

## The Selective Carbothermic Reduction of Chromite

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### INTRODUCTION

The selective carbothermic reduction of Transvaal chromite in a DC arc furnace was the subject of an extensive investigation undertaken by Middelburg Steel and Alloys (now incorporated into Samancor Ltd) between 1982 and 1988.

The project arose from chromite smelting trials conducted at Tetronics Research & Development Ltd in 1979, using a 1,4 MVA DC arc furnace(1). These results had demonstrated that selective carbothermic reduction of chromite to partially separate Cr and Fe was possible, by decreasing the fixed-carbon to chromite ratio in the feed. Slags containing 25 per cent Cr<sub>2</sub>O<sub>3</sub> with Cr:Fe ratios of 4:1 were produced from Transvaal chromite with a Cr:Fe ratio of 1.6:1. The use of this high Cr:Fe ratio slag (HISLAG) as a synthetic ore to produce ferrochromium alloys with chromium contents greater than 65 per cent was considered to be a potentially useful means of widening the range of alloys which could be produced from the low Cr:Fe ratio Transvaal chromites. This was of particular interest for low-carbon ferrochromium alloys where high chromium contents are the market norm.

### Background

The selective reduction of chromite was the subject of a patent by M.J. Udy(2), in 1937 in which, typically, a submerged-arc furnace was used to produce a high Cr:Fe ratio slag and a correspondingly low Cr:Fe ratio metal. The subsequent reduction of the high Cr:Fe ratio slag was usually carried out in an open-arc furnace silicothermically. Coetzee and Smit(3) reported in 1961 on the production in South Africa of a slag with a Cr:Fe ratio of 3.3:1 from an ore of Cr:Fe ratio 2.0:1. A metal of Cr:Fe ratio 1.1:1 with a 7.6 per cent carbon content was simultaneously produced. The authors state that 'the only real problem in the large scale application of this process is to find a market for the reject metal from the first melt'.

Hunter and Banning(4) reported on the use of a similar technique to 'upgrade' U.S. chromites in 1962, while more recently Lectromelt Corp(5) and SKF Steel Engineering(6) have filed patents describing furnace designs capable of carbothermically selectively reducing chromite.

### Theory

The greater stability of chromium oxides compared with iron oxide forms the basis for the selective carbothermic reduction of chromite. The extent to which the iron and chromium may be distributed between the slag and metal phases at equilibrium was not known for slag-metal systems involving natural chromites and the most relevant experimental data was that of Rankin and Biswas(7). An estimate was made using their data of the Cr:Fe ratio expected in a slag in equilibrium with an Fe-Cr-Si alloy as a function of the Cr content of the alloy and the CaO:SiO<sub>2</sub> ratio of the slag (see Figure 1). Rankin and Biswas' data was however derived from CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> master slags and carbon-free alloys containing less than 30 per cent Cr. The presence of MgO in the slag and carbon in the alloy will undoubtedly affect the Cr:Fe ratio that can be achieved but this data served as a useful first estimate. This extrapolation indicated that at 1600°C for an alloy containing 40 per cent Cr that an equilibrium Cr:Fe ratio of between 25 and 55 could be attained for CaO:SiO<sub>2</sub> ratios from 0.3 to 1.5 respectively.

The kinetic factors affecting the approach to equilibrium were unknown and especially so in a DC arc furnace but it was recognised that these factors could drastically reduce the Cr:Fe ratios attainable.

### Process Applications

Various process options were considered to produce a 65 per cent low carbon ferrochromium, which are summarised in Figure 2.

The objection raised by Coetzee and Smit(3) regarding the economic sale of the low Cr:Fe ratio metal produced can be overcome by an integrated stainless-steel producer. This would enable such a producer to shift iron units from the ferro-alloy to the stainless-steel product lines. All the process options benefit by maximising the HISLAG Cr:Fe ratio and chromium content since the material is essentially a synthetic ore and as such competes with natural high-grade chromites.

### Equipment

Three DC arc furnaces rated at powers of between 30 kW and 1.2 MW were used at Mintek(8) together with a 300 kVA a.c. arc

