Implementation of a Novel Technology for the Recovery of Cobalt from Copper Smelter Slags

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Abstract

In January 2001, Chambishi Metals commissioned a 40MW DC arc furnace using selective carbothermic reduction for processing reverberatory furnace slag stockpile of 20 million tons containing 0.34 to 4.5% cobalt, and an average of 1.1% copper. Cobalt occurs as faylite whereas copper occurs as oxide and sulphide. An atomizer unit to atomize furnace product, molten Co/Cu/Fe alloy, and a pressure oxidation leach process to leach cobalt and copper and separate iron as goethite was also commissioned. Cobalt and copper containing solution is processed in the refinery for production of metals.

The commissioning and ramp up period was much longer than projected due to premature failure of the hearth and other operational problems associated with the feed system, cooling system and power control. Furnace availability was low and affected the throughput and metal production. This had put tremendous pressure on the company due to poor cash flow and non repayment of the capital resulting in sale of 100% of its share in July 2003. A systematical analysis initiated then, to de-bottleneck the furnace operation, was successful, resulting in attainment of design throughputs. The Plant Historian Database (PHD) was used for the analysis.

Commercial application of the DC arc furnace on smelting of copper smelter slag was unique and therefore required extensive literature search to broaden the knowledge of the theory and the practice.

The thesis shows improvements and modifications carried out on feed system to create charge bank, selection of flux to modify the slag chemistry, modification of alloy chemistry, re-configuration of the power control system and increased atomization

capacity. Following the implementation of these, the furnace performance attained design levels.

Extended Abstract

1.0 Introduction

After 1991, at the time of the commencement of the privatization process of the mining conglomerate “Zambia Consolidated Copper Mines”, Chambishi Cobalt Plant was packaged with the 20 million tonnes slag stockpile. The cobalt grade of the slag ranged from 0.34% to 4.5% where as copper averaged 1.2%.The stockpile was created over a period of 60 years since 1935 by dumping the slag generated from the Rokana Copper Smelter. Anglovaal Mining of South Africa purchased this package in 1998. Due to declining production of Cu/Co sulphide concentrates which was the traditional feed to the plant, an addition of a process for treatment of slag for production of cobalt and copper, to sustain Chambishi’s viability, became essential.

Carbothermic reduction was selected to be an economically viable option. Pilot scale test work was conducted at Mintek, RSA, using a DC arc furnace for determination of the operating parameters. The project was then executed and a 40MW DC furnace was commissioned in 2001.

The commissioning period was much longer than projection of three months. Until July 2003, only 50% of the annual throughput target rate of 300000 tonnes could be achieved. The furnace suffered failures of hearth lining, upper sidewall lining and copper cooling elements in the slag/metal zone. These major failures restricted the de-bottlenecking of the operation.

In July 2003, the ownership changed to Enya Holding when a systematical analysis was undertaken for de-bottlenecking, the throughput started approaching target levels almost immediately. Extensive literature search was carried out to study all aspects of smelting operation and relate those to the plant data extracted from Plant Historian Datasheet (PHD). Several improvements in the operations and the modifications carried out are discussed.

2.0 Mineralogy of the Slag

Mineralogical analysis of the slag carried out by MINTEK, RSA, is shown in the table 1, indicate that the cobalt is present as faylite (Iron Silicate Matrix) where as copper is present as oxide, sulphide and metal. Presence of significant level of sulphide and metallic copper are due to entrained losses.

Table-1: Mineralogical composition of the Rokana Reverberatory Slag

Group Total Co	Mineral Phases	% of Total Cu	% of Total Co
Slag	Fe, Ca, Al (Mg, K, Co, Cu) - Silicates	46.6	94.6
Spinel	Fe(Al, Cr, Ti, Ca, Co, Cu) - Oxides	1.1	5.2
Sulphide	Cu(Co, Fe) - Sulphide	39.3	0.2
Metal	Cu(Co, Fe) - Metal	13.0	<0.1
	Total	100.0	100.0

Figure 1 below is the picture of the Rokana slag dump. The cobalt grade varied significantly as shown in figure 2. The tonnages and the grades were estimated using metallurgical accounting records of Rokana copper smelter. Few drill samples were taken for chemical analysis due to cost and time constraints. The chemical analysis of those samples indicated resemblance with the analysis obtained from the smelter records.

Fig.1: Picture of the Rokana Slag Dump- View from Ndola-Kitwe Road Side

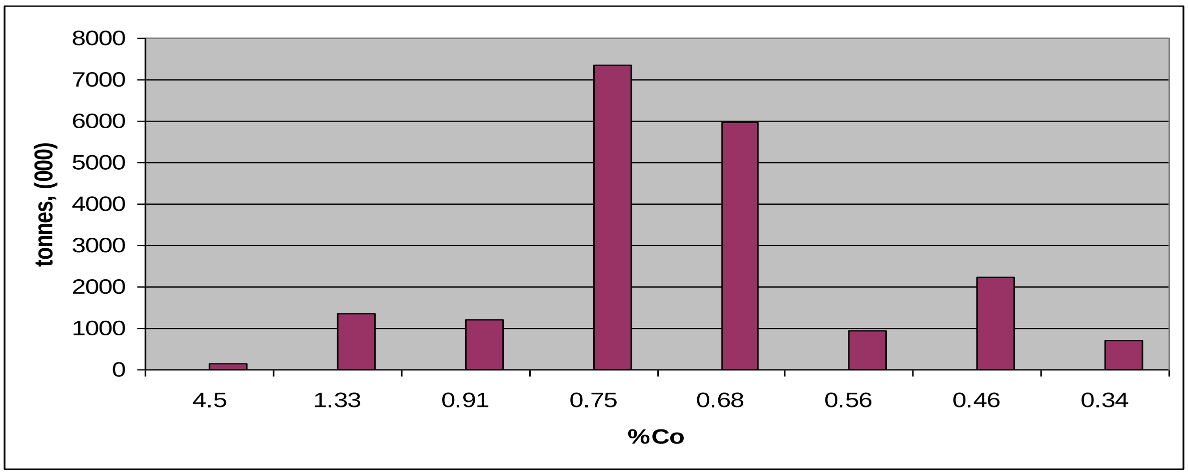


Fig.2: Estimated Tonnage and Grade Distribution on the Rokana Slag Dump

The cobalt grades were as high as 4.5% reducing to 0.34%. Majority of the slag averaged 0.7% Co. The variations were due to variations in the concentrates feed mix to the Rokana Copper Smelting furnaces.

3.0 Theory of Carbothermic Reduction

The chemical reactions occurring in metallurgical processes such as reduction of metal oxides can be explained in terms of free energy in thermodynamics. The reduction of metal oxides is obtained using carbon which is available cheaply in reduced form as coal / coke. Moreover, when carbon reacts with oxygen, it forms gaseous oxides i.e. Carbon monoxide and carbon dioxide, therefore the dynamics of its oxidation is different from that of metals whose oxidation has a more negative ∆G at higher temperatures. Carbon is therefore acts as reductive agent both in element phase and in monoxide phase.

Figure 3, Ellingham Diagram, shows the conditions under which a metal oxide can be reduced to a metal. The standard Gibbs free energy of formation of the oxide is considered, for example, $M+½O_2 \rightarrow MO$ The value of ΔG is plotted against temperature. In general, the result is a straight line. In some cases, there is an abrupt change in the line’s slope at a point because of a phase change. The value of ΔG for the reducing agent is also plotted. For example, if the reducing agent is carbon forming carbon dioxide, it is ΔG for the reaction $C+O_2 \rightarrow CO_2$. Reduction can occur in the range of temperatures in which the carbon curve is lower than the metal curve.

