Spinel Removal from PGM Smelting Furnaces

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Abstract – As Merensky reef ores are replaced by UG2 ores, chromium levels in PGM smelting furnace feeds have steadily increased. Increased chromium levels lead to operating problems. Attempts to increase the chromium solubility in the slag by a variety of techniques create other difficulties. The authors have developed a technique for removal of the chromium spinel interface along with the matte for subsequent separation outside the smelting furnace by utilising differential solidification in the ladle. The process has been patented internationally with support from the Innovation Fund.

INTRODUCTION

All non-ferrous smelting processes deal to some extent with the presence of chromium in the furnace. Some of the chromium is present in the feed material, and some originates from refractory wear, particularly where converter slag is returned to the furnace. The degree to which chrome presents a problem in the operation is, to a large extent, a function of the quantity of chrome involved.

Platinum smelting operations have 'lived' with chromium for many years, but in the past 20 years, as the exploitation of UG2 reef ores has increased, the severity of the problem has increased.

Some operators have opted for radical changes in furnace design and operation in attempts to deal with manifestations of the problem, with limited success.

Others have chosen to accept that the chrome content places limits on ore blends, and adapt their mining and smelting plans accordingly. This places constraints on mine life and furnace throughput, which in turn negatively affects profitability.

As low-chrome ore resources dwindle, the problem becomes more severe, and, to date, none of the major players in the PGM industry have satisfactorily solved the problem**.**

This paper firstly reviews some of the existing methods of chromium control, and the problems associated with these methods, and then presents an alternative that the authors consider viable for existing producers.

CHROMIUM IN PGM SMELTING

Background

In conventional submerged-arc smelting of PGM –bearing concentrates, the key operational step in smelting is to achieve a fully molten bath consisting of a dense sulphide-containing matte phase, which contains the maximum amount of PGMs, and a lighter slag phase containing gangue elements and a minimum amount of PGMs. Clean separation of slag from matte is desirable, and flux additions aim at improving slag properties to achieve this. In addition the slag functions as the electrical resistance for the current, so electrical properties are also important. Comprehensive reviews of current operating practice have been provided by Jones,[4,5] along with relevant operating data.

Unfortunately, the ideal is not achieved, and certain oxides, particularly the trivalent Fe and Cr oxides, have high density, high viscosity, low solubility in silicate slags, high melting points, and partial solubility in matte (and vice versa). These properties result in the formation of an intermediate zone in the furnace at the slag-matte interface, where these elements concentrate. Their high density keeps them in this area, and their high viscosity results in matte entrainment. Over time, this material, which is only partially liquid at normal smelting temperatures, settles to the furnace bottom and lower sidewalls, resulting in reduced crucible capacity and irregular matte tapping. This material has become known in the industry as 'bottom', 'false bottom', 'mush', 'magnetite', or 'spinel', owing to its tar-like consistency. All these terms refer to the same problematic material. For simplicity, this material is referred to as 'spinel' in this paper. In extreme cases, the build-up results in the premature termination of the furnace campaign.

Current philosophies for dealing with high chrome contents

PGM–containing ores as found in Southern Africa are generally of two varieties:

(a) The conventional ore (Merensky reef) contains little chromium. These ores have been successfully treated in the conventional process for decades. Merensky reef ores are becoming depleted and more costly to mine.

(b) The second variety (UG2 ore) is actually a chromite ore containing large quantities of PGMs. These UG2 ores are a rich resource, but processing them through the conventional route described above is problematic, for a number of reasons, mostly associated with the concentrate chemistry.
Typical Concentrate analyses are shown in Table I below:

Table I: Concentrate analysis, mass %

Ore type	Al_2O_3	CaO	Fe	MgO	SiO_2	Cr_2O_3
Merensky	1.8	2.8	18	18	41	0.4
UG2	4.4	2.7	13.7	22.3	49.6	3.8
Blend(30:70)	3.6	2.7	15	22	47	2.8

Chromite (generally $MO.N_2O_3$ where M is Fe^{2+} or Mg^{2+} and N is Al^{3+} Cr^{3+} Fe^{3+}) is a spinel mineral that has a high melting point (*i.e.* it is 'refractory') as well as high density and viscosity. Consequently, concentrates containing large amounts of chrome spinel are difficult to melt, and cause operational problems in the smelting furnace:

- difficulties in obtaining clean separation of matte and slag
- high operating temperatures
- shortened furnace life
- high operational cost
- build up of sticky high chrome compounds in the furnace, restricting capacity and shortening furnace life
- high maintenance costs and lengthy repair periods.

