

ASPECTS OF DC CHROMITE SMELTING AT MINTEK – AN OVERVIEW

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e-mail: IsabelG@mintek.co.za**ABSTRACT**

Ferrochromium alloy smelting in a DC open-arc furnace, principally for the direct processing of ore fines, has come of age in the past 30 years. From relatively humble beginnings in Mintek's first DC pilot-plant facility in the 1980s to commercial pilot-plant testwork today, Mintek's DC research work has led to the implementation of a new technology in industry that has revolutionised the processing of fine ores. In the past 10 years, Mintek has conducted chromite smelting testwork on seven types of chromite ore and processed more than 700 metric tons of concentrate in its test facilities. A wide variety of chromite ores has been tested, varied not only in origin but also with large variations in the total and relative amounts of chromium and iron, which relates to ore grade (in terms of total chromium oxide) but also Cr/Fe ratio. The Cr/Fe ratio largely determines the chromium content of the ferrochromium alloy produced. The variations in composition also affect the relative ease of reduction of the ore. For example, increasing amounts of magnesium compared with iron in the divalent site will make the spinel more difficult to reduce. Conversely, increasing amounts of iron in the trivalent site, replacing aluminium, will increase the reducibility of the spinel. The overall results from processing of chromite concentrates with origins in Southern Africa, India, Kazakhstan, and North America are discussed in terms of the inherent variations. Smelting recipes, alloy compositions and grades, and general observations are evaluated in the context of the DC open-arc smelting regime. The relative independence of power supplied by the open-arc allows for a wide variety of compositions to be processed, whilst the optimum slag composition can be selected to achieve recovery targets and alloy composition.

KEYWORDS: DC arc furnace, chromite, smelting, ferrochromium, Mintek, South Africa, Zimbabwe, India, Kazakhstan, North America.

1. INTRODUCTION AND BACKGROUND

Ferrochromium alloy smelting in a DC open-arc furnace, principally for the direct processing of ore fines, has come of age in the past thirty years. Mintek's DC research work in the mid- to late 1970s led to the implementation of new technology that revolutionised processing of fine chromite ores. In the early 1980s, Mintek and Middelburg Steel & Alloys (now incorporated in Samancor Cr) developed the DC open-arc process for the production of ferrochromium, with the objective of smelting chromite ore fines. This work led to the commissioning of the first DC smelting furnace (16 MVA) in 1983, followed by a 40 MVA installation in 1988. Thirty years later, DC smelting has become a mature and accepted technology, recognized for features such as the ability to handle fines, allowance for use of cheaper reductants, and the ability to process a wide variety of feed compositions whilst achieving very high chromium recovery. At the same time Mintek's pilot-plant facilities grew from relatively humble beginnings in the 1980s to commercial pilot-plant facilities with a wide range of flexible configuration options.

In view of this major 30-year milestone, an overview of chromite smelting testwork at Mintek seemed appropriate. This paper aims to review the history and progress and highlight the flexibility of DC chromite smelting by comparing the results from smelting tests conducted on a selection of

varied chromite ores. In the past 10 years Mintek has conducted chromite smelting test work on seven different chromite ores, smelting more than 700 metric tons of chromite ore. The chromite ores not only varied in origin but also in composition. Results from the pilot-plant smelting tests for chromite originating from South Africa, Zimbabwe, India, Kazakhstan and North America are discussed in light of the inherent variations and the relative ease of smelting. Smelting recipes, alloy compositions, and general observations are evaluated in the context of the DC open-arc smelting regime. Figure 1 shows the general origins of the ores tested at Mintek on a simplified world map.



Figure 1: World map indicating the origins of chromite ores tested using Mintek’s DC pilot facilities

The flexibility of the DC furnace process is reviewed by comparing different smelting projects, and the various fluxing recipes utilised, from the perspective of alloy composition and operational parameters. Table 1 summarises a selection of pilot-plant smelting tests executed at Mintek in the past 10 years and identifies the types of chromite according to their region of origin, Cr/Fe ratio, general characteristics, and the equipment configuration utilised during the tests.

2. CHARACTERISATION OF CHROMITE ORES TESTED

Chromium ore, or chromite ore, occurs in rocks formed by the intrusion and solidification of molten lava or magma that is very rich in heavy, iron-containing minerals such as pyroxene and olivine. Within these rocks, often referred to as ultramafic igneous rocks, chromium occurs as a chromium spinel, a highly complex mineral made up, in its basic form, of magnesium and aluminium oxides. However, the magnesium can be substituted in varying proportions by divalent iron, and the aluminium can be substituted, also in varying proportions, by trivalent chromium and trivalent iron. Thus the chromium spinel may be represented as: $(\text{Fe},\text{Mg})\text{O} \cdot (\text{Cr},\text{Fe},\text{Al})_2\text{O}_3$. Large variations in the total and relative amounts of chromium and iron in the lattice occur in different deposits. These affect the ore grade not only in terms of the chromium oxide content, but also in the Cr/Fe ratio. The Cr/Fe ratio largely governs the chromium content of the ferrochromium produced. The variations also affect the relative ease of reduction of the ore. For example, increasing amounts of magnesium compared with iron in the divalent site will make the spinel more difficult to reduce. Conversely, increasing amounts of iron in the trivalent site, replacing aluminium, will increase the reducibility of the spinel.

Commercial chromite deposits are found mainly in two forms: stratiform seams in basin-like intrusions, often multiple seams through repeated igneous injections, and the more irregular podiform or lenticular deposits. The best-known example of a stratiform deposit is the Bushveld Igneous Complex, a saucer-shaped deposit in the northern part of South Africa. Chromite ore is mined along the eastern and western rims of the complex that consists of three primary layers (upper, middle, and lower). The Great Dyke of Zimbabwe, traversing nearly the length of the country, is very similar and has been linked to the Bushveld in geological history. These two features are well known also for their important and very large commercial deposits of platinum-

group metals. Other stratiform deposits occur in Canada, Madagascar, and in the Orissa district of India. Stratiform deposits are generally very large complexes. Podiform deposits are relatively small in comparison and may be shaped as pods, lenses, slabs, or other irregular shapes. Many have been extensively altered to serpentine, and they are often faulted. They are generally richer in chromium than the stratiform deposits and have higher Cr/Fe ratios. Ore reserves in Kazakhstan are of the podiform type. Podiform ores were originally highly sought after, especially those from the deposits in Zimbabwe, as the best source of metallurgical grade chromite for high-carbon ferrochromium. These ores also tend to be massive (hard lumpy) ores, as opposed to the softer, more friable ores from the stratiform deposits.

A summary of the various ore types tested is presented in table 1. The summary includes an overview of the types of reductant, fluxes, duration, and scale of the test work, and also summarises the electrode configurations utilised (single solid, single hollow, and solid twin electrodes). Ores with Cr/Fe ratios ranging from 1.3 to 3.8 were tested. The duration of the test projects ranged from about 10 to 28 days, depending on the quantities of ore available for smelting. Preparation of bulk samples for pilot testing is expensive and time consuming, especially so for new projects, and, depending on availability, the scale of the tests is often determined by cost and time constraints, thereby limiting the quantities of raw materials smelted.

