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An Investigation into the Pretreatment Methods for the Extraction of Platinum (Pt) from Platinum Oxide Ores

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Abstract

Platinum (Pt) is known to be one of the rarest metals in the world.lt's unique physical and catalytic properties make it largely valued across a number of various demand segments and technologies. The four main segments of Pt demand are automotive (30-40%), industrial (27-36)%, jewelry (23-30%), and investment ~10%. There has been a global Pt demand with automotive demand being on the highest rising to 16% in 2023 and predicted to grow in 2024. To meet the current rising demands, there has to be an increase in the production of platinum however, there has been a fast depletion of platinum group metals (PGMs) bearing sulfide ores which has activated interest in exploring the likelihood of the recovery of PGMs from near-surface oxidized PGM ores. In Zimbabwe and South Africa, there is an estimated resource of over 500MT of PGM oxides that is either unmined, mined, stockpiled, or discarded as overburdened waste. The recovery of these PGMs has shown to be difficult to process by conventional means as an alternative source to sustain the production of PGMs. Several attempts to process the oxidized ores via conventional hydrometallurgical methods by concentrator plants in Zimbabwe and South Africa have been made. The attempts saw some PGM values that fall within the floatable size range not being floated and successively reporting to the tailings. Attempts to process oxidized PGM ore have been made worldwide using different methods. This paper scrutinizes the different hydrometallurgical methods previously used to process the oxidized PGM ores and their recoveries, the challenges encountered and the research gaps to be considered for future research. Recommendations for future research will also be given based on current research techniques in the mineral processing field.

Keywords: PGM (Platinum Group Metals), Oxidised PGM ores, Mineral Processing, Hydrometallurgy, Recovery)

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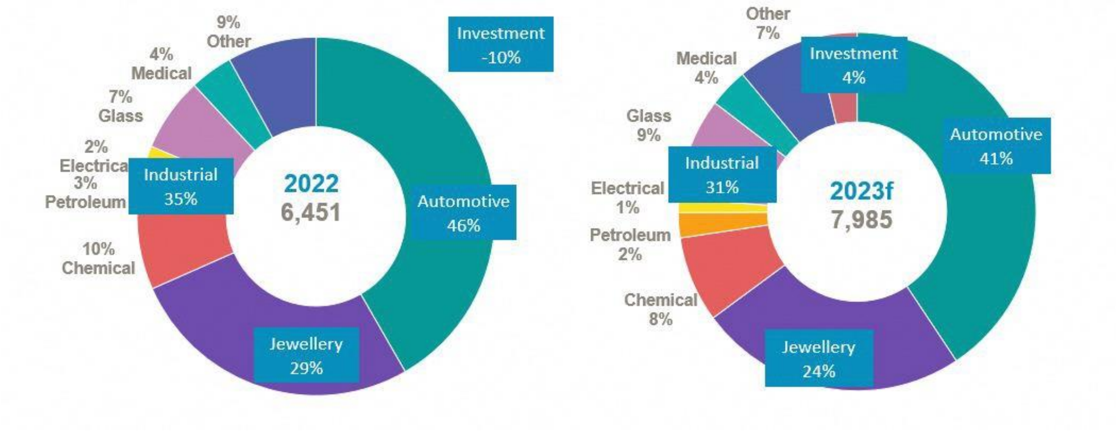
1. Introduction

Platinum group metals (pgms) or elements commonly refer to ruthenium, rhodium, palladium, osmium, iridium, and platinum[4].These platinum elements are used for many industrial applications such as automobiles, jewelry, electronics, fuel cells, and pharmaceuticals. Among the PGE elements, platinum and palladium are in high demand as they play an important role as catalysts in the auto industry, the glass industry, and industrial catalysts (Aspola,et al.,2020). The platinum elements are contained in minerals such as sperrylite,braggitte, cooperite, laureates, etc [24] and these minerals do not occur as independent natural ores but are mainly associated with sulfides, tellurides, arsenides, antimonides, and various complicated mineral phases [11]. According to [24], for many decades the platinum group metals have outshone all other elements in their unparalleled range of applications due to their unique properties such as catalytic qualities, corrosion resistance, good electrical conductivity, and high melting points. The world's largest deposit of platinum group metals (pgms) is the Bushveld igneous complex (bic) which is located in

South Africa. This is followed by the main sulfide zone (msz) of the Great Dyke in Zimbabwe. The Bushveld complex comprises three main reefs, the Merensky reef, the Upper Group 2 (UG2) reef, and the Platreef. The reef that has been highly exploited is the Merensky reef as it contains high pgm grade as compared to the other two. The platreef is known for having high palladium and base metals but lower pgm values [12]. The UG2 reef has significantly high levels of platinum but its main disadvantage is having high concentrations of chromite which has limits and penalties at smelters due to problems that arise as a result of roasting the chromite-containing ores [14]. The concentrations of platinum group elements (pge) in the Great Dyke are restricted to sulfide dissemination of the Main Sulphide Zone (MSZ).Pristine sulfide-bearing ores are mined underground (Mimosa Mine) or from the surface (Ngezi Mine). The near-surface oxidized ores have a large potential at an estimated resource of 400Mt of ore. Attempts to extract the PGE from this type of ore proved uneconomic due to low pge recoveries achieved by conventional metallurgical methods [22].