In order to mitigate these problems, current operations are forced to either limit the amount of UG2-originating concentrate fed to the smelting unit, or to modify the flotation process to minimise the amount of chrome contained in the concentrate. This results in a lower recovery of PGMs in the concentrate, and a higher operating cost.

Numerous attempts have been made to modify operational conditions within the smelting furnace, particularly to lower the partial pressure of oxygen (pO_2) in the furnace by the addition of reductants. These modified operations have not met with complete commercial success, and the economic viability of UG2 processing is somewhat jeopardised, as is the profitability of these mining operations heavily dependent on UG2 ores for their PGM reserves.

Chromium control with respect to slag chemistry
It is not the intention of this paper to comprehensively review the physico-chemical aspects of PGM smelting, but to try to explain why attempts to control chromium in the furnace have met with limited success.

Since chromium reports in the form of the trivalent oxide, and reduction to the metallic form is thermodynamically virtually impossible under normal matte smelting conditions, chemical chrome control depends on creating a slag in which the maximum amount of chrome is dissolved in the slag. Highly siliceous slags (*i.e.* acid slags) have high viscosity, poor chrome (III) solubility, and tend to have relatively high liquidus temperatures.

The temptation in terms of operation is to reduce the amount of lime addition to cut costs, but this is counter-productive. Not only are the slag properties unsuitable for chrome removal, but the smelting rate drops off as the kWh/t energy requirement skyrockets. Slag skimming becomes messier, and metal losses to the slag increase dramatically. This becomes particularly significant in situations where no converter slag is returned, as the lack of iron in the slag tends to result in a very siliceous slag.

Generally, the viscosity, liquidus temperature, and resistivity of the slag increase with increasing silica (SiO_2) content, but the density decreases. The

chromium-containing spinel phase is amphoteric, and its behaviour is therefore influenced by the general slag basicity.

Conditions inside non-ferrous smelting furnaces do not encourage the reduction of Cr^{3+} to Cr^{2+}, and only partial reduction of Fe^{3+} to Fe^{2+}. An essential feature of furnace control would be the regular reporting of Fe^{3+} levels in the slag, rather than just Fe (total) as is common practice in PGM smelters. Without adequate iron control, chrome control is well nigh impossible.

Investigations into operations clearly indicate that furnace fluxing is often inadequate - insufficient lime addition being the usual problem. It may be that this stems from a misunderstanding of the fundamentals of extractive metallurgy. The purpose of flux is just that: - the addition of a specific compound that improves fluidity and permits the melting of the gangue elements. If a fluxless operation were possible, it would obviously be preferable from an economic point of view. Unfortunately, the reality is that, without flux, the gangue is so refractory that it cannot melt, and the production rate drops while operating temperatures skyrocket. Only once the basic slag composition is satisfactory can attempts at finessing the composition to control chromium distribution be attempted.

Many research articles have examined the effect of flux addition on furnace performance in efforts to optimize operation. A pertinent report by Pulling and Hopkins[1] on similar non-ferrous slags in the 1970s showed that an additional 3% addition of lime, which reduced the slag SiO_2 content from 62% to 59%, resulted in a 300% improvement in smelting rate. Similar (confidential) studies on South African platinum operations confirmed this trend. The old adage "make a good slag and the metal (matte) will look after itself" remains as true today as 100 years ago. Nell[2] more recently reviewed the pertinent slag chemistry issues, highlighting the dilemma faced by operators. Addition of reductant could be made in the belief that this will reduce the spinel and remove build up. The result however is that iron in the slag becomes reduced to the metallic form and alters the matte to a 'malloy' composition (sulphur deficient). This superheated 'malloy' has the potential to dissolve copper coolers where installed and cause severe erosion of the coolers above the matte cooling blocks. It could also possibly result in segregation of high-melting-point iron from the matte with absorption of PGMs, as well as a decrease in basicity.

