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Extraction of Platinum Group Metals

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Abstract

About 80% of the worlds' reserves for platinum group metals (PGMs) are in South Africa's Bushveld Igneous Complex. Processing of PGM involves comminution, flotation, smelting, converting, base metals refinery and precious metals refinery. Due to increasing chrome content in the feed and the challenges associated with operating high chrome feed, alternative routes to smelting of PGM are being investigated. Some hydrometallurgical routes have been proposed. However, none of the reported potential routes have yet been commercialised.

Keywords: platinum group metals, chrome, smelting, UG2, Merensky

1. Introduction

Platinum group metals (PGMs) are a group of six elements, namely iridium (Ir), osmium (Os), platinum (Pt), palladium (Pd), rhodium (Rh) and ruthenium (Ru) [1, 2]. PGMs together with gold and silver are classified as noble or precious metals because of their high corrosion and oxidation resistance [1–3]. The world's reserves of platinum group metals/elements are estimated at 100 million kilogrammes, of which over 80% is contained in South Africa's Bushveld Igneous Complex [4]. Summary of the PGM reserves by country is shown in **Table 1** [5]. PGMs are used in a number of industrial processes and commercial applications including automotive, jewellery, electronics, dentistry, catalysts, needles, pivots, temperature measurements, special crucibles and investments amongst others [5–7].

Country	PGM reserves (kg)
United States	900 000
Canada	310 000
Russia	1 100 000
South Africa	63 000 000
Other countries	800 000
World total (rounded)	66 000 000

Table 1. World’s reserves of PGM [5].

2. Geology

In South Africa, the PGM ore is mined in the western and eastern limb of the Bushveld Igneous Complex [8]. Within the Bushveld Igneous Complex, the Merensky reef, the Platreef and Upper Group 2 (UG2) reef are exploited for platinum production [1, 4, 9]. Merensky and Platreef have similar chemical and mineral composition [6, 10]. These reefs typically have fairly low contents of sulphides. UG2 differs from the two reefs in that it has low nickel and copper content [3]; compared to UG2, Merensky reef has higher amounts of chalcopyrite, pentlandite and pyrrhotite [8]. Chromite spinel can be up to 4% by mass in a UG2 concentrate, while a Merensky concentrate can have <1% by mass chromite spinel [8, 10].

Mineral	Formula
Sulphide minerals	
Chalcopyrite	CuFeS_2
Pentlandite	$(\text{Fe, Ni, Co})_9\text{S}_8$
Pyrite	FeS_2
Pyrrhotite	$\text{Fe}_{1-x}\text{S}_x$
Gangue minerals	
Alteration silicates	Hydrated minerals
Chromite spinel	FeCr_2O_4
Pyroxenes	$(\text{Mg, Fe})\text{SiO}_3 - \text{Ca}(\text{Mg, Fe})\text{Si}_2\text{O}_6$
Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$
Plagioclase/feldspar	$\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$
Quartz	SiO_2
Haematite	Fe_2O_3

Table 2. Sulphide and gangue mineralogy of a typical PGM concentrate [11].

A typical mineralogy of the flotation concentrate blend is shown in **Table 2** [11]. Eksteen (2011) [8] has given the fractions of typical minerals in the UG2 and Merensky concentrates. The abundant gangue minerals in a typical PGM concentrate are orthopyroxene, talc, clinopyroxene and plagioclase [8]; other gangue minerals are <5% by mass [8].

3. Sources of PGM

The principal sources of PGM are sulphide and arsenide minerals such as PtAs_2 , PtS , $\text{Pt}(\text{AsS})_2$, $(\text{Pt,Pd})\text{S}$, $(\text{Pt,Pd,Ni})\text{S}$, RuS_2 and Pd_3Sb and elemental ruthenium [3, 7]. Noble metals together with cobalt (Co), copper (Cu), iron (Fe) and nickel (Ni) belong to the class of transition metals in the periodic table [6]. Geologically, PGM associates with base metal sulphides such as chalcopyrite (CuFeS_2), millerite (NiS), pentlandite ($\text{Fe,Ni}_9\text{S}_8$), pyrite (FeS_2) and pyrrhotite (Fe_{1-x}S) [3, 12, 13]. Troilite carries trace amounts of iridium, while chalcopyrite has trace amounts of Ru, Pd, Ir and Pt [13]. Gangue minerals associated with PGM-containing minerals are feldspar, biotite, plagioclase and pyroxene [12].

4. PGM ore processing: an overview

Typical process route for treating PGM ore with the approximate PGM grade in each process is shown in **Figure 1** [1, 7, 9].

