The Effect of Roasting on the Recovery of PGMs from Chromite Ore

NG Kyungu and Elvis Fosso-Kankeu

***Abstract*—** This research investigates the effect of roasting on the recovery of platinum group metals (PGMs) from a chromite ore (UG2). The study uses hydrochloric acid (HCl) leaching, a hydrometallurgical technique, to extract PGMs from the ore. It compares the recovery of palladium (Pd) from direct leaching of an unroasted concentrate with the recovery from leaching after a roasting pre-treatment step using sodium carbonate ($Na_2\ CO_3$).

The results show that roasting at 1273K (1000°C) leads to near-zero Pd recoveries, suggesting the formation of refractory compounds or increased Pd adsorption at this temperature. Leaching the unroasted concentrate yields moderate Pd recoveries (up to 90%), indicating that roasting under these specific conditions hinders rather than enhances PGM recovery.

The study highlights the complexity of the Pd leaching process from chromite ores and the critical need to optimize roasting conditions to achieve effective PGM recovery. It suggests further research into the impact of different roasting temperatures, detailed characterization of the roasted concentrate such as X-ray diffraction, SEM-EDS, and exploration of alternative lixiviants to maximize PGM recovery.

***Keywords*—** Chromite Ore, Concentration, Roasting, Palladium, Leaching Kinetic, Rate Limiting Factor.

I. Introduction

Platinum group metals (PGMs) comprise of six metallic elements, which are commonly divided into two distinct subgroups: the iridium-group platinum-group elements (IPGEs: osmium, iridium, ruthenium) and the palladium-group platinum-group elements (PPGEs: rhodium, platinum and palladium). These metals are known for their unique physical and chemical properties, making them highly valuable in various industrial applications [1]. They are used in automotive catalytic converters, chemicals, jewelry, and medical devices, among other things [2]. One primary source of PGMs is chromite ore, but they can also be extracted from sulfide ores, such as pyrrhotite, pentlandite, and chalcopyrite [3].

Most of the South African's PGMs are extracted from chromite ore deposits found in the Bushveld Complex located in the northern part of South Africa [4]. The composition of chromite ore varies depending on the geological formation and location of the deposit. The chromite ore rich with PGMs is located in the eastern and western limb of the Bushveld Igneous Complex (BIC) [5]. Within the BIC, the Upper Group 2 (UG2), Platreef and the Merensky reef are mined for PGM production [6].

Chromite ore is usually extracted through underground mining or open-pit mining methods, and then processed through various beneficiation techniques to concentrate the valuable minerals. Platinum group metals are typically extracted from chromite ores through a multi-step process that involves roasting and leaching. The roasting process involves heating the ore in the presence of air to oxidize the base metals and convert the PGMs into a water-soluble form [4]. The dissolution process on the other hand involves the use of acids and other solvents to dissolve the PGMs, which can then be separated and purified through refining processes [7]. However, this recovery process is often hindered by rate limiting factors, thus affecting the efficiency of the extraction process.

The dissolution of PGMs from roasted chromite ore is a complex process that involves various kinetic factors, which can be elucidated through kinetic models [8-18]. The rate limiting step in this process is crucial to understand, as it determines the overall efficiency of PGM extraction [19]. Kinetic models, such as the shrinking core model can be applied to investigate the dissolution process of PGMs. This model considers factors like chemical reaction, product layer diffusion and film diffusion, allowing for the identification of the specific factor that may be affecting the dissolution of PGMs [13]. Understanding this rate limiting factors is essential for optimizing the extraction process and maximizing the economic value of PGM deposits in South Africa.

This study aims to determine the rate-limiting factor during the dissolution of PGMs from roasted chromite ore, in order to optimize their extraction process and improve the overall efficiency.