Figure 1

EXPECTED SLAG Cr:Fe RATIOS BASED ON RANKIN AND BISWAS DATA<sup>[7]</sup>

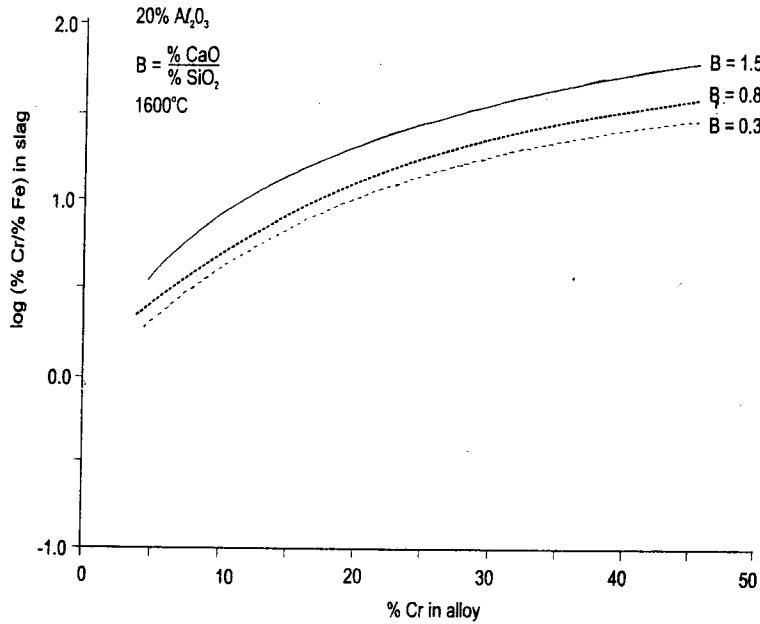


Figure 2  
 POSSIBLE ROUTES FOR PRODUCTION OF A 65% GRADE  
 LOW-CARBON FERROCHROMIUM

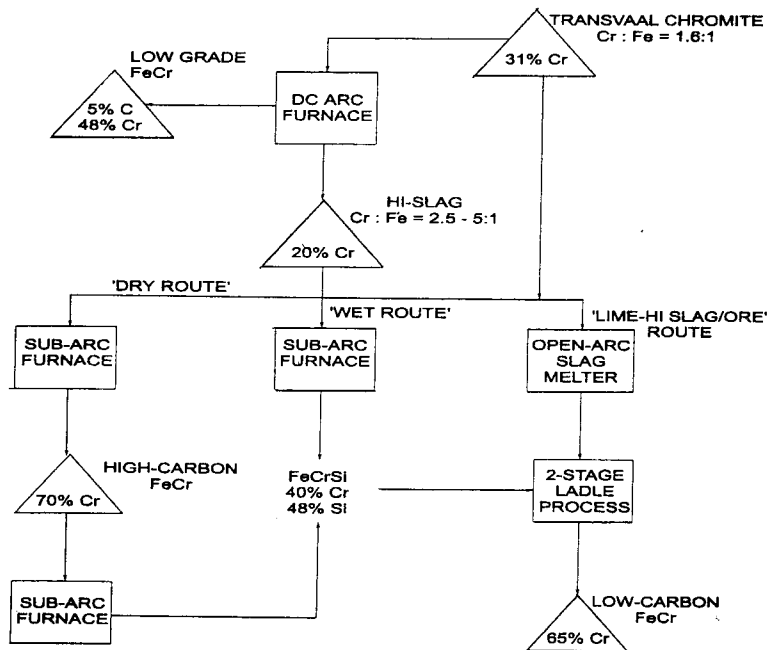


Figure 3. Arrangement of the 100kVA DC-arc furnace

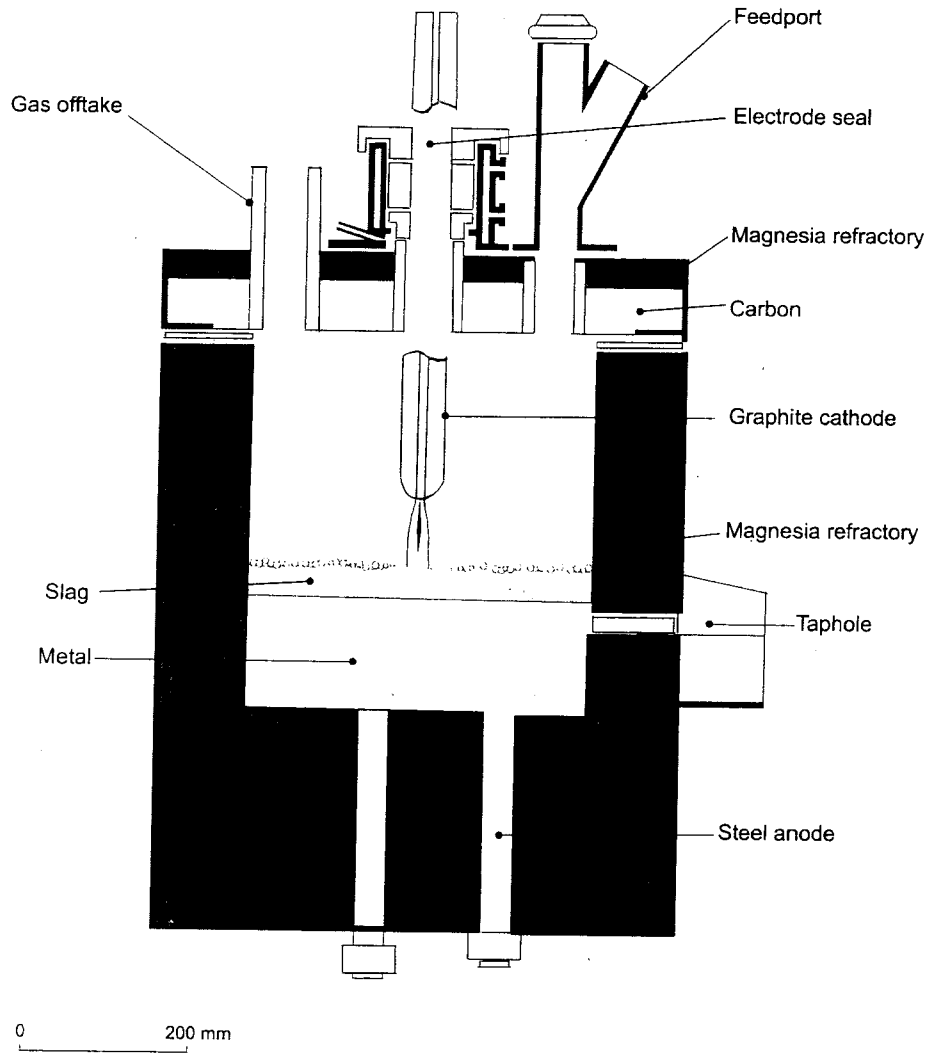


Figure 4. 200 KVA DC-arc furnace arrangement

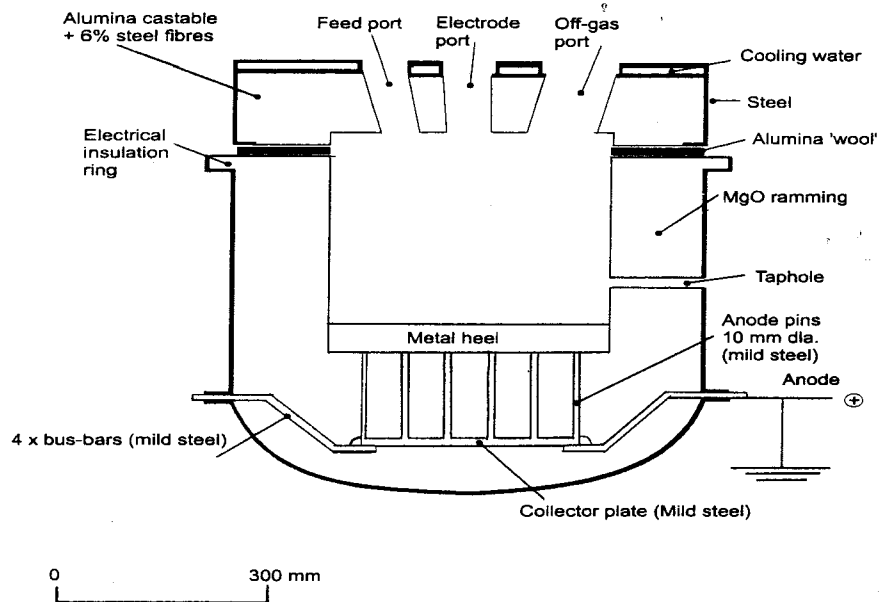
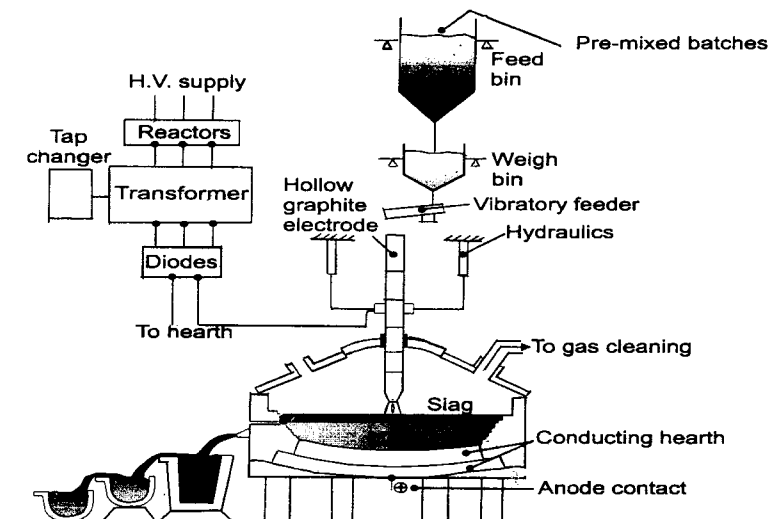


Fig.5 Schematic diagram of the 16 MVA DC- arc furnace



furnace. A 16 MVA DC arc furnace(9) was used at Samancor's Krugersdorp plant. (See Figures 3, 4 and 5). These furnaces have been extensively described in the literature(8,9,10,11).