Table 1: Summary of smelting testwork and general characteristics of the chromite ores tested

Origin	Kazakhstan	Zimbabwe	India A	India B	N. America	SA (UG-2)	SA (MG)
Chromite size	-6 mm	-2 mm	-2 mm	-2 mm	-1 mm	-1 mm	-2 mm
Cr/Fe ratio	3.8	3.3	2.8	2.5	2.1	1.4	1.3
Refractory index	4.1	4.4	4.2	3.9	2.9	2.3	2.1
Cr ₂ O ₃ , mass %	51.2	48.4	53.5	50.6	44.0	42.6	42.9
FeO, mass %	11.9	13.1	16.9	17.9	18.2	27.5	28.5
Reductant type	A, C	A, C	A	C+A, A	A	A	C+A, A
Reductant size	-5 mm	-10 mm	-12 mm	-12 mm	-10 mm	-12 mm	-10 mm
Fluxing regimes	S	S+L	S+L	S+L	S, S+L	S+L	S+L
Shell diameter	1m & 2.5m	1m	2.5m	2.5m	2.5m	2.5m & 1m	2.5m
Ore processed, t	185.6 [#]	7.0	68.2	83.4	144.4	126.9 ⁺	117.2 [#]
Duration, days	9 & 27	7	6	10	21	17 & 4	21 & 7
Equipment	Twin, solid Single, solid	Single, solid	Twin, solid	Hollow Twin, solid	Single, solid	Hollow Twin, solid ^{\$}	Single, solid

Reductant type

A=anthracite, C=coal

Fluxes

S=silica, L=limestone

Single, solid

Single (1) solid electrode; fed via roof

Twin, solid

Twin (2) solid electrodes; fed via roof

Hollow

Single hollow electrode; fed via electrode

Note \$

Hot feed and cold feed (all other tests with cold feed only)

Note #

Totals reflects two separate projects smelting the same sample

Note +

Totals reflects two separate projects different UG-2 concentrate samples

Chromite C & D

Processed during same project (India A – concentrate, India B – off-spec fines)

Shell ID

Shell diameter without refractory lining (typical refractory thickness 230 mm)

Refractory index

$$\frac{\text{Cr}_2\text{O}_3 + \text{MgO} + \text{Al}_2\text{O}_3}{(\text{Fe}_{\text{total as FeO}}) + \text{SiO}_2}, \text{ mass \% ratio, chromite composition}$$

All test furnaces were configured in DC mode with the electrode or electrodes acting as the cathode, and with a pin-design bottom anode installed in the hearth of the furnace. While the pin anode design is used with great success in Mintek's test furnaces (figure 3 a typical installation diagram and photograph of pin anode and roof), a commercial installation is more likely to use a conductive hearth design. The majority of the tests were conducted in a 2.5 m diameter furnace (shell diameter) with some work executed in a smaller 1 m diameter furnace for cases where the quantity of available ore was limited (about 10 to 15 metric tons).

Table 2: Average chemical composition of chromite ores tested, mass %

Origin	Kazakh.	Zimbabwe	India A	India B	N.America	SA (LG §)	SA (UG-2)	SA (MG)
Cr ₂ O ₃	51.2	50.8	53.5	50.9	44.0	46.4	42.6	42.9
Fe _{Total} as FeO	11.9	13.3	16.9	17.9	18.2	25.0	27.4	28.5
MgO	19.8	17.9	11.4	10.9	12.8	10.8	9.3	8.8
Al ₂ O ₃	6.5	12.7	11.4	12.7	12.5	15.1	14.9	15.7
SiO ₂	6.9	3.9	1.3	1.2	5.9	0.6	1.2	3.0
Cr/Fe	3.8	3.4	2.8	2.8	2.1	1.6	1.4	1.3
MgO/Al ₂ O ₃	3.1	1.4	1.0	0.9	1.0	0.7	0.6	0.6
	1.5	1.1	0.9	0.8	0.7	0.7	0.9	0.5

Note LG, MG and UG-2 (Lower, Middle and Upper Groups from the Bushveld Igneous Complex)

§ SA chromite reference material (for reference only, not tested); Origin = Winterveld Chrome Mines, Steelpoort

The compositions of the various ores tested are projected on the MgO-Al₂O₃-SiO₂ ternary phase diagram (excluding all other oxides for purposes of this comparison) (figure 2). The ores as projected have liquidus temperatures exceeding 1950°C, extending into the stable periclase and spinel fields. In general for the tests performed at Mintek, the aim was to operate within the forsterite/spinel field, at or above the slag liquidus temperature, allowing for a superheat of up to 200°C as required (indicated by the dashed elliptical area on the phase diagram). The chemical compositions of the ores depicted in figure 2 are presented in table 2, ranked (left to right) according to decreasing Cr/Fe ratio. As expected, decreasing grades (Cr₂O₃) are associated with an increase in total iron (typically expressed as iron oxide (FeO)). The MgO/Al₂O₃ ratio of the South African chromite ores is about 0.6, while the ratio of MgO/Al₂O₃ for the rest ranges from about 1 to 1.4. The only notable exception is Kazakhstan ore with a ratio of more than 3. The three zones (MgO/Al₂O₃ ratios) are indicated on the phase diagram (figure 2). The variations in composition affect the relative ease of reduction of the ore.

3. PILOT-PLANT EQUIPMENT

The pilot-plant furnace used most commonly comprises a refractory-lined cylindrical steel shell with an outside diameter of 2.5 m. The furnace has separate tap-holes for the removal of alloy and slag. The furnace is fed more or less continuously, and is tapped intermittently. Graphite electrodes are used as the cathode, and the anode at the bottom of the furnace is made up of a number of steel pins that protrude through the refractory hearth to come into intimate contact with the molten alloy. The gas leaving the furnace passes through a bag-house to remove the entrained dust. The particular furnace used in the work reported here is equipped with film water cooling on the lower part of the sidewalls while the sidewalls in the freeboard zone is equipped with closed channels (forced water circuits).

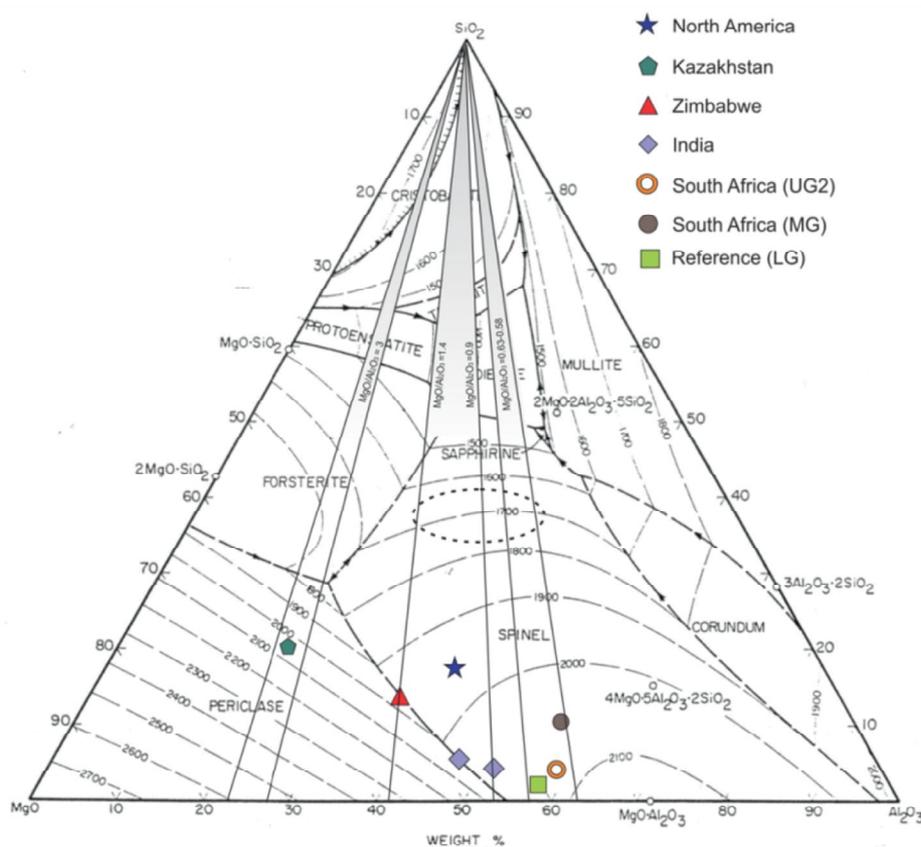


Figure 2: Chromite ore compositions projected on a $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ternary phase diagram

The furnace was generally operated with slag temperatures between 1700 and 1850°C, and metal temperatures about a hundred degrees cooler than this. Anthracite and coal were used as the reducing agents, either exclusively or as a blend, and, for the most part, fluxes consisted of silica and limestone. If fluxes or reductants were available from the region of origin, these were tested preferentially.

