

Table VI: Composition of the reductant used for all tests (mass %)

Fixed Carbon	Moisture	Volatiles	Ash	Al_2O_3	CaO	Fe_2O_3	MgO	SiO_2	TiO_2
80.5	1.6	6.2	11.7	2.9	0.5	0.7	0.1	5.4	0.2

Test conditions

The amount of anthracite required as a reductant was calculated on the basis of the total amount of carbon required for full reduction of Cr_2O_3 (as FeCr_2O_4 and MgCr_2O_4) and FeO_x (as FeCr_2O_4 and Fe_3O_4) to Cr and Fe respectively; these are known as low-carbon cases (18% reductant in this case). As reduction of SiO_2 and B_2O_3 was expected, a number of tests referred to as high-carbon cases were also done, where the amount of anthracite added was 1.5 times (*i.e.*, 27%) on a mass basis than that used in the low-carbon case. For the conventional recipe, 25% of the feed was anthracite.

The amount of flux was based on the amount required to fully dissolve residual MgAl_2O_4 in the slag as predicted using the thermochemical calculations done in FactSage, but the amount of HGC was varied between 3 and 9% to check sensitivity of the smelting process with varying amounts of flux compared to the conventional recipe. Fluxes tested were:

- SiO_2 only (10%)
- Varying amounts of pure B_2O_3 (3, 4.3, 5, and 8%)

- Varying amounts of HGC (3, 6, and 9%)
- A fixed amount of LGC (which would be suitable as per the prediction)
- CaO+SiO₂ (conventional recipe of 9.5% SiO₂ + 7.5% CaO)

Tests were done at 1650°C and 1750°C for all the tests with borate minerals, and only at 1750°C for the conventional recipe.

Furnace set-up and test procedure

Raw materials were milled in a swing mill after drying overnight at 105°C in a muffle furnace. Mixing of the ores was done in small plastic bags, after weighing, and the mixtures placed into either a high-density pure MgO or a graphite crucible. Material was compacted mechanically into the crucibles, and small holes made in the material bed to ease release of the gas evolved during testing.

The prepared crucibles were loaded in batches of four into a 30 kW induction furnace. The four crucibles were placed inside a large graphite crucible that is used as a susceptor inside the water-cooled coil of the induction furnace. The large susceptor is insulated using more bubble alumina and an insulating castable material. A graphite lid was placed over the graphite susceptor. A B-type thermocouple was placed through the lid to measure the temperature inside the furnace, and argon gas was used for purging through an alumina lance placed through the lid as well. A ceramic blanket was used as additional insulation, to avoid excessive radiative energy losses. The furnace power was initially set from 2.5 kW and increased every 30 minutes by 0.5 kW until the required test temperature of 1650°C or 1750°C was reached. The test was left to run at the required temperature for one hour, after which the furnace was switched off and left to cool overnight.

The metal and slag was then recovered from the crucible after breaking the crucibles apart. The slag was not always fully recovered, due to attack on the crucible. Where possible, all bulk pieces of metal were collected for weighing. The metal and slag were analysed by means of ICP-OES for Cr, Fe, Si, Mn, Ti, and V; LECO for C and S; and ICP-MS for B.

RESULTS AND DISCUSSION

Laboratory-scale crucible tests

Three factors were compared to one another for the smelting tests. These are the relative amount of bulk alloy that formed, the %Cr in the metal, and main impurity levels, in this case Si and B. The relative amount of bulk alloy formed serves as an indication of the effectiveness of the flux used to facilitate metal-slag separation.

The amount of bulk alloy formed refers to the recoverable lump of alloy that settles at the bottom of the crucible after testing. Metal entrained in the slag phase is often difficult to separate physically and is not, on laboratory scale, deemed appropriate to compare based on previous experience at Mintek. As the slag is contaminated with metal in most cases (as will be shown later in this section), the slag analysis was disregarded in all calculations. Consequently, the mass recovery of Cr is also not calculated. The bulk alloy phase was found to be more homogeneous (little entrainment of slag particles found) and therefore used for comparison. For all practical purposes, a comparative study of the quality of the alloy was more suitable, as recovery of elements in industrial processes is almost always different from laboratory tests.



