Towards bioleaching of PGMS

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ABSTRACT

This paper explores bioleaching as a viable method for extracting precious group metals (PGMs) with potential advantages over the traditional energy-intensive extraction processes that cannot cope with the depletion of high-grade ores. The proposed bioleaching process consists of three main steps: base metal removal, bio-decomposition of silicates and PGM extraction using biogenic cyanide. Base metals form stable complexes with cyanide under similar oxidative conditions required for PGM leaching. Such that efficient removal of base metals minimizes biogenic cyanide consumption, while the subsequent decomposition of silicates prevents PGM loss. The use of mixed thermophilic microorganisms enhances kinetics during base metal removal, resulting in a base metal-free residue for PGM bioleaching. For PGM bioleaching, a decoupled approach was proposed, involving biogenic cyanide production, followed by its utilization for PGM leaching. This accommodates the different conditions required by cyanide-producing microorganisms and those for PGM leaching. A conceptual flowsheet was drawn to illustrate the bioleaching of PGMs. The challenges related to the influence of PGM mineralogy on the flowsheet were brought to attention, along with their respective solutions.

1. Introduction

Traditionally, pyrometallurgical processes have dominated metal extraction from ores, especially the sulphidic type. However, these processes are electrical energy intensive and as such, their application is more suited for high-grade ores as their use on low-grade ores is uneconomical. Furthermore, the ongoing power disruptions in South Africa pose a serious threat to the world's leading producer of platinum group metals (PGMs). In contrast, hydrometallurgical processes can economically beneficiate high and low-grade and also complex ores.

Although hydrometallurgy has replaced pyrometallurgy in the extraction of many metals, there are still some metals like the PGMs that are not currently extracted industrially without some pyrometallurgical pre-treatment steps. PGMs are a family of six structurally and chemically similar elements that are most valued for their wide range of industrial, medical, and electronic applications (Glaister and Mudd, 2010). They are: Pt, Pd, Rd, Ru, Ir and Os. Together with silver and gold, PGMs are classified as noble metals due to their high oxidation potential and corrosion resistance (Xiao and Laplante, 2004; Glaister and Mudd, 2010).

Pyrometallurgy requires large volumes of high-grade feed for economic processing. The depletion of high-grade ores, therefore, implies decreased feed rates to the pyrometallurgical stages and consequently decreased productivity and profitability. The production of PGMs is primarily controlled by Southern Africa (South Africa and Zimbabwe) and Russia. However, due to the Ukraine war, there is a potential risk to Russian PGM sales. Additionally, in South Africa, frequent electricity load-shedding poses a significant threat to the electrical PGM smelting process. Consequently, this situation serves as a crucial catalyst for exploring alternative options that are less reliant on electricity consumption. Furthermore, with the ever-fluctuating metal prices, the profitability of metal processing is compromised even further. Thus, partial or total replacement with a low-cost hydrometallurgical alternative is imperative. To further improve the environmental friendliness of hydrometallurgy, bio-hydrometallurgy has attracted a lot of interest due to its inherent advantage of using naturally occurring microorganisms to produce lixiviants, with less environmental concerns associated with production and handling. Moreover, the process has been noted to have lower energy consumption (Bosecker, 1997; Rawlings, 2005). Furthermore, the re-use of microorganisms ensures a constant supply of the required lixiviant (Ndlovu, 2008).

Considering the economic and environmental advantages of bio-

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hydrometallurgy, it would be beneficial to expand the application of this technology in the processing of PGMs (Mwase and Petersen, 2017) (Mpinga et al., 2018). An additional incentive to explore the bio-processing of PGMs stems from the imminent depletion of high-grade ores that yield concentrates suitable for smelting. The current approach involves blending Merensky Reef ores with UG2 ores to address smelting challenges.

The Merensky Reef is exceptionally rich in platinum group elements, occurring in the form of sulphide minerals like cooperate and braggite (Cramer, 2001). It also contains chromite and sulphides. In terms of conventional PGM processing methods, the Merensky Reef is the most economically viable option (Cramer, 2001). For instance, the Merensky Reef is ten times more abundant in base metal sulphides (BMS) than the UG2 Reef (Solomon et al., 2011). However, as the Merensky Reef is being depleted, it becomes crucial to utilize other PGM reserves.

The Platreef also holds a significant amount of economically viable PGMs, albeit at a lower grade compared to the Merensky and UG2 Reefs. The mineralogy of the Platreef is highly complex, with sperrylite being the most common PGM mineral (Cramer, 2001). The Platreef also contains substantial quantities of pyrrhotite (Cramer, 2001). On the other hand, the UG2 Reef primarily consists of chromite, with PGMs occurring as sperrylite, braggite, and cooperate (Mpinga et al., 2018). In the UG2, low-grade PGM concentrates are sometimes associated with high chromite contents. The high pyrrhotite content in Platreef ores and the elevated chromite levels in UG2 ores pose challenges to smelter efficiency (Mwase et al., 2012a).

In some cases, PGMS are locked in silicates and report to the tailings. For example, it has been reported that almost 50% of PGMs in the Platreef ores deport to silicate minerals (Bryson, 2008) resulting in a significant fraction of PGMs being lost to the tailings. There is, therefore, a need to also look into silicate-destroying microorganisms when developing a bioleaching process for PGMs. In other cases, the reefs are associated with mineral grade inconsistencies, meaning that some regions might have very low PGM grades that are not suitable for the concentrator-smelter-refinery route. Grade inconsistency has also been reported for the Platreef ores (Mwase et al., 2012b). All the challenges mentioned above suggest that there is a significant need to look at other PGM processing alternatives.

