SOME ASPECTS OF THE PRODUCTION OF FERROCHROME ALLOYS IN PILOT DC ARC FURNACES AT MINTEK

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ABSTRACT

Ferrochrome alloy is predominantly produced in AC submerged-arc furnaces where the electrodes are buried in the burden of lumpy materials comprised of chromite ores or pellets, reductants and fluxes. Mintek has developed and patented the smelting of chromite ores in DC electric open-arc furnaces; principally for the processing of ore fines of sizes less than 1 mm without the need for agglomeration.

Since the inception of this process, the DC arc furnace test facilities at Mintek have been employed to test varying composition, grade and mineralogy of chromite ores using different slag and metal chemistries, resulting in the production of ferrochrome alloys of varying composition and grade. The results of these campaigns primarily demonstrated the robustness and flexibility of the DC arc furnace for the processing of chromite ores and secondly provided a useful database pertaining to the smelting of chromite ores.

Using the data collected over a series of DC arc furnace campaigns, the metallurgical control of the alloy composition is discussed. In particular, the reporting of Si and C to the alloy is evaluated based on the smelting conditions and thermodynamic principles. This article attempts to evaluate the results of DC arc smelting of chromite ores, and compare these results with the guidelines proposed in the literature for submerged-arc furnaces.

1 INTRODUCTION

In the conventional production of stainless steels, chromium is generally introduced to the process in the form of Cr-Fe-C-Si alloys, principally as high-carbon ferrochrome or charge chrome. The level of carbon and silicon in the above alloys is important especially when refining is carried out by blowing oxygen in the melt.

High-carbon and charge chrome alloys are generally produced in the conventional smelting process by carbothermic reduction of ferrochrome ores using AC submerged-arc and DC open-arc electric furnaces.

In AC submerged-arc furnaces, the energy to the furnace is predominantly supplied in a resistive heating mode. The main features of this mode are the electrical resistivity of the slag and the slag liquidus temperature that are strictly selected to operate the process comfortably; these two parameters also impose some limitations to the smelting process in terms of operating temperature.

The energy to a DC open-bath furnace is mainly supplied in an arcing mode. This energy is largely independent to the slag chemistry; thus providing more freedom in the selection of the slag composition and process temperature. This freedom has conferred to the DC open-arc furnace a greater ability to control silica reduction more closely by slag chemistry. A reasonably large range of process temperatures can be achieved in DC open-arc as opposed to AC submerged-arc furnace; subliquidus and superheated slags can be produced in the smelting process. Superheated slag would improve to a certain extent the kinetics of chemical reactions and the slag-metal separation whilst subliquidus slag will have a favorable effect on the furnace lining. Whilst change to the slag chemistry is possible, this is generally restricted by the economics of the process.

This paper summarizes some of the aspects of the presence of C and Si reduction in the ferrochrome alloys learnt through the pilot smelting tests of ferrochrome at Mintek.

2 EQUIPMENT AND METHODOLOGY OF TESTWORK AT MINTEK

2.1 Equipment

Ferrochrome alloys were produced in the 3.2 and 5.6 MVA DC open-arc pilot plant facilities at Mintek. A description of the 3.2 MVA facilities is given here and schematically presented in Figure 1. The power supply to the facilities consisted of an 11 kV vacuum breaker, 2 isolators, 2 contactors, 2 x 1.6 MVA transformers and 2 x 5 kA thyristor rectifiers able to be configured for single or twin electrode operation. The pilot plant facilities consisted of the batching plant feeding through two final feeders into a furnace with a 2m diameter hearth. The furnace crucible was lined with magnesia based bricks and its hearth consisted of high magnesia namable with steel pins through the hearth serving as anode. The roof was cast in namable alumina. Two tapholes were used to tap metal and slag separately. Lined and cast iron ladles were used for containing metal and slag, respectively. Process control and data logging were managed through the Delta V control system.