Figure 9: An example of the bulk alloy pellet that forms and is collected from a smelting test (bright grey/silver = alloy)

The %Cr values in the alloys were compared to one another. It is important to realise that the absolute value of the Cr content can be affected by the method of analysis. In this project, the standard deviation on the %Cr for the method used was ± 0.15 .

The level of major impurities plays an important role in the value of high-carbon ferrochromium. Anything that is not Cr is not paid for, and penalties are payable when the material does not meet the required specification. For comparative purposes, the total %Si and %B were compared, as these are interdependent. The standard deviations on the analysis error for Si and B are $\pm 0.1\%$ and ± 10 ppm respectively.

Results are presented in bar-chart format for easy comparison. Where no bar is presented on the chart, the test (or set of tests) failed. Failed tests are tests where no discernibly separate metal and slag phases could be identified and separated, due to severe entrainment. These 'failed' tests were repeated at least once, to ensure that the result was consistent. Error bars on the charts indicate the standard deviation for the particular quantity. Where no error bar exists, a single test was done for the particular case. The variability of these tests was usually confirmed by a similar case. This was done for two reasons: firstly to do a test that would be more industrially relevant for actual furnace operations, and secondly to keep the number of tests within the limit that could be carried out within the budget for this project.

Results for tests using chromite ore with a high Cr/Fe ratio

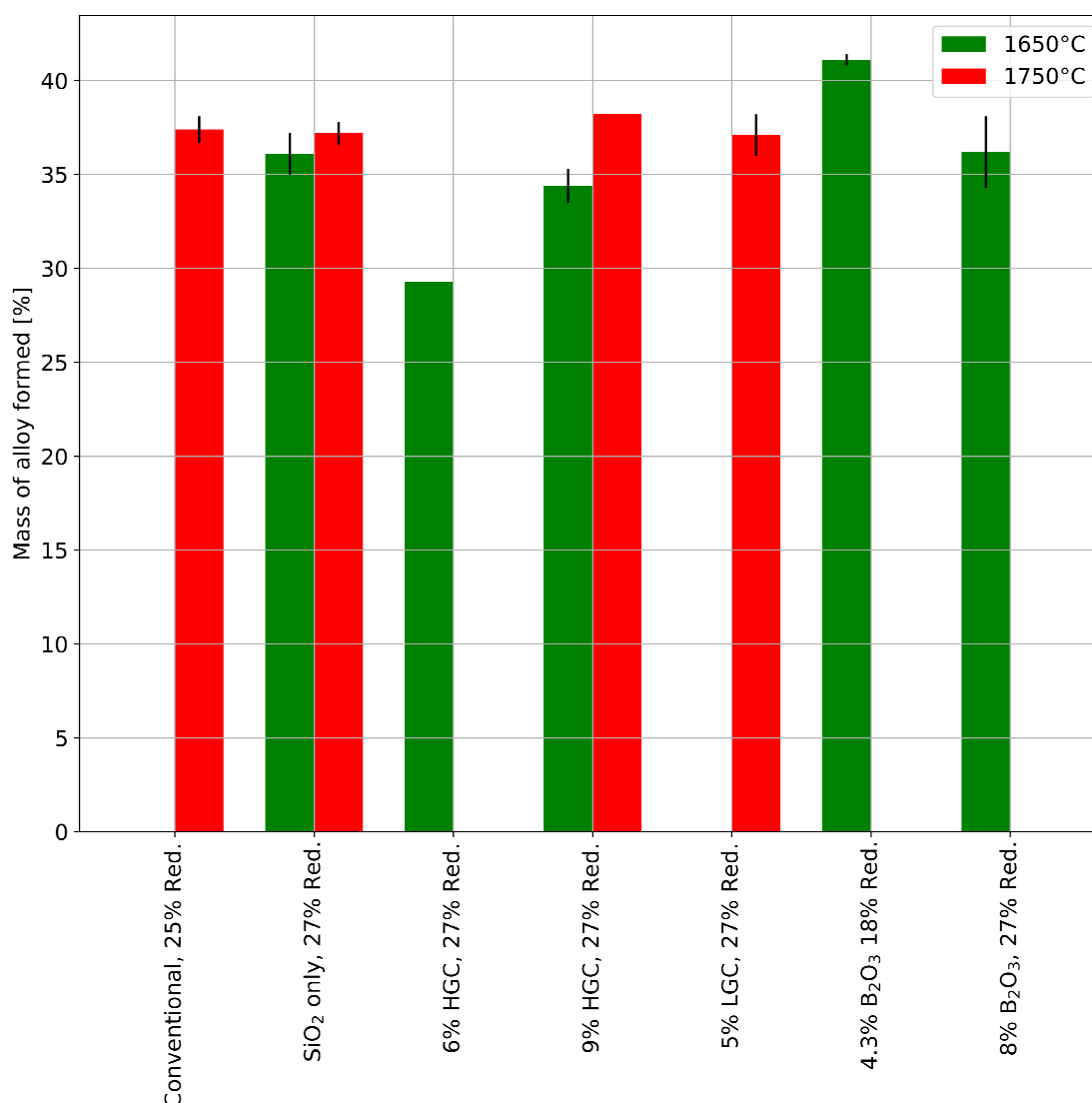