The effects of a shortage of flux on operability are severe:
- Specific power requirements increase
- Specific melting rates drop
- Matte and slag temperatures increase dramatically
- Matte and slag launders suffer frequent burn-through by superheated matte
- Metal recoveries drop as a result of poor matte/slag separation
- The furnace lining suffers erosion damage.

An exhaustive review of the principles of slag control is beyond the scope of this paper, but reference to a few pertinent phase diagrams will illustrate clearly how flux deficiency affects the operation. The major gangue element in the feed is silica, with magnesia the next most abundant, and ferrous oxide third. Since these three constitute the major oxide components in the feed, reference will be made primarily to the MgO-FeO-SiO_2 system.

MgO and FeO are mutually soluble but there are vast differences in their respective melting points (as shown in Figure 1), as well as those of their respective silicates.
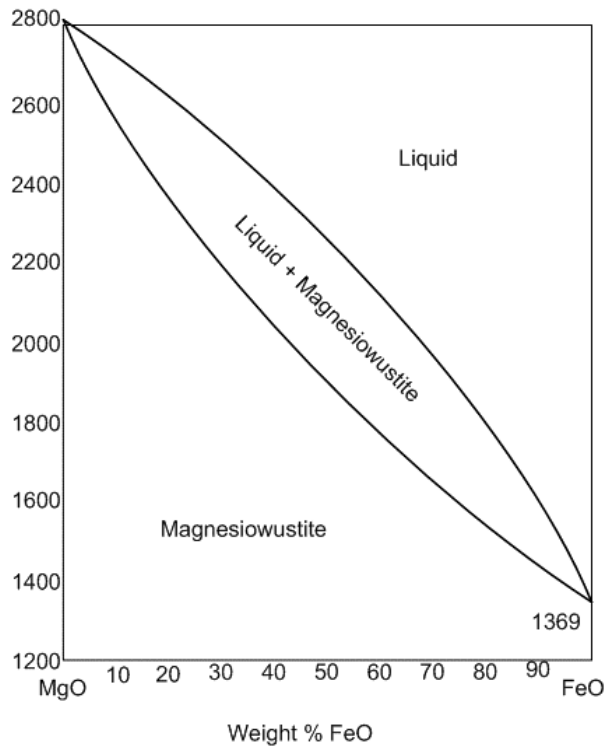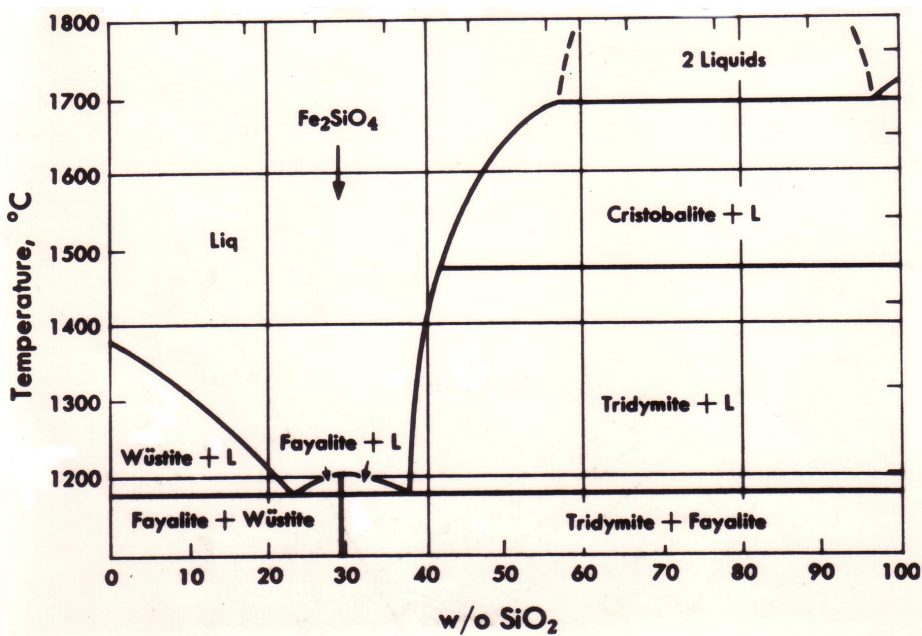