Since the installation of the first commercial DC smelting furnace in South Africa, multiple upgrades and new furnaces have been installed successfully, with more installations in the pipeline. Despite the general acceptance of the technology, many misconceptions remain regarding aspects or features of DC arc smelting. Recently, Jones *et al*¹ addressed some of the features associated with DC smelting and contextualised the relevance of certain myths or assumptions regarding DC smelting.

A good example is the common belief that a DC furnace requires a hollow electrode and stabilising gas to operate. The first commercial DC-arc smelting furnace treating chromite fines indeed used a hollow electrode arrangement with feed fed through the electrode. Subsequent upgrades were also implemented with hollow electrode installations. The assertion that a hollow electrode configuration was integral to successful smelting in a DC furnace was first investigated at Mintek in 1996. During various subsequent smelting campaigns, a comparison was done by switching between feeding fines through feed ports in the roof and feeding the fines via the hollow electrode. No significant metallurgical benefits could be attributed to either method, thus debunking the idea that the hollow electrode configuration and a stabilising gas is a critical process requirement for successful DC smelting. A slight increase in dust losses was observed when not feeding through the electrode, but it is clear that there are many advantages to utilising a solid electrode that significantly outweigh the possibility of a slight increase in dust losses. Avoidance of

the additional manufacturing cost of hollow electrodes and the more complex feed arrangement that is required are amongst the most persuasive arguments.

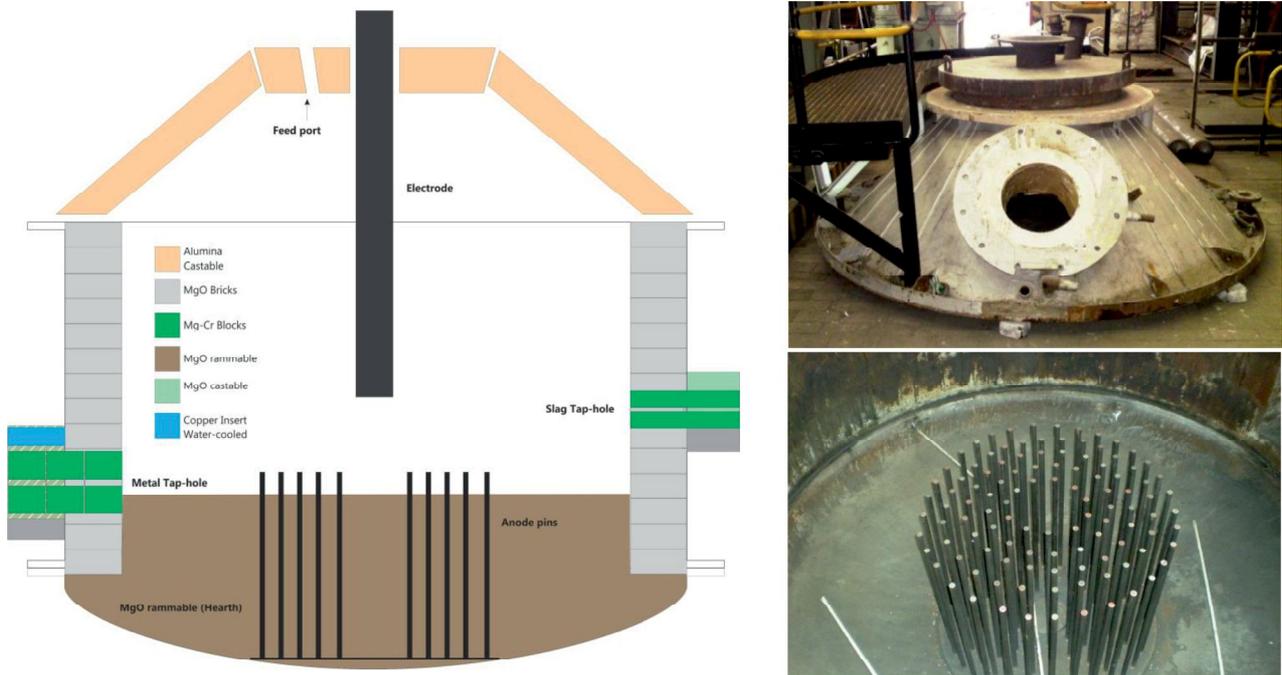


Figure 3: Generic diagram of single (solid) electrode installation (left), photographs of Mintek’s pilot furnace pin anode design (bottom right) and water-cooled furnace roof (top right)

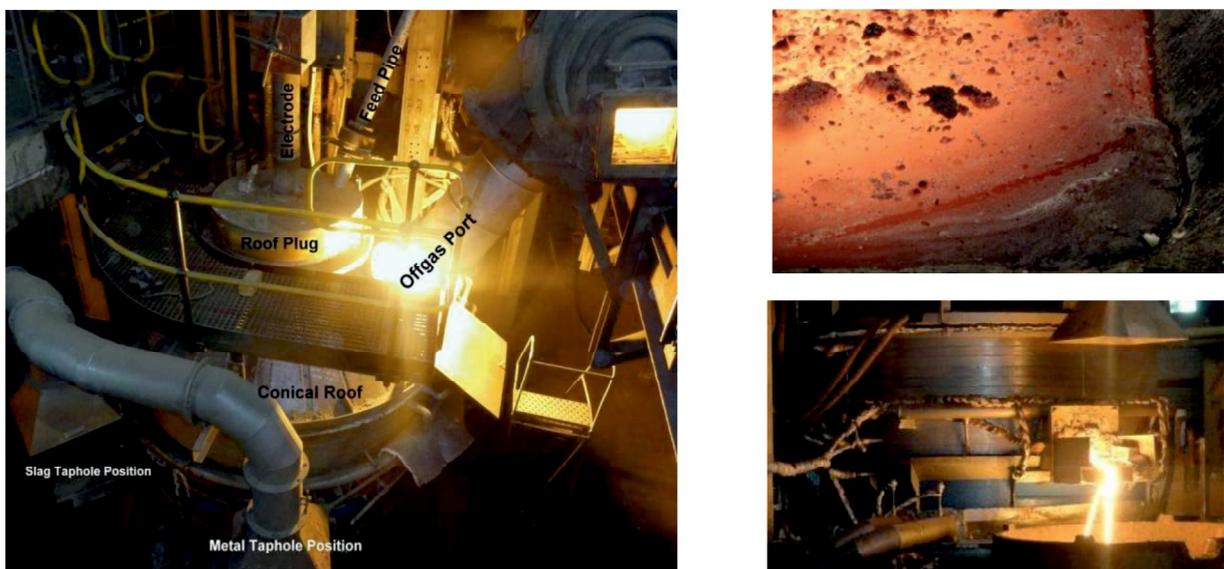


Figure 4: Test furnace with single, solid electrode and feed pipe connections (left), tapped ferrochromium metal (top right) and tapping slag (bottom right)

With advances in the field of engineering and the rising cost of electricity, scale-up to large “mega” smelters is becoming a trend which presents some challenges to the designer. Solutions to the electrode size limitation problem include operating multiple furnaces on a site, or using multiple electrodes in a single cylindrical furnace. The latter design has been successfully implemented by

the steel industry in the form of the so-called twin-electrode furnace. This permits such a furnace to operate at twice the existing power limit imposed by available electrode diameters. Testwork conducted at Mintek utilising two electrodes configured as two cathodes with a bottom electrode acting as the anode is referred to as using twin-electrodes (a configuration with one of the electrodes acting as the anode and the second electrode being the cathode is referred to as dual-electrodes, a design that is being considered to convert existing AC furnaces to DC where installation of an anode in the hearth is not an option).