Conventional leaching of the platinum group metals has been through use of chlorides (Tuncuk et. al., 2012) or cyanide (Hourn and Turner, 2012). Thus, if a bioprocessing route would be developed, it follows then that chlorine or cyanide-producing microorganisms might be a good option. However, whereas cyanogenic microorganisms have been identified and isolated, chlorine-producing microorganisms have not yet been identified. Therefore, the use of cyanide producing microorganisms is the best starting point in developing a process for the bioleaching of PGMs.

The importance of recovering PGMs is evident in the circular model of metal resource recovery from urban wastes. Due to their high value and depletion of deposits, PGMs are among the metals that have been targeted for metal recycling. The recycling of PGMs may be done by conventional chemical recovery methods or new technologies such as biotechnology (Dodson, 2015; Karim and Ting, 2021). The low-cost requirements and environmental friendliness of biotechnology make this option attractive (Liang and Gadd, 2017). However, the aim of this paper is to provide the necessary knowledge for the bioleaching of PGMs from primary sources. The sections that follow provide a background of the mineralogy of PGM ores and their conventional processing, a description of the bioleaching of the major mineral phases associated with PGMs, the challenges and opportunities of PGM bioleaching and a suggested processing route for the bioprocessing of PGM ores.

2. PGM occurrence

Proterozoic and Archaean age layered intrusions (e.g. the Bushveld Complex, South Africa and the Great Dyke, Zimbabwe) are the world's foremost sources of PGMs (Oberthür et al., 2018). Over 80% of the earths reserves are contained in the Bushveld Complex of South Africa (Junge et al., 2015). Generally, PGMs are associated with either chromitites or sulfide-rich rocks (Scoon and Teigler, 1994; Naldrett and Naldrett, 2004). In chromite environments, PGMs occur in alloys, sulphides, arsenides, sulpharsenides (Junge et al., 2014; 2016; Barnes et al., 2016). Bismuthotellurides are generally found in base metal sulphide systems such as the Merensky Reef, the Great Dyke and the Platreef (Kinloch, 1982; Oberthür et al., 2003; Holwell and McDonald, 2007; Osbahr et al., 2013; Junge et al., 2015). PGM sulphides and arsenides are also found in base metal sulphide systems (Junge et al., 2019).

Although, silicates are a high constituent in PGM ores (Fig. 1), and sometimes contain most PGMs, generally PGMs are associated with the sulphide phases, as reported in previous work (Seymour and O'Farrelly, 2001; Schouwstra and Kinloch, 2000). They exist within base metal sulphide (BMS) minerals or at BM-silicate grain boundaries. For this reason, milled PGM ores can be floated to recover PGMs (Junge et al., 2019). Generally, PGMs are associated with the BMS (Lee, 1996). Virgin ores consist mainly of pyrrhotite ($Fe_{1-x}S$) (~75%), pentlandite (Fe, $Ni)_9S_8$), chalcopyrite ($CuFeS_2$) and minor quantities of pyrite (FeS_2) (Junge et al., 2019).

Some PGMs are also found in oxides that form as weathering products of sulphide ores (Oberthür et al., 2013). During weathering of sulphide ores, there is a redistribution of PGMs and a substitution of base metal sulphides by iron oxides or hydroxides (Junge et al., 2019). The base metal sulphides are oxidised when there is low fugacity of sulphur (Augé and Legendre, 1992). As can be seen in Fig. 1 (based on Junge et al., 2016), the most common non-sulphide phases in PGM ores are silicates and chromites.

3. Conventional processing of PGMs

Conventional processing of PGM ores consists of mineral beneficiation (flotation), pyrometallurgical processing (matte smelting) and hydrometallurgical extraction (leaching) (Crundwell et al., 2011). A typical flowsheet showing the main processes involved in the processing of PGMs is shown in Fig. 2 (based on Cramer, 2008).

Smelting sub-processes include concentrate drying, electric arc smelting to remove slags, converting of matte to reduce sulphur and iron, gas cleaning, production of H_2SO_4 from SO_2, matte granulation and crushing of matte. Base metal refining consists of sub-processes such as sulphate leaching, impurity removal, copper electrowinning, cobalt removal and recovery, nickel electrowinning or hydrogen reduction and sulphuric acid production from SO_2. PGM separation and refining consists of sub-processes such as leaching, solvent extraction, ion exchange, precipitation, distillation, effluent treatment and metal preparation for dispatch.
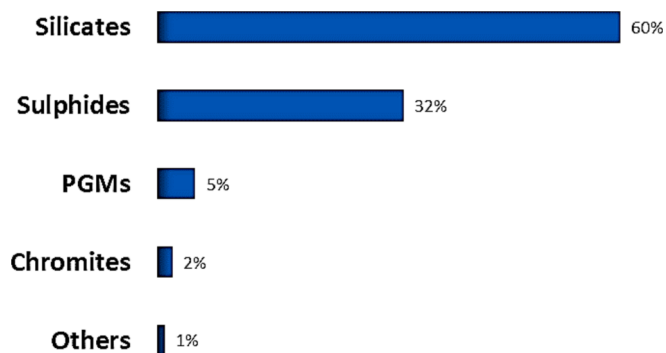