Figure 1: FeO-MgO Phase Diagram

Figure 2: FeO-SiO₂ phase diagram

While the Fe$_2$SiO$_4$ (fayalite) phase melts at 1178°C, (shown in Figure 2), the lowest-melting MgSiO$_3$ is only liquid above 1543°C, and Mg$_2$SiO$_4$ only melts at 1860°C. Small quantities of Al$_2$O$_3$ (below about 7%) have virtually no influence on the melting temperatures. Lime silicates melt at lower temperatures than magnesia silicates (about 1464°C). Lime is exclusively used as furnace flux in PGM smelting.

The presence of Cr$_2$O$_3$ particularly (Figure 3), and Fe$_2$O$_3$ to a lesser extent, increases the melting point of the slag dramatically. The presence of 5% Cr$_2$O$_3$ raises the liquidus temperature of a magnesium silicate slag to over 1800°C.
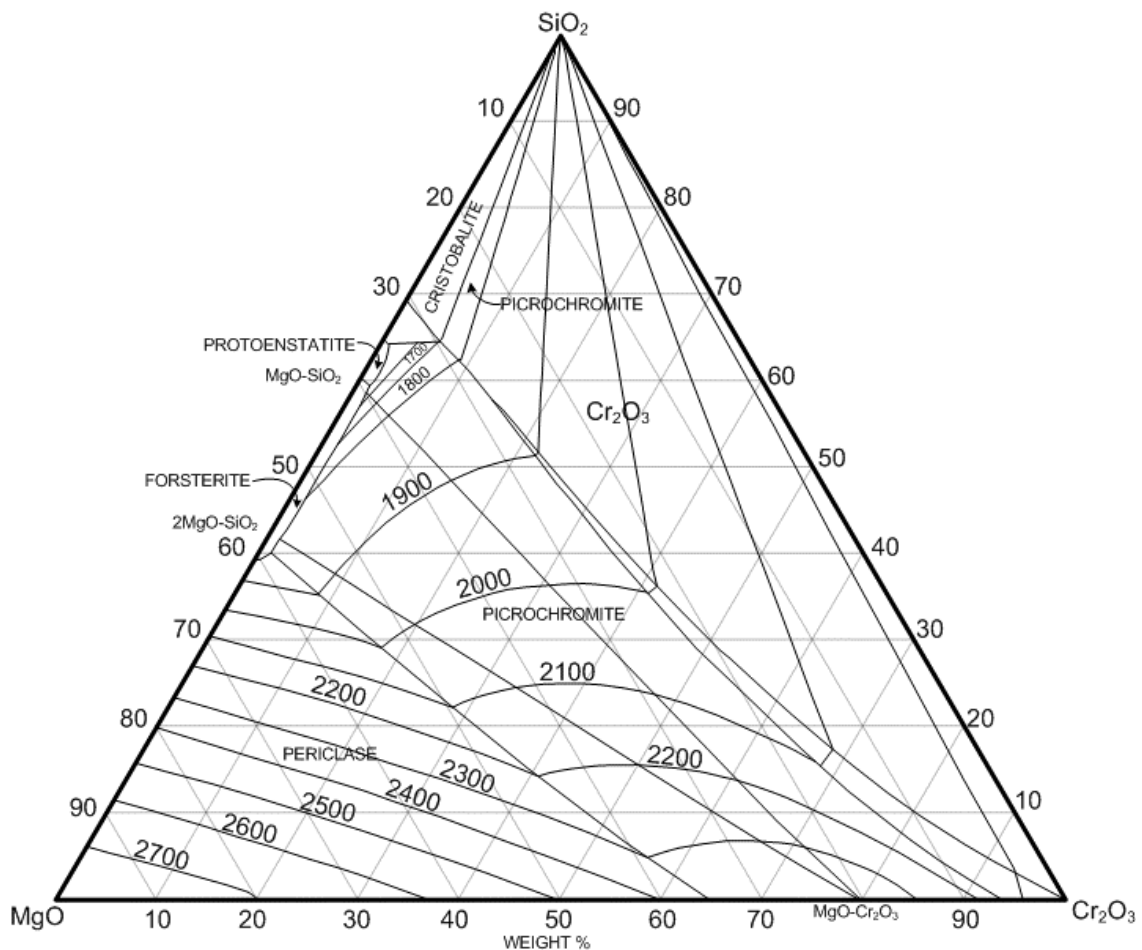