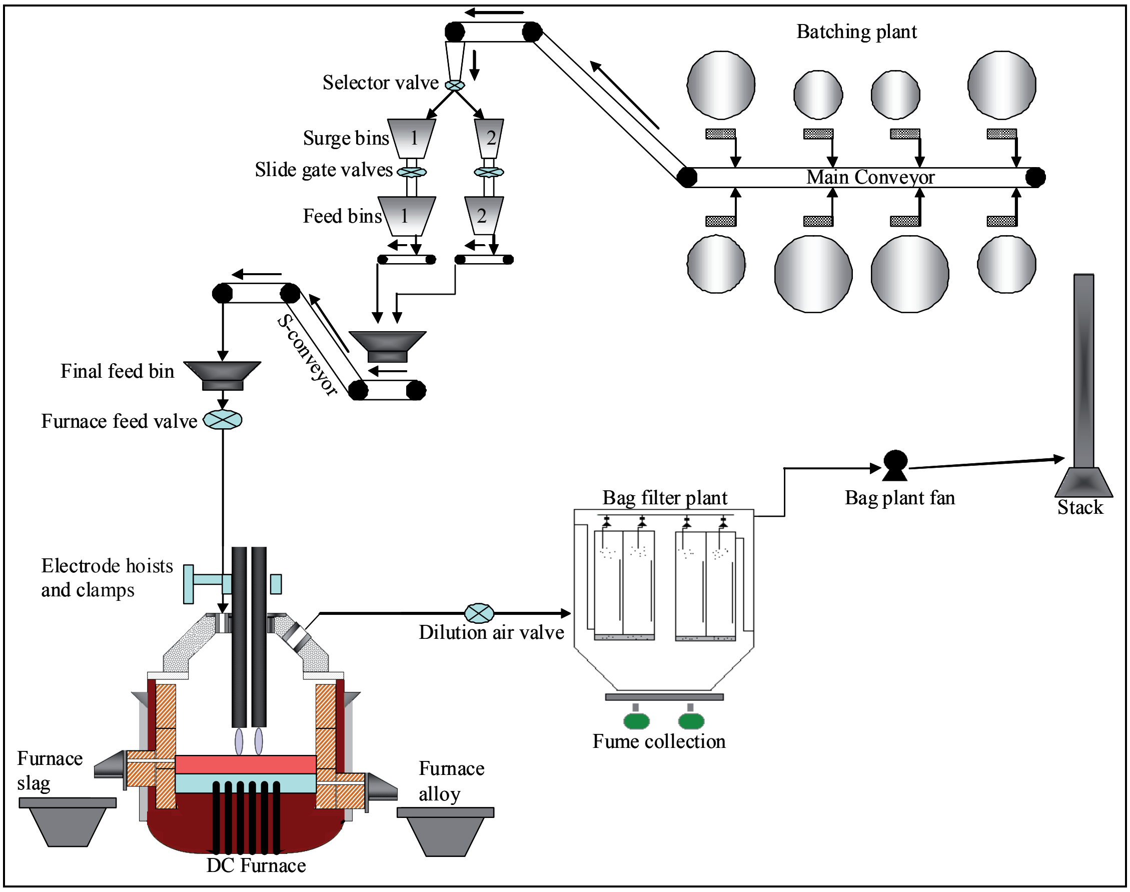

Figure 1: Schematic of Mintek DC Arc Furnace pilot plant facility

2.2 Testwork Methodology

The test recipes were simulated by Pyrosim, a Mintek developed thermodynamic process simulation package, to obtain the required flux and reductant additions in order to produce liquid slags and metals in the specified operating temperature range. The simulations also provided the process energy required. Excess carbon was allowed in practice to compensate for air ingress into the furnace and reductant inefficiencies.

The furnace was slowly warmed up to required temperature prior to undertaking the testwork program. During the electrical warm-up period, the feed was initially introduced into the furnace at lower rates; these rates were progressively increased with subsequent increase of power to the target levels towards the end of this period. After the warm-up period has been completed, slag and metal analyses were used to optimize the smelting recipe. Once stable conditions have been reached and maintained long enough to collect sufficient data, the smelting recipe and/or the power was changed to investigate the subsequent target condition. Throughout the tests, the feed rates of the input materials and the power input to the furnace were balanced to maintain liquid metal and slag at required temperatures without compromising the integrity of the refractory lining of the furnace.

3 PROCESS METALLURGY FOR THE PRODUCTION OF FERROCHROME

The production of ferrochrome metal from chromite ores using a carbonaceous reductant reduces oxides to metal in order of reactivity.

The main reactions involved in the reduction of iron, chromium and silicon to the metal phase are briefly presented below (subscripts x and y indicate that carbides of varying stoichiometry form).

The alloy product is likely a mixture of different carbides.
$FeO.Cr_2O_3 \rightarrow Fe_xC_y + Cr_2O_3 \rightarrow CrO \rightarrow Cr_xC_y$
$MgO.Cr_2O_3 \rightarrow MgO + CrO \rightarrow MgO + Cr_xC_y$
$Cr_2O_3 \rightarrow CrO \rightarrow Cr_xC_y$

This is followed by the reduction of silica as follows:
$SiO_2 + 2C \rightarrow Si + 2CO$ or
$SiO_2 + 3C \rightarrow SiC + 2CO$
The influence of the partial pressure of O_2 and CO on the reduction of SiO_2 may be seen in Figure 2.

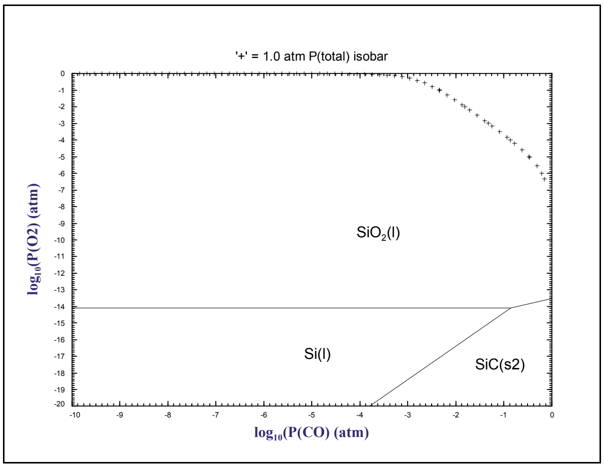

Figure 2: Si predominance diagram for differing O_2 and CO partial pressures at 1750ºC, FACTSage 5.4

4 RESULTS OF TESTS AT MINTEK

4.1 Overview of the Testwork Campaigns

A number of ferrochrome smelting campaigns were carried out at Mintek. These smelting campaigns produced in total about 229 tonnes of metal alloys and 207 tonnes of slag. The most significant campaigns were carried out in a 2 m diameter furnace operating at a power flux of between 450 and 550 kW/m^2. The furnace was operated in both single and twin electrode (cathode) configurations and both hollow and solid electrodes were used during the tests.