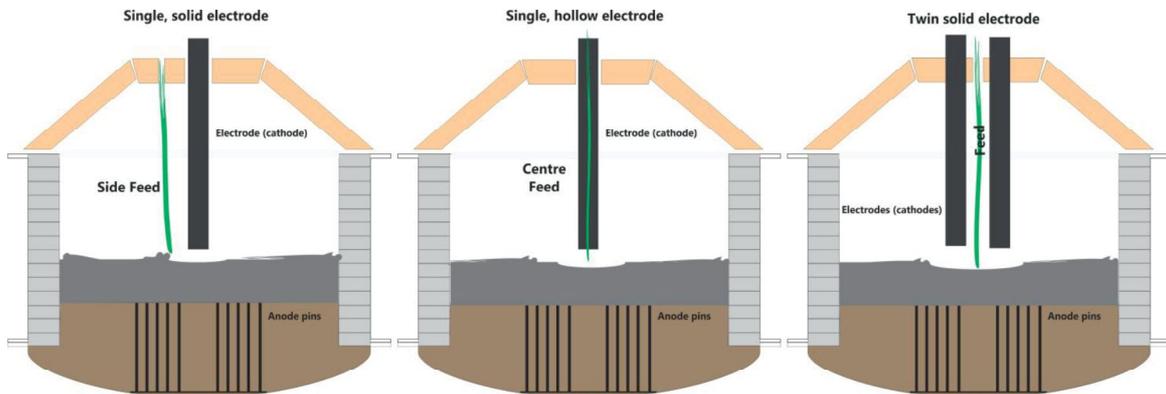


Figure 5: Contrasting furnace feed positions associated with single (solid or hollow) and twin-electrode configurations as tested at Mintek

Mintek investigated the twin-electrode mode of operation during various pilot-plant smelting tests in the past decade. Overall though, no significant metallurgical differences could be attributed to any specific configuration. The electrode configuration also directly relates to the point at which feed is introduced into the pilot-plant furnace, and Mintek’s facility is designed to test a variety of possible feed and electrode configurations. Figure 5 shows the three electrode configurations used during chromite smelting campaigns at Mintek, indicating the position at which feed was added to the furnace. The diagrams are simplified to illustrate the general configuration of feed addition, and do not explore the mechanical set-up of the feed system. Additional side feed ports located nearer to the sidewalls could be utilised for any of the scenarios depicted. As the size of the furnace increases, distribution of a portion of the feed closer to the sidewalls has been shown to be a useful tool to manage radiation losses from the bath surface.

4. PILOT-PLANT TEST RESULTS

The results from the various pilot-plant tests conducted in the past decade were collated, and various aspects were compared. Slag and metal compositions were compared and correlated. Although each project had specific project-related objectives, the common testwork methodologies and smelting techniques utilised at Mintek allow for a unique comparison between the various data sets. Metal composition is a function of the degree of reduction achieved, the Cr/Fe ratio of the chromite ore, and the slag composition. Table 3 summarises the alloy compositions (weighted averages as produced during stable periods), together with the corresponding residual chromium and iron oxides in slag, and chromium recovery, for all the ores tested. Sub-periods are included when substantially different operating conditions or equipment configurations were utilised.

As is typical for chromite smelting, recovery of chromium and iron is maximized whilst taking care to limit reduction of silica and magnesium oxide. These reactions are energy intensive side-reactions favoured under heavily reducing and high temperature conditions. The degree of reduction is practically monitored via the residual chromium oxide and iron oxide in the slag, and

adjustments to the carbon (reductant) addition are made to control the degree of reduction (or recovery). For each test campaign, the characteristic smelting behaviour of the ore (reducibility) and reductant (reactivity) are evaluated. The compositions reported in table 3 exclude results from start-up periods, in order to report the average compositions resulting from stable conditions more accurately.

Table 3: Weighted average compositions of metal and slag produced (mass %), stable operating periods

Chromite Origin	Metal Composition, mass %				Slag Composition, mass %		Cr/Fe metal	Cr Recovery %
	Cr	Fe	C	Si	Cr ₂ O ₃	FeO		
Kazakhstan	71.0	19.0	7.6	0.2	6.6	1.8	3.7	88
Zimbabwe	63.7	23.0	8.7	0.3	5.2	2.2	2.8	90
India Type A	61.0	26.7	7.9	3.3	4.4	1.5	2.3	93
India Type B	64.7	24.0	7.8	2.7	4.3	1.3	2.7	92
N. America Basic	60.4	29.8	8.0	0.1	4.8	1.5	2.0	91
N. America Acid	58.4	27.6	6.4	5.5	3.8	2.1	2.1	94
SA (UG-2) Hollow	51.4	38.2	8.8	0.3	3.9	2.8	1.3	95
SA (UG-2) Twin	49.5	37.2	7.7	2.8	3.7	2.4	1.3	95
SA (MG)	49.8	39.7	8.4	1.0	3.8	2.3	1.3	94

During the start-up phase of a test, carbon addition is adjusted to achieve the desired degree of recovery and product composition. Simultaneously, slag composition and operating temperature are managed to achieve the desired operational targets. This process involves a variety of systematic approaches to determine the best operating regime as quickly as possible. The following graphs, figure 6 and figure 7, present slag and metal compositions for two test campaigns to illustrate how slag typically initially contains relatively high levels of chromium and iron oxide which then gradually decrease as the process chemistry stabilises. The resulting impact on the metal composition is also of interest and is presented on the basis of Si, C and Cr content.

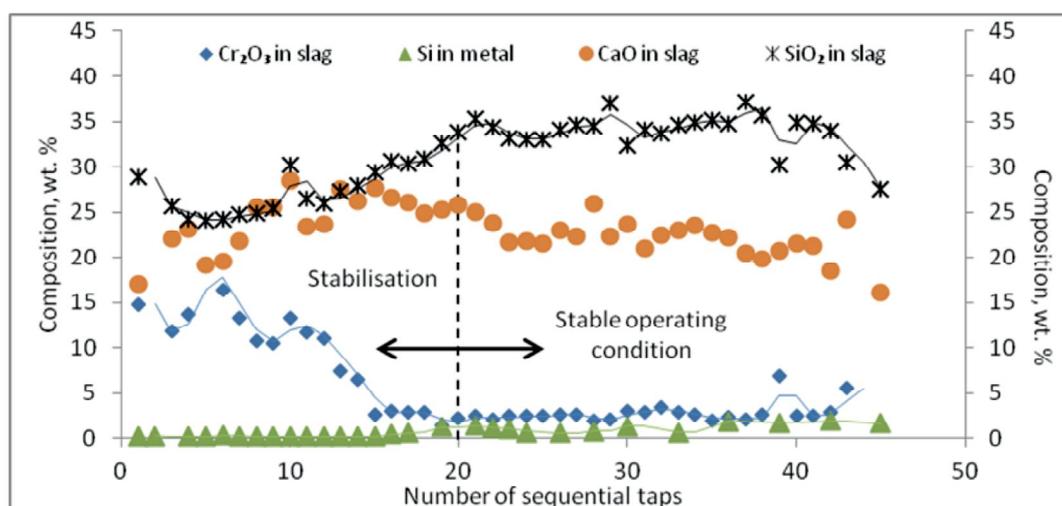


Figure 6: Features of the slag and metal compositions for the SA (MG) chromite smelting project illustrating slag stabilisation and the corresponding metal behaviour