Fig. 1. Mineral association proportions based on MLA data for a PGM concentrate from the Bushveld Complex of South Africa.
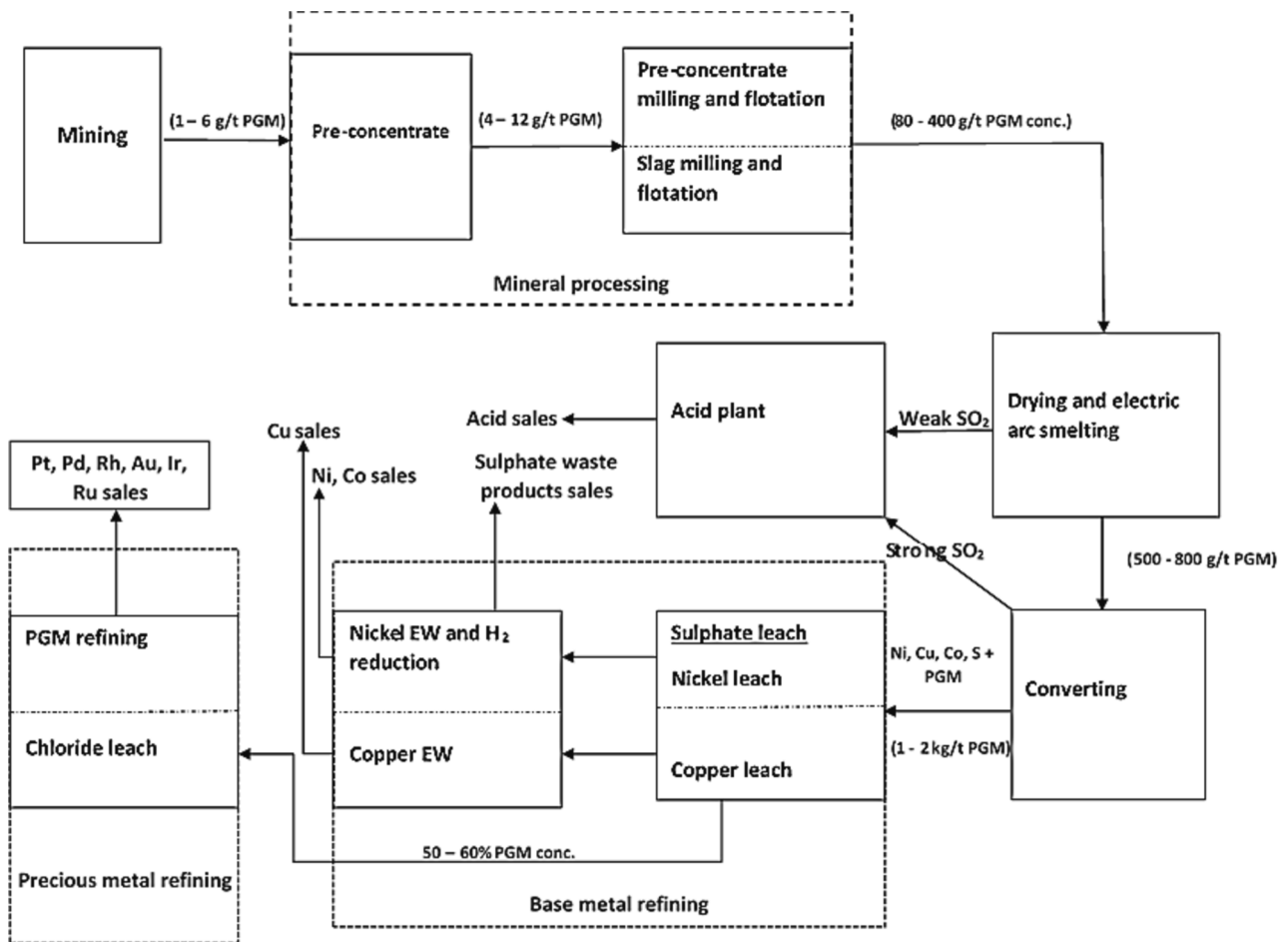
Fig. 2. Conventional Processing of PGMs.

4. Direct leaching of PGMs

Several hydrometallurgical approaches have been proposed for the extraction of PGMs (Mpinga et al., 2015). The complex PGM mineralogy has made the development of a universally feasible process difficult. Of relevance to this paper are those processes that use cyanide for the extraction of PGMs as it is anticipated that leaching with biogenic cyanide will require more or less the same parameters as those for inorganic cyanide leaching.

Hydrometallurgical extraction of PGMs is motivated by the need to profitably process low-grade and mineralogically complex ores within strict environmental regulations. Conventional smelter-based operations are only applicable to high-grade, low-chromite, large resources and long life-of-mine operations (Mpinga et al., 2015). Several direct
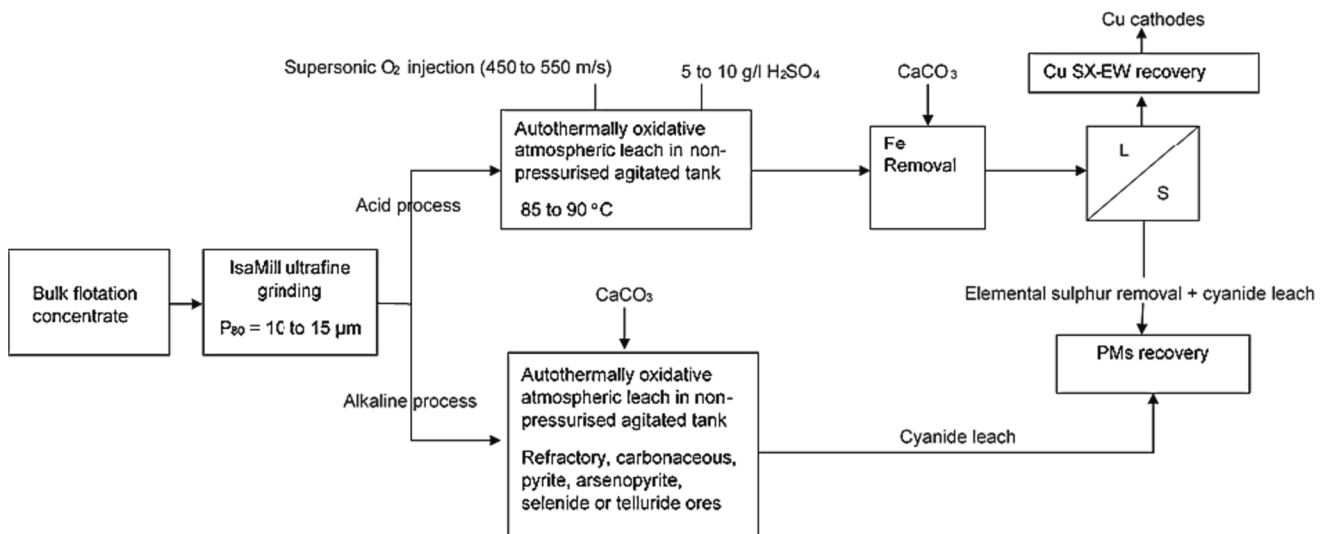