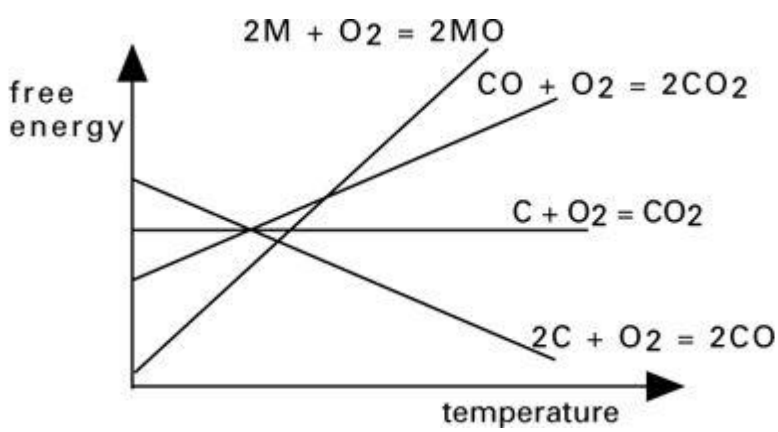


Fig.3: Gibb’s Free Energy-Temperature Diagram (Ellingham Diagram)

Jones, et el [7,47] developed relationship between carbon addition and nickel, cobalt and iron recoveries. Taking advantage of the finding that the cobalt reduction is much faster than iron, a relationship between % iron reduction and cobalt recovery was developed as shown in figure 4.

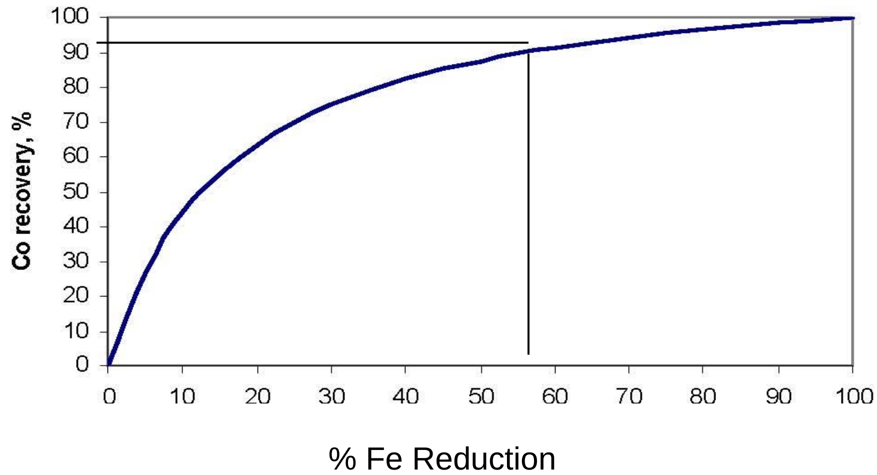


Fig.4: % Fe Reduction vs. % Cobalt Recovery

In order to maximize cobalt recovery and minimize iron recovery, this work became the basis of optimal coal addition. Coal addition rate to achieve 56% iron recovery to the alloy, almost 90% cobalt recovery was achieved. It was necessary to optimize down stream processing plant size and efficiency. Higher iron content in the product would increase the cobalt losses through the residue, goethite.

4.0 Process Description

Following commissioning of the 40 MW DC Arc furnace in the year 2001, the Chambishi operation's flow sheet is shown in figure 5.

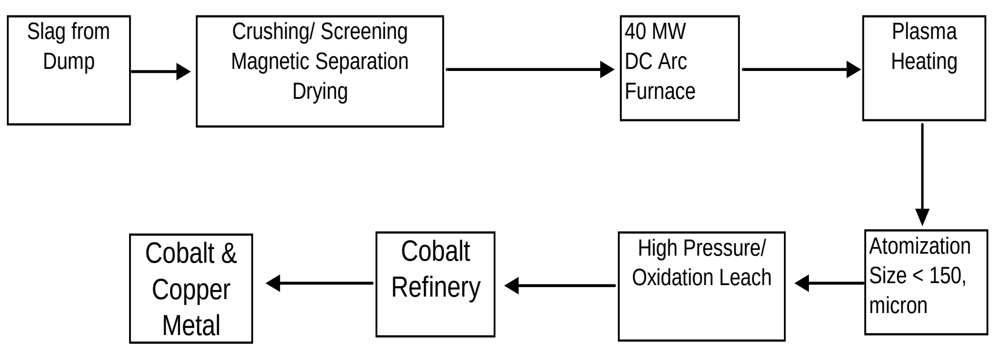


Fig.5: Simplified Flow Chart of Chambishi Operation after 2001.

The slag excavated from the dump, crushed and screened to +6, -16mm particle size, beneficiated to high grade the furnace feed by 15 – 20%, dried to reduce moisture to <1%, is fed to the furnace. Furnace product is an alloy of cobalt, copper and iron. Molten alloy is tapped and atomized to <150 micron particle size which is pumped to the pressure/oxidation leach plant for leaching cobalt and separating iron as goethite. The leach solution containing cobalt, copper and other trace impurity elements is processed in cobalt refinery for cobalt and copper metal production.

5.0 Commissioning and Ramp Up

Figure 6 indicate that the projected furnace power was only attained in the year 2003. The attainment of design power level of 40MW was the first necessary step to achieve design throughput. The projected total energy consumption was only attained after July 2003 with the start of systematical analysis and de-bottlenecking. With the progress of improvements, the furnace power exceeded the projected levels.

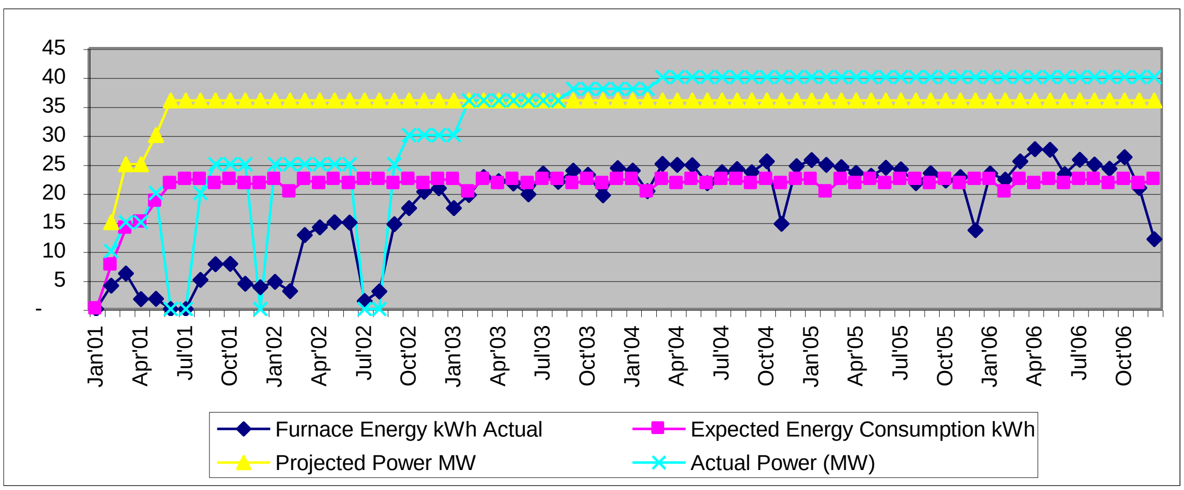
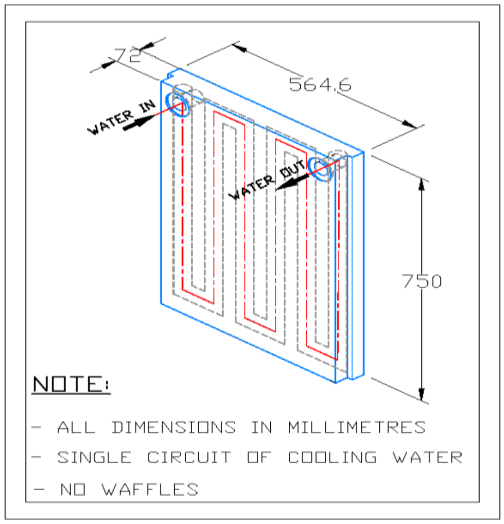