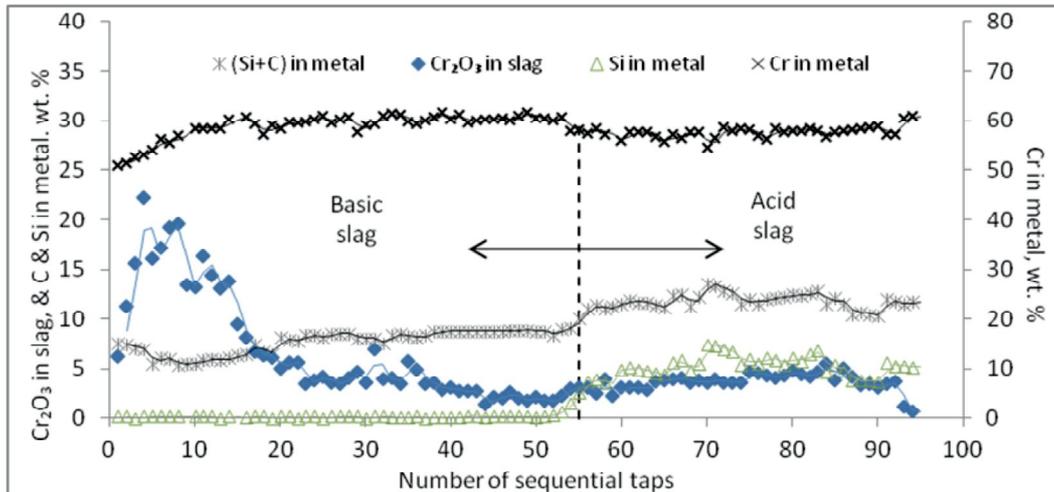


Figure 7: Features of slag and metal compositions for the North American chromite smelting project

A gradual increase in reductant addition results in a gradual increase in carbon in the alloy (as the residual chromium oxide decreases) up to the point of saturation. From figure 7, this correlation is clearly illustrated. As the chromium oxide content of the slag decreases (batches 1 to 20) associated with increased reductant addition, carbon in the metal slowly increases once the operation stabilises (batches 20 to 30).

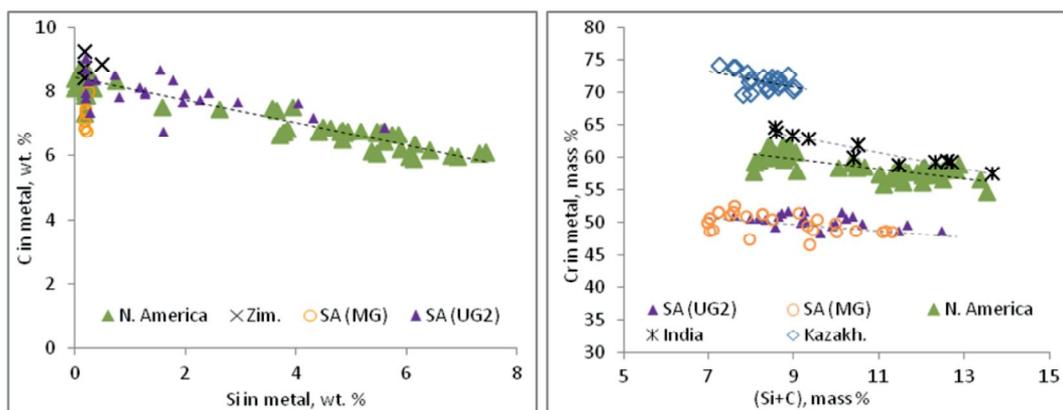


Figure 8: Associated C, Cr, and Si contents of the ferrochromium alloys from various smelting tests

It is only once the carbon content of the metal is closer to the saturation level that significant reduction of silica is achieved, at which point carbon content is controlled by the C-Si equilibrium. In general, the level of carbon in the metal is a result of the equilibrium between carbon and silicon, as most of the smelting tests were conducted under highly reducing conditions, *i.e.*, with low concentrations of residual chromium oxide and iron oxide in the slag. For low-silicon alloys, the carbon content was found to be about 8 to 9%, while typically (for stable periods of operation) increased silicon reduction resulted in lower carbon contents ranging from about 6 to 8%, depending on the conditions.

The chromium and iron contents of all alloys produced during the various test campaigns are presented in figure 9, expressed as a function of the Cr/Fe ratio of the related chromite ore. The data

includes all metal tapped during the various campaigns, including the start-up metal products for each ore type. As the chromium content of the alloy increases, the corresponding iron concentration decreases, primarily due to dilution associated with increased chromium recovery. During start-up, chromium recovery is typically relatively low (50 to 80%), but, as the process is stabilised, recoveries exceeding 85% (typically greater than 90%) are targeted.

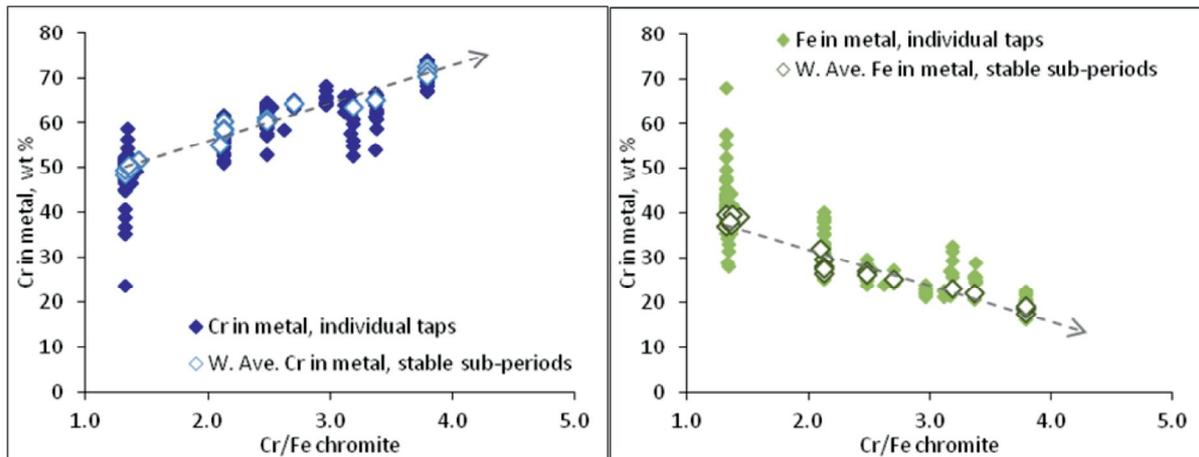


Figure 9: Fe and Cr content of alloys produced from the various chromite ores (Cr/Fe ratio), including stabilisation and start-up conditions

The objective of flux addition is to modify slag composition to achieve a suitable smelting regime. A suitable regime would include, for example, acceptable slag properties (physical, electrical, and chemical), and compatible slag and metal liquidus temperatures. Although slag basicity has lost a lot of the theoretical importance originally attributed to it, it is still used as a controlling variable in many smelting operations. High silica in the slag (*i.e.*, low basicity values) will theoretically lead to three-dimensional chains and networks of silicate polymers promoting high slag viscosities. These slags are said to be very acidic. Basic oxides such as CaO and MgO increase the basicity of the slag, breaking chains and networks, and generally lower the viscosity of the resulting slag. Addition of relatively small quantities of silica (as illustrated on the MgO-SiO₂-Al₂O₃ ternary diagram) modifies the slags significantly, especially in the spinel field. The data presented in figure 2 illustrates these changes associated with the addition of silica (indicated by the dashed lines towards the silica apex). With the exception of the Kazakhstan chromite, addition of silica effectively equalizes the compositions of the various ores within the spinel field (as illustrated by elliptical area on the diagram). A DC furnace, however, allows for the treatment of feed materials with a wide variety of compositions, due to the relative independence of the power supplied by the open plasma arc, thus allowing more flexibility in the selection of a fluxing regime as it allows for selection of an operating temperature relatively independent from the slag composition.