4.2 Chrome Ores

Chromite ores and concentrates smelted at Mintek were characterized by the Cr grade, Cr/Fe ratio and gangue elements as presented in Table 1. The chromite ore Cr/Fe ratio is of importance as it directly affects the alloy Cr grade whilst the gangue elements affect the melting energy and rate as well as the slag chemistry. The chromite spinel ore morphology can be described stoichiometrically as $(Fe, Mg)(Cr,Al,Fe)_2O_4$ and chromite ores often contain gangue elements of SiO_2 and MgO.

Table 1: Composition range of major oxides in chromite ores and concentrates smelted at Mintek DC pilot plant facilities

	MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	Cr/Fe
	wt %	wt %	wt %	wt %	wt %	wt %	mass/mass
Min	9.4	6.5	0.6	0.1	42.2	11.9	1.3
Max	20.5	16.9	6.9	0.3	53.8	27.3	3.8

4.3 Slag Composition

From Table 1 it can be seen that if the iron and chromium oxides were totally reduced to the alloy phase, the major components left in the slag would be MgO, Al_2O_3 and SiO_2. The unfluxed slags that would be produced from the complete reduction of iron and chromium oxides are graphically illustrated on the ternary phase diagram, calculated using FACTSage 5.4 Solution databases (Bale, et al., 2002)[1], in Figure 3 by a red outline. From the phase diagram, it may be seen that the unfluxed slags have liquidus temperatures exceeding 1900ºC and extending into the areas of stable periclase and spinel phases. In general, it was targeted for the tests performed at Mintek, to operate within the forsterite/spinel slag area, at or above the slag liquidus temperature and allowing a superheat of up to 200°C.

The slags produced during testwork at Mintek were either $MgO-Al_2O_3-SiO_2$, shown in Figure 4, or $MgO-Al_2O_3-SiO_2-CaO$ types. The latter slag type is presented in Figure 5 and Figure 6. Fluxing to produce the required slag composition was carried out using either silica or a combination of silica and lime (in the form of burnt lime or limestone). The resulting ternary slag contained in mass percent about 30-40% MgO, 30-40% Al_2O_3 and 20-30% SiO_2. In the quaternary slag, (MgO+CaO) was in general about 30 – 40%, the other constituents Al_2O_3 and SiO_2 as specified above remaining at the same levels.

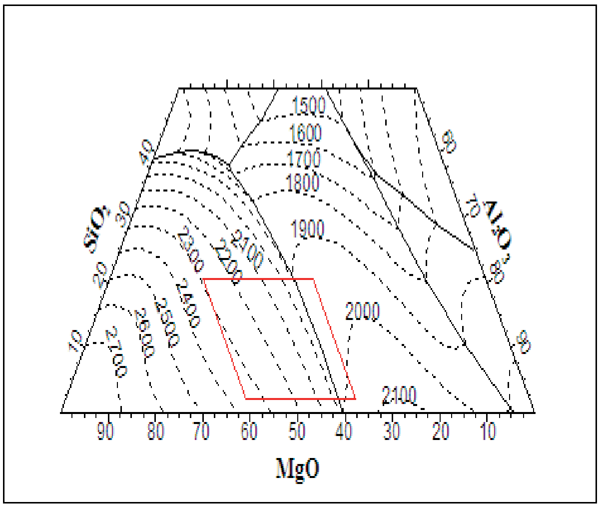

Figure 3: Range of un-fluxed slags indicated on the Al_2O_3-MgO-SiO_2 ternary phase diagram in red.

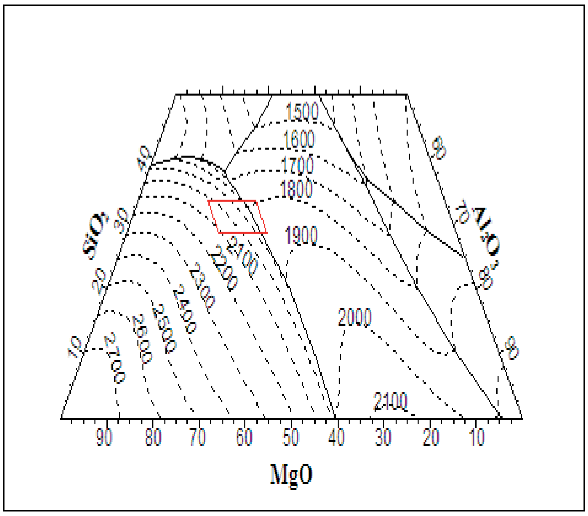

Figure 4: Average fluxed slags tapped from DC pilot plant furnace where silica fluxing were practiced