Source: Market News Insights JPX, "Commodities Analysis,"

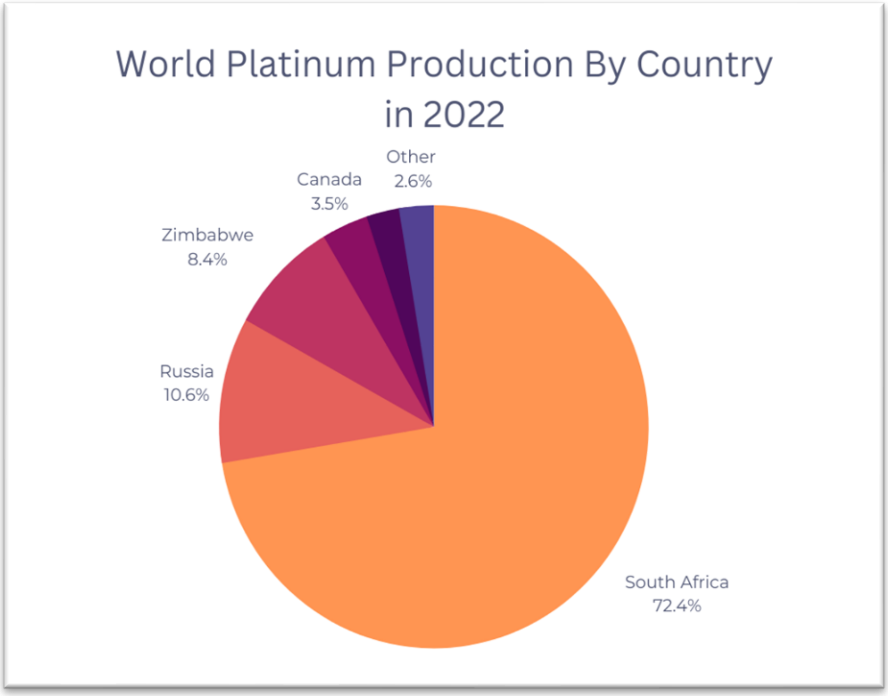
Fig:1 Sources of platinum demand 2022 versus 2023

1.1 Global Platinum Demand

Platinum elements have become important in many modern industrial applications such as jewelry, electronics, fuel cells, and automobiles. According to Mordor Intelligence, the global platinum group metals market size is estimated at 625.03 tons in 2024 and is expected to reach 778.16 tons by 2029, growing at a CAGR of 4.48% during the forecast period (2024-2029). The automotive industry is currently the largest consumer of PGMS, especially platinum and palladium. These PGM's are used in catalytic converters to reduce harmful emissions from vehicles, Kinas [13] mentioned that platinum-group-metal catalysts help facilitate important reactions such as the conversion of harmful pollutants into less toxic substances, thus contributing to environmental sustainability and this leads to growth in the automotive sector which is being driven due to the stricter emission regulations. New Age Metals mentions that another cause of the increase in demand has been the shift towards hybrid and electric vehicles (HEVs/EVs). Although the HEVs/EVs use fewer PGMs than the traditional fuel cars , they still require them in their catalytic systems and this shift is also expected to influence the PGM's demand in the future. Emerging technologies like Hydrogen fuel cells, which utilize platinum as a catalyst also hold promise for future clean energy applications and would contribute to PGM demand growth.

1.2 Major Global Sources of Platinum

Platinum group metals are found mainly from natural primary sources about 80% and secondary sources about 20% which are recycled catalytic converters for example. South Africa is known as the largest producer of platinum in the world, In 2023 alone production from South Africa was an estimated 120 metric tons. Russia came in a distant second place, producing some 23 metric tons that same year [28]. Matthey [16] states that currently there is a PGM deficit and that their global reserves are decreasing.This supply deficit has led companies to turn to platinum recycling and finding alternative ways of processing the available platinum oxides.A review was made on the different sources of secondary platinum.The authors mentioned that waste catalysts used for chemical reactions are one of the most abundant secondary sources of PGMs,they also suggested that automotive catalytic convetors are also known to contain a much higher concentration of Pt, Pd, or Rh than the primary sources.The other secondary sources from which the catalysts can be recovered include computer motherboards,mobile phones and jewellery [13].