**SELECTIVE CARBOTHERMIC REDUCTION**

The testwork conducted to produce a high Cr:Fe ratio slag (HISLAG) from Transvaal chromites was carried out at progressively larger scales.

**50 kW to 100 kW Tests**

These tests were carried out on the 100 and 200 kVA DC arc furnaces and the three most significant campaigns are described below.

**Particle size**

This campaign was carried out on the 100 kVA furnace and used two different average particle sizes of chromite to determine the effect of this parameter upon the slag Cr:Fe ratio. The two chromite samples were prepared by screening Winterveld chromite fines (100% < 6mm) at 3mm and at 0.25mm. The fraction below 0.25mm was used in the first part of the campaign and the fraction between 0.25mm and 3mm was used in the second part. The chemical analyses of the two chromite fractions are given in Table 1 as well as the other raw materials i.e.

coal, limestone and quartz which were all screened at 6mm. The furnace was fed continuously until 50kg of feed had been added, at an approximately constant power of 50 kW. The furnace was then tapped and the process repeated until the end of the campaign. The power and feedrate were adjusted to ensure that a fluid bath of molten slag was present across the entire internal diameter of the furnace at all times and that the tapping temperatures remained relatively constant. A summary of the operating conditions for the campaign is given in Table 2.

A summary of the feed and product data is given in Table 3. A fixed carbon-to-chromite ratio of approximately 0.1 and a total (SiO<sub>2</sub> + CaO) flux addition of ~ 29 per cent of the chromite mass was used.

The slag produced from the finer chromite had a Cr:Fe ratio of 11.7 compared with the coarser chromite with a Cr:Fe ratio of 4.1. The Cr<sub>2</sub>O<sub>3</sub> contents of the two slags were also significantly different (29.3 per cent and 35.8 per cent) for the finer and coarser chromite feed respectively. This represents different degrees of reaction (despite similar fixed-carbon additions) which was reflected in the lower chromium content of the metal produced (32 cf. 41 per cent). The carbon contents of the two alloys were however similar (5.7 per cent and 5.4 per cent). The strong effect of particle size suggested a kinetic limitation on the process under these smelting conditions.

**Table 1: Raw material compositions for the selective reduction tests (% by mass)**

| Material              | Average particle size mm | Cr <sub>2</sub> O <sub>3</sub> | FeO  | SiO <sub>2</sub> | CaO  | MgO  | Al <sub>2</sub> O <sub>3</sub> | F.C. | S    | P    |
|-----------------------|--------------------------|--------------------------------|------|------------------|------|------|--------------------------------|------|------|------|
| Chromite (Winterveld) | 0.8                      | 46.3                           | 24.1 | 1.1              | 0.2  | 11.5 | 14.5                           | -    | -    | -    |
| Chromite (Winterveld) | 0.1                      | 43.3                           | 23.0 | 4.6              | 1.0  | 12.3 | 14.1                           | -    | -    | -    |
| Chromite (TCL)        | 0.8                      | 44.5                           | 25.2 | 2.7              | 0.2  | 11.1 | 13.0                           | -    | -    | -    |
| Chromite (HGX)        | 0.2                      | 43.6                           | 25.7 | 3.6              | 0.4  | 9.8  | 15.2                           | -    | -    | -    |
| Coal                  | 3.0                      | -                              | 0.3  | 7.7              | 0.4  | 0.2  | 2.7                            | 54.3 | -    | -    |
| Coal                  | 10.0                     | -                              | 0.3  | 7.7              | 0.4  | 0.2  | 2.7                            | 53.3 | 0.65 | 0.02 |
| Anthracite            | 12.0                     | -                              | -    | 6.5              | -    | -    | 3.6                            | 73.5 | -    | -    |
| Quartz                | 2.0                      | 0.1                            | 0.4  | 99.1             | -    | -    | 0.3                            | -    | -    | -    |
| Quartz                | 10.0                     | -                              | -    | 99.6             | -    | -    | -                              | -    | -    | -    |
| Limestone             | 2.0                      | -                              | 0.5  | 0.2              | 55.0 | 1.0  | -                              | -    | -    | -    |
| Limestone             | 10.0                     | -                              | -    | 0.8              | 52.4 | -    | -                              | -    | -    | -    |

\* F.C. = Fixed carbon

**Table 2: Summary of the operating data from the selective reduction campaigns**

| Campaign Title         | No of Taps | Power kW | Current A | Furnace thermal efficiency % | Batch mass, kg | Fixed carbon addition % of chromite | Feedrate kgh <sup>-1</sup> | Feed flux* kgh <sup>-1</sup> m <sup>-2</sup> |
|------------------------|------------|----------|-----------|------------------------------|----------------|-------------------------------------|----------------------------|--|
| Particle size (fine)   | 7          | 50       | 550       | 36                           | 50.0           | 10.5                                | 33                         | 260  |
| Particle size (coarse) | 8          | 50       | 550       | 36                           | 50.0           | 11.5                                | 33                         | 260  |
| High basicity          | 24         | 60       | 800       | 38                           | 46.3           | 9.5                                 | 30                         | 240  |
| 100kW scale            | 71         | 96       | 900       | 43                           | 65.7           | 11.4                                | 51                         | 260  |
| 1MW scale (TCL)        | 48         | 830      | 2440      | 60                           | 1117           | 13.9                                | 643                        | 360  |
| 1MW scale (HGX)        | 53         | 958      | 2580      | 64                           | 1121           | 13.3                                | 700                        | 396  |
| 8MW scale              | 39         | 7600     | 23300     | 69                           | 20800          | 14.0                                | 5540                       | 350#   |

\* Based on molten bath diameter = furnace internal diameter

# Based on a molten bath diameter = 4.5m

Table 3: A summary of the feed and product data from the selective reduction campaigns