II. METHODOLOGY

A. Sample preparation

A UG2 chromite run of the mine sample was obtained and taken through comminution for size reduction. After comminution, the reduced sample (reduced via crushing) was weighed and collected for characterization (i.e., XRF). From the crushed ore, a portion was also obtained for the determination of the presence and concentration of PGMs using fire assay. During fire assay, 50g of sample was prepared with the addition of fluxes such as borax, sodium carbonate, litharge and carbon. The prepared mixture was put in the furnace at a temperature of

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1100°C. After heating, buttons were obtained which were then hammered into cubes and loaded back to the furnace for cupellation. The remaining sample was the weighed and prepared for further comminution through wet milling. In the milling step, 5 runs were carried out at different time frames, *vis* 5 minutes, 15 minutes, 30 minutes, and 60 minutes respectively. This was done to achieve the optimum milling time to meet the required PSD of 80% passing 75 microns for preparation of the leaching process. After wet milling, the sample was collected and a milling curve was plotted.

The preceding step from the milling was the rough froth floatation step. The aim of floating was to concentrate the sulfide before it could be taken for roasting and leaching. SIBX and copper sulphate reagents were prepared for the flotation circuit. The mixed reagents were allowed a time of 5 minutes for conditioning. After 5 minutes, the sample was poured into the flotation circuit of mixed water and reagents which made up to 3L of the total volume of the cell. The sample was floated for 20 minutes up until little to no froth could be collected. This was to avoid any mass loss at all costs. The floated sample was dried separately with the tailings. After drying, the tailings were discarded while the concentrates were split and taken for the subsequent steps, characterization and LRL (leach-roast-leach) route."

B. Direct leaching (unroasted concentrate)

The concentrate was subjected to leaching at a solid/liquid ratio of 20% with hydrochloric acid (HCl) as lixiviant at a constant pH of 1.5, with varying temperatures (25, 40, 55, and 70°C) and different leaching times (30, 60, 90, 120, and 150 minutes) to recover the PGMs. It was constantly agitated at constant speed of 320rpm using a magnetic stirrer. The resulting pregnant liquor, containing the dissolved PGMs, was separated from the solid residue (gangue) through filtering and then taken for atomic absorption spectrometry (AAS) analysis.

C. Roasting and leaching

In this step, the concentrate was first subjected to a roasting pre-treatment with Na_2CO_3 at 1000°C for 2 hours at a ratio of 15% mass of the concentrate. This roasting step aimed to alter the ore's properties and enhance PGM recovery. This step was then followed by the direct leaching step process, described prior.

III. RESULTS AND DISCUSSION

A. Ore Characterisation

Chromite ore, naturally occurring with a spinel structure, can be represented by the formula $(Fe^{2+}, Mg)(Cr, Al, Fe^{3+})_2O_4$. This indicates that chromite is essentially a solid solution composed of various oxides, including $FeO{\cdot}Cr_2O_3$, $MgO{\cdot}Cr_2O_3$, $FeO{\cdot}Al_2O_3$, and $MgO{\cdot}Al_2O_3$. In addition to these primary constituents, chromite ore also contains impurities such as hydrated magnesium silicate ($3MgO{\cdot}2SiO_2{\cdot}2H_2O$), silicon dioxide ($SiO_2$), and iron oxide ($Fe_2O_3$) [20]. This UG2 chromite sample which was analysed using x-ray fluorescence had the following elemental composition before flotation (Table 1) and before roasting (Table 2) presented below respectively.

TABLE I: UG2 CHROMITE ORE ELEMENTAL COMPOSITION BEFORE FLOTATION

Component	MgO	Al_2O_3	SiO_2	SO_3	CaO
Weight (%)	8.66	10.38	24.74	0.40	4.76
Component	Cr_2O_3	Fe_2O_3	Co_2O_3	NiO	CuO
Weight (%)	20.33	25.77	0.05	0.27	0.24

TABLE II: UG2 CHROMITE CONCENTRATION ELEMENTAL COMPOSITION BEFORE ROASTING

Component	MgO	Al_2O_3	SiO_2	SO_3	CaO
Weight (%)	14.56	5.84	37.86	1.13	3.76
Component	Cr_2O_3	Fe_2O_3	Co_2O_3	NiO	CuO
Weight (%)	4.09	30.46	0.04	0.68	1.75

The most striking difference is the increase in SiO_2 content from 24.74% in the raw ore to 37.86% in the concentrate. This indicates that flotation effectively separated silicate minerals, which are typically associated with the gangue, from the heavier chromite minerals. The significant reduction in Cr_2O_3 (from 20.33% to 4.09%) and the increase of Fe_2O_3 (from 25.77% to 30.46%) confirms the successful removal of chromite ($(Fe^{2+}, Mg)(Cr, Al, Fe^{3+})_2O_4$) during flotation. While Fe_2O_3 is still present, its increase suggests that a portion of iron oxide is associated with the chromite mineral and was floated along with it.