Source: Suisse Gold, "The Platinum Market in 2023,"

Fig 2:Global Platinum Production 2022

1.3 Platinum Group Metals Recovery Methods

Platinum group metals are recovered using many methods. The two main groups of recovery include hydrometallurgical methods and pyrometallurgical methods. Hydrometallurgical methods use the dissolution of PGMs from waste materials or the dissolution of a carrier containing PGMs. Mixtures of acids and oxidizers, cyanides, and various additives are employed to achieve this effect [8]. The main operation mode of hydrometallurgical processes for PGM recovery is the selective dissolution of a part of or the entire treated raw material by a chosen procedure. One method is the direct transfer of PGMs from a given raw material into a solution and etching it out; another method is the precipitation of the already dissolved PGMs [13].Recent studies have also found the possibility of recovery using biological methods. Authors [7], [19], [25] conducted research work and mentioned that biometallurgical methods were among some of the growing PGMs recovery methods. Methods such as biosorption, bioleaching, and bioreduction were some of the mechanisms being actively used. The mechanism of biosorption is based on the physical and chemical interactions between metal ions and the functional groups present on the surface of the organic matter.

2. The Research and Development in the Treatment of PGM Oxides

2.1 Overview

Platinum Group-bearing ores have for years been treated using conventional metallurgical processes such as grinding, milling, floatation, smelting, and the production of matte and chemical refining [22]. Once extracted from the ground, the ore is crushed, milled, and concentrated by flotation to recover the valuable platinum group elements (PGE) that are hosted either in discrete platinum group minerals (PGM) or in a solid solution with the base metal sulfides (BMS), namely chalcopyrite, pentlandite, pyrrhotite and minor pyrite (e.g. solid solution Pd in pentlandite,[23]. According to [28] the success of PGM concentration by floatation from these pristine unweathered sulfide ores is largely due to the occurrence of PGMs in close association with base metal sulfide minerals like chalcopyrite, pentlantite, and pyrrhotite which are easily floatable and recoveries achieved during flotation of pristine ores are generally greater than 85%. The depletion of sulfide PGM-bearing minerals has led to a widespread interest in exploring alternative possibilities for recovery of the PGMs from near-surface oxidized PGM ores. According to research conducted, the processing of PGM oxides has proved to be more difficult to process by conventional means [5]. Many attempts to process the oxidized PGM ores by conventional flotation methods achieved poor recoveries (typically less than 50 %).

2.2 Minerology of PGM oxides

The oxidized ores are mainly found on the surface of the pgm ores sometimes 15-30mm deep. They are altered and oxidized due to exposure to atmospheric conditions and acidic ground waters. Research has suggested that the main process taking place during oxidation is said to be the decomposition of base metal sulfides and the formation of iron oxyhydroxides [22].The alteration and oxidation of base metal sulfides are known to affect the chemical properties of the particle surface. This alteration of the particle surface reduces the ability of the oxidized ore to interact and react with floatation reagents such as sulfide collectors.[2]Authors suggests that the Pd remobilization in oxidized PGM ores is also one of the reasons for reducing floatation efficiency by changing the Pt: Pd ratio.

2.3 Pretreatment methods previously employed.

Research has been conducted on the pretreatment of oxidized ores using different techniques such as floatation, sulphidisation of the oxidized ores, leaching, and acid pretreatment. Pretreatment methods are employed as a method to condition or dissolve the hindering oxidized layer from the mineral surfaces so that floatation reagents can easily penetrate the new sulfide layer.

2.3.1 Sulphidisation

Sulfidisation is a process in which a non-sulfide mineral surface is converted to a sulfide-like surface. It involves the reaction of sulfidising agents such as sodium sulfide (Na_2S) or sodium hydrogen sulfide (NaHS) with the oxidized mineral surface. Sodium sulfide then hydrolyses and dissociates in the pulp releasing hydroxide ions (OH^-), hydrosulfide ions (HS^-), and sulfide ions S^{2-}ions into the solution as follows:

$$Na_2S + 2H_2O \rightleftharpoons 2NaOH + H_2S \qquad 1$$

$$\mathrm{NaOH} \rightleftharpoons \mathrm{Na+} + \mathrm{OH^-} \qquad 2$$

$$\mathrm{H_2S} \rightleftharpoons \mathrm{H+} + \mathrm{HS^-} \qquad 3$$

$$\mathrm{HS-} \rightleftharpoons \mathrm{H+} + \mathrm{S_2S^-} \qquad 4$$

Another mechanism suggested for sulfidation is the adsorption of the produced hydrogen sulfide ions on the oxidized mineral surface then a formation of sulfide surface takes place through anionic exchange. Research [28] suggested that controlled potential sulfidation (CPS) limits the chances of excessive sulfide concentration in the pulp. The main challenge posed by CPS is poor production of optimum sulphidisation conditions because of sensitivity to conditioning times, sulphidiser type, and concentration. Consequently, many workers have reported various optimum subsidizing potentials for the processing of oxidized copper ores [18].

2.3.2 Acid Pretreatment

A study was conducted by [20] on the effect of acid pretreatment of oxidized PGM ore. This study used sulfuric acid (H_2SO_4) to pretreat the oxidized ore in a Denver floatation machine while agitating at the same time. Filtration was then conducted to separate the leach residue and used acid. He added potassium Hydroxide (KOH) before floatation. The experimental results showed an increase of 20% in floatation recoveries compared to 17% when floatation was conducted using untreated ore. The main disadvantage of acid pretreatment is its highly corrosive properties. Acid pretreatment needs specialized equipment made of stainless steel or other acid-resistant materials.

2.3.3 Ammonium Pretreatment

The pretreatment of the oxidized PGM ores was investigated using ammonia [17]. This study showed that ammonia pretreatment was not viable because alteration phases of the ore (Fe oxides/hydroxides) were not leached from the particle surfaces during the pretreatment. The results showed a marginal recovery of the PGMs.

3. Conclusion

The pretreatment techniques show that the effectiveness of treatment methods lies in a technique that can penetrate and break the alteration phases of the Fe oxides/hydroxides. The methods carried out have only been able to slightly improve recoveries but cannot be adopted for commercial use.

Refrences

[1] D. L. P. Arrobas, K. L. Hund, M. S. McCormick, J. Ningthoujam, and J. R. Drexhage, *The Growing Role of Minerals and Metals for a Low Carbon Future.* Washington, DC: World Bank, 2017.

[2] M. Becker, J. Wiese, and M. Ramonotsi, "Investigation into the mineralogy and flotation performance of oxidised PGM ore," *Minerals Engineering,* vol. 65, pp. 24–32, 2014.

[3] M. Becker, P. Harris, J. Wiese, and D. Bradshaw, "Mineralogical characterisation of naturally floatable gangue in Merensky Reef ore flotation," *International Journal of Mineral Processing*, vol. 93, no. 3, pp. 246–255, 2009.

[4] C. O'Connor and T. Alexandrova, "The geological occurrence, mineralogy, and processing by flotation of platinum group minerals (PGMs) in South Africa and Russia," *Minerals*, vol. 11, no. 1, p. 54, 2021.

[5] Cramer, "The extractive metallurgy of South Africa's platinum ores," *The Journal of The Minerals, Metals & Materials Society (TMS),* vol. 10, pp. 14–18, 2001.

[6] S. Castro, J. Goldfarb, and J. Laskowski, "Sulphidizing reactions in the flotation of oxidized copper minerals, I. Chemical factors in the sulphidization of copper oxide," *International Journal of Mineral Processing*, vol. 1, no. 2, pp. 141–149, 1974.

[7] N. Das, "Recovery of precious metals through biosorption—a review," *Hydrometallurgy*, vol. 103, no. 1–4, pp. 180–189, 2010.

[8] H. Dong, J. Zhao, J. Chen, Y. Wu, and B. Li, "Recovery of platinum group metals from spent catalysts: a review," *International Journal of Mineral Processing*, vol. 145, pp. 108–113, 2015.

[9] M. Ericsson, J. Drielsma, D. Humphreys, P. Storm, and P. Weihed, "Why current assessments of 'future efforts' are no basis for establishing policies on material use—a response to research on ore grades," *Miner Econ.*, vol. 32, no. 1, pp. 111–121, 2019.

[10] H. Hao *et al.*, "Securing platinum-group metals for transport low-carbon transition," *One Earth*, vol. 1, no. 1, pp. 117–125, 2019.

[11] M. S. Jena, J. K. Mohanty, P. Sahu, R. Venugopal, and N. R. Mandre, "Characterization and pre-concentration of low grade PGE ores of Boula area, Odisha using gravity concentration method," *Transaction of the Indian Institute of Metals*, vol. 70, pp. 287–302, 2017. doi:10.1007/s12666-016-0998-1

[12] R. Jones, "An overview of Southern African PGM smelting," in *Nickel and Cobalt 2005: Challenges in Extraction and Production*, 2005, pp. 147–178.