| Parameter                               | Campaign Title       |                        |               |             |           |       |           |
|---|----------------------|------------------------|---------------|-------------|-----------|-------|-----------|
|   | Particle size (fine) | Particle size (coarse) | High basicity | 100kW scale | 1MW scale |       | 8MW scale |
|   |                      |                        |               |             | (TCL)     | (HGX) |           |
| Chromite average particle size mm       | 0.12                 | 0.8                    | 0.8           | 0.8         | 0.8       | 0.2   | 0.2       |
| Chromite mass/batch kg                  | 33.0                 | 32.0                   | 30.5          | 48.7        | 795       | 800   | 14650     |
| <b>BATCH COMPOSITION/100KG CHROMITE</b> |                      |                        |               |             |           |       |           |
| Coal/anthracite kg                      | 21                   | 23                     | 19            | 21          | 26        | 25    | 19        |
| Quartz kg                               | 26                   | 28                     | 16            | 14          | 15        | 15    | 8         |
| Limestone kg                            | 4                    | 6                      | 16            | -           | -         | -     | 15        |
| SLAG MASS/TAP kg                        | 25.5                 | 32.4                   | 23.8          | 32.0        | 503       | 509   | 10850     |
| <b>SLAG COMPOSITION (MASS %)</b>        |                      |                        |               |             |           |       |           |
| Cr <sub>2</sub> O <sub>3</sub>          | 29.3                 | 35.8                   | 32.6          | 35.8        | 29.0      | 29.2  | 27.4      |
| FeO                                     | 2.2                  | 7.6                    | 10.1          | 6.2         | 6.4       | 5.7   | 9.2       |
| SiO <sub>2</sub>                        | 36.2                 | 29.9                   | 21.2          | 26.6        | 28.5      | 27.1  | 16.6      |
| CaO                                     | 4.0                  | 3.3                    | 9.0           | 0.4         | 0.5       | 0.6   | 12.2      |
| MgO                                     | 13.4                 | 11.3                   | 12.6          | 17.0        | 15.9      | 13.1  | 13.3      |
| Al <sub>2</sub> O <sub>3</sub>          | 16.4                 | 14.9                   | 15.8          | 21.0        | 20.2      | 23.4  | 21.7      |
| Cr:Fe Ratio                             | 11.7                 | 4.1                    | 2.8           | 5.1         | 4.0       | 4.5   | 2.6       |
| (CaO + MgO)/SiO <sub>2</sub>            | 0.48                 | 0.49                   | 1.02          | 0.65        | 0.58      | 0.51  | 1.54      |
| METAL MASS/TAP kg                       | 10.1                 | 8.3                    | 8.4           | 12.8        | 273       | 285   | -         |
| <b>METAL COMPOSITION (MASS %)</b>       |                      |                        |               |             |           |       |           |
| Cr                                      | 40.7                 | 32.2                   | 44.5          | 42.0        | 46.1      | 45.1  | 47.0      |
| Fe                                      | 49.8                 | 60.0                   | 49.4          | 53.1        | 46.9      | 48.5  | 46.4      |
| Si                                      | 0.84                 | 0.59                   | 0.58          | 0.46        | 0.35      | 0.28  | <0.1      |
| C                                       | 5.7                  | 5.4                    | 3.1           | 2.3         | 4.9       | 4.9   | 5.3       |
| S                                       | -                    | -                      | 0.080         | 0.12        | 0.13      | 0.13  | 0.17      |
| P                                       | -                    | -                      | 0.010         | -           | 0.008     | 0.008 | 0.005     |

**High basicity**

This campaign was also conducted on the 100 kVA DC arc furnace using Winterveld chromite (coarse fraction) and coal, quartz and limestone screened at 6mm (Table 1). The campaign was conducted to test the feasibility of operating with a higher slag basicity (1.0 instead of 0.5) and was carried out under very similar conditions to the previous campaign (see Table 2). The slag Cr:Fe ratio was only 2.8 and the slag contained 32.6 per cent Cr<sub>2</sub>O<sub>3</sub>. The metal contained 44.5 per cent Cr, 3.1 per cent C, 0.08 per cent S and 0.01 per cent P (see Table 3).

**Scale up to 100 kW**

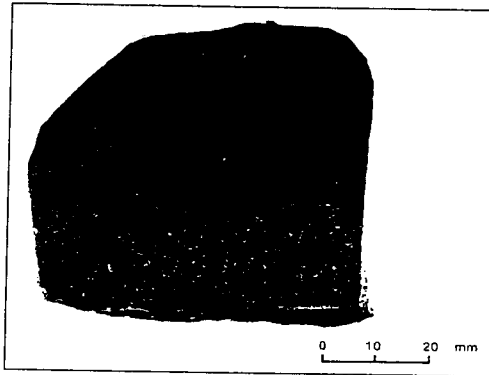
This campaign was carried out on the 200 kVA DC arc furnace. It was designed to scale the process up to the 100 kW level, maximise both the slag Cr:Fe ratio and the Cr<sub>2</sub>O<sub>3</sub> content, and demonstrate the feasibility of operation with low slag basicities when using a magnesia refractory. The raw materials were coarse Winterveld chromite, coal and quartz fines (see Table 1), and the operating parameters are given in Table 2. An average power (over 71 taps) of 96 kW was attained at a furnace thermal efficiency of 43 per cent.

The slag produced contained 36 per cent Cr<sub>2</sub>O<sub>3</sub> at a Cr:Fe ratio of 5.1 and a basicity of 0.65 (see Table 3). The metal contained 42 per cent Cr, 2.3 per cent C and 0.12 per cent S. The furnace showed extremely good refractory wear and a mineralogical study showed that a protective layer of picrochromite (MgO.Cr<sub>2</sub>O<sub>3</sub>) had formed at the slag/refractory boundary. It was concluded that the presence of at least 25 per cent Cr<sub>2</sub>O<sub>3</sub> in the slag under the mildly reducing conditions of the process rendered the slag inert with respect to the MgO lining. The slag was found to consist of two distinct layers, a glassy upper layer with a Cr:Fe ratio of 21 containing recrystallized spinels and a 'sugary' lower layer with a Cr:Fe ratio of 2.2 containing undissolved, partly reduced chromite spinels (Figure 6).

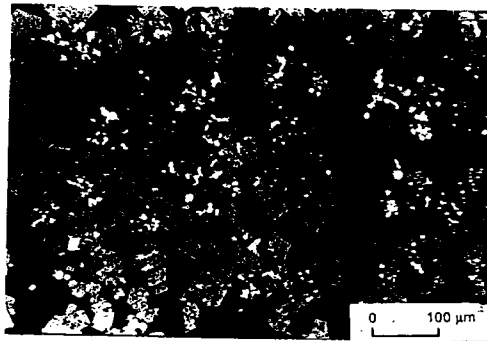
**The 1 MW Demonstration Campaign**

This campaign was undertaken to demonstrate the process at the 1.0 MW scale using the 3.2 MVA DC arc furnace. Two chromite types were used (TCL and HGX). The compositions and approximate average particle sizes of the chromites and other raw materials (10mm coal and 2mm quartz) are shown in Table 1. The furnace was operated (see Table 2) at between 830 kW and 960 kW for a total of 101 taps each consisting of 1120kg of feed material. The thermal efficiency was about 62 per cent and the feedrate varied between 640 and 700kg/h.

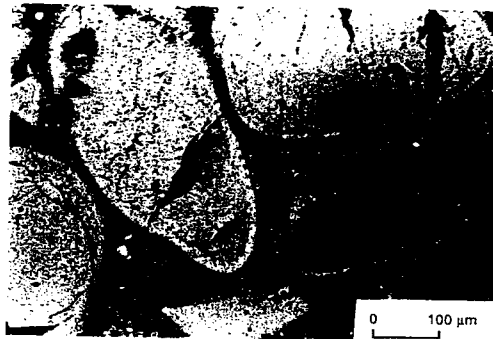
Figure 6  
NATURE OF SLAG FROM THE 100kW SCALE-UP CAMPAIGN



Bulk appearance



Optical micrograph of upper layer



Optical micrograph of lower layer

The two different chromites, TCL and HGX yielded similar Cr:Fe ratios (4.0 and 4.5) and Cr<sub>2</sub>O<sub>3</sub> contents (29.0 and 29.2 per cent) respectively. The Cr:Fe ratios did not however show the strong effect on Cr:Fe ratio with particle size as the earlier campaign.