Fig. 3. Albion process for the hydrometallurgical extraction of PGMs (Mpinga et al., 2015).

leaching approaches to PGM extraction have been proposed, but of interest to this paper are the commercial applications that use the cyanide lixiviant (Albion process (Fig. 3) and the pressure oxidation processes (Fig. 4)). Several authors have also looked at direct PGM extraction techniques from secondary materials, especially spent automotive catalyst. Table 1 provides additional pre-treatment steps that have yielded improved PGM recoveries.

5. Postulating the bioleaching of PGMs

5.1. First step - bioleaching of base metal sulphides associated with PGMs (Pretreatment of PGM concentrates)

The removal of base metals prior to the PGM extraction process is important in order to minimise their interference during the PGM leaching stage. Base metal removal can be done using mesophilic and thermophilic microorganisms. With respect to base metal leaching from PGMs, previous work (Mwase et al., 2012a; 2012b; Mwase et al., 2014, Eksteen et al., 2014) on Platreef PGM concentrates, used columns of granite coated with slurry and a mixture of thermophiles and mesophiles. Recoveries of 91.1% Cu, 98.5% Ni and 83.5% Co were achieved after 88 days of leaching at 65 °C. The setup for the leaching tests is shown in Fig. 5 (Mwase et al., 2012a).

After successful removal of base metals from PGM concentrates, the next stage is the leaching of PGMs. However, since, as reported earlier, some PGMs report to silicates, and get lost to the tailings, it would be important to biochemically decompose the silicate minerals, prior to the extraction of PGMs.

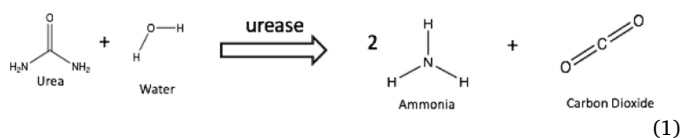### 5.2. Second step – Decomposition of silicates

The advantages of using microorganisms, instead of chemicals, for silicate decomposition include environmental friendliness, cost-effectiveness and high selectivity. Silicate-decomposing microorganisms are known to be much more environmentally gentle compared to toxic chemicals, resulting in significantly reduced environmental impact (Dwyer et al., 2012). Moreover, employing silicate-decomposing microorganisms instead of chemicals offers overall cost-effectiveness since microorganisms can be cultivated using low-cost substrates such as agricultural waste. Other studies (Wonyen et al., 2018; Faramarzpour et al., 2022) have reported improved selectivity and enhanced process efficiency with the use of microorganisms, and the same is anticipated with the use of silicate-decomposing microorganisms. The effectiveness of microorganisms for silicate decomposition can vary depending on the specific mineral composition, pH, temperature, and other environmental factors (Lauwers and Heinen, 1974). Therefore, there is a need to explore various experimental options for the use of microorganisms for silicate decomposition in PGM ores.

According to Henne and co-researchers (2018), *A. ferrooxidans* are able to solubilise some Fe^{2+}-bearing silicates such as chlorite and amphiboles that are also associated with PGMs. It is, therefore, likely that some degree of silicate decomposition will take place during the bioleaching of PGMs with either mesophilic or thermophilic microorganisms. Henne and co-researchers (2018) found that the dissolution of silicates provided access to sulphides trapped within the silicates. Earlier work by Welch and Ulman (1996) also revealed the possibility of solubilising a number of silicates using *A. ferrooxidans* and *F. acidarmanus*.

Dopson and co-workers (2009) were also able to solubilise silicates using *F. acidarmanus* and *A. ferrooxidans*. The authors reported that the microorganisms tend to grow on the dissolution of the silicate minerals. They found that during the dissolution of the silicate mineral olivine, there was a release of Fe^{2+} that might have become a substrate for the microorganisms resulting in increased leaching rates. The finding by Henne and co-workers (2018) that *A. ferrooxidans* tend to attack Fe^{2+} silicates is consistent with those by Dopson and co-researchers (2009). However, since some major silicates associated with PGMs such as serpentine and are not iron-bearing, these might not be amenable to dissolution with *A. ferrooxidans*. The tendency of silicate minerals to dissolve in the presence of acidophilic microorganisms has also been reported by several other researchers (Bhatti et al., 1993; Bhatti et al., 1994; Tasa et al., 1995; Bigham et al., 2001; Santelli et al., 2001; Welch and Banfield, 2002). Using a mixed culture of acidophilic iron- and sulphur-oxidising bacteria, Bhatti and collaborators (1993) bioleached mixed silicates that were mostly phlogopite whereas Bigham and co-workers (2001) were able to solubilise mica. Using similar microorganisms, Bhatti and collaborators (1994) and Tasa and co-workers (1995) solubilised mixed silicates whereas Santelli and co-researchers (2001), Welch and Banfield (2002) targeted the silicate fayalite.