Within a specific smelting period, slag compositions (or the silica activity) are managed carefully which typically results in fairly consistent slag and metal compositions. The objectives of these stable operating periods include evaluation of product quality and composition, recovery of chromium, and determination of the energy requirement for a desired operating regime. Although it is possible at pilot scale to demonstrate the effects of changes in the slag composition, optimization is typically not possible due to limited availability of raw materials and the costs associated with pilot-plant test work. Typically, adjustments to the slag composition are limited to one or two primary operating conditions to minimize transition periods where the slag and metal products are

not at equilibrium. Transition and stabilisation periods are frequently excluded when evaluating sub-periods for trends, although the transition periods are often of interest.

Fluxing strategies for the pilot tests conducted at Mintek normally consisted of silica (typically quartz/silica sand) and lime (as limestone) in a desired ratio. As it is possible to produce metal with ultra-low silicon in a DC furnace, most pilot tests were designed to demonstrate this aspect. While most of the test projects were designed with both limestone and silica additions as slag modifiers, notable exceptions are the test campaigns for Kazakhstan (entire campaign) and North American ore (sub-periods). Kazakhstan ore was smelted with silica as the only modifier. In the case of the North American ore, both scenarios were tested. The transition from a basic to low-lime slag was achieved by systematically decreasing the limestone addition while continuing to operate the furnace. It is important to note that while the Kazakhstan ore was smelted with silica addition only, the magnesium oxide content of this chromite is significantly higher than most other types tested – as presented in figure 2.

The various periods highlighted in table 4 summarise stable operating periods during which the slag and metal compositions remained relatively unchanged. Each sub-period represents a specific operating window or condition. The summary of these operating periods includes product compositions (mass %), flux additions (% of chromite) as well as some production information for context.

Table 4: Smelting test results for various chromite projects, highlighting acid and basic fluxing

Basicity	Low	Low	High	High	High	High	High	High
Configuration	Solid	Twin	Hollow	Twin	Solid	Solid	Twin	Solid
Origin	N.Amer ica	India	SA (UG-2)	SA (UG-2)	SA (MG)	N.Amer ica	Kazakh.	Zimbab we
Recipe, % of chromite ore								
Silica	11.1	13.0	8.5	9.6	8.6	8.0	5.6	13.6
Limestone	-	9.7	15.1	15.0	23.5	20.0	-	28.9
Fixed Carbon	23.8	25.8	26.8	26.3	24.9	25.1	22.1	28.1
Duration, days	5	2	2	2	2	8	20	2
Ore processed, t	44	22	17	22	14	49	163	1.3
Slag composition, mass %								
Cr ₂ O ₃	3.8	4.2	4.1	3.5	6.2	4.0	6.0	4.2
FeO	2.1	1.1	3.2	2.0	2.3	1.4	1.4	2.6
MgO	31.1	22.7	15.9	16.4	15.4	23.0	42.7	21.6
Al ₂ O ₃	33.5	28.9	35.5	38.4	28.6	24.1	18.6	21.7
SiO ₂	27.8	29.2	21.8	21.2	23.7	27.3	28.1	25.4
CaO	1.1	12.0	14.9	16.2	20.6	18.6	0.7	22.4
Metal composition, mass %								
Cr	58.4	64.5	51.1	50.4	51.1	60.2	71.0	63.8
Fe	27.6	24.8	38.4	37.3	41.0	29.7	18.7	23.0
C	6.4	7.8	8.7	8.1	6.7	8.2	7.8	8.8
Si	5.5	3.3	0.33	1.5	0.20	0.14	0.17	0.45
P	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01
Slag Temp. °C	1800	1796	1831	1815	1807	1770	1828	1760
Metal Temp. °C	1740	1562	1586	1574	1694	1730	1800	1718
Slag basicity ratio								
$\frac{(\text{CaO} + \text{MgO})}{(\text{Al}_2\text{O}_3 + \text{SiO}_2)}$	0.53	0.60	0.54	0.55	0.69	0.81	0.93	0.93
$\frac{(\text{CaO} + \text{MgO})}{\text{SiO}_2}$	1.16	1.19	1.41	1.53	1.52	1.52	1.55	1.73

The silicon content of a ferrochromium alloy is a function of the silica content of the slag. Furthermore, the distribution of silicon between the metal and slag phases depends on the degree of reduction, with higher temperatures favouring reduction of silica, and hence favouring the formation of alloys with higher silicon contents. In addition, silica activities for the types of slags summarised in the previous tables increase with increased residual silica in the slag. Despite these complex interdependent relationships, the pilot-plant test work conducted at Mintek demonstrated that it is relatively easy to modify the slag composition to achieve a different metal product composition (silicon content specifically). The North American chromite test specifically included an objective to deliberately change over from a basic slag to an acid (low lime) slag. Figure 10 illustrates the changeover from basic slag (left) to low lime slag (right) via the systematic decrease in limestone addition. As the CaO concentration in the slag decreased, MgO and Al₂O₃ concentrations increased. In order to manage the slag properties, the silica addition was adjusted simultaneously.

The normalised slag compositions (MgO, Al₂O₃, SiO₂, and CaO) presented in figure 10 are detailed in table 5 together with the flux and reductant additions (expressed as fixed carbon) for sub-periods during the North American trial to demonstrate the change.

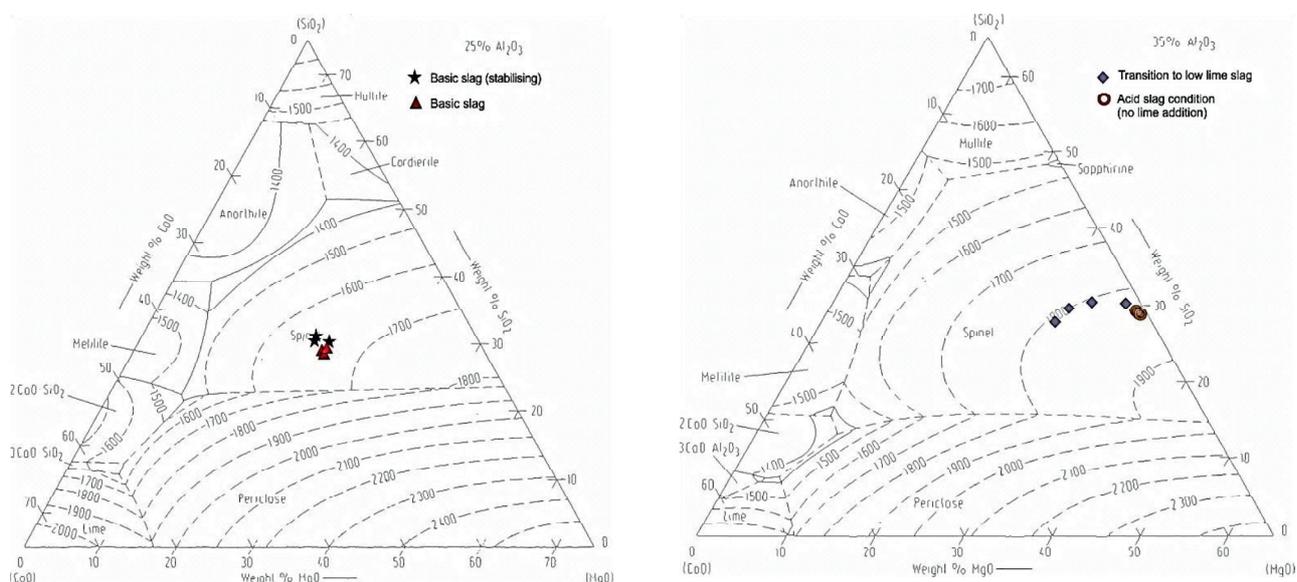


Figure 10: Slag composition change for North American chromite basic and low lime slags - projected on MgO-CaO-SiO₂ phase diagram, 25% Al₂O₃ (left) & 35% Al₂O₃ (right)