The metal produced contained 46 per cent Cr, 5 per cent C, 0.3 per cent Si, 0.13 per cent S and 0.008 per cent P (see Table 3). The Cr distribution between slag and metal was approximately 42 per cent and 52 per cent respectively while the iron distribution was 18 per cent and 75 per cent respectively. The rammed magnesia lining performed extremely well despite being in direct contact with a low basicity slag (0.55) throughout the campaign. An electrode consumption of 1.6kg/MWh was measured.

An examination of the tap-to-tap data showed a statistically significant correlation of higher Cr:Fe ratios with higher tapping temperatures and lower feedrates. This result tends to support the evidence from particle size campaign and the slag mineralogy observed previously that the process is kinetically limited.

#### The 8 MW Industrial Trial

A ten-day industrial trial was carried out at the Palmiet Ferrochrome Plant of Samancor on the 16 MVA plasma furnace in January 1987, shortly before a shut-down. The raw materials were HGX chromite, 12mm anthracite, 10mm quartz and limestone (see Table 1). The major campaign operating parameters are given in Table 2. An average power of 7.6 MW was attained with an 88 per cent availability at feedrates of approximately 5.5 t-h<sup>-1</sup>. A furnace thermal efficiency of between 65 per cent and 73 per cent was estimated for this campaign. The molten pool diameter increased rapidly during the campaign. A decrease in power contained this erosion of the 'banks' and the mass balance indicated that a new steady state furnace condition was being established. The hearth temperatures also rose sharply indicating a lowering of the freeze line in the metal heel but the subsequent dig-out of the furnace hearth did not indicate any abnormal wear or penetration of the hearth. The electrode consumption was high at 4.4kg/MWh compared with 1.6kg/MWh measured at Mintek.

The metallurgical results are summarised in Table 3 for comparison with the earlier campaigns. The slag contained 27 per cent Cr<sub>2</sub>O<sub>3</sub>, had a basicity of 1.5 and a Cr:Fe ratio of 2.6. The Cr<sub>2</sub>O<sub>3</sub> content of the slag was lower than expected from the 1 MW testwork and indicated an effective increase in the carbon addition which was possibly derived from the electrode or the banks of frozen material. The metal contained 47 per cent Cr, 5.3 per cent C, <0.1 per cent Si, 0.17 per cent S and 0.005 per cent P of which only the higher sulphur content differed greatly from the smaller scale results, particularly in view of the higher slag basicity used.

This trial demonstrated the industrial feasibility of the carbothermic selective reduction of Transvaal chromite in a DC

arc furnace to yield a slag with 27 per cent Cr<sub>2</sub>O<sub>3</sub> at a Cr:Fe ratio of 2.6 and a slag basicity of 1.5.

#### Discussion

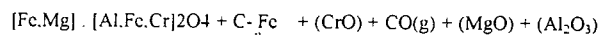
Consideration was given to the development of a reaction mechanism which adequately describes the results obtained. The major characteristics of the process are:

- \* increasing Cr:Fe ratio as slag basicity or chromite particle size decreased
- \* increasing Cr:Fe ratio as temperature and residence times increased
- \* decreasing alloy carbon content as the slag Cr<sub>2</sub>O<sub>3</sub> content increased

The mineralogical study of the product HISLAG after cooling in the tapping tray revealed that chromium existed in the slag in two major forms (see Figure 6). Firstly as crystallised spinel associated with small metal droplets in the upper part of the slag and secondly as essentially undissolved chromite spinels at the bottom of the slag just above the slag-metal interface. The alloy carbon content was observed to be in the range between 2.3 and 5.3 per cent which is substantially lower than the 7 to 8 per cent encountered in smelting Transvaal chromites. These facts led to the following proposed mechanism.

a) chromite falling onto the slag surface sinks largely unreacted through the slag layer to accumulate at the slag-metal interface.

b) the chromite particles dissolve and reduce (virtually simultaneously) by the following schematic reaction:



where [ ] denotes spinel crystal

— denotes dissolution in liquid

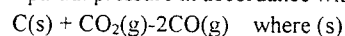
alloy

( ) denotes dissolution in liquid

slag

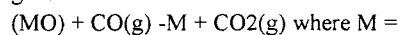
and (g) denotes a gaseous phase

c) the carbon falling onto the slag surface maintains a low oxygen partial pressure in accordance with the Boudard reaction:



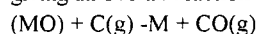
denotes a solid phase

Carbon monoxide then reduces the dissolved oxides of chromium (principally CrO) and iron to form droplets of metal according a general reaction:



Cr or Fe

giving an overall reaction as follows:



The metal droplets are likely to nucleate at the slag-carbon interface allowing carbon dissolution into the metal droplets to take place.



d) these chromium rich alloy droplets descend through the slag and enter the bulk alloy phase raising the chromium and carbon contents.

The rate limiting step in the mechanism is probably the dissolution of chromite which requires two co-existing conditions:

- (i) a sufficiently low oxygen partial pressure to reduce  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  to substantially CrO and Fe; and
- (ii) a slag with sufficient solubility for the MgO,  $\text{Al}_2\text{O}_3$  and CrO species resulting from the chromite dissolution.

This is supported by the presence of substantial quantities of partially reacted spinel which effectively reduces the overall Cr:Fe ratio in the slag. Therefore higher temperatures and smaller chromite particle sizes (which should favour faster dissolution) should improve the overall Cr:Fe ratio, as observed. The effect of a lower slag basicity is to increase the solubility of CrO in the slag relative to FeO and thereby increase the overall Cr:Fe ratio.

The oxygen partial pressure at the slag-alloy interface is determined by the carbon and silicon contents of the alloy together with the activity of CrO in the slag. Healy(12) has shown that the activity of carbon in Fe-Cr-C alloys decreases rapidly as the carbon content decreases. The oxygen partial pressure in the system therefore increases. When there is insufficient carbon in the feed mixture to reduce the CrO in the slag the equilibrium carbon content of the bulk alloy decreases and the resulting higher partial pressure of oxygen inhibits further dissolution of chromite(13).

#### **SMELTING 'HISLAG' TO HIGH-CARBON FERROCHROMIUM**

The production of high-carbon ferrochromium (HCFeCr) from HISLAG was of importance primarily to provide a high Cr:Fe ratio ferrochromium to serve as a raw material for the production of ferrochromium silicide ( $\text{FeCrSi}$ ) via the so-called 'dry' process (see Figure 2). A high Cr:Fe ratio  $\text{FeCrSi}$  in turn forms the reducing agent in the silicothermic reduction of a lime-ore melt to produce low-carbon ferrochromium (Perrin-type process).