The moderate increase in MgO content (from 8.66% to 14.56%) suggests that some magnesium-bearing minerals were retained in the concentrate. This could be due to the presence of magnesium in other valuable minerals or its association with the silicate minerals. The relatively minor changes in other components, such as Al_2O_3, CaO, SO_3, NiO, CuO, and ZnO, indicate that flotation had a limited impact on their distribution. These elements are likely present in both the valuable minerals and the gangue, resulting in less significant changes after flotation. The XRF analysis alone could not detect nor quantify the PGM content in the ore and for that reason, fire assay analysis was done to determine the present PGM and its concentrations before flotation and after. The concentrations are presented in Table 3 and 4 below respectively."

TABLE III: PALLADIUM CONCENTRATION IN THE CHROMITE ORE

Concentration	Measured (mg/L)
Averaged	1,213681

TABLE IV: PALLADIUM CONCENTRATION IN THE CHROMITE CONCENTRATE

Concentration	Measured (mg/L)
Averaged	1,68112

From Table 3 and 4. it was observed that the concentration of palladium increased after flotation from 1,213681 to 1.68112755 mg/L. This indicates that the flotation process was efficient.

B. PGM leaching

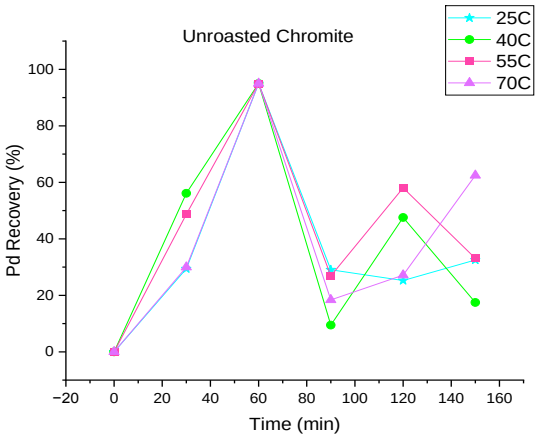

Fig. 2: %Recovery of palladium for an unroasted chromite concentrate

The graph illustrates the recovery of palladium (Pd) from an unroasted UG2 chromite concentrate leached with HCl at a pH of 1.5, under varying temperatures (25°C, 40°C, 55°C, and 70°C) and leaching times (0 to 160 minutes). The initial steep rise in Pd recovery within the first 20-40 minutes across all temperatures suggests that a significant portion of the Pd is readily accessible and rapidly leached by HCl. This could be attributed to the presence of some Pd in easily soluble forms or located on the surface of the chromite particles, as highlighted by [21]. However, each temperature exhibits a peak recovery point followed by a decline, indicating that prolonged leaching leads to re-precipitation or loss of the already leached Pd. This phenomenon could be due to the re-adsorption of Pd onto the chromite matrix or the formation of insoluble Pd compounds at longer leaching times, as suggested by [22]. As expected, higher temperatures generally result in both higher peak recovery and faster leaching kinetics.

This aligns with the understanding that higher temperatures enhance reaction rates and the solubility of Pd [23]. It's important to note that while the graph shows high recoveries of 95% for palladium at 60 minutes across all temperatures, this might not represent the complete picture. Kakavas et al [24] mentions that PGMs can be enclosed within the refractory chromite matrix hindering their accessibility to leaching solutions. Therefore, the observed high recovery might only reflect the easily accessible Pd, while a significant portion could remain trapped within the chromite."