Silicon in metal dramatically increased as the slag composition changed to the targeted low-lime slag. In addition, significant adjustments were required with respect to the carbon addition and energy requirements, as the decomposition of limestone impacts both. Reductant addition had to be reduced significantly, as there was significant evidence of SiO fuming (high temperatures and very reducing conditions) once limestone addition was ceased. These factors all contributed towards increased silicon deportment to the metal. Attempts were made to limit the reduction of SiO₂ by systematically decreasing carbon addition, but feed material was limited in quantity, and optimized additions of silica and reductant were not targeted. The slag composition change was managed to minimize disturbing the furnace operation, *i.e.*, managing slag properties to allow smelting to continue uninterrupted. The expected changeover from ultra-low levels of silicon in the metal to relatively high levels was fairly dramatic. The relationship between the slag composition,

(expressed as the mass % ratio of $((\text{MgO} + \text{CaO}) / \text{Al}_2\text{O}_3)$, and silicon in metal is presented in figure 11 (including data from the Indian, Zimbabwean, and Kazakhstan trials for comparison).

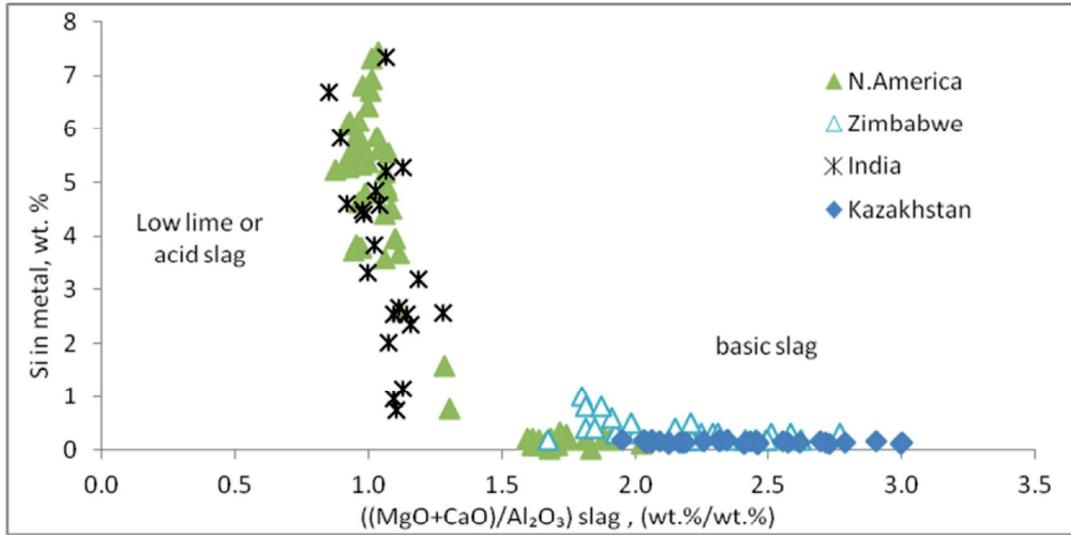


Figure 11 : Influence of slag composition on Si content of ferrochromium metal

Adjustments to the fixed carbon addition and flux additions for the North American ore are presented in figure 12, illustrating the change from basic to low-lime slag conditions and the resulting impact on slag and metal compositions. On the right, the switch from low Si to high Si metal occurred within 10 batches, during which about 7.7 metric tons of chromite ore was processed. This illustrates the responsiveness of open-bath, open-arc smelting.

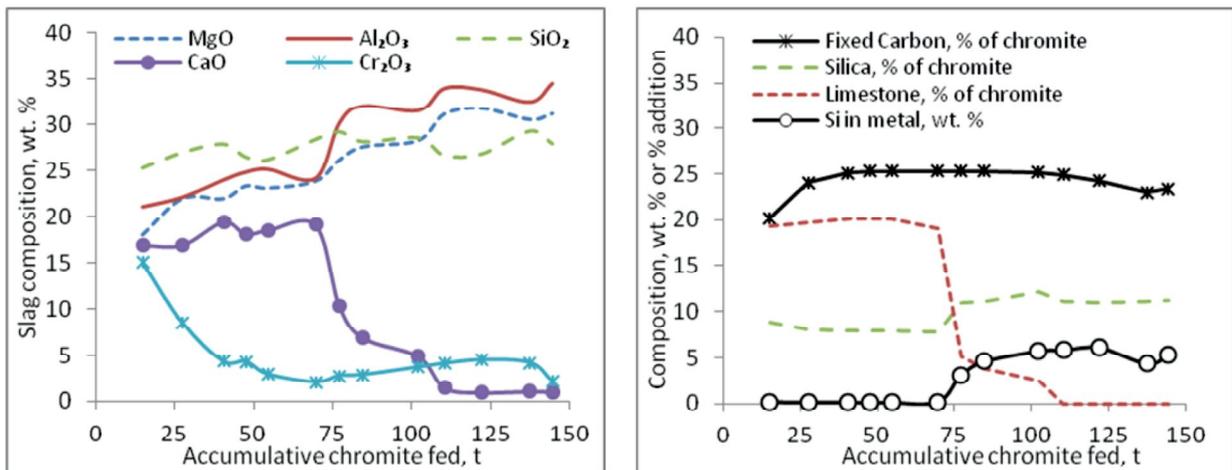


Figure 12: Slag composition for the North American chromite smelting test; basic and low-lime conditions (left). Carbon, limestone, and silica addition and the corresponding Si in metal (right)

The results from hollow-electrode and twin-electrode configurations, namely the Indian and South African UG-2 ores, are compared in table 6.

The results indicate that the feed and electrode configuration may also have a role to play in the degree of silicon department to the metal phase. Although it is difficult to separate all the factors at play (slag composition, degree of reduction, operating temperatures, and electrode and feed configuration), a trend is observed in that it appears that when switching from a single hollow

electrode to a twin-electrode configuration there is a significant increase in silicon department to the metal phase. (Note that switching produces an inevitable disturbance in the operation – transition data is excluded in this comparison.) Results from twin-electrode and solid, single-electrode test campaigns for the South African MG and Kazakhstan ores (single and twin respectively) are also included for comparison.

Table 5: Slag composition and flux additions for stable sub-periods – North American chromite test

Chromite mass fed t chromite	Fixed Carbon	Silica addition	Limestone addition	Weighted average slag composition, mass %			
				MgO	Al ₂ O ₃	SiO ₂	CaO
	kg per t chromite						
15	202	88	194	18.1	21.1	25.2	16.9
13	240	81	197	22.0	22.1	26.9	16.9
13	251	79	200	22.0	24.0	27.8	19.4
7	253	79	201	23.3	24.8	26.4	18.1
7	253	79	201	23.1	25.2	26.1	18.5
15	253	78	190	23.9	24.2	28.3	19.1
8	253	109	51	26.2	30.2	29.2	10.3
8	253	111	38	27.6	32.0	28.1	6.9
17	252	121	24	28.3	31.5	28.5	4.9
8	249	110	0	31.1	34.0	26.6	1.5
12	242	110	0	31.8	33.8	26.8	1.0
15	230	110	0	30.5	32.5	29.3	1.1
7	234	112	0	31.2	34.5	27.9	1.0

Table 6: Comparative results for hollow-electrode and twin-electrode configurations