The two methods of carbothermally smelting HISLAG to HCFeCr that were considered in this investigation were, firstly, the conventional submerged-arc furnace practice and, secondly, DC arc smelting. The HISLAG raw material would in either case constitute a synthetic chromite ore. The open-bath DC arc furnace route would be necessary if the HISLAG were to be processed direct as a liquid material while the submerged-arc furnace route would be a natural choice for a solid lumpy HISLAG material. The determination of the smelting behaviour of HISLAG in each of these two furnaces, both operationally and metallurgically, was the objective of this section of the investigation.

##### **Submerged-Arc Smelting**

Seven smelting campaigns on the 300 kVA a.c. arc furnace were carried out using both low and high basicity HISLAG and various fluxes (limestone, magnesite and dolomite). The following conclusions were drawn from the tests.

\* The batch smelting of HISLAG with both a high (1.4) and low (0.5) basicity in a 300 kVA arc furnace posed no problems, and from an electrical point of view both behaved in a very similar manner.

\* It was observed that neither types of HISLAG smelted like a natural ore in the submerged-arc furnace operated under dry-top conditions because of the low liquidus temperature of these materials compared with natural chromite. Because of their lack of refractoriness these materials melted away rapidly from around the electrodes. Soon after starting each smelt a bath of molten slag formed under a layer of unreacted coke and flux. The reduction presumably takes place at the interface. It was not possible to operate the furnace under dry top conditions because of this rapid formation of slag high up in the furnace bed. This effect was probably worsened by the limited depth of charge that could be carried in the furnace, imposed by the geometry of the furnace shell.

\* The submerged-arc smelting of both types of HISLAG was characterised by low chromium oxide contents in the slags. An average of 1.3 per cent  $\text{Cr}_2\text{O}_3$  was obtained for a series of smelts on the low basicity HISLAG and 3.0 per cent for the series of smelts using the higher basicity material. The alloy produced from the low basicity HISLAG contained typically 62 per cent Cr, 10 per cent Si and 7 per cent C, while the alloys from the more basic HISLAG contained typically, 58 per cent Cr, 6 per cent Si and 8 per cent C.

##### **DC Arc Furnace Smelting**

Two campaigns were undertaken on the 200 kVA DC arc furnace with the specific objectives of determining whether a 65 per cent Cr content HCFeCr alloy with its associated higher solidus temperature could be tapped from a DC arc furnace. It was also hoped that alloys having less than 4 per cent Si could be produced, unlike the submerged-arc furnace results.

The campaigns utilised both high and low basicity HISLAG materials and proceeded smoothly. The slags produced contained an average of 5.5 per cent  $\text{Cr}_2\text{O}_3$  while the alloys contained 66 per cent Cr, 0.8 per cent Si and 7.6 per cent C for the low basicity campaign and 60 per cent Cr, 3.2 per cent Si and 8.1 per cent C for the higher basicity campaign.

#### **THE PRODUCTION OF LOW-CARBON FERROCHROMIUM**

The production of a low carbon ferrochromium alloy (LCFeCr) containing greater than 65 per cent chromium, was the overall goal of the investigation because this represents the most valuable ferroalloy product. The investigation was undertaken in three parts. The first part simulated the commercial reladling process in a DC arc furnace operated at the 35 kW power level. The second part involved a preliminary plant trial, where the chromite coolant used in the exothermic plant reladling process was replaced with 500kg batches of HISLAG. The third and final part consisted of a full-scale plant trial where a large portion of the natural chromite ore in the lime-ore melt, was substituted with HISLAG.

### 35 kW Pilot-Plant Testwork

The pilot-plant investigation of the use of HISLAG to produce a high-grade LCFeCr product, involved three distinct stages of experimental testwork, namely:

- STAGE I: Simulation of the existing plant operation, using plant raw materials, in a single-stage DC arc furnace.
- STAGE II: Simulation of the substitution of HISLAG for chromite ore in the lime-ore melt.
- STAGE III: Evaluation of the effect of the high carbon content of HISLAG on a proposed plant scale lime-ore /HISLAG melt test.

#### Stage I: Simulation of the existing plant operation

The Middelburg plant operates a modification of the classical Perrin process in which a lime-ore melt and FeCrSi are reacted in a multiple reladling operation to produce LCFeCr. Obviously, a complete simulation of the plant process is extremely difficult to perform on a pilot plant. Consequently, the process was simplified by assuming that it was only necessary to simulate the "refining" ladle.

Plant raw materials were employed and the 100 kVA DC arc furnace with a 200mm internal diameter was used. Chemical analyses of the raw materials employed for the testwork, are shown in Table 4. The charge recipes tested were based on a lime-ore ratio of 0.67, and a silicon-to-reducible species (Cr<sub>2</sub>O<sub>3</sub> + FeO) ratio of 0.24. A technique of stagewise melting as opposed to co-melting was employed, because it results in a higher Cr recovery, but a poorer Cr:Fe ratio, presumably due to the greater selectivity for the reduction of oxides of Fe than Cr in the liquid slag (a similar effect was observed by Volkert)(14). This involved the formation of a lime-ore melt at the 35 kW power level over 45 minutes, followed by stagewise addition of cold FeCrSi over 15 to 30 minutes and was used in all subsequent 35kW pilot plant testwork.

The result of the best test performed indicated that the production of LCFeCr could be simulated in a single-stage operation. The metal produced was very similar in composition to that being produced at the plant (see Table 5), although the slag contained a higher level of Cr<sub>2</sub>O<sub>3</sub> (9.1 per cent) than the prevailing plant slag (5.1 per cent).

#### Stage II: Replacement of ore by HISLAG in the lime-ore melt

Two types of HISLAG were used (see Table 4), a low basicity (0.6), medium Cr:Fe ratio (4.9) material (HISLAG 'A') and a specially selected high basicity (1.1) but high Cr:Fe ratio (10.0) material (HISLAG 'B').

Chemical analysis of the HISLAG material produced earlier revealed that these slags had a high carbon content (0.11 to 0.77 per cent, see Table 4). Mineralogical examination of the slags showed that entrained metallics were the major source of carbon contamination. The alloy produced during the tests in which a mild steel anode was used contained as little as 0.06 per cent carbon however (see Table 5).

The major conclusions of the stage II testwork to investigate the production of LCFeCr, by substitution of HISLAG for ore in the lime-ore melt can be summarised as:

- \* The high level of carbon contamination of the HISLAG (by entrained metallics), did not appear to adversely affect the final alloy carbon content.
- \* The desired degree of silicon refining of the alloy (1 per cent Si) was found to be primarily a function of good slag-metal contact and enhanced interfacial mass transfer rates (achieved through rocking the furnace and "cocktailing" its contents).
- \* Excessive lime additions were not necessary to achieve effective refining of the silicon content of the alloys produced from low basicity HISLAG.
- \* The low total reducible oxides (Cr<sub>2</sub>O<sub>3</sub> and FeO) content of the HISLAG manifested itself in a slag-to-metal ratio almost twice as high as the existing plant practise (5.6 compared to 2.1).
- \* Experimentally the use of mild steel anodes in the furnace permitted low alloy carbon contents to be attained, at the expense of diluting the alloy Cr:Fe ratio, while the use of graphite and graphite impregnated magnesia anodes permitted tight control over the alloy Cr:Fe ratio, at the expense of alloy carbon contents.