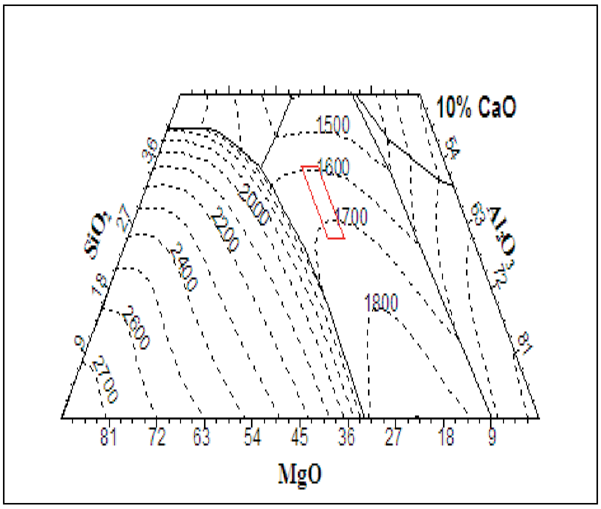

Figure 5: Quaternary phase diagram showing liquidus surface plots for slag compositions with 10% CaO

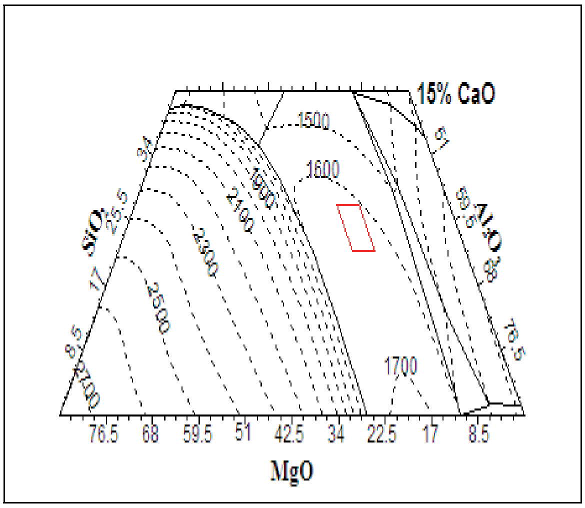

Figure 6: Quaternary phase diagram showing slag compositions with 15% CaO

The slag tapping temperatures are compared to the slag liquidus temperatures (for slag composition normalised to SiO_2, MgO, Al_2O_3, CaO – FeO and CrO/Cr_2O_3 neglected) in Table 2.

Table 2: Slag liquidus temperature vs slag tapping temperature for specific campaigns

	Slag liquidus temperature range	Slag tapping temperature range
	ºC	ºC
Chromite 1	1600 – 1700	1642 – 1928
Chromite 2	1600 – 1750	1661 – 1898
Chromite 3	1800 – 2000	1739 – 1953

4.4 Ferrochromium Alloys Produced from Pilot Tests at Mintek

The alloys produced are summarized in Table 3 in terms of chromium grade, Cr/Fe ratio, and carbon and silicon contents.

Table 3: Overview of metal alloys produced in Mintek's testwork

Item	Cr grade, %	Cr/Fe ratio	C, %	Si, %
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

5 DISCUSSIONS

5.1 Evolution of Carbon and Silicon in the Alloy with Gradual Increase of Carbon Addition

The impact of carbon addition on the smelting results and alloy quality was investigated in all the campaigns. The evolution of C and Si contents in the charge chrome produced from the smelting of low grade Chromite ore 1 was of particular interest when anthracite input to the recipe was gradually increased to optimize the process as can be seen in Figure 7. Carbon in the alloy was steadily increasing while silicon remained low and unaltered with the increase of anthracite input prior to reaching the alloy carbon saturation level. It is only closer to saturation level that significant reduction of silica really started. From that point onwards, the alloy carbon content was controlled by the C-Si equilibrium. It is believed that the above silicon behavior in the production of charge chrome in a DC open-arc furnace by carbothermic reduction may also be observed in the production of high carbon ferrochrome. The optimal carbon level prior to significant silicon reduction in the alloy is a transition point between the two different behaviors of silicon in the alloy. The impact of the furnace operating conditions, ore reducibility, reductant reactivity and some other parameters on this transition point is not well understood.