Fig.6: Furnace Power – Actual vs Projected

Prior to the year 2003, major change undertaken, was the replacement of copper cooling elements in the slag/metal bath in the year 2002. The original Fuch's coolers (fig.7) were replaced with Hatch coolers (fig.8). Fuch's coolers had single water cooling circuit with the flat copper plate facing the molten slag/alloy whereas Hatch coolers had double cooling circuit with waffles. The waffles helped in an efficient formation of the freeze layer as well as retained it firmly to protect the cooling element. Despite this change, the furnace performance did not improve significantly as shown in figure 9. Even at lower furnace power, the heat flux on the copper cooling elements were very high at 4 - 5MW against design of 2 - 2.5 MW causing stoppages. Continued exposure of copper coolers to heat could have resulted in catastrophic failure, water ingress in the molten bath and therefore explosions. The downward trend only started after July 2003 when the improvements commenced. The high heat flux, sensed by the rate of change of water temperature was causing furnace stoppages due to safety reasons. A systematical analysis was then initiated for de-bottlenecking.



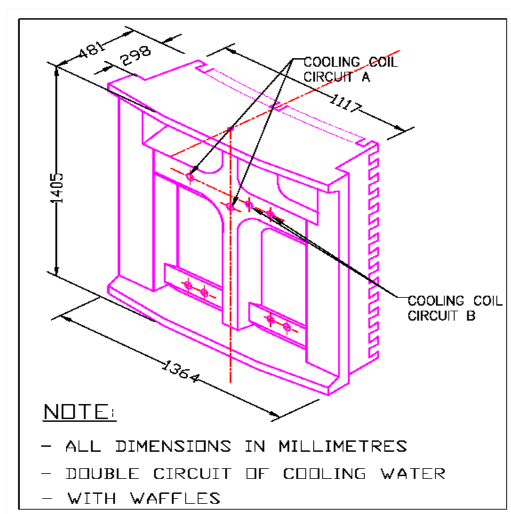


Fig.7: Sketch of the Fuch's Coolers

Fig.8: Sketch of the Hatch Coolers

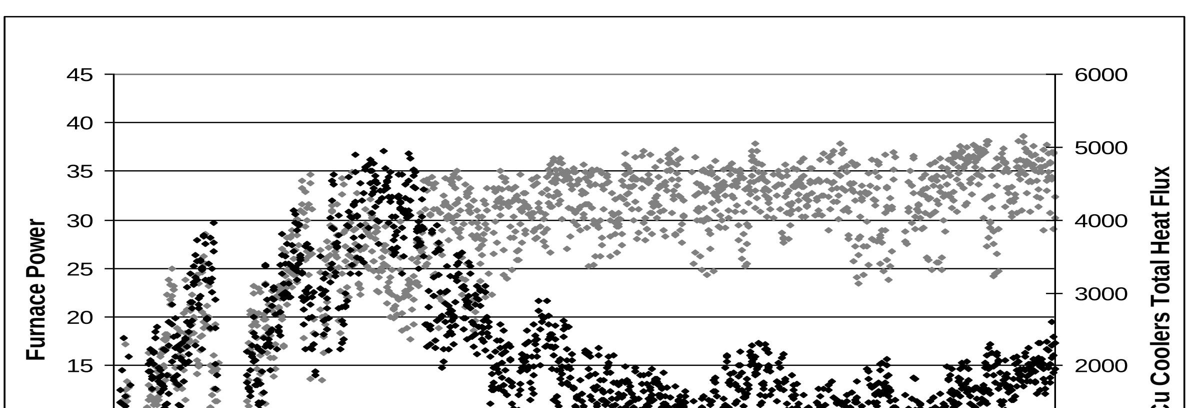


Fig.9: Furnace power vs. Copper Coolers total Heat Flux.

6.0 De-bottlenecking

De-bottlenecking commenced with the analysis of the root causes of the furnace stoppages. The analysis of maintenance and operational activities (fig.10) clearly indicated that main reasons for furnace stoppages were operational.

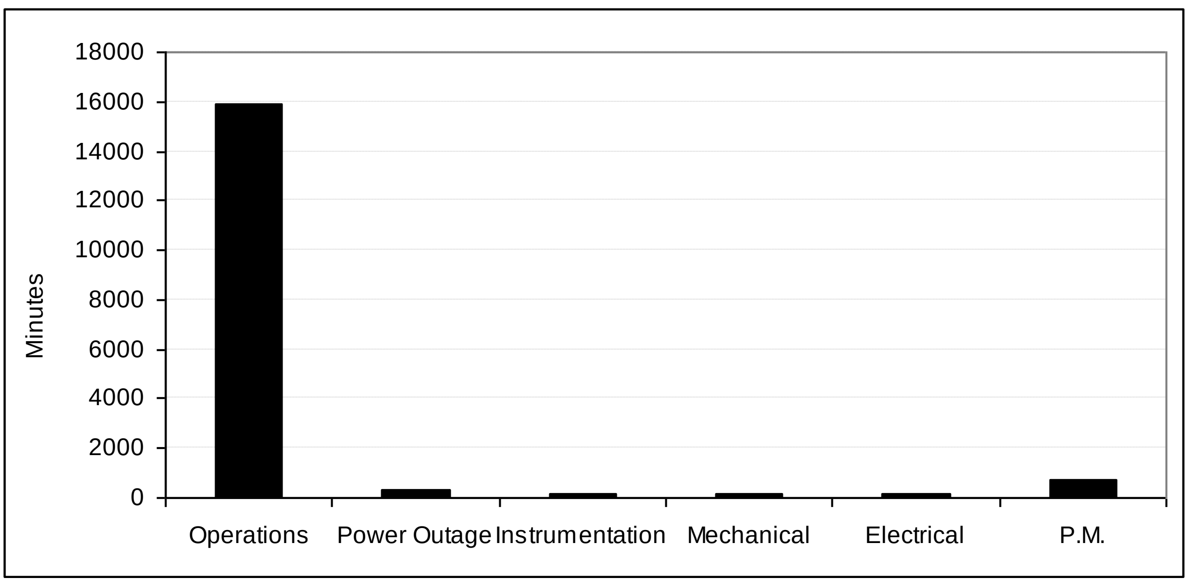


Fig. 10: Furnace Stoppage due to Maintenance Activities

The analysis of the operational activities (Figure 11) shows the major causes for furnace stoppages as:

1. Power trip outs due to copper coolers experiencing high heat flux above set point.
2. Plasma torch failures/maintenance causing alloy tapping constraint which resulted in high level in the furnace and necessitated feed reduction/ power off.
3. Faster wear out of the feed pipes resulting in feed slag spillages on the dome and roof panels needed frequent and longer stoppages for replacement.