[13] S. Kinas, D. Jermakowicz-Bartkowiak, P. Pohl, A. Dzimitrowicz, and P. Cyganowski, "On the path of recovering platinum-group metals and rhenium: A review on the recent advances in secondary-source and waste materials processing," *Hydrometallurgy*, vol. 106, p. 106222, 2023.

[14] K. S. Liddel and M. D. Adams, "Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates," *Journal of the Southern African Institute of Mining and Metallurgy*, pp. 2225–6253, 2012.

[15] L. Little *et al.*, "Investigating the effects of particle shape on chromite entrainment at a platinum concentrator," *Minerals Engineering*, pp. 46–52, 2016.

[16] J. Matthey, "PGM market report May 2016," *Johnson Matthey Technology Review*, vol. 60, no. 3, pp. 209–210, 2016.

[17] K. J. Musonda, *Ammonia Leaching as a Pre-Treatment for the Processing of Oxidised PGM Ores*, M.S. thesis, University of Cape Town, Cape Town, 2015.

[18] D. Nagaraj and R. Farinato, "Evolution of flotation chemistry and chemicals: A century of innovations and the lingering challenges," *Minerals Engineering*, vol. 96, pp. 2–14, 2016.

[19] C. K. Ng, T. K. C. Tan, H. Song, and B. Cao, "Reductive formation of palladium nanoparticles by Shewanella oneidensis: role of outer membrane cytochromes and hydrogenases," *RSC Advances*, vol. 3, no. 44, pp. 22498–22503, 2013.

[20] M. Ramonotsi, *Characterisation of the Effect of Alteration on the PPM Platinum Ore and Evaluation of Selected Strategies to Improve Metallurgical Performance*, M.S. thesis, University of Cape Town, Cape Town, 2011.

[21] T. Raymond, E. Sterck, and B. Clifford, "Platinum essentials: fuel cell electric vehicles are forecast to drive material long-term demand growth for platinum," WPIC, London, 2022.

[22] T. Oberthür, F. Melcher, T. W. Weiser, and L. Gast, "Distribution of PGE and PGM in oxidized ores of the Main Sulfide Zone of the Great Dyke, Zimbabwe," in *9th International Platinum Symposium, Ext. Abstr.*, Boudreau, A., Ed., 2002, vol. 333.

[23] I. Osbahr, T. Oberthür, R. Klemd, and A. Josties, "Platinum-group element distribution in base-metal sulfides of the UG2 chromitite, Bushveld Complex, South Africa—a reconnaissance study," *Mineralium Deposita*, vol. 49, pp. 655–665, 2014.

[24] C. O'Connor and T. Alexandrova, "The geological occurrence, mineralogy, and processing by flotation of platinum group minerals (PGMs) in South Africa and Russia," *Minerals*, vol. 11, no. 1, p. 54, 2021.

[25] P. Sahu, M. S. Jena, N. R. Mandre, and R. Venugopal, "Platinum group elements mineralogy, beneficiation, and extraction practices – an overview," *Mineral Processing and Extractive Metallurgy Review*, vol. 42, no. 8, pp. 521–534, 2021. doi:10.1080/08827508.2020.1795848

[26] I. Yakoumis, M. Panou, A. M. Moschovi, and D. Panias, "Recovery of platinum group metals from spent automotive catalysts: A review," *Cleaner Engineering and Technology*, vol. 3, p. 100112, 2021.

[27] M. Locmelis, F. Melcher, and T. Oberthür, "Platinum-group element distribution in the oxidized main sulfide zone, Great Dyke, Zimbabwe," *Mineralium Deposita*, vol. 45, pp. 93–109, 2010.

[28] M. H. Jones and J. T. Woodcock, "Perxanthates—a new factor in the theory and practice of flotation," *International Journal of Mineral Processing*, vol. 5, no. 3, pp. 285–296, 1978.

[29] *Platinum Group Metals Market,* Mordor Intelligence. [Online]. Available: https://www.mordorintelligence.com/industry-reports/platinum-group-metals-market. [Accessed: Nov. 9, 2024].

[30] *Hydrogen Energy Impact on Platinum Metals,* New Age Metals. [Online]. Available: https://newagemetals.com/hydrogen-energy-impact-platinum-metals-new-age-metals-river-valley-palladium/. [Accessed: Nov. 9, 2024].

[31] *Global Mine Production of Platinum,* Statista. [Online]. Available: https://www.statista.com/statistics/273645/global-mine-production-of-platinum. [Accessed: Nov. 9, 2024].