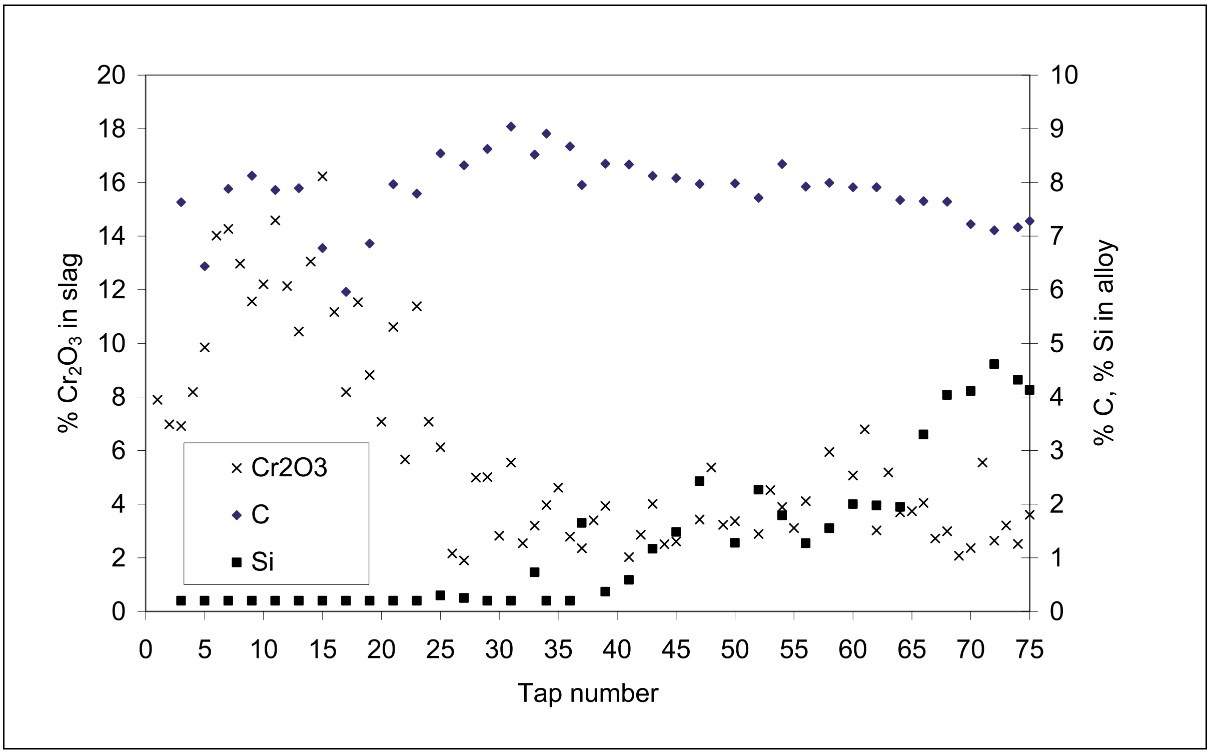

Figure 7: Evolution of C and Si in chromite smelting

Prior to the transition point, the level of carbon is proportional to the relative amount of chromium and iron carbides in the alloy; the main carbides being $(Cr,Fe)_3C_2$, $(Cr,Fe)_7C_3$ and $(Cr,Fe)_{23}C_6$ as observed by Wedepohl[2]. The capacities of the carbides Cr_7C_3 and $Cr_{23}C_6$ for incorporation of iron into their lattices are 55 and 30 per cent respectively[3].

The ratio in which different carbides and elemental Fe, Cr or Si form is affected by the furnace conditions (temperature, configuration, power density, partial pressures of O_2 and CO), ore reducibility, reductant reactivity, slag chemistry, silicon reduction and other minor parameters is not well understood. The variability of the above parameters might also have some effect on the carbon and silicon content in the alloy. The above shows that the silicon distribution and carbon presence in the ferrochrome alloy are occurring in a complex mechanism.

5.2 C-Si Equilibrium

In general the level of carbon in the alloy is controlled by the equilibrium between silicon and carbon when the smelting of chromite ores is carried out with an excess carbon above the stoichiometric requirement. Although this was observed through various conditions of the smelting of chromite ores and considering the operation of a similar furnace size and power density, it appeared that the Si and C values at equilibrium were variable and dependent on the ore type. At almost similar ferrochrome alloy silicon contents, the carbon content differed from one ore to another as can be seen in Figure 8.