Figure 10: Results summary (mass of alloy formed) for chromite with high Cr/Fe ratio (error bar indicated standard deviation on tests). The % values stated refer to the amount of material added as a percentage of the amount of ore added (*e.g.*, “6% HGC, 27% Red” refers to a case where 6 grams of flux and 27 grams of reductant was added to 100 grams of ore).

No separable bulk alloy could be produced at 1650°C using the conventional recipe or levels of less than 6% of either lower- or higher-grade colemanite. The best result achieved, in terms of the amount of metal, was where 4.3% pure B₂O₃ was used. Whether it would be cost-effective to use pure B₂O₃ as flux is yet to be explored, as it is even more expensive than colemanite or a combination of conventional fluxes.

From the tests done at 1750°C, there was no statistically significant difference between using low- or high-grade colemanite versus conventional fluxes. Operating at a temperature of 1750°C also defeats one of the major aims of the project: operating at lower temperatures.

The amount of alloy formed is not the only parameter that needs to be considered. Grade is assessed by not only the total amount of Cr in the product, but also the level of impurities, in this case Si and B, present, as this would affect the customer downstream.

The amount of Cr in the metal for each of the cases where bulk alloy was formed is shown in Figure 11. It was found that, in all but one case, the minimum specification for charge chrome of 50% Cr was achieved. Just as for the amount of metal formed, it does seem that there is no statistically discernible difference when comparing conventional smelting at 1750°C to using ~9% high- or 5% low-grade colemanite at 1650°C. However, the fact that an alloy can be formed at 1650°C using HGC with this ore is promising, as this implies that the overall operating temperature can be decreased, yielding more or less the same result as using conventional fluxes at 1750°C.