Fume duct blockages and inspections were considered necessary activities to ensure timely corrective action for safety of the furnace. Stoppage for electrode addition was a routine and standard requirement.

In view of the above analysis, the focus was to enhance protection of the copper coolers from heat, increase plasma heating capacity and replacement of feed pipes with stronger wear resistant material. Later on, cooling of the roof panels was also improved.

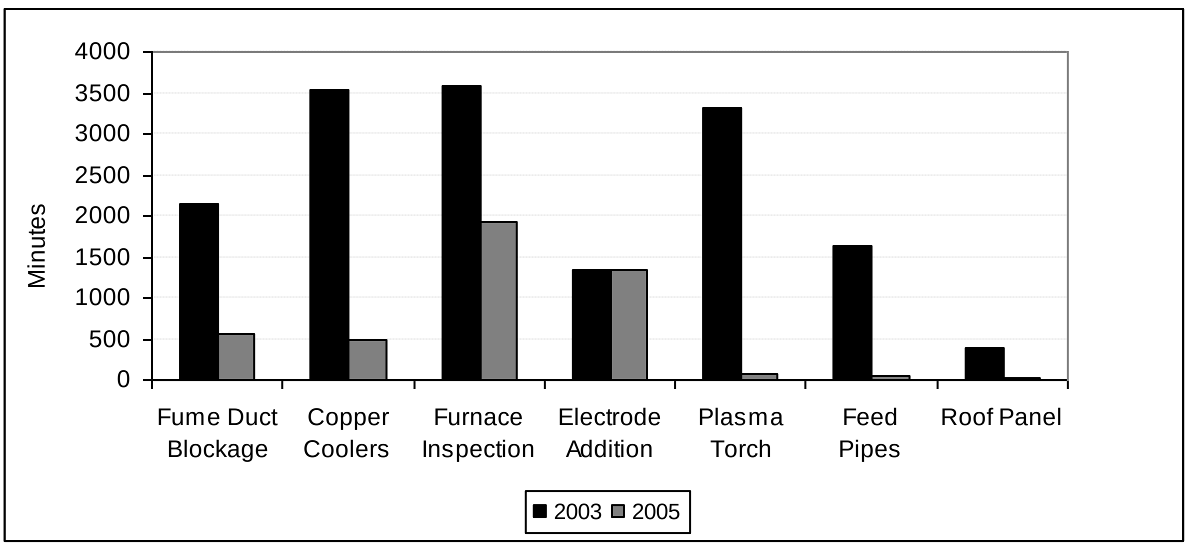


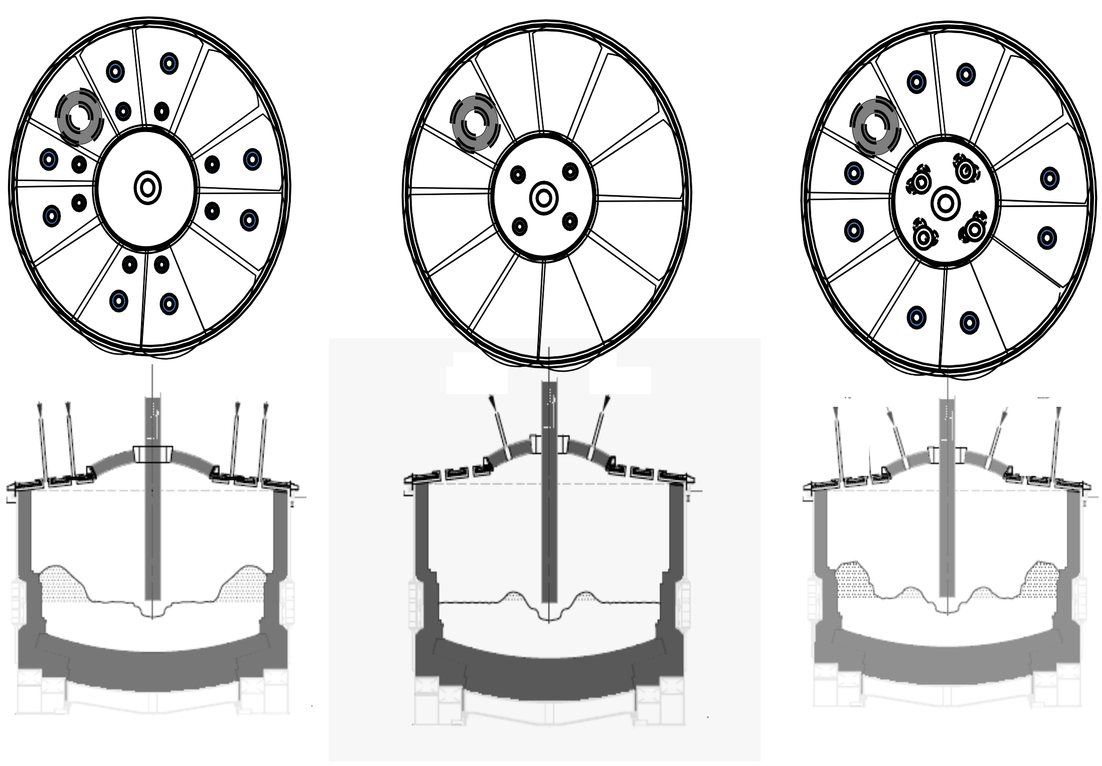
Fig.11: Furnace Stoppage due to Operational Activities

It can be clearly seen that by the year 2005, there was a significant reduction in the furnace stoppages which consequently increased throughput.

6.1. Rearrangement of the Feed Points

Rearrangement of the feed points was the quickest medication which resulted in quenching the bath in front of the copper coolers and reducing the radiant heat on the upper side wall. In the original design, the feed points were located around the inner periphery (fig.12-A). Due to slow flow of the slag towards the arc and not totally shrouding it, the intense radiant heat was damaging the side wall brick work and the shell. Furnace roof was then modified to open feed points around the electrode (fig.12-B) to feed 100% of the material to ensure that the arc is totally shrouded. This had an additional advantage of faster melting rate because of all the material directly entering the arc. The radiant heat, still, could not be contained due to open arc operation and damage to the furnace wall continued resulting in long stoppages. The submerged arc operation was not possible due to Fuch's copper coolers not able to retain freeze layer resulting in high heat flux on them posing safety risks.

In July 2003, the closed feed points on the inner periphery were re-opened and the 10% of the feed was directed through those, keeping 90% through the points around the electrode (fig.12-C). This improved the protection on the side wall resulting in increased furnace availability.