An indirect mechanism was proposed for the dissolution of silicates by bacteria (Avakyan et al., 1985). Avakyan and co-researchers (1985) dissolved silicon using the bacteria *Sarcina ureae* and observed the production of ammonia that in turn resulted in an alkaline medium which then disrupted the siliceous bonds. The formation of ammonia by *Sarcina ureae* is as shown in **Equation (1)** (Cook, 2017).

$$\underset{\text{Urea}}{H_2N-\overset{O}{\overset{\|}{C}}-NH_2} + \underset{\text{Water}}{H-O-H} \xrightarrow{\text{urease}} 2 \underset{\text{Ammonia}}{\overset{H}{\underset{H}{N}}-H} + \underset{\text{Carbon Dioxide}}{O=C=O}$$

(1)

Avakyan and co-researchers (1985) also found a similar result with the bacteria *Paenibacillus mucilaginosus* which was able to release silicon
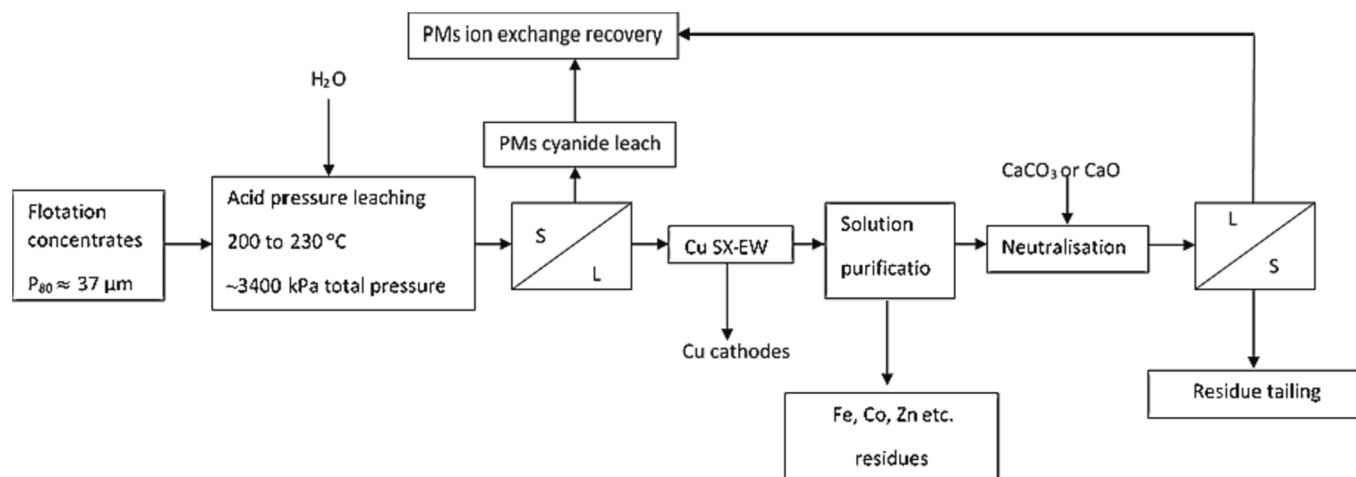

Fig. 4. Total Pressure Oxidation process for the hydrometallurgical extraction of PGMs (Mpinga et al., 2015).

Table 1

The extraction techniques employed for the pre-treatment and subsequent recovery of precious metals (PGMs) from secondary sources.

Material used – and metals extracted	Pre-treatment method	Highlights	References
Spent automotive catalyst – Pt, Pd and Rh	Ultrasound assisted nitric acid	80% ultrasonic power, 37 kHz ultrasonic frequency, 6 M HNO₃, 50 min. Accelerated leaching, improved recoveries, reduced reagent consumption, lowering temperature requirements. Recoveries of 38% Pt, 44% Pd and 91% Rh were achieved.	Karim and Ting (2022)
Spent automotive catalyst – Rh	Oxidation followed by reduction	Oxygenation by addition of hydrogen. Resulted in Increased dissolution rates. Recoveries of 56% Rh were attained.	Chen et al. (2014)
Spent automotive catalyst – Pt, Pd, Rh	Use of formic acid	PGMs were leached with electro-generated chlorine after pretreatment of spent automotive catalyst with formic acid. High extractions are achieved at low concentrations of formic acid. Recoveries of 97% Pt, 94% Pd and 90% Rh were attained.	Upadhyay et al. (2013)
Spent automotive catalyst – Pt, Pd, Rh	Zn vapour deposition	Zn vapour treatment of spent automotive catalytic converters prior to acid leaching. Resulted in improved recoveries of 98% Pt, 97% Pd and 65% Rh.	Sasaki and Maeda (2014)
Spent automotive catalyst – Pt	Coke oxidation	Burning of the carbonaceous material supporting the catalysts. Resulted in 100% Pt solubilisation.	de Sá Pinheiro et al. (2004)
Na₂PtO₃ – Pt	Calcination	Formation of a (Na,Li)₂PtO₃ solid solution by heating Pt in the presence of Li₂CO₃ at 800 °C. Ability to dissolve in relatively safe lixiviants such as HCl. Resulted in 96 – 97% Pt recovery.	Kasuya et al. (2014)
Spent automotive catalyst – Pt, Pd, Rh	Mechanochemical activation	Done in the presence of an oxidising agent – details still concealed. Resulted in 77.2% Pt, 97.4% Pd and 62.1% Rh.	Wei et al. (2019)

from quartz. The dissolution of silicon by *Paenibacillus mucilaginosus* was later investigated by Liu and co-workers (2006). They found that two processes were responsible for the decomposition of silicate minerals, i. e., the production of organic acids and polysaccharides by bacteria, followed by the adsorption of organic acids and SiO₂ by the polysaccharides. The two processes altered the equilibrium between the mineral and liquid phases, and this caused the solubilising of silicon.

In addition to bacteria, it has been proven that fungal species such as *Aspergillus* and *Penicillium* are able to dissolve silicate minerals (Castro et al., 2000). Castro and collaborators (2000) found better extractions with *A. Niger* than with bacteria. They attributed the improved leaching kinetics of *A. Niger* to the production of citric acid by the fungal species. The citric acid produced by the fungal species results in the formation of complexes with metals (Castro et al., 2000). The complexation of metals in turn results in the rearrangement of the mineral structure and the consequent release of silicon (Ehrlich and Rossi, 1990). Other studies have also reported complexation in the decomposition of silicates by bacteria (Webley and Taylor et al., 1963, Henderson and Duff, 1963).