#### Stage III: The effect of the carbon content of HISLAG in a lime-ore/HISLAG melt

Calculations of the use of a blend of HISLAG and chromite ore in a lime/ore-HISLAG melt, had predicted that the final alloy produced from such a melt could have a carbon content substantially above the maximum allowable 0.05 per cent specification. Therefore a more detailed series of test were undertaken to investigate this important aspect.

A series of seven, 15kg lime/ore-HISLAG melts were produced at the 35 kW power level, in a DC arc furnace campaign, using ratios of HISLAG to chromite of between 50:50 and 75:25. A mild steel anode was used in the furnace to ensure that tight control could be achieved on the overall carbon balances of each test.

Table 4 : Raw materials analysis, (% by Mass) for the LCFeCr testwork

| ANALYSES                       | FeCrSi       | Chromite     | HISLAG 'A'    | HISLAG 'B'   | LIME          | HISLAG 'C'   | HISLAG 'D'<br>(after jiggling) |
|--------------------------------|--------------|--------------|---------------|--------------|---------------|--------------|--------------------------------|
| <b>Oxides</b>                  |              |              |               |              |               |              |                                |
| Cr <sub>2</sub> O <sub>3</sub> | -            | 47.0         | 36.47         | 32.03        | -             | 26.1         | 29.2                           |
| FeO                            | -            | 20.7         | 6.58          | 2.82         | 0.35          | 3.8          | 10.62                          |
| SiO <sub>2</sub>               | -            | 3.65         | 25.30         | 22.15        | 2.20          | 27.4         | 16.5                           |
| CaO                            | -            | 0.36         | 0.52          | 0.76         | 95.40         | 0.8          | 8.3                            |
| MgO                            | -            | 12.2         | 15.49         | 23.40        | 1.75          | 16.5         | 12.8                           |
| Al <sub>2</sub> O <sub>3</sub> | -            | 11.1         | 19.51         | 17.44        | 0.35          | 20.6         | 18.79                          |
| MnO                            | -            | 0.23         | 0.35          | -            | 1.04          | -            | -                              |
| <b>Metallics</b>               |              |              |               |              |               |              |                                |
| Cr                             | 28.80        | -            | -             | -            | -             | -            | -                              |
| Fe                             | 20.75        | -            | -             | -            | -             | -            | -                              |
| Si                             | 48.25        | -            | -             | -            | -             | -            | -                              |
| C                              | 0.09         | 0.13         | 0.77          | 0.11         | 0.67          | 0.27         | 0.57                           |
| <b>Ratios</b>                  |              |              |               |              |               |              |                                |
| B*                             | -            | 3.44         | 0.63          | 1.09         | -             | 0.63         | 1.28                           |
| Cr:Fe                          | 1.39         | 2.00         | 4.88          | 10.00        | -             | 3.96         | 2.42                           |
| <b>TOTAL</b>                   | <b>97.89</b> | <b>95.37</b> | <b>104.98</b> | <b>98.71</b> | <b>101.76</b> | <b>97.47</b> | <b>96.82</b>                   |

\* B = Basicity ratio (% CaO + %MgO)/%SiO<sub>2</sub>

Table 5: Summary of results from the LCFeCr testwork

| Test Conditions                 |                                   |                      |   |                        | Average product analyses (mass %) |      |       |       |                                |      | Slag/meta<br>l<br>ratio |
|---------------------------------|-----------------------------------|----------------------|---|------------------------|-----------------------------------|------|-------|-------|--------------------------------|------|-------------------------|
| Test<br>type                    | HISLAG<br>type                    | Anode type           | Si/<br>(Cr <sub>2</sub> O <sub>3</sub> +FeO)<br>ratio | Lime<br>'ore'<br>ratio | Metal                             |      |       | Slag  |                                |      |                         |
|                                 |                                   |                      |   |                        | Cr                                | Si   | C     | Cr/Fe | Cr <sub>2</sub> O <sub>3</sub> | FeO  |                         |
| Plant in<br>June '85            | Chromite<br>only                  | N/A                  | 0.24  | 0.67                   | 61.6                              | 0.91 | 0.04  | 1.63  | 5.1                            | <1.0 | 2.1                     |
| 35 kW                           | Chromite<br>only                  | mild steel           | 0.24  | 0.67                   | 57.9                              | 1.12 | 0.05  | 1.50  | 9.1                            | 0.14 | 2.8                     |
| 35 kW                           | HISLAG<br>'B'                     | mild steel           | 0.25  | 0.67                   | 52.8                              | 12.4 | 0.06  | 1.67  | 10.5                           | 0.68 | 8.2                     |
| 35 kW                           | HISLAG<br>'A'                     | conducting<br>hearth | 0.20  | 0.76                   | 65.3                              | 0.66 | 1.1   | 2.14  | 6.0                            | <0.8 | 5.6                     |
| Plant<br>coolant<br>trial       | Chromite<br>only                  | N/A                  | -   | -                      | 58.0                              | 0.5  | 0.025 | -     | 5.6                            | 0.4  | -                       |
| Plant<br>coolant<br>trial       | HISLAG<br>'C'                     | N/A                  | -   | -                      | 59.7                              | 0.50 | 0.024 | -     | 5.1                            | 0.4  | -                       |
| Plant<br>coolant<br>trial       | HISLAG<br>'D'<br>Blend 1<br>(50%) | N/A                  | -   | 0.7                    | 61.9                              | 0.84 | 0.047 | -     | -                              | -    | -                       |
| Full<br>scale<br>plant<br>trial | HISLAG<br>'D'<br>Blend 2<br>(75%) | N/A                  | -   | 0.7                    | 63.7                              | 0.98 | 0.053 | -     | -                              | -    | -                       |
| Full<br>scale<br>plant<br>trial | HISLAG<br>'D'<br>Blend 3<br>(75%) | N/A                  | -   | 0.7                    | 63.9                              | 0.82 | 0.045 | -     | -                              | -    | -                       |

The highest carbon content recorded for a lime-ore/HISLAG melt was 0.04 per cent. Calculation of the carbon balance over the melts showed that more than 91 per cent of all the carbon introduced into the system had been removed by oxidation. It appeared that oxidation of carbon occurred either by surface oxidation of the melt, or by carbon dioxide gas, released into the melt by decomposition of the residual CaCO<sub>3</sub>. If the latter was the dominant mechanism, the efficiency of oxidation of carbon demonstrated on the pilot-plant scale should be repeated on the plant.