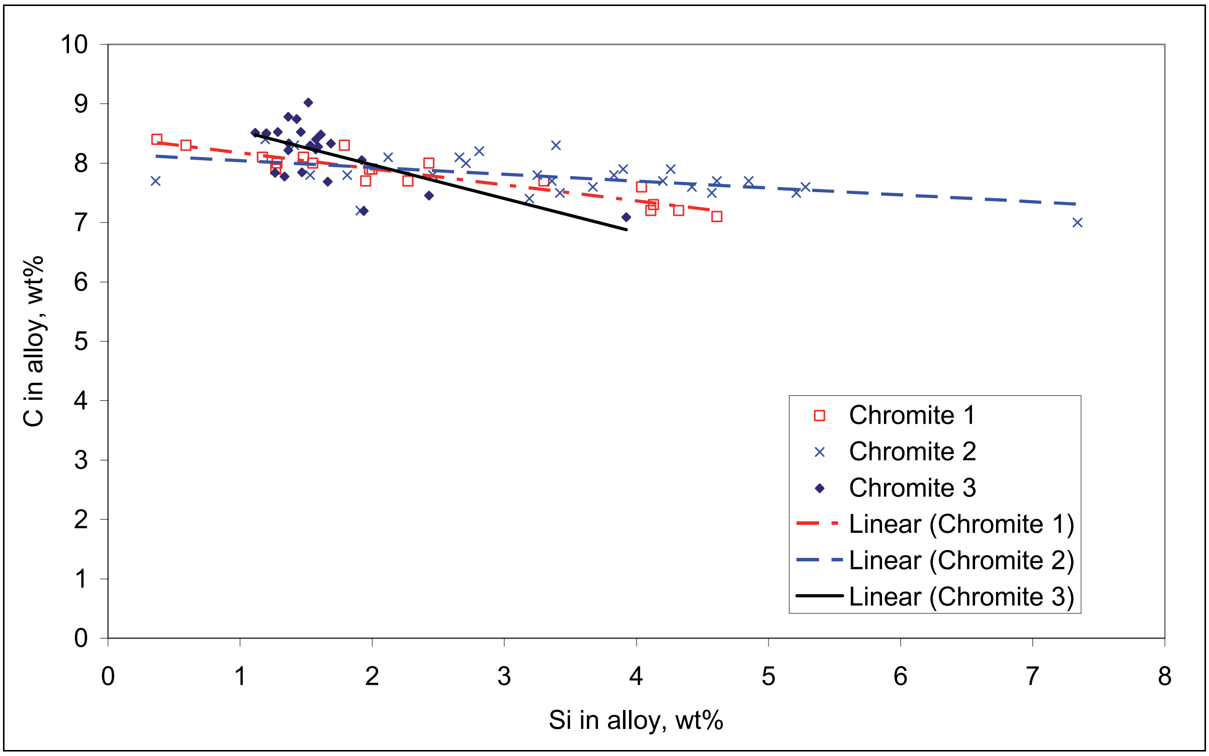

Figure 8: C versus Si in ferrochrome alloy from the smelting of different chromite ores

In practice, the excess reductant in the smelting process can be quantitatively evaluated by the residual contents of Cr_2O_3 and FeO in the slag. The latter are generally related to the main parameters of the smelting process such as chrome recovery to the alloy, alloy grade, etc. The Cr_2O_3 content in the slag can also be related to the silicon content in the alloy as presented in Figure 9.

In the testwork at Mintek, SiO_2 reduction was significant when residual chromium oxide in the slag was below 5% for the smelting of Chromite 1 and below 3% for the smelting of Chromites 2 & 3; this threshold level was observed by.HJ Kammeyer[4] to be 3% in South African commercial production of charge chrome using DC open-arc furnaces. Other factors could have played a role in the commercial furnace such as the furnace size and geometry, feeding configuration, arc characteristics, furnace hydrodynamics that are difficult to mimic on the pilot plant facilities. Since silica reduction increases the energy and reductant consumptions, it is important to minimize it.

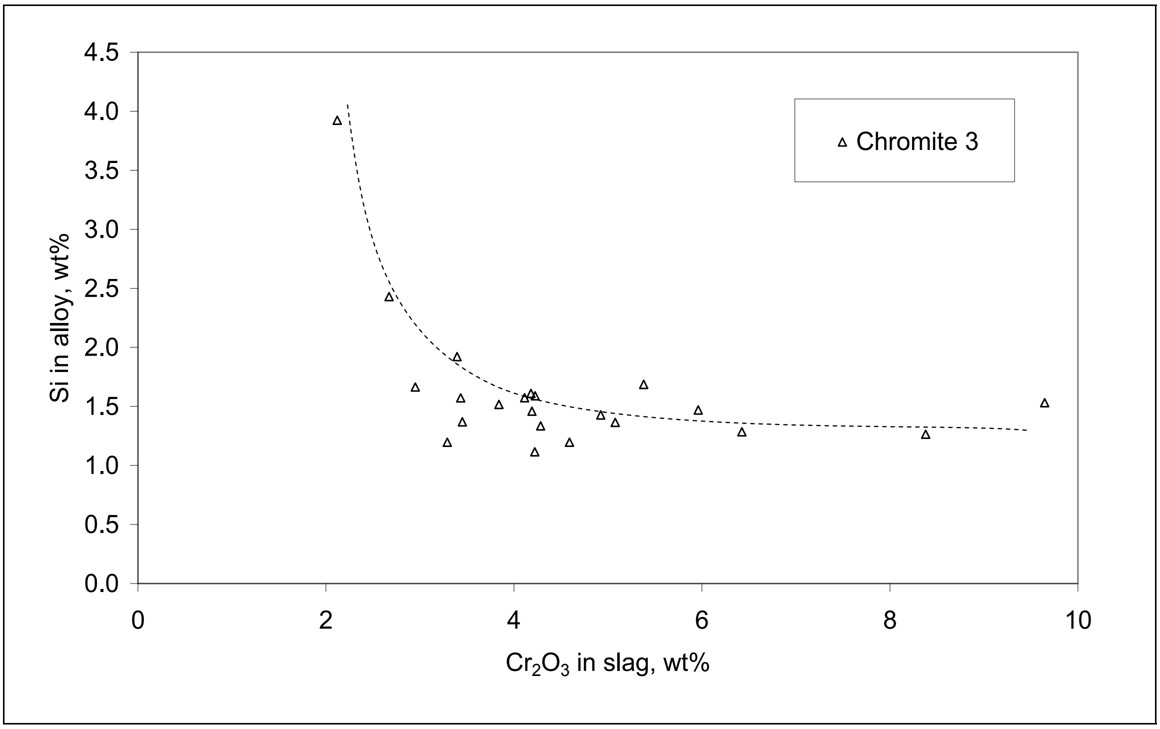

Figure 9: Slag Cr_2O_3 versus alloy Si

5.3 Impact of the Reductant on the Si and C in the Ferrochrome Alloy

The use of reductant is commonly investigated in most of the smelting campaigns. Whilst the change of the reductant type in a specific campaign, based on equivalent fixed carbon amount, could produce almost similar alloy Cr grade, it was observed that it affected the content of carbon and silicon to the alloy. This could be a result of the change in the reduction rates of the reducible oxides in the chromite ore. At consistent ore mineralogical composition (thus a specific ore reducibility) and slag composition (i.e. silica reactivity), the reduction of Fe, Cr and Si would be affected by the reductant reactivity (See Table 4).