However, the use of silicate-decomposing microorganisms also presents some disadvantages. These include challenges associated with process optimization and longer processing times compared to chemical methods. Microorganisms are highly sensitive to environmental changes, which can make it challenging to consistently maintain their efficacy (Dwyer et al., 2012). Achieving optimal conditions for microbial activity, such as strain selection, growth conditions, pH, temperature, and nutrient availability, requires careful monitoring and optimization. Additionally, the slower kinetics of microbial silicate decomposition can contribute to longer processing times compared to chemical-based methods. These factors highlight the need for ongoing research and development to address these challenges and improve the efficiency of using silicate-decomposing microorganisms in mineral processing.

It is also known that the dissolution of silicates is likely to influence conditions such as pH and viscosity, and might result in the production of fluoride ions, associated with the silicates, that might inhibit the further dissolution of other mineral sulphides (Dopson and collaborators, 2008). Dopson et al., 2009 also reported on the release of toxic fluoride elements during silicate decomposition. The thickening of leach liquor by silica was reported by Pietrobon and co-workers (1997). Brierley (2001) and Salo-Zieman and co-researchers (2006) reported the passivation of sulphide minerals by jarosite during silicate dissolution. The formation of jarosite might be due to the low pH created during the oxidation of sulphide species associated with silicates and the dissolution of the iron associated with the silicates (Dopson et al., 2008). Given the challenges associated with silicate dissolution, the decomposition of silicates may be done as a separate stage, since the pH for silicate dissolution (3 to 5) (Henne et al., 2018) is higher than the pH for base

metal leaching (~1.5). Furthermore, it is known that acidophilic microorganisms preferentially attack sulphide minerals over silicate minerals (Edwards et al., 2000), perhaps due to the easier release of Fe²⁺ from the iron-sulphide bond.

It is anticipated that after the decomposition of silicates, the PGMs will be more amenable to bioleaching. The next section looks into the bioleaching of PGMs following the pretreatment stages. A background of PGM cyanide leaching chemistry is presented followed by a closer look into the possible approaches for the bioleaching of PGMs.

5.3. Third step – Bioleaching of PGMs

5.3.1. PGM cyanide leaching chemistry

Almost all transition metals form complexes in the presence of cyanide (Marsden and House, 2006). These complexes show high water solubility and chemical stability. It can be deduced that the reactions are similar to those of gold. However, the thermodynamic aspects of PGMs are different from those of gold, being associated with much higher oxidation potentials (Dorin and Woods, 1991; Marsden and House, 2006). Leaching of PGMs is not possible at room temperature and pressure due to poor kinetics (Chen and Huang, 2006). It is also known that the PGMs, namely Pd, Pt and Rh leach to different extents during pressure cyanidation, with Pd having the highest extraction efficiency and Rh having the least (Chen and Huang, 2006). Huang and collaborators (2006) also reported that the chemical stabilities of the PGM-CN complexes at high temperature were in the order Rh > Pt > Pd. The higher chemical stability of $Rh(CN)_6^{3-}$ than $Pd(CN)_4^{2-}$ is ascribed to different geometrical structures, with $Rh(CN)_6^{3-}$ having an octahedral structure and $Pd(CN)_4^{2-}$ having a planar structure (Huang et al.., 2006). The octahedral structure for $Rh(CN)_6^{3-}$ implies the need to firstly break Rh-CN bond before oxidation (Huang et al.., 2006), unlike the planar structure $Pd(CN)_4^{2-}$ that would not require breakdown of any bonds before oxidation (Huang et al.., 2006). The higher chemical stability for $Pt(CN)_4^{2-}$ compared to $Pd(CN)_4^{2-}$ is due to $Pt(CN)_4^{2-}$ being heavier, and therefore being more thermodynamically and kinetically more stable (Huang et al.., 2006). Marsden and House (2006) and Mountain and Wood (1988) gave the stability constants (Log β_4) for $Pt(CN)_4^{2-}$ and $Pd(CN)_4^{2-}$ as 78 and 63, and both were higher than that for $Au(CN)_4^{-}$ (56). The E_h-pH diagrams for Pd and Pt (Dorin and Woods, 1991) reveal wide stability regions for both the Pd and Pt cyanide complexes. The metal/metal-CN complexes are pH dependent up to a pH of 9.2, beyond which they become independent of pH (Dorin and Woods, 1991). It can also be deduced that the formation of complexes will require oxygenated cyanide solutions, since the metal complexes exist below the oxygen
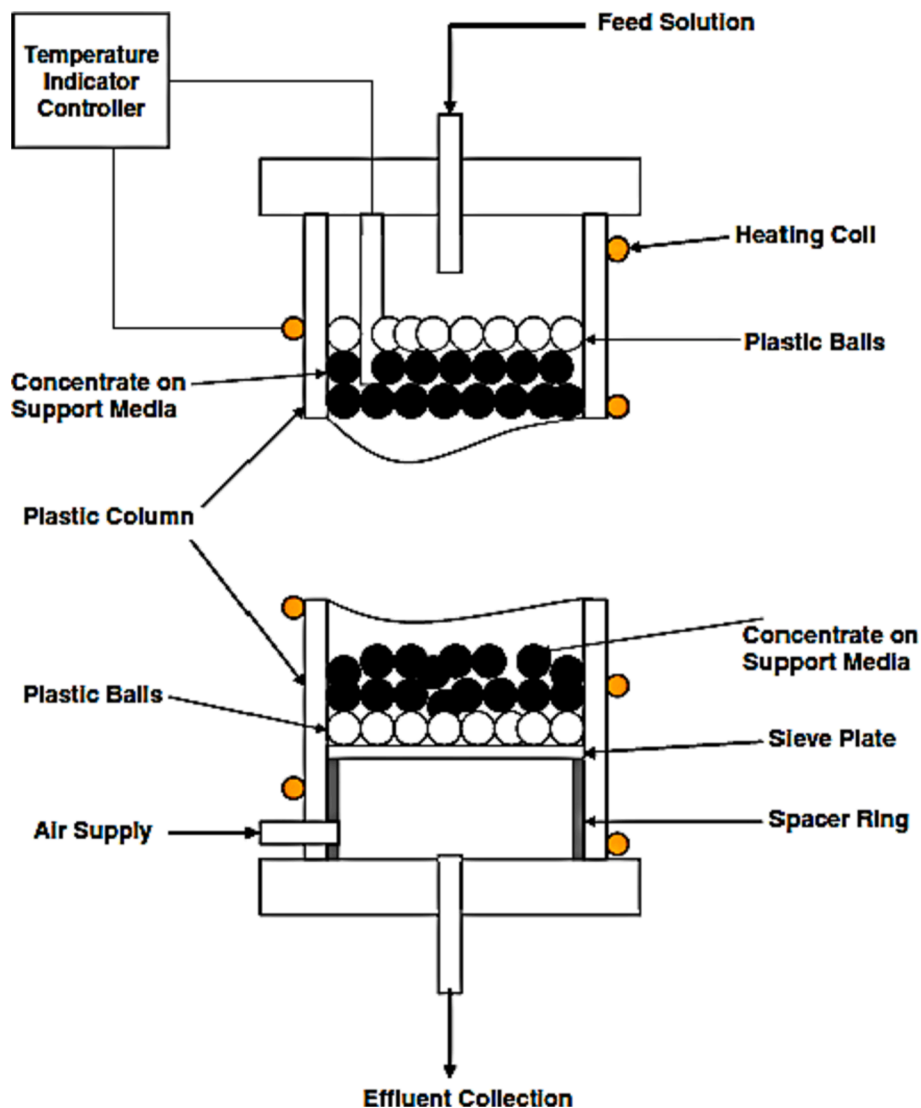
Fig. 5. Schematic layout of the It can be deduced from this paper that from PGMs (Mwase et al., 2012a).