MgO-Cr$_2$O$_3$-SiO$_2$ Phase Diagram
Figure 3: MgO- Cr$_2$O$_3$-SiO$_2$ phase diagram

The higher the silica content, the higher the viscosity, and reference to any of the binary diagrams will show that the silica-rich phase is still solid at temperatures well above the furnace operating temperature. What happens in practice is that the available lime, magnesia, and iron oxides partially flux the silica, producing a very low-melting and fluid slag, which drains rapidly from the feed, leaving a matrix of virtually pure solid silica floating on top of the slag. This silica is virtually inert and refractory, resisting dissolution into the slag unless it has an excess of base. Since this material floats on top of the bath, it is never skimmed off, and slag samples from the launder indicate an apparently correct slag composition. Only by performing a comprehensive
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mass balance, can the silica retention be demonstrated, but by this time the furnace has already become 'constipated', and operational difficulties begin to manifest themselves.

Most non-ferrous operations have relied, over the years, on returning iron-oxide-rich converter slag to the smelting furnace, and, although this has increased the chrome burden on the furnace, it has had the beneficial effect of reducing the slag liquidus temperature.

An unfortunate side effect of the addition of reductant is that while it was primarily aimed at reducing the spinel, it has resulted in a dramatic conversion of iron oxide to metallic iron, with a consequent increase in the liquidus temperature of the slag, and this is further exacerbated if lime additions have been kept low to try to increase the solubility of Cr (II) into the slag, as mentioned by Nell.[2] In addition, the carbon causes a reaction:

$$C + FeO \rightarrow Fe + CO$$
$$\Delta H^0 = +137 kJ/mol \qquad\qquad [1]$$
$$\Delta G^0 = -117 kJ/mol$$
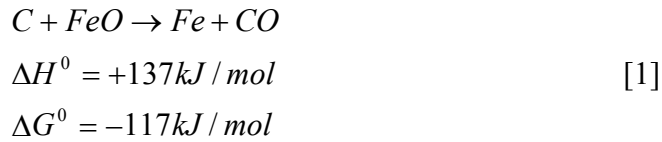
which is highly endothermic, absorbing 11.42 MJ per kg of carbon added. The reaction is thermodynamically spontaneous, in contrast to the reaction:

$$C + Cr_2O_3 \rightarrow CrO + CO \qquad\qquad [2]$$
$$\Delta G^0 = +358 \ kJ/mol$$

$$\Delta H^0 = +766 kJ/mol$$
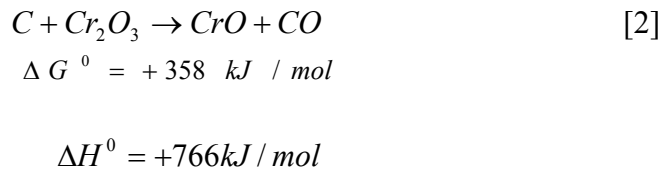
Whether the reductant addition actually does assist in chrome removal is doubtful, but it definitely reduces the available smelting power and has a very negative impact on slag fluidity, as a consequence of the removal of iron.