As observed by Yonggao[5], the factors affecting C and Si are complex and would depend on the development of the reduction and refining processes taking place in the furnace. Contrary to the submerged-arc furnace where the primary metal from the smelting reactions is subjected to refining as the metal droplets filter through the viscous chromium oxide-rich slag above the alloy; it is believed that most of the refining in the open-bath furnace could be happening at the interface between metal and slag. The latter does not permit refining reactions to proceed to any significant extent; the limiting factors being the surface area, residence time and temperature. It was observed that the increase of the residence time together with the decrease of the specific feed rate of chromite ore per surface area, particularly in the period of warm-up and ramp-up to target regime, was able to decrease to an appreciable extent the carbon content in the alloy.

Table 4: Impact of chromite type, alloy Cr/Fe ratio and reductant on FeCr alloy carbon content

Type of chromite	Cr/Fe ratio	C	Si	Fluxes	Type of reductant
Chromite 4 (LG)	1.56	8.23	1.65	Burnt lime/silica	SA Anthracite
Chromite 5 (HG)	2.46	8.33	1.53	Burnt lime/silica	SA Anthracite
Chromite 5 (HG)	2.75	8.82	1.35	Burnt lime/silica	SA Coal
Chromite 1 (LG)	1.51	7.23	1.71	Burnt lime/silica	SA Coal
Chromite 1 (LG)	1.33	8.02	1.55	Limestone/silica	SA Anthracite

LG= Low Grade; HG= High Grade

Assuming that there is insignificant refining in the open-bath smelting process, the extent and rate of reduction would play a significant role in the determination of the levels of carbon and silicon in the chrome alloy produced in a DC open-arc furnace. In practice, the reduction is related to the operating temperature, chromite ore reducibility and grain size of the ore and reductant reactivity. The ore grains were in most of the tests 60% -1mm size and their effects were assumed insignificant.

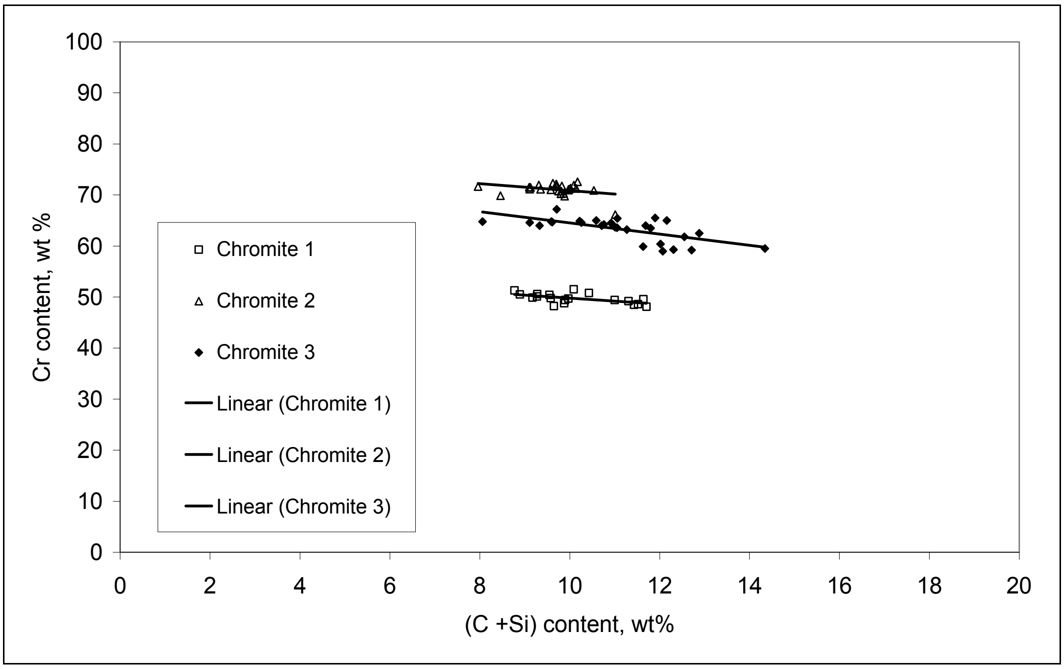

Figure 10: Variation of (C+Si) with alloy Cr grade

5.4 Impact of both C And Si on the Alloy Cr Grade

The alloy chromium grade generally affects the content of both C and Si. The amount of these two elements increases with the decrease of the alloy Cr grade as can be seen in Figure 10 for the cases investigated. At constant Cr/Fe ratio, the variation of the grade is dependent on the content of both silicon and carbon.