A – Original Design (100% Feed in Front of- Copper Coolers)

B – Changed in Yr.2001 (100% Feed around the- Electrodes)

C – Changed in Yr.2003 (Split Feed – Current)

Fig. 12: Furnace Feed Configurations (Feed Ports shown as Circles-Electrode in the Centre)

6.2 Replacement of Feed Pipes

After the feed ports were reconfigured, the throughput increased but the increased wear rate of the feed pipes resulted in furnace stoppages for clearing spillages and replacements of pipes. A trial on the use of ceramic lined pipes was successful. Photographs of the original wear resistant pipes and the ceramic lined pipes are shown in figure 13.

(A)-4 inch I.D., Original Abrasion Resistant Pipes

(B)-5 inch I.D., Ceramic Lined Pipes

Fig.13: Furnace Feed Pipes

6.3 Stabilization of the Furnace Power

Furnace was experiencing severe power fluctuations which caused erratic feed rates. This resulted in difficulties in controlling slag bath temperature to 1500 – 1550^{0}C. Overfeeding was causing cooling of the bath whereas underfeeding causing high temperature, both changing the resistance. This frequent swing in the bath resistance triggered the electrode movement to maintain power set point, causing power fluctuations. Figure 14 gives the circuit control diagram originally built in PLC. The power fluctuations were experienced due to a sudden drop in resistance causing the power to begin to drop. The controller would try to compensate by increasing the current, thus maintaining the power at the set point, until it eventually reached a maximum limit for the tap position. Once the current reached the maximum limit then the power would fall in line with the resistance. Under these circumstances the tap changer should tap down, thus increasing the allowable current. The ABB controller prevented the transformer from tapping down below tap 10. This was designed to limit the maximum current such that the current density remained under 300A/m2, specified by the supplier. The ABB was convinced to remove the tap changer control from their custom PLC. Chambishi then engineered this functionality into the PlantScape control system.

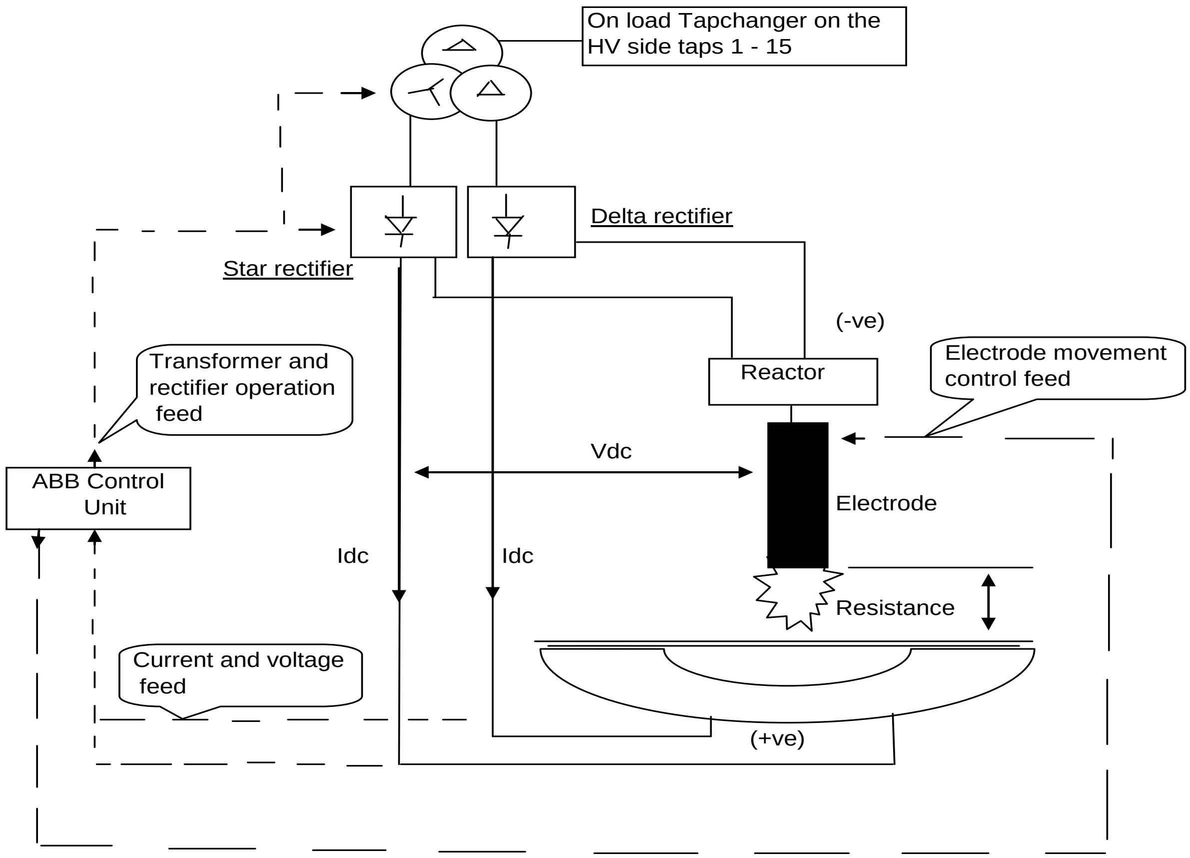


Fig.14: Schematic electrical/control diagram for electrode movement for power control

The advantage of this change was that Chambishi had the flexibility to alter the philosophy whilst retaining the integrity of the safety features built into the ABB control system. The PlantScape system requests a tap change from the ABB system, which executes it if it is safe to do so. The maximum limit for current was set at 70 kA ($250A/m^2$). This meant that the tap setting could safely go down to position 3 (fig. 15) with no safety risks to electrical equipment.

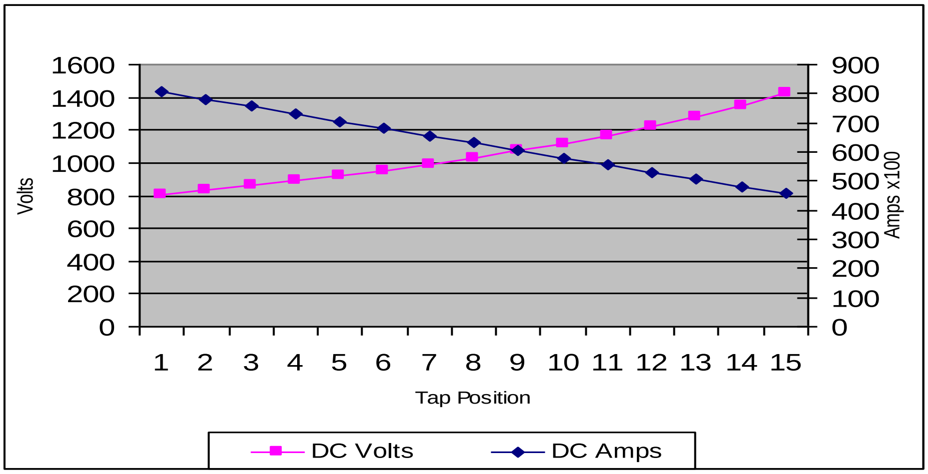


Fig 15: Voltage and Current limits for Tap Positions, 1 – 15.

After this change was made to stabilize the power, the standard deviation improved to 0.84 from 1.6 in the year 2005, indicating a significant improvement as shown in figure 16. The standard deviation improved from 1.6 to 0.847 by the end of the year 2006. The standard deviations are calculated for 6 monthly averages at 40MW power only.