Electrode setup Origin	Hollow India	Solid Twin India	Hollow SA (UG-2)	Solid Twin SA (UG-2)	Solid Twin Kazakhstan	Solid Single SA (MG)
Silica, %	11.8	12.1	8.5	10.1	5.6	10.6
Limestone, %	9.8	9.8	15.1	15.0	-	21.6
Fixed C, %	24.0	26.1	26.8	26.3	22.1	26.3
Duration, days	1.0	3.2	2.0	5.2	20.3	2.9
Ore processed, t	10.8	32.3	17.2	37.8	163	16.7
Slag Composition, mass %						
Cr ₂ O ₃	5.4	4.9	4.1	3.8	4.2	4.7
FeO	1.4	1.8	3.2	2.3	2.6	2.5
MgO	21.1	22.1	15.9	16.3	21.6	13.9
Al ₂ O ₃	28.1	32.3	35.5	37.6	21.7	30.7
SiO ₂	28.4	24.1	21.8	21.5	25.4	24.6
CaO	10.2	11.7	14.9	15.8	22.4	21.5
Metal Composition, mass %						
Cr	63.7	60.4	51.1	50.3	63.8	49.4
Fe	27.3	25.8	38.4	37.4	23.0	40.6
C	8.4	7.6	8.7	8.0	8.8	7.7
Si	0.4	4.5	0.3	1.5	0.5	0.7
Slag Temp., °C	1832	1807	1831	1813	1760	1796
Metal Temp., °C	1557	1562	1586	1581	1718	1739
Slag basicity	0.55	0.60	0.54	0.54	0.93	0.64

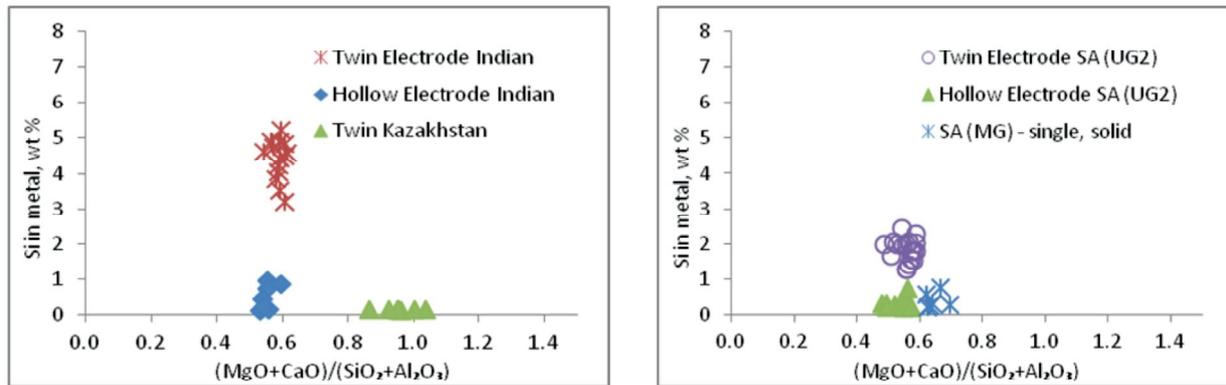


Figure 13: Influence of twin-electrode and single-electrode operation on Si in metal as a function of basicity

Silicon in metal for the periods detailed in table 6 is presented in figure 13, as a function of slag basicity. The observed increase in silicon department to the metal for the two twin-electrode operations appears to indicate that the twin-electrode operation has an effect on the chemistry over and above the aspects already discussed. However, slag composition governs the overall outcome as the Kazakhstan and South African (MG) smelting results demonstrated that low-silicon metal could be produced with either single- (hollow or solid) or twin-electrode configurations. There is, however, clear evidence that the twin-electrode configuration results in increased silicon department to the metal, for a given slag composition and operating regime (India and UG-2 examples). The increased silicon in metal for a given slag regime is likely due to the increased size of the intense melting zone underneath the twin-arcs, if compared directly.

Photographs showing some of the characteristics of twin- and single-electrode arcs have been published by Reynolds and Jones [3,4,5] and three photographs related to this discussion are presented in figure 14. The arc photographs clearly show the relative size difference between the twin- and single-electrode smelting zone. A DC plasma arc is the principal energy source in the furnace, and is struck between the end of the graphite electrode and the surface of the electrically conductive molten bath. Energy escapes from the arc via a multitude of mechanisms, but most importantly thermal radiation from the hot plasma gas, and convection to the molten bath surface. The plasma arc is a very effective way of heating process material, as much of this energy is delivered to a localised area directly beneath the arc (often referred to as the “arc attachment zone”). The size of this arc attachment zone underneath the electrodes increases when two arcs are involved. The smelting zone underneath the electrodes is characterised by high temperatures and intense stirring, which would favour the reduction of silica under the highly reducing conditions associated with chromite smelting. An increase in the size of the smelting zone is therefore most likely the source of the additional silicon department, as was observed during the SA (UG-2) and India test campaigns.



Figure 14: Photographs of twin-electrode arcs (left, middle) and a single-electrode arc (right)

Twin DC arcs, like parallel current-carrying conductors, experience attractive forces (figure 14) while in the case of a dual-electrode setup, the arcs tend to deflect away from each other as the anode and cathode arc jets carry current in opposite directions and repel each other. This phenomenon may bring with it further interesting variations with regards to the smelting behaviour, but, for chromite smelting, where bigger is typically more efficient, dual-electrode applications may be limited to retrofitting of circular AC furnaces, as the power limitations are similar to single electrode applications.

The increased silicon reduction observed when switching from single- to twin-electrodes elegantly illustrates some of the principles of the DC furnace “engine room” and highlights the need for a good understanding of the arc and its behaviour – an aspect that Mintek has been investigating in parallel with the advancement of DC smelting technology over the past decade.

5. CONCLUSIONS

Mintek’s involvement in chromite smelting goes back to the original implementation of DC smelting for chromite ore fines 30 years ago. Mintek continues to provide large-scale pilot-plant testwork services to industry, and, in the past decade, Mintek’s testwork projects have included the smelting of a variety of chromite ores from all over the world.

The results from various pilot-plant tests confirm that for the smelting of chromite ore fines, open-arc DC furnaces have some key advantages over conventional submerged-arc furnaces, both technical and economic. These include:

- The use of unprocessed chromite ore fines as well as the use of finely sized fluxes and reductants. Testwork conducted at Mintek typically smelted chromite fines 100% passing 2 mm, for example.

- The use of anthracite and coal as reducing agents, removing the reliance on expensive metallurgical coke and char. The selection of a reductant can therefore address phosphorus content, for example, as a wider choice is available if anthracite and coal sources can be considered.

- High chromium recovery; with residual chromium oxide in slag typically ranging from 3-5% in the discard slags.

- The DC furnace’s relative independence from slag electrical resistivity constraints (typically associated with submerged-arc furnaces) allows for the selection of the process temperature through control of the power level and feed rate, irrespective of the raw materials and their physico-chemical properties. A reasonably wide range of operating temperatures can therefore be achieved.

- The rapid response time and greater flexibility in the process make it possible for a DC open-arc furnace to produce a wider range of alloy compositions than can be produced in a submerged-arc furnace. The smelting metallurgy could be adapted to achieve a desired product quality or to minimize costs. Energy consumption is typically similar or higher than in the conventional operations, but savings related to the raw material costs and potential premiums with respect to product quality could offset the energy consumption issue, especially if flux addition could be minimized. A reduction in flux addition would also reduce operating costs (a reduction in reductant and electrical energy consumption, for example).

Pilot-plant test work conducted at Mintek demonstrated that chromite ore fines from a wide variety of origins could be smelted successfully while achieving high chromium recoveries. The relative independence of power supplied by the open-arc allows for a wide variety of compositions to be processed, while the optimum slag composition can be selected to achieve targets regarding recovery and alloy composition. The testwork conducted at Mintek underlines the suitability of DC smelting for chromite ore fines, aptly concluded at the birthplace of DC chromite smelting.

6. ACKNOWLEDGEMENTS

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