C. PGM Leaching (Roasted sample)

The unexpectedly low palladium (Pd) recovery observed which are presented in table 5 found in the appendix after leaching the UG2 chromite concentrate roasted with $Na_2\ CO_3$ at 1273K (1000°C) could be attributed to several factors arising from the high-temperature roasting process. This outcome aligns with previous research indicating potential challenges associated with roasting chromite ores at elevated temperatures [25]. Firstly, the high roasting temperature may have induced undesirable phase transformations within the chromite mineral structure. As described by Rodney (n.d), chromite, a complex spinel composed of iron, magnesium, chromium, and aluminium oxides, can undergo significant alterations at elevated temperatures. While moderate roasting can liberate PGM particles trapped within the chromite lattice [26], excessive heat may lead to the formation of highly stable or even refractory compounds, rendering the encapsulated PGMs inaccessible to leaching solutions. This could explain the initial negative recovery observed in the 1000°C roasted samples, where Pd was seemingly lost from the leachable fraction, potentially due to the formation of insoluble Pd-bearing phases. Secondly, the high temperature might have promoted sintering or fusion of the chromite particles. Sintering, the process of forming a solid mass of material by heating without melting it to the point of liquefaction, can reduce the porosity and surface area of the concentrate. This decrease in accessible surface area could hinder the penetration of the leaching solution, limiting its contact with the Pd particles and thus reducing the leaching efficiency [27]. Even if the roasting process successfully liberated some Pd particles from the chromite lattice, the subsequent sintering might have encapsulated them again within a denser, less permeable matrix.

Thirdly, the interaction of the roasting additives with the chromite ore at high temperatures could have led to the formation of new phases that are resistant to HCl leaching. As noted in the literature, additives like sodium carbonate can facilitate the formation of new compounds, such as sodium chromate [23]. While these new phases might be beneficial under certain leaching conditions, they could also prove unfavourable if they encapsulate or react with the Pd, forming insoluble or less reactive compounds. This could further explain the low Pd recovery observed in the 1000°C roasted samples, where the formation of such phases might have hindered the effectiveness of the HCl lixiviant.

Finally, strong adsorption of Pd onto mineral surfaces or within the pores of the roasted concentrate could be another contributing factor. While roasting can alter the surface characteristics of PGM-containing minerals, influencing their behaviour with leaching solutions [23], excessive heat might increase the adsorption capacity of certain minerals, leading to stronger binding of Pd. This could render the adsorbed Pd inaccessible to the HCl lixiviant, resulting in low recovery. The initial negative recovery observed in the 1000°C roasted samples might be partly attributed to this strong adsorption, where Pd is initially removed from the solution and bound to the mineral surfaces.

IV. Conclusion

This study investigated the recovery of palladium (Pd), a Platinum Group Metal (PGM), from a UG2 chromite concentrate through hydrochloric acid (HCl) leaching, both with and without a roasting pre-treatment using $Na_2\ CO_3$. Roasting at 1273K (1000°C) resulted in near-zero Pd recoveries, likely due to the formation of refractory compounds and increased Pd encapsulation or adsorption within stable oxide or silicate phases at this high temperature. In contrast,

leaching the unroasted concentrate yielded moderate Pd recoveries (up to 90%), indicating that roasting at extreme temperatures may hinder the leaching process rather than facilitate it. The lack of applicability of the shrinking core model (SCM) in this scenario further underlines these findings. The SCM assumes a predictable diffusion and reaction path through a shrinking, permeable layer, which was disrupted in the roasted concentrate due to structural densification, sintering, and the formation of impermeable, refractory compounds. This model could not describe the leaching process effectively because the Pd became encapsulated within dense, stable phases, blocking the HCl lixiviant from reaching unreacted Pd. The contrasting behaviour between unroasted and 1273K roasted samples highlights the complexity of Pd leaching and the importance of optimizing roasting conditions to avoid creating non-leachable phases. Future research should focus on exploring different roasting temperatures, conducting detailed characterizations of roasted concentrates, experimenting with alternative lixiviants, and performing in-depth kinetic studies to maximize Pd recovery.

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