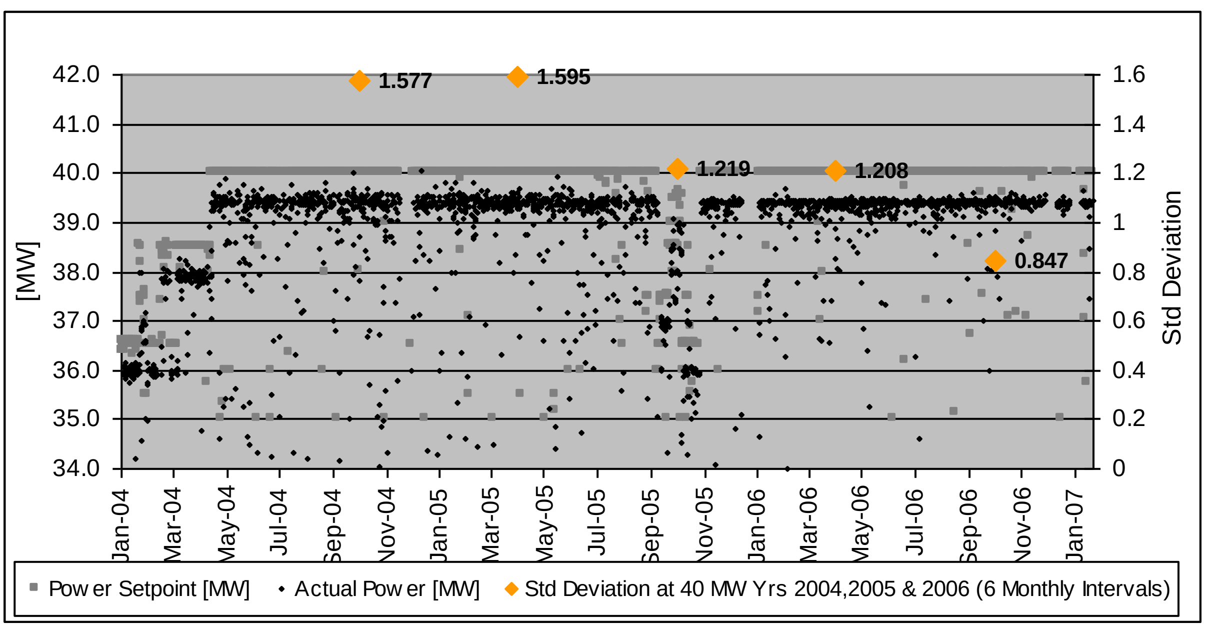


Fig.16: Furnace power set point vs. Actual power (Jan'04 – Jan'07)

6.4 Selection of Flux

Due to availability locally and low price, burnt lime (CaO) was being used to flux iron oxide and silica. The lower melting temperature of the resultant slag, CaO-FeO-SiO_2, at the operating temperature, the formation of the freeze layer was not sufficient for the protection of the Hatch copper coolers. The substitution of the burnt lime with burnt magnesite (MgO) gave adequate freeze layer. The slag MgO-CaO-FeO-SiO_2 has a higher melting temperature spinel phase (1600^{0}C). At an operating temperature of 1500 – 1550^{0}C, the change in the slag chemistry assisted in efficient formation of freeze layer as the same cooling water flow rates to the coolers. Due to the waffle on the Hatch coolers (17-A) the freeze layer is retained securely (fig.17-B), providing better protection against heat flux from the molten bath. Figure 9 clearly shows the benefit of this that the heat fluxes on the copper coolers came down to the 2MW levels which was the specified limit for operation at 40MW power levels.

A- New Hatch Coolers

B- Picture of the Hatch Cooler, Showing Freeze Layer

Fig.17: Hatch Waffle Coolers

6.5 Changing Chemical Composition of the alloy

Due to the slag temperature of 1500 – 1550^{0}C and alloy temperature of 1220 - 1240^{0}C, it was also necessary to modify the chemical composition of the alloy as well such that the tapping is smooth and the atomization is efficient. At lower temperatures, the tapping was difficult resulting in high levels in the furnace and excessive skull formation in the launder and in the atomization unit. Alloy therefore had to be sufficiently fluid to minimize such problem. Mintek, through the test work developed an empirical relationship between the chemical composition and the alloy liquidus as follows:

Liquidus Temperature, ^{0}C = N – 1.6[%Cu – 10] – 26[%S] –80[%C] –8.5[%Si]

Where, N is 1474 for Cu < 12% and 1435 for Cu equal to or greater than 12%. This suggested that higher the copper, lower will be the liquidus.

It was therefore necessary to keep Cu levels above 12% to lower the liquidus such that the plasma heating time is reduced. This eventually reduced tap to tap time and increased furnace out put. It was not commercially recommended to exceed copper concentration beyond 12% because of additional costs. Additionally, there is also a loss of copper through the furnace waste slag. The option of increasing alloy temperature in the furnace by operating at higher slag temperature would not only have adversely affected the productivity but also would have increased wear rate of the lining.

6.6 Installation of the Second Plasma Heating and Atomizer Stations

The second plasma heating and the atomizer station was incorporated to provide flexibility for maintenance such the one unit was always available for operation. This improved tapping from 5 taps a day to 14 taps a day as shown in figures 18 and 19 and completely removed the tapping constraint.

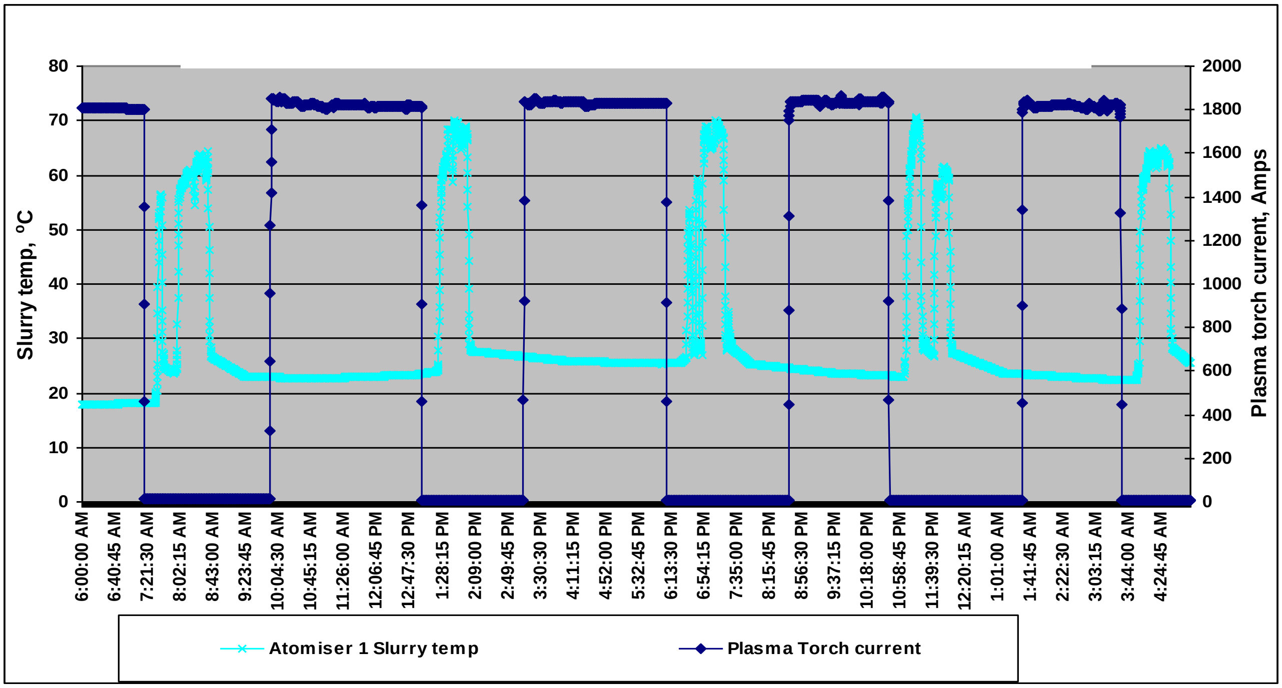


Fig.18: Alloy tapping profile with one plasma torch station and one atomizer (25/12/2005)