4.1. Comminution

The PGM ore is initially treated in primary and secondary crushers after which it is sent to rod and ball milling circuits. The milled PGM ore is treated using gravity separators and flotation cells; xanthate and dithiophosphate collectors are typical reagents used for flotation at a pH of 7.5–9 [1]. A sulphide-rich PGM concentrate is produced in the flotation cells [6].

Typical composition of UG2 and Merensky flotation concentrate is shown in **Table 3** [14]. A typical PGM content in the flotation concentrate is in **Table 4** [9]. The UG2 concentrate has higher chrome content when compared to the Merensky as seen in **Tables 3** and **4**. UG2 also has higher PGM content than the Merensky concentrate. The concentrate from the flotation cells is dried and smelted to separate the sulphides from the silicates [9].

4.2. PGM ore smelting

To separate the PGM-rich sulphides from the gangue minerals, smelting is used. Rectangular six-in-line or circular three-electrode electric furnaces are typical in the PGM industry [12]. Smelting is a high-temperature process step where the sulphides (valuable minerals) are separated from the silicates (gangue minerals). Energy required for melting the concentrate is provided by Joule heating when an electric current is passed through the resistive bath [15]. The electrodes are used for electrical connections between the power supply and the bath. Graphite electrodes are inserted into the resistive bath such that when a current is applied through the electrodes, thermal energy is generated [6, 15].