5.5 Impact of the Slag Chemistry

The silicon content in the metal alloy is a function of the silica content of the slag when complete equilibrium is established, and the silicon distribution between slag and metal depends on the CO pressure. The silica activities in the slags produced in the two slag systems were calculated using FACTSage 5.4 and plotted in Figure 11. Within any of the slag systems used in the testwork at Mintek, the silica activity increases with the increase of silica in the slag. At similar residual silica content in the slag, the silica activity was higher in the high lime slag than in the low lime slag.

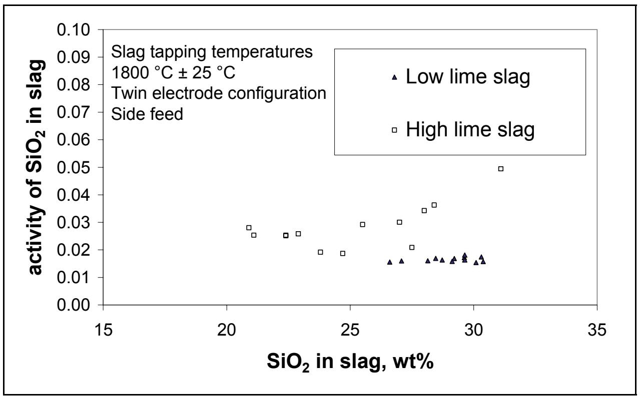

Figure 11: Calculated activities of SiO2 in the slags (FACTSage 5.4) for the low and high lime slag systems

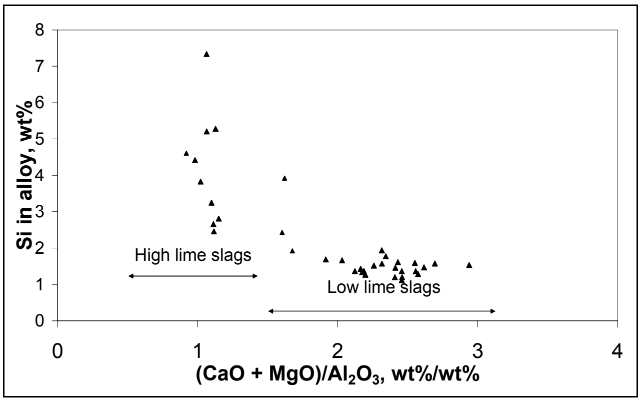

Figure 12: Slag (MgO+CaO)/Al_2O_3 versus Alloy Si

(CaO+MgO)/Al_2O_3 ratio in slag is one of the key factors for the determination of the slag melting point and viscosity; thus the smelting rates. This ratio was lower for the high lime than for the low lime slag. Increasing the above ratio in the slags will decrease the alloy silicon content. Whilst this trend could be observed, it was however not significant for ratios above 2 as can be seen in Figure 12.

The above would suggest that within the range of the observed parameters, the low lime slag has a slightly lower impact on the silica reduction than the high lime slag. The alloy silicon contents were more sensitive to variations of carbon inputs to the smelting recipe for ratios below 2; this was particularly observed for the high lime slag.

Within a specific smelting condition, the slag compositions or the silica activity was quite consistent so that any significant variation of silicon content in the alloy would be as a result of the variation of either the temperature and carbon addition or both.

5.6 Impact of the Furnace Configuration

Table 5: Impact of the furnace configuration on Si and C in the alloy for the smelting of Chromite 1

Electrode arrangement	Cr/Fe ratio	C	Si	Fluxes	Type of reductant
Hollow electrode / Centre feeding	1.30	8.10	0.38	Limestone/silica	SA anthracite
Twin electrodes / Side feeding	1.34	8.02	1.55	Limestone/silica	SA anthracite

The impact of the furnace configuration on carbon and silicon in the alloy was investigated for the smelting of Chromite 1. Side feeding in a twin electrode configuration as compared to center feeding through a single hollow electrode seemed to increase the carbon and silicon to the alloy. This may however be partly due the operational difficulties experienced with hollow electrodes leading to longer residence times and most probably promoting the refining reactions. The twin electrode configuration increases the arc attachment zone and the amount of materials effectively exposed to the arc; this is able to increase the silicon reduction to the alloy.

6 CONCLUSIONS

The data collected from the smelting testwork of chromite ores in DC open-arc furnaces at Mintek were used to investigate the silicon reduction and carbon presence in the ferrochrome alloys.
It was observed that carbon and silicon in the production ferrochrome alloys using DC open-arc furnace are occurring in a complex mechanism. The impacts of the ore reducibility, reductant reactivity, slag chemistry, furnace configuration were observed. The ore and reductant types included the chemical and mineralogical compositions whilst the slag chemistry was evaluated on the basis of the silica activity in the low and high lime slag comprised of Al_2O_3-SiO_2-MgO and Al_2O_3-SiO_2-MgO-CaO as a function of (MgO+CaO)/Al_2O_3 ratio. The furnace configuration was comprised of the centre feeding through a single hollow electrode or side feeding using twin electrode configuration. Besides the above, there might be a number of minor uncontrollable factors that would also affect the reduction rates of the chromite ores, factors linked to the variability of the mineralogical composition of the feed materials.

7 REFERENCES

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