Addition of reductant is therefore unsuitable for modifying slag chemistry to increase chromium solubility in slag. Dramatic increases in slag temperature do assist in increasing chrome removal via slag, but result in increased operating cost and shorter campaign lives. It also does not allow complete removal of chrome as the schematic chrome balance (Figure 4) below shows, which is based on published data from Nell.[2]

Table II: Chrome distribution within the furnace (Typical acid slag, UG2 /Merensky Blend)

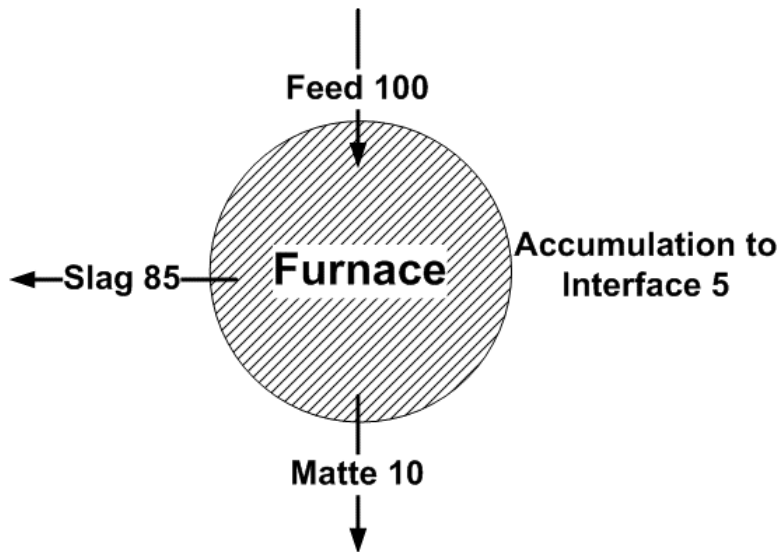| PHASE	Relative Volume	Density	% Cr_2O_3	Cr Distribution
Slag	10	3	2.4	50
Spinel Interface	1	5	12	34
Matte	2	5	2.4	16

Figure 4: Chrome balance

PROPOSED ALTERNATIVE SOLUTION

The proposed method involves the removal of chromium and iron oxides from platinum matte smelting furnaces by selective solidification of the oxides, and subsequent separation from the molten matte or alloy outside the furnace.

The novelty of the invention lies in that the chrome removal takes place in the matte handling stage of the processing operation rather than inside the furnace or in the slag handling stage, as is common practice.

All metallurgical extraction techniques rely on a physical or chemical property difference to effect separation of compounds from one another - the flotation process relies on differences in wettability, the matte-slag separation relies on differences in density, and the converting process on different affinities for oxygen.

The proposed process relies on the fact that high chrome-containing compounds have high melting points, while mattes have relatively low melting points, and separation takes place by means of **differential solidification.** This method relies only partially on a small difference in density between the slag and the matte, but far more significantly on the differences in melting point. The chrome balance has already indicated the significant lock up of chrome in the spinel interface. These differences are shown schematically in Figure 5.
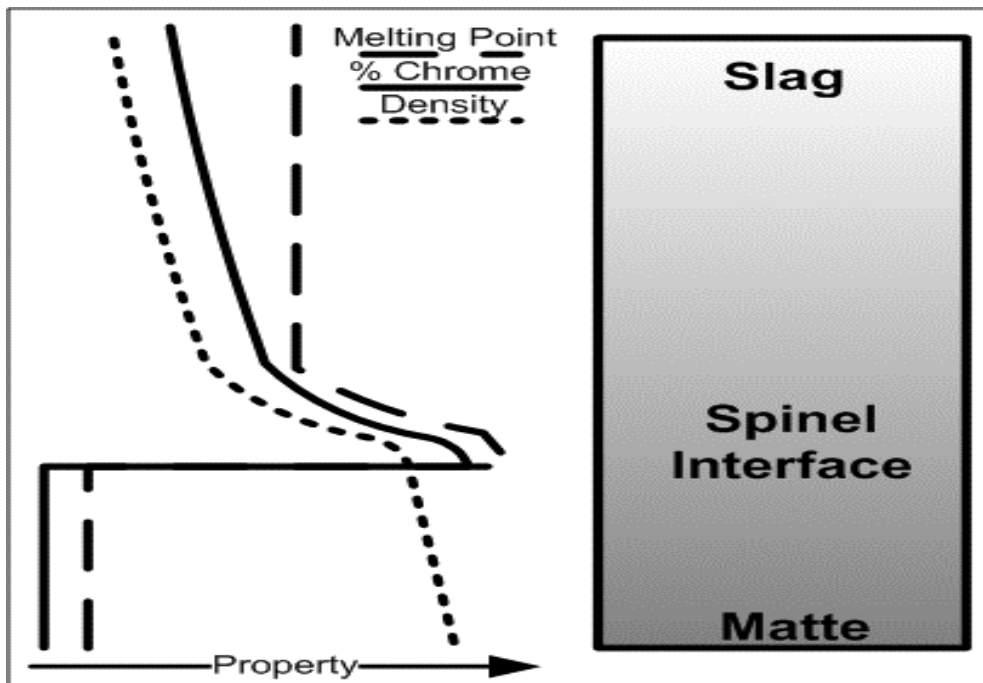
Figure 5: Property differences – Slag, Matte, and Spinel