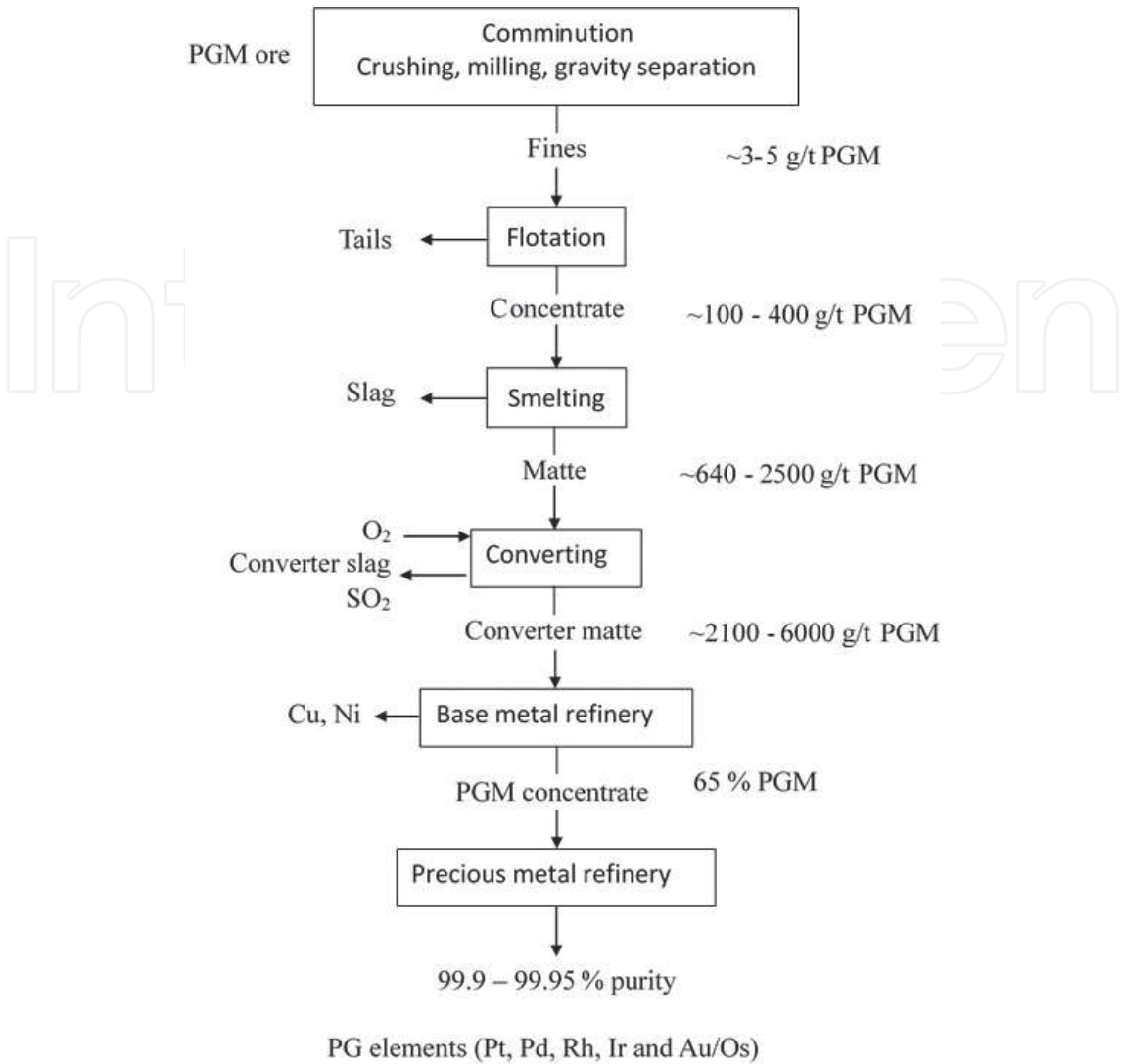


Figure 1. Typical process flow diagram for PGM ore processing [9, 12].

	Al ₂ O ₃	CaO	Cr ₂ O ₃	Cu	FeO	MgO	Ni	S	SiO ₂	PGM (g/t)
Merensky	1.6	2.2	0.3	2.1	22.3	18.2	3.2	9	41.4	100 - 250
UG2	5.0	2.4	2.9	0.8	12.6	21.0	1.7	3.6	44.0	300 - 600

Table 3. Typical composition of Merensky and UG2 concentrate [14].

The PGM concentrate is introduced into the smelter through the feed ports situated on the furnace roof. The concentrate forms a thick bed (~400 mm) on top of the molten bath. The heat generated in the resistive bath causes the concentrate bed to melt gradually [8].

The operating temperature of the smelter at the concentrate zone can range from 600 to 900°C [16]. The liquidus temperature of base metal sulphides associated with PGMs is 850–875°C, whereas the liquidus temperature of the corresponding silicates is approximately 1350°C [16]. The sulphides in a PGM concentrate start melting at the concentrate bed since temperature at

Assay	Merensky	UG2	Platreef
PGM-4E	200	200	120
Pt-% of 4E	63.5	56.7	45.1
Pd	28.1	29.4	45.7
Rh	4.4	13.0	3.2
Au	4.0	0.9	6.0
Ir	0.6	1.6	1.0
Ru	6.8	9.6	3.5
Ni %	6.0	1.4	4.9
Cu	3.4	0.7	2.5
Co	0.15	0.05	0.2
Cr ₂ O ₃	0.6	3.0	0.3
Sulphur	15-20	4-6	10-15
USD value/tonne	14009	16526	7397

Table 4. Typical content of a PGM flotation concentrate [9].

the concentrate zone can exceed the liquidus temperature of the sulphides. The silicate minerals melt when they reach the molten bath (concentrate-slag interface) [16]. The silicates and sulphides are immiscible; upon melting they form two separate layers.

The molten silicates and oxides form a fayalitic-forsteric slag layer, while the PGM-containing sulphides form a matte layer [16]. The specific gravity of matte ranges from 4.8 to 5.6, and that of slag ranges from 2.8 to 3.8 [6, 15]. Owing to the difference in specific gravities of matte and slag, the slag forms a top layer. Matte being denser than slag falls through the slag layer and settles underneath the slag. Matte consists of base metal sulphides (cobalt, copper, iron and nickel). Matte serves as a collector for the PGMs [6, 7, 14].

Operating temperature of matte and slag varies with the composition of the concentrate [8]. Typical smelter operating temperature for matte varies from 1380 to 1600°C, and that of slag varies from 1500 to 1680°C [8].

The molten slag and matte are tapped out of the smelter through the tap holes situated at the side-wall of the furnace. After tapping, the matte either can be fed directly to the converters as tapped or can be granulated before the conversion step; matte treatment varies with the producers.

4.2.1. Industrial PGM-furnace matte

Anglo American Platinum (Amplats), Impala Platinum (Implats) and Lonmin are three major producers of PGM in South Africa [9]. Typical compositions of matte from selected smelters are shown in **Table 5**. Matte from different smelters seems to have comparable amounts of major components (Cu, Fe, Ni and S). The slight difference is that the amount of iron in Amplats matte is slightly higher than the iron in a Lonmin matte (**Table 5**).

	Co	Cr	Cu	Fe	Ni	S
Amplats-Waterval	0.5	0.5	9.0	41.0	17.0	27.0
Lonmin-Merensky/UG2	0.5	0.2	9.7	37.0	17.0	28.0
Lonmin-UG2	0.5	0.3	9.8	35.0	17.0	28.0

Table 5. Typical chemical composition of industrial matte from selected smelters (% by mass) [12].