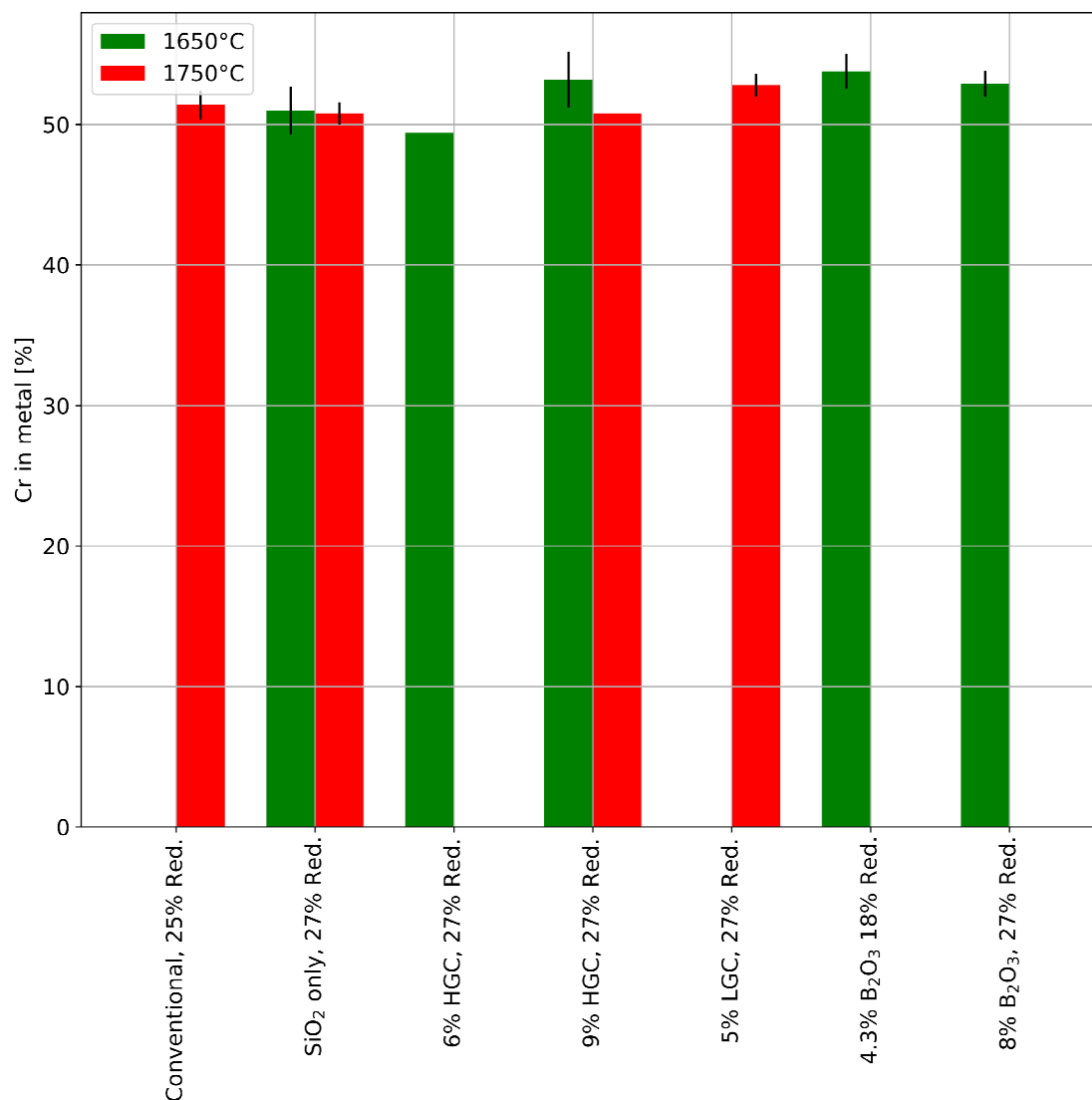


Figure 11: Results summary (Cr grade) for chromite with high Cr/Fe ratio (error bar indicated standard deviation on tests)

As part of the thermodynamic calculations in FactSage 7.1, the energy requirement for smelting was also calculated. The results of that calculation are given in Table VIII, along with the expected viscosity of the slag, also calculated using the Viscosity module of FactSage 7.1. Smelting chromite at 1650°C with 9% HGC would save roughly 3% on the total energy requirement when compared to smelting using conventional fluxes at 1750°C. The reason that this value is lower than expected is due to the fact that some 25-30% by mass of the colemanite is present as crystal water. Calcination of colemanite before use in a furnace would reduce the energy requirement even more. However, if one takes a longer-term view, the reduced operating temperature can have significant benefits for a smelter.