line. The thermodynamic driving force for the formation of $Pd(CN)_4^{2-}$ is greater than that for $Pt(CN)_4^{2-}$ since there is greater difference in potential between $Pd(CN)_4^{2-}$ formation and oxygen reduction reaction (Chen and Huang, 2006).

Mclnnes and co-researchers (1994) worked on ground ores (80% $-74\,\mu m$) containing Pt, Pd and Au, and they observed the best recoveries for Pd (85%) at pH of 9.5 and at ambient conditions using NaCN lixiviant. However, Pt could not be extracted beyond 20% at the same ambient conditions. From the findings, it was observed that Au recoveries were higher than for both Pd and Pt, due to the weaker metallic bonding strength associated with Au (Huang et al.., 2006). Earlier work by Bruckard and co-workers (1992) realized 88 – 92% Pd recoveries and 73 – 79% Pt recoveries at 100 °C, pH of 9.5 – 11.5 for 4 – 6 h using atmospheric air. They reported that optimum leaching temperatures were between 100 and 125 °C. It is quite evident that high temperatures (>100 °C) are necessary for efficient PGM extraction. Huang et al. (2006), firstly removed base metals using acidic pressure leaching and then subjected the residue to pressure cyanidation for selective dissolution of PGMs, and subsequent zinc cementation to produce a Pt-Pd concentrate. Zinc cementation was done at 60 – 80 °C, pH 9.5 – 10, 2 h and 1 atm. Recoveries of $> 95\%$ and $> 99\%$ were attained for Pt and Pd, respectively, after the leaching stages. The leaching conditions by Huang et al. (2006) are summarised in Table 2.

Mwase et al., (2012a) used a laboratory scale column to investigate heap leaching of residual PGM concentrate following base metal removal with a mixed culture of thermophiles and mesophiles. They observed that some Rh and Pd, and to a much less extent Pt, were co-extracted with base metals. Dorfling et al., (2011) also reported similar co-extractions for sulphate based PGM refining. The subsequent cyanide leaching column tests were done at 23 °C (room temperature), and after 21 days, recoveries of 20.3% Pt, 87% Pd and 46% Rh were attained.
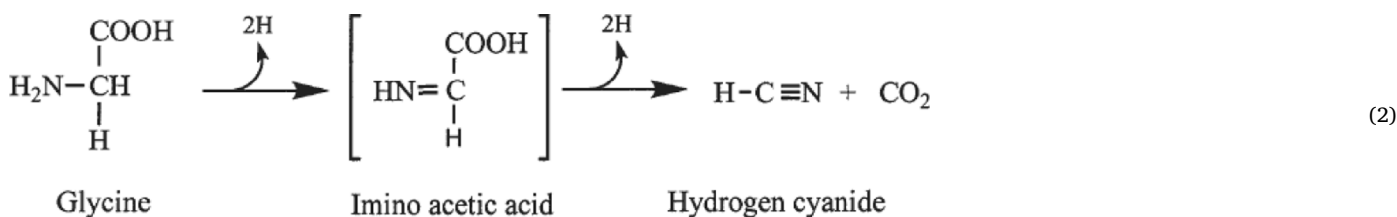
For the heap leaching of residual PGM concentrate, Mwase et al., 2012a deduced that Pd leached the most, with very little extractions for Pt and Ru. It can also be deduced from the figure that for both Pt and Rh, there was still leaching taking place when the tests were ended. Mwase and co-researchers (2012a) also inferred that during cyanide leaching of PGMs, not much of the gangue elements are leached. The relatively lower recoveries of Pt were attributed to its deportment to cyanide insoluble sperrylite. After increasing the leaching temperature to 50 °C and the leaching period to 45 days, Mwase and co-workers (2012b) were able to increase PGM recoveries. For example, the recovery of Pd increased to 96.5% and Pt recovery increased to 35%. After 60 days, recoveries of Pt and Pd were increased to 57.8% and 99.7%, respectively (Mwase et al., 2014). The cyanide leaching of PGM therefore appears to follow first order kinetics, and higher temperatures (>100 °C) should be

Table 2
Leaching conditions for a PGM-bearing sulphide concentrate.