	Al ₂ O ₃	CaO	Co	Cr ₂ O ₃	Cu	FeO	MgO	Ni	S	SiO ₂
Amplats-Waterval	3.3	6.4	0.1	0.8	0.1	31.0	15.0	0.2	0.5	46.0
Lonmin-Merensky	2.0	9.8	0.1	1.2	0.1	28.0	19.0	0.2	0.0	44.0
Lonmin-UG2	3.9	13.0	0.0	2.4	0.1	9.2	22.0	0.1	0.0	47.0

Table 6. Typical chemical composition of industrial slag from different smelters (% by mass) [12].

4.2.2. Industrial PGM-furnace slag

Gangue minerals associated with PGM-containing minerals are feldspar, biotite, plagioclase and pyroxene ([Ca,Na]Al₁₋₂Si₃₋₂O₈) [12]. During smelting these gangue minerals form a slag that is a silicate rich phase. Typical composition of a PGM-furnace slag from different smelters is shown in **Table 6** [12]. The oxide compounds in Amplats and Lonmin-Merensky slag are comparable; Lonmin-UG2 slag has higher Cr₂O₃, CaO and MgO; and its FeO content is significantly lower when compared to that of the slag from Amplats and Lonmin-Merensky ore.

4.3. Converting

After smelting, the furnace matte is treated in Pierce-Smith converters or Ausmelt process where iron sulphide is oxidised to ferrous oxide and sulphur is oxidised to sulphur dioxide [9]. Sulphur dioxide is removed as an off-gas, and iron oxide is removed as a fayalitic slag. The slag phase of the converter contains significant amounts of entrained PGM and is recycled to the smelting furnace to recover the entrained PGM. The converter matte is cooled, milled and treated in base metals refinery (BMR) [1, 9].

4.4. Purification

Typical hydrometallurgical processes used for PGM purification are as follows: dissolution-precipitation (pressure oxidation leach), solvent extraction and ion exchange and molecular recognition technology [17]. Pressure oxidation leach is a typical hydrometallurgical process used to separate base metals from the PGM residue. The base metals are leached, while the PGMs remain in the residue. The PGM residue is sent to a precious metal refinery where various solution extraction and precipitation methods are used to separate individual metals [1]. Solvent extraction is another method by which PGMs can be separated from the base metals [7].

5. Operational challenges facing PGM industry

South Africa is faced with increasing cost of electricity which has direct impact on the energy-intensive processes such as smelting [1, 18]. South African PGM producers generally process a Merensky concentrate where available; otherwise, the Merensky and UG2 concentrates are blended together to achieve the required feed composition for the smelter. In recent years, the depletion of the Merensky reef has forced the PGM producers to mine the UG2 reef that has up to 60% chromite. As a consequence, the concentrate from the floatation cells has high chrome content than the amount that the smelters are designed to handle. In reducing conditions, the operating temperature limits the solubility of Cr_2O_3 in a typical slag. At 1450–1650°C the solubility of Cr_2O_3 in slag is limited to 1.8% by mass. As such the smelters have battled with numerous challenges owing to the treatment of a high chrome concentrate [9, 19].

5.1. Challenges associated with smelting high chromite concentrate

The challenges associated with high chrome feed to the smelter are the following [19]:

- Formation of chromite spinels which are insoluble in slag.
- Chromite spinels have high melting points as such they increase the liquidus temperature of the slag and they lower the fluidity of the slag [19].
- Chromite spinels increase the overall temperature of the constituents (slag and matte) [8].
- When the matte temperature is above the liquidus temperature of the slag freeze-lining, the matte dissolves the freeze-lining; this leads to corrosion of the refractories by corrosive PGM melt [8].
- There are FeO- and CrO-based spinels; the proportion of Fe and Cr in the spinel may vary, as such there are spinels that are heavier than the matte, while other spinels are slightly lighter than matte. Spinel which are denser than matte settle on the hearth; the accumulation of spinels on the hearth reduces the volume of the furnace [8].
- Spinel with intermediate density form a 'mushy' layer at the slag-matte interface; this leads to the entrainment of matte in slag [8].
- High chrome decreases electrical conductivity of the bath leading to electrical control problems in the furnace [19].
- Higher chrome levels affect the matte temperatures during conversion step (matte temperatures above 1355°C have been observed); this causes damage to the refractory lining. Cold dope (revert) is normally used to lower the temperature of the matte during conversion [16, 19].