Table VIII: Theoretical slag viscosity, and energy requirement for smelting

Fluxing regime	1650°C		1750°C	
	Slag Viscosity [poise]	Energy requirement [MWh/t FeCr]	Slag Viscosity [poise]	Energy requirement [MWh/t FeCr]
Conventional	1.8	3.15	1.7	3.45
SiO ₂ only	2.7	3.29	1.8	3.60
6% HGC	1.5	3.27	0.9	3.60
9% HGC	1.3	3.33	0.8	3.64
5% LGC	1.8	3.25	1.1	3.58

Finally, the amount of contamination of the product needs to be assessed. The amounts of Si and B, the main impurities in the alloy, are given in Table IX. As expected, less Si is present in tests where borates are used. This could be attributed to two factors – firstly, less SiO₂ is present to be reduced in the first place; secondly, B₂O₃ is preferentially reduced to SiO₂. The amount of B present in the alloy is higher at 1750°C than at 1650°C, which was also expected.

Table IX: Impurity levels for alloy formed from chromite with a high Cr/Fe ratio

Fluxing regime	T = 1650°C		T = 1750°C	
	%Si (±SD)	%B (±SD)	%Si (±SD)	%B (±SD)
Conventional	-	-	1.03 ± 0.22	-
SiO ₂ only	5.38 ± 1.47	-	7.71 ± 0.8	-
6% HGC	1.26 ± 0.07	-	-	-
9% HGC	2.98	1.21	3.1	4.9
5% LGC	-	-	1.8 ± 0.6	0.18 ± 0.01

One question remains regarding B-contamination of the alloy. There is no formal boron specification for HCrFe that the authors could find in any standard or literature. However, during the production of stainless steel, there might be a very tight specification on the amount of boron present. This is beyond the scope of this particular paper, and is being investigated. The authors did do some initial tests on converting of HCrFe with the aim of boron removal.

The full details of the decarburisation testwork are not given here, as the results need to be confirmed. In brief, a sample of ferrochromium metal produced during testing was decarburised in an alumina crucible in an induction furnace. An alumina lance was used to inject pure oxygen into the melt. A synthetic slag of 40% CaO – 40% SiO₂ – 10% MgO – 10% Al₂O₃ was added to the melt periodically, to aid the converting process. A temperature of 1600°C was maintained. Samples were taken, and analysed using ICP (for metal components) and LECO for C. The initial and final compositions of the alloy sample are given in Table X.

Table X: Initial and final compositions of the alloy melt subjected to decarburisation using pure oxygen

t (min)	% Cr	% Si	% Mn	% Fe	% P	ppm B	% Cr	% Ti
0	8.54	1.23	0.27	44.3	0.04	1815	46.2	0.27
32	7.32	0.63	0.23	48.0	0.20	480	48.7	0.21

A plot of the boron content as a function of time (Figure 12) shows that boron removal follows an exponential rather than a linear relationship, indicating possible first order kinetics for removal. After 32 minutes of blowing time, the boron content of the melt was reduced to 25% of the original value, showing that removal of boron from the melt

is indeed possible. A side effect of this process is the increased concentration of impurities such as P, which will have to be removed at a later stage of blowing, or in a separate process step. This implies that steelmakers would necessarily have to adjust parameters in their operations when using boron-containing ferrochromium.