The core of the problem with chrome-containing slags is that their density approaches the density of the matte, and they are also partially soluble in the matte, resulting in a sticky, semi-molten intermediate layer, referred to as 'spinel'.

The novel step is to deliberately tap the spinel interface, together with entrained matte, via a dedicated tap hole situated between the matte and slag tap holes.

The partially separated matte/slag mixture is tapped into a ladle fitted with a teapot spout while a second conventional ladle is positioned immediately next to and slightly below the first. The relatively quiescent conditions in the ladle allow the spinel to solidify on the top and sides of the ladle, while the fluid molten matte collects in the bottom portion of the ladle, and overflows via the teapot spout into the second ladle. The second ladle, when filled with matte, is transferred to the converter as normal. The first ladle is allowed to stand for a suitable period (from 30 minutes to 2 hours) to ensure that all the slag has solidified as a result of the partial cooling of the ladle and its contents. At this stage, the ladle is tilted and the molten matte decanted into the second ladle and transferred to the converter. The first ladle is up-ended, bumped on a suitable bumping block to remove the solidified slag, and replaced in position for the next spinel-removal campaign sequence.

The collected solid slag, rich in spinel, can be treated by whichever method is in practice for converter slag treatment, barring return to the smelting furnace - crushing followed by milling and flotation is the preferred method of treatment.

This process can be performed intermittently and independently from the normal process of matte tapping, specifically to remove spinel accumulation

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from the furnace. The process can be applied in conjunction with other spinel removal practices such as bath agitation, or high power density 'burns'.

Specific advantages of the process
- Adoption of this modified process permits unrestricted exploitation of all PGM containing ore bodies.
- The chrome content of the concentrate is not restricted.
- The flotation process can be optimised to extract maximum PGM recovery into the concentrate.
- The furnace can be operated in a mode that maximises energy efficiency, PGM recovery, and furnace life, rather than in a mode specifically to eliminate chrome. This results in lower production costs, improved throughput, and enhanced profits.
- Furnace life is extended.
- Personnel safety is improved - lower operating temperatures in the furnace reduce the risk of catastrophic failure of the furnace lining.

The concept as presented was considered sufficiently novel that it has been patented internationally under the Patent Co-operation Treaty, Patent No. WO 2005/031013 A1 [3], with financial assistance from the Innovation Fund, since the idea is considered to have considerable potential commercial benefits for South Africa. A South African patent has also been filed. Since then, two additional provisional patents, covering further modifications and refinements, have been lodged.

Discussions with respect to commercial implementation are currently taking place with PGM producers. Certain specific details of the techniques used to monitor chrome accumulation, and operational practice, remain confidential at this stage, and, unfortunately, certain practical details relating to know-how cannot yet be disclosed. This includes information on how tapping of the interface is successfully concluded.

CONCLUSIONS

In the opinion of the authors, the proposed solution has much to offer, and almost nothing to lose on the part of operators. Implementation is relatively easy, with minimal disruption of furnace operation, and spinel control becomes a complementary operation - it does not replace normal matte and slag tapping.

The proposed control method can be initially tested on any currently operating furnace, following the installation of the intermediate tap hole, and level sensing can be added at any time, even if the tap hole is not installed. Ladle modifications are a refinement, but the method can be implemented on a trial basis before modified ladles are installed.

Negotiations at executive level with existing producers are exploring a mutually acceptable contract to commence a programme aimed at the eventual full implementation of the proposed chrome control methods.

ACKNOWLEDGEMENTS

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