A number of approaches have been investigated to deal with the chrome problem. The following actions have eased chromite problem in the smelters:

- Deep electrode immersion operating at high power densities causes sufficient mixing which keeps the solids in suspension [8, 21], but high power densities adversely affect the refractory life. To minimise the effect of high power input on the refractory life of the sidewall lining, the phase voltage is increased without increasing the current levels [19].
- Some producers stopped recycling the converter slag to the furnaces since the converter slag has high chrome content [19, 20].
- The flux addition in the furnace was discontinued since lower CaO levels increased the solubility of the chromite in the slag [19, 20].
- The control of furnace inputs and control of furnace parameters (power, furnace availability) are essential in controlling chrome content [19].
- Selective reduction improves the solubility of chromium in the slag [20].
- Tapping out the intermediate layer intentionally [22].
- Decreasing the chromium input to the smelters [20].
- Another innovation able to manage chrome-rich ores is the ConRoast process. This process involves removing and capturing sulphur from the concentrate prior to smelting in a DC arc furnace. Roasting a concentrate makes smelting more environmentally friendly; it also enables furnaces to accept any proportion of chromite, resulting in more efficient and cost-effective platinum production [9, 23].

5.2. Premature failure of refractory lining

Due to high operating temperatures (1350 to >1600°C) [8] associated with PGM smelting, the smelter has to be lined with refractories at the hot face. To prolong the service life of the refractories, sufficient cooling of the refractories is required at the cold face of the refractory wall. Copper waffle coolers are typically used in the cold face of the refractories to extract heat away from the refractories [24]. Due to high operating temperature and corrosiveness of the PGM melt, premature failure of the waffle copper coolers has been experienced in PGM smelters [24] in the upper sidewall region. Failure of waffle copper coolers causes explosions, loss of production and costs associated with furnace rebuild. The failure of waffle copper coolers was preceded by the consumption of conventional refractory bricks ($\text{MgO}_x\text{-CrO}_x$) which were used to form the furnace lining. The refractory brick ($\text{MgO}_x\text{-CrO}_x$) had low resistance to chemical attack by liquid PGM melt. To prevent the occurrences of copper cooler failures, conventional bricks have been replaced by the graphite blocks in recent designs of PGM smelter refractory walls [25]. Graphite blocks are only applied at the hot face of the upper sidewall (against the concentrate and the slag zone).

With the graphite block lining, a frozen protective skull forms at the hot face of the refractory. The formation of the protective skull is attributed to the efficient cooling of the refractory wall by waffle coolers. The frozen skull is the melt that solidified due to the surface temperature of the graphite that was lower than the liquidus temperature of the melt [25].

Graphite blocks have increased the service life of the waffle copper coolers through the formation of a protective layer. However, high infiltration of melt is still observed at the matte-slag tidal zone. This is a challenge that still needs to be addressed; currently, conventional bricks or monolithics are used at lower sidewall of the PGM smelter refractory. It is desired to extend the graphite blocks to the lower sidewall of the PGM smelter refractory wall against the matte zone [25]. It is envisaged that using carbon-based refractory at the hot face of the matte zone (lower sidewall) will improve the service life of the furnace lining in PGM smelters [25].

6. Opportunities in PGM processing

The PGM industry faces challenges with increasing chrome content in the feed and premature failure of refractory lining in the smelter. Alternative ways to process the PGM have become attractive due to the challenges associated with the conventional smelting process [1, 18]. A hydrometallurgy (Kell) process has been probed as an alternative to smelting PGM. The Kell process has three stages: stage 1 is the leaching of base metal sulphides in an acidic sulphate medium (pressure oxidation); stage 2 is roasting of the residue from stage 1; and stage 3 is atmospheric leaching of PGMs in a chloride media. The leached precious metals are further treated in refineries to recover metals [18]. Other hydrometallurgical routes have been discussed in Ref. [1]. These hydrometallurgical processes have advantages over the smelting process since they reduce the operating costs drastically [1]. However, the alternative hydrometallurgical routes of processing PGMs have not yet been commercialised [1].

7. Conclusions

In this chapter, an overview of PGM processing has been presented. The conventional smelting process has challenges with high chromium feed, premature failure of refractory lining and increased operating cost associated with increasing cost of electricity in South Africa. The Kell process is an alternative way to process a PGM concentrate, and it has a number of advantages such as less energy consumption, less energy cost, less electricity consumption, less CO₂ emissions and no restriction on chrome content of feed. Other hydrometallurgical routes have been investigated, but none has been commercialised yet.

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