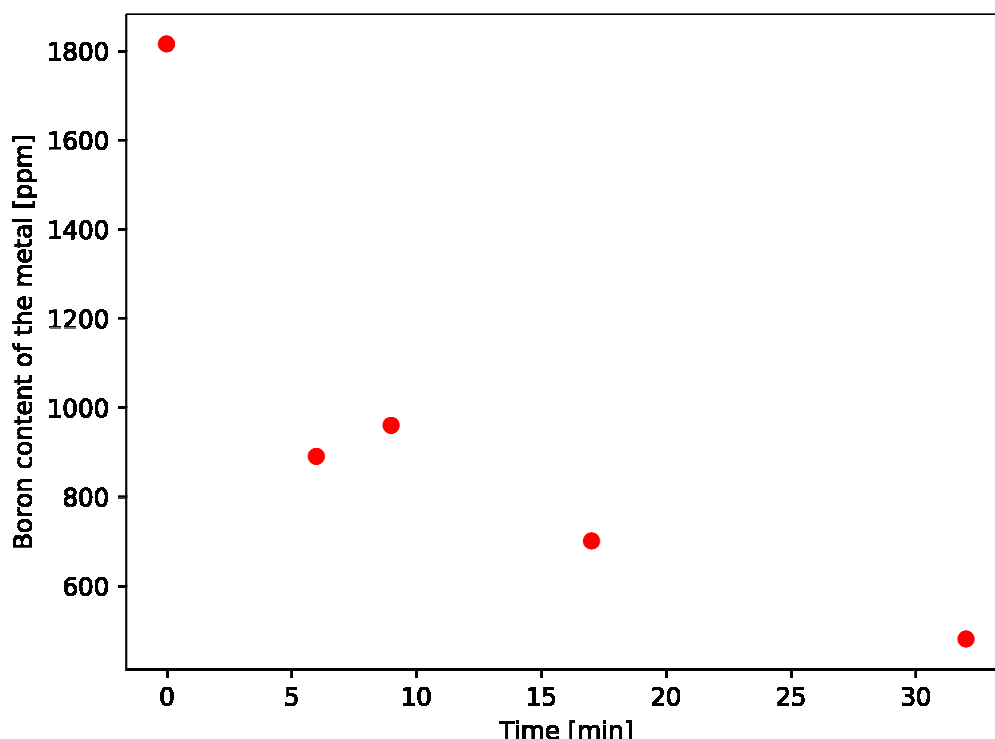


Figure 12: Boron removal from a ferrochromium alloy at 1600°C in contact with a synthetic slag

CONCLUSIONS AND FUTURE WORK

Fluxing of chromite ore with borate ores shows promise, but many factors need to be taken into account to gain maximum benefit from it. Results from laboratory tests show that it is indeed possible to reduce operating temperatures from 1750°C to 1650°C using colemanite in place of conventional fluxes. The amount and grade of alloy formed when using colemanite as flux at 1650°C was more or less the same when compared to the conventional smelting case at 1750°C. In some cases (*e.g.*, with pure B_2O_3 as flux), it was found that the grade of the alloy was increased by some 1–2% Cr, which does imply that some more testwork with borates is required to get a full picture of the potential benefits. Boron contamination of up to 1% could pose a problem, but it seems that boron removal might be possible, and this should be studied in more detail.

Furthermore, tests need to be conducted on pilot scale on a longer-term campaign to confirm the results found on laboratory scale. This is especially important to determine the optimal level of flux and reductant relevant to furnace operations, and to account for other factors such as the conductivity of the slag when B_2O_3 is present. The ultimate success of colemanite as a flux will depend greatly on the relative cost of fluxes balanced against the short- and longer-term benefits realised, especially as conventional fluxes are cheap and sourced locally, when compared to borates, which would have to be sourced from, for example, Turkey.

ACKNOWLEDGEMENTS

This paper is published with the permission of Mintek. The authors would like to thank Mintek, ERAMIN, and the South African Department of Science and Technology for sponsoring the work. The contributions of our colleagues are gratefully acknowledged.

Finally, the authors wish to thank the all of the partners of the BOFLUX consortium (Ab Etiprodukt Oy, Finland and Siyanda Chrome Company Pty Ltd) for their support with material and endless discussions during the project – without them, this project would not have been possible. Mintek also acknowledges the support of the National Intellectual Property Management Office (NIPMO) in the ongoing maintenance of its IP portfolio.

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