#### Preliminary Industrial Trial

A preliminary small-scale trial was conducted at the Middelburg plant, whereby 500kg of HISLAG 'C' was added as coolant for four consecutive taps (see Table 4 for chemical analysis of this HISLAG). The major objective of the trial was to evaluate the effect of the high carbon content (0.27 per cent) of the HISLAG

on the final alloy carbon content. A subsidiary objective was to compare the alloy chromium grade obtained from the HISLAG with that obtained using Transvaal chromite fines as the coolant.

The series of four consecutive tests was far too short for a quantitative interpretation to be made of the results achieved. However, the results were extremely encouraging in that carbon contamination of the alloy did not occur. An average alloy carbon content of 0.024 per cent was achieved over the 4 tests conducted.

A further encouraging feature of the trials was that the chromium added via the coolant stream effectively reported to the alloy, to improve the alloy chromium content from 58.0 per cent to 59.7 per cent Cr. The low chromic oxide content of the discard slag (1.8 per cent Cr<sub>2</sub>O<sub>3</sub>) supported this conclusion. However, a 500kg chromite coolant addition effectively introduced less than 5 per cent of the total chromium units to the process. A HISLAG coolant addition in excess of 3.lit would have been required to

achieve greater than 65 per cent Cr in the final alloy. Such a coolant addition could not be accommodated on the plant, so that the use of HISLAG as a coolant could not be considered a realistic means of achieving a 65 per cent chromium grade alloy.

#### Full-scale Industrial Trial

After careful evaluation of the results of the preliminary pilot-plant testwork, a lime/(ore + HISLAG) ratio of 0.7 was selected for the full-scale plant trial. Three blends of chromium source material were selected for investigation, namely:

- Blend 1 - HISLAG/Marico ore = 50/50
- Blend 2 - HISLAG/Marico ore = 75/25
- Blend 3 - HISLAG/TCL ore = 75/25

Marico chromite ore had a Cr:Fe ratio of 1.71 compared with the 1.55 ratio in TCL chromite. The slag was processed through a jiggling plant prior to the testwork and 8 per cent by mass metallics and sand was removed. This resulted in HISLAG 'D' containing a Cr:Fe ratio of 2.42, (see Table 4) which was considerably lower than the Cr:Fe ratio in the original material (2.86).

Thirty taps of Blend 1, 18 taps of Blend 2 and 7 taps of Blend 3 were successfully processed in the LCFeCr reladling operation. High chromium (>65 per cent Cr) LCFeCr was successfully produced for 15 taps out of the total trial of 55 taps, at a 27,3 per cent success rate. No doubt a higher success rate would have been achieved had the Cr:Fe ratio of the HISLAG been as high as the 2.8 value initially expected. Higher success rates would also have been achieved had the trial been conducted under a more stable furnace operating condition, especially with regards to the lime/(ore + HISLAG) ratio and the feed/power ratio of the furnace.

The average final alloy carbon analyses achieved after the plant trial, revealed that carbon levels were generally normal (<0.053 per cent C, see Table 5). However, the sulphur content of the final LCFeCr alloy increased progressively throughout the trial, from 0.011 per cent for Blend 2 to 0.024 per cent for Blend 3. The precise reasons for the increased sulphur levels in the alloy still require further clarification, but entrained metallics could have been responsible.

The silicon content of the alloy was found to be less than 1 per cent Si on a daily average and this demonstrated that effective refining of the alloy could be achieved, with only a marginally higher lime addition, when the silica-rich (16.5 per cent SiO<sub>2</sub>) HISLAG was used. Furthermore, the final discard slag was effectively stripped to 2.14 per cent Cr<sub>2</sub>O<sub>3</sub> and 0.47 per cent FeO on average.

Finally, as expected, the lower total reducible species (Cr<sub>2</sub>O<sub>3</sub> and FeO) content of the HISLAG manifested itself in a slightly lower nett alloy throughput of 4.1 t/tap, compared to 4.8 t/tap achieved in conventional plant operation. Thus, it could be concluded that HISLAG could be used to produce high grade (>65 per cent Cr) LCFeCr.

#### PROCESS EVALUATION

The most economically attractive product was a low-carbon ferrochromium (LCFeCr) with a 65 per cent Cr content using HISLAG material to replace the increasingly expensive high Cr:Fe ratio chromite ores required to attain this grade. The use of HISLAG to attain this target can be achieved in at least three different ways (see Figure 3) and a preliminary economic evaluation of the optimum route was undertaken.

Mass and energy balances were used to calculate a detailed process flowsheet for each of the three process options considered. The most reliable available data were used, but where insufficient information existed, particularly with regard to dust and fume losses, assumed values were used.

The raw material and energy costs for each route were calculated from these flowsheets and compared with the existing process. All the new process routes have costs per ton of LCFeCr that depend very strongly on the selling price of the intermediate, low-chromium content FeCr alloy co-produced with the HISLAG (see Figure 3). The mass of this alloy per ton of LCFeCr varies between 0.70t and 0.75t for the three routes considered.

The 'wet' route emerged as the lowest cost route in terms of raw materials and energy, principally because it involves one fewer process step than the other routes, but is technically the most uncertain. The 'dry-route' was the next lowest in cost but probably the most costly in capital and manpower requirements because of the number of process steps. The technical feasibility appears to be good based on the Mintek testwork but the production of HCFeCr from HISLAG has not been tested at a plant scale. The 'lime-ore/HISLAG' route was the most costly in raw materials and energy but has been demonstrated at full industrial scale and involves fewer additional process steps than the 'dry-route'.

All the process routes have in common a DC arc furnace (to produce the necessary HISLAG) which would need to be rated at between 10 and 12 MW to produce 20 000 tons per annum of LCFeCr with a 65 per cent Cr grade.

#### CONCLUSIONS

6.1 The production of a slag (HISLAG) containing up to 30 per cent Cr<sub>2</sub>O<sub>3</sub> at a Cr:Fe ratio of between 2.6 and 4.5 has been demonstrated at scales between 1 MW and 8 MW from Transvaal chromites with a Cr:Fe ratio of 1.6 by selective carbothermic reduction in a DC arc furnace.

6.2 The carbothermic reduction of this HISLAG material to form a high-carbon ferrochromium has been accomplished with good metallurgical recoveries at the 300 kVA level in a pilot plant submerged-arc furnace and in a DC arc furnace. The HCFeCr produced from the submerged-arc furnace generally contained between 5 and 10 per cent silicon, depending on the basicity of the HISLAG, while the DC arc furnace yielded silicon contents of between 1 and 3 per cent.

6.3 The replacement of up to 75 per cent of the chromite by HISLAG in the lime-'ore' melting furnace at Samancor's Middelburg plant was successfully demonstrated. Additional lime was not required and the subsequent production of LCFeCr with a 65 per cent Cr content was accomplished without an increase in the alloy carbon content and with unimpaired chromium recovery.

6.4 The economic viability of the various methods of using HISLAG to produce a high-grade LCFeCr depends very strongly on the cost effective use in the stainless steel plant of the low Cr:Fe ratio ferrochromium alloy by-product (at the rate of ~0.73 t/t of LCFeCr).

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