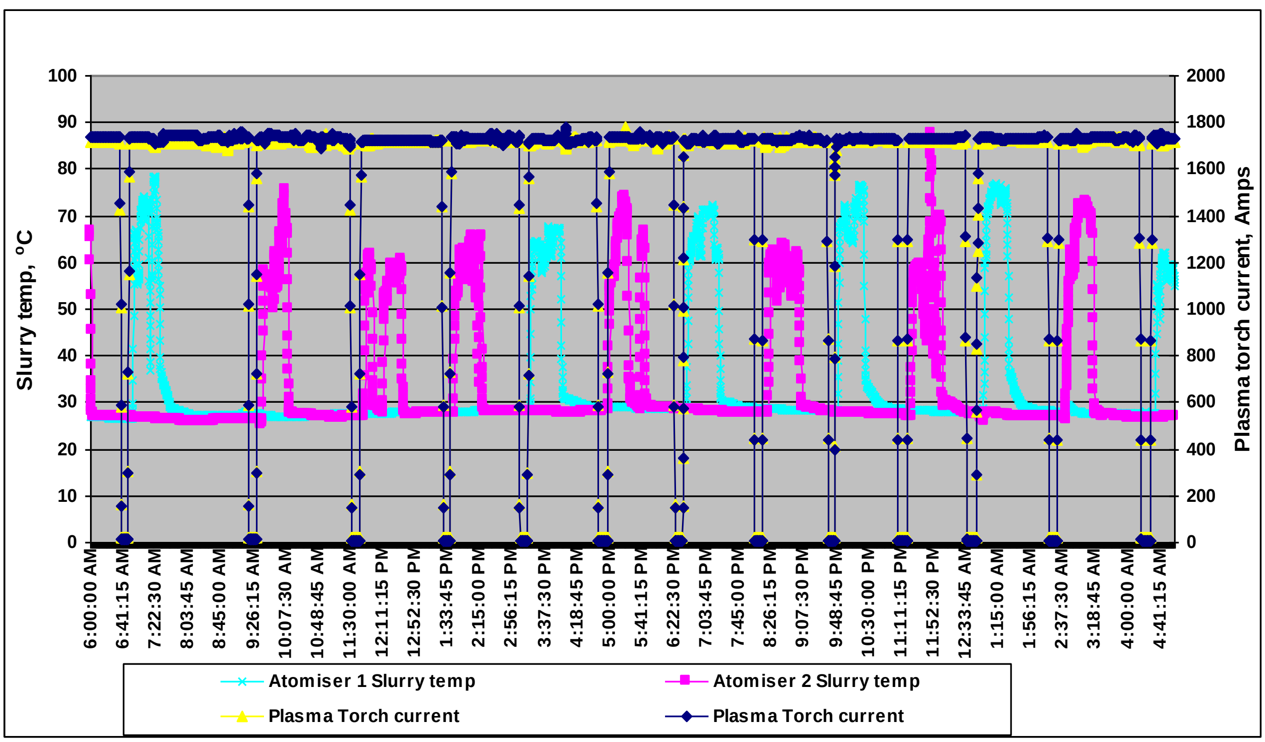


Fig.19: Alloy tapping profile with two plasma torches and two atomizer stations (15/11/2006)

6.7 Improvements in Roof Panels and Electrode Cooling

The original roof panels had single cooling coil. The brush arc mode of operation was casing burning of the refractory and the cooling coil due to flames which resulted in frequent furnace stoppages for replacements. In 2005, the panels were redesigned to have twin cooling coils. The advantage of this was the much longer operating life of panels due to improved cooling and also the flexibility of a planned replacement in the event of failures which avoided unplanned stoppages. The flames were damaging the electrode sealing ring and the dome bricks resulting in premature failures of the dome. Replacement of the dome required extended furnace stoppage. Water cooling around the electrode, above the sealing ring was introduced. This increased the life of the electrode seal and therefore less wear and tear on the dome bricks. The dome replacement frequency was reduced significantly as shown in figure 18. The first replacement was in 2004 after the power was ramped up to 40MW in the later half of the year 2003. There were two replacements in 2004 reducing to one in 2005 and nil after that.

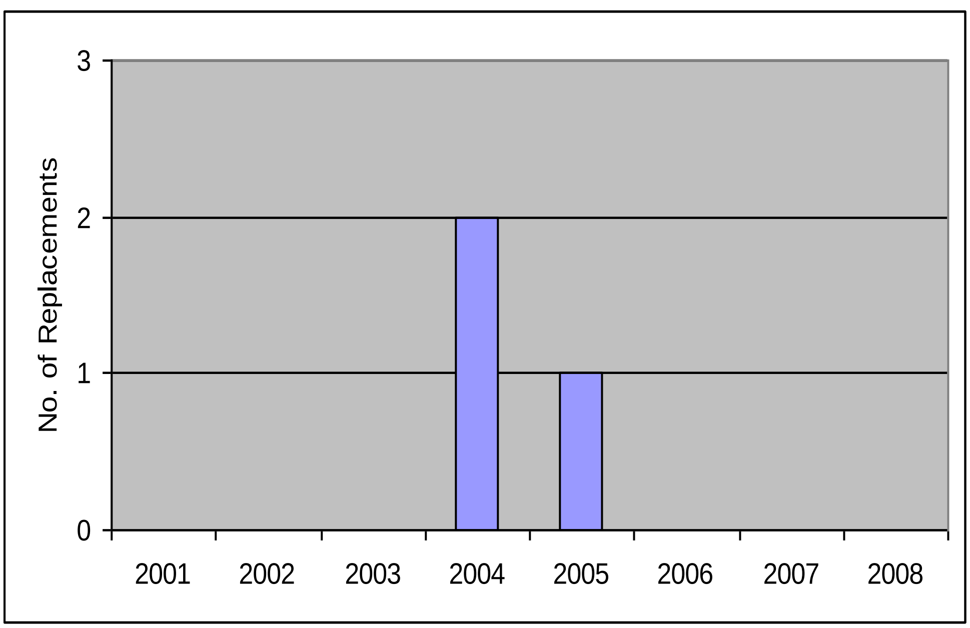


Fig.20: Furnace Dome replacements frequencies from 2001 to 2008

7.0 Fume Extraction

The performance of the fume extraction system improved after power stabilization and the improved integrity of the roof panels and the electrode seal due to improved cooling. Damages to the roof panels and the electrode seal caused air ingress in the furnace resulting in increased gas volume which posed gas handling capacity constraint. This resulted in furnace pressurization and reduced feed for safety and environment controls. The performance further improved by selection of coal which had lower volatiles.

8.0. Results

8.1 Energy Utilization and Throughput

The de-bottlenecking exercise resulted in increase in energy utilization ratio due to improved furnace utilization which eventually increased throughput to design levels as shown in figures 21 and 22.

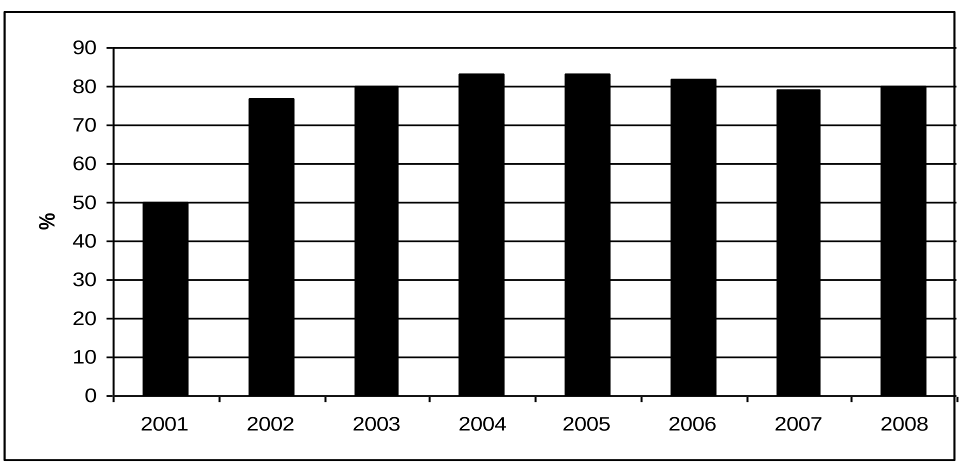


Fig.21: Yearly Energy Utilization Ratios

The energy utilization ratio increased from 50% in 2001 to 80% in the year 2003. Even when there were stoppages in the years 2007 and 2008, the energy utilization still remained at 80% level.

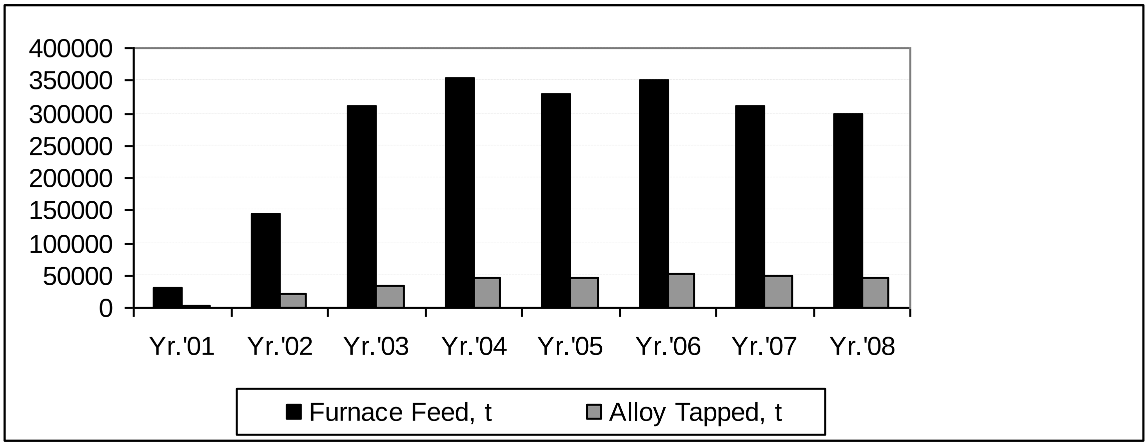


Fig.22: Yearly furnace throughput

Throughput in the year 2005 was marginally affected by a 3 week shut down of the pressure leach plant for relining of the autoclaves. In the year 2007, the hearth lining failure in January which required relining in a 5 weeks shut down affected the throughput whereas in the year 2008, the furnace was stopped in November due to economic down turn and crash in the metal prices making the operation unviable.

8.2 Electrode Consumption

The graphite electrode consumption improved from 2.2 kg/t of slag feed to 0.7 kg/t, a 68% reduction as shown in figure 23 due to stability in furnace power.

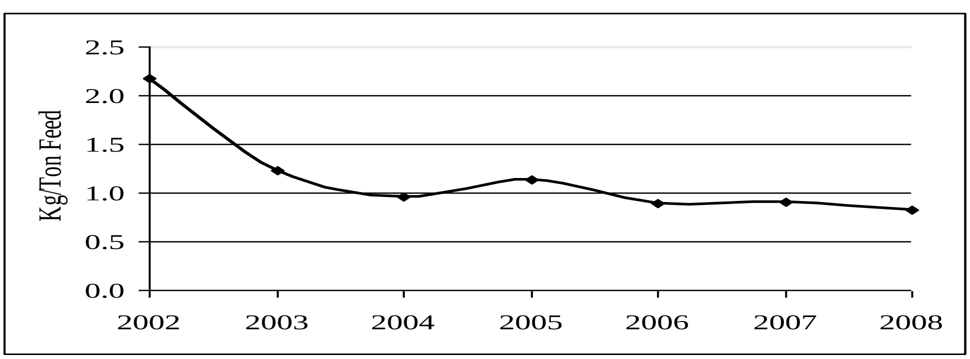


Fig.23: Yearly Graphite Electrode Consumption

8.3 Furnace Campaign Life

The furnace campaign life is defined as the operating time between the two furnace rebuilds. It is the indicator of the productivity of the furnace as well as safe operating practices. The history of the furnace campaign is as follows:

	Commissioned	**Failed**	**Life (Years)**
First Lining	January 2001	April 2001	0.3
Second Lining	July 2001	July 2002*	1.0
Third Lining	October 2002	January 2007	**4.3**
Fourth Lining	February 2007		to-date

* the lining was modified to incorporate Hatch Waffle Coolers.

Although the campaign life of 4.3 years achieved is the highest so far, it is lower than the standard 7 – 8 years being achieved in the steel industry. The reason for shorter life was the failure of the hearth lining due to massive volume of water ingress in the furnace caused by failure of two copper coolers in November 2005. The skew bricks underwent thermal shock resulting in gradual washing away of lining below the copper coolers. Furnace operated for another 14 months before the lining gave way resulting in a run away from a point about 400mm below the metal tap hole.

9.0 Conclusions

A systematical approach to de-bottleneck furnace operation was successful in attaining furnace throughput to design levels. Despite extensive pilot test work was conducted at Mintek, all the information regarding the applicability could not be established. The extrapolation of the information to the commercial unit was difficult. There was no such process existed worldwide to gain experience. The learning time therefore was too long. Such unique technology for which no operating knowledge available, involvement of all the specialist institutions engaged in electric arc furnace smelting could have been very useful to gather technical and operating experiences before even design stage.

Abbreviations

Aq.	- Aqueous
AVMIN	- Anglovaal Mining
Cons	- Concentrates
CRU	- Copper Research Unit
DTA	- Differential Thermal Analysis
g/t	- gram per tonne
HS	- High Speed
I.D.	- Internal Diameter
IX	- Ion Exchange
LIM	- Low Intensity Magnetics
ml/s	- Milliliter per second
Pptn	- Precipitation
SX	- Solvent Extraction
TPA	- Tonne per annum
TPD	- Tonne per day
TPM	- Tonne per month
R.L.E.	- Roast Leach Electrowin
RSA	- Republic of South Africa
XRD	- X-Ray Diffraction