Stage	Temperature (°C)	Lixiviant concentration (g/l)	Time (h)	O$_2$ pressure (MPa)	L:S ratio	Recoveries
Pressure acid leach (with H$_2$SO$_4$)	200	12.5	6	1.8	4:1	>99% Cu, Ni and Co
Two-stage cyanidation (with NaCN)	160	6.25	1	1.5	4:1	>95% precious metals

expected to yield good recoveries for all PGMs.

Since NaCN leaching of PGMs has been found to be feasible, the use of cyanide-generating bacteria may result in an even more environmentally friendly process. The most common cyanogenic bacterial species are *C. violaceum, Pseudomonas fluorescens, Pseudomonas plecoglossicida, Pseudomonas aureofaciens, Pseudomonas putida, Pseudomonas syringae, Pseudomonas aeruginosa, Bacillus megaterium*, archaea *Ferroplasma acidarmanus* and *Ferroplasma acidipholum*, and some fungal species like *Clitocybe s*p, *Marasmius oreades*, and *Polysporus* sp. (Knowles, 1976; Askeland and Morrison, 1983; Paterson, 1990; Faramarzi et al., 2004; Faramarzi and Brandl, 2006; Hol et al., 2011). It is worth noting that several cyanide-based alternatives have been proposed for the leaching of PGMs. Shaik and Petersen (2017) conducted a comparison of SCN$^-$ + CN$^-$ + [Fe(CN)$_6$]$^{3-}$, SCN$^-$ + CN$^-$, and SCN$^-$ + [Fe(CN)$_6$]$^{3-}$ and found that SCN$^-$ + CN$^-$ + [Fe(CN)$_6$]$^{3-}$ exhibited the highest effectiveness. These findings could be valuable for enhancing the bioleaching of PGMs using biogenic cyanide.

that contained 10 mM glutamate, 2–3 mM glycine and 0.2–0.5 mM methionine. The Fe^{2+} concentration also increased the cyanide production with concentrations of 30 μM FeSO$_4$ being used. The phosphate concentration of 68 mM was determined to be optimal for the production of cyanide by *C. violaceum*. However, this phosphate concentration seemed to inhibit the growth of *P. aeruginosa* as concentrations of >10 mM were inhibitory. In order to adapt the microorganisms to the concentrate, small amounts of concentrate (0.1 g) are generally added to the bacterial culture over a few months and the culture then transferred biweekly to sterile nutrient medium (Yopps and Baglin, 1991). The biogenic cyanide may be harvested by centrifugation of bacterial cells at 10 000 rpm for 15 min. The supernatant may be filtered and stored at 4 °C before being analysed for cyanide concentration and pH. Generally, it is not necessary to store the supernatant at 4 °C if measurements are to be done immediately after centrifugation. However, if the measurement equipment is not ready or the supernatant has to be sent somewhere else then there is need for refrigeration to prevent regrowth of cells.

$$(2)$$

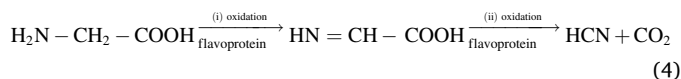### 5.3.2. Production of biogenic cyanide

A large number of bacteria and fungi are able to produce cyanide (Møller and Seigler, 1999) and cyanide-producing microorganisms such as *C. violaceum* have been used for the bioleaching of gold from pre-oxidised refractory mineral ores (Lawson et al.., 1999). This is largely based on the historical effective and economic application of cyanide in the leaching of gold ores. Cyanide producing microorganisms such as *C. violaceum* that have been used for the bio-heap leaching of gold from low grade ores (Lawson et al., 1999), are therefore potential candidates for the bioleaching of PGMs since it is known that the gold and PGMs react with cyanide in a similar way (McInnes et al., 1994). A study conducted by Mwase and co-researchers (2012 a and b) proposed a heap chemical cyanidation process of PGM's from low grade concentrates. This paper will therefore focus on bio-cyanidation of PGMs.

It is known that cyanide production only happens under micro-aerophilic conditions (Clawson and Young, 1913). The production of cyanide by *C. violaceum* is affected by glycine and oxygen concentrations as well as pH and temperature (Castric, 1975; Castric, 1994) with a near neutral pH showing higher cyanide production (Campbell et al., 2001). The α-carbon of glycine is responsible for the stimulation of cyanide production by cyanogenic bacteria (Brysk et al., 1969; Ward and Thorn, 1966).

It is also known that the cyanide producing bacteria work by oxidative decarboxylation as (Knowles and Bunch, 1986; Blumer and Haas, 2000). From **Equation (2)**, it can be deduced that glycine is the direct antecedent of cyanide that is metabolised by proteobacteria such as *C. violaceum*. Rodgers and Knowles (1978) showed optimal production of cyanide by *C. violaceum* when it was grown on minimal medium

Liu and co-researchers (2016) observed that a mixed culture of *Pseudomonas aeruginosa* and *C. violaceum* showed the highest bioleaching capabilities. Shin and co-workers (2015) conducted a study on bio-cyanidation of PGMs from spent automotive catalysts. They produced cyanide in a continuous culture with the use of *C. violaceum*. The maximum biogenic cyanide concentration produced was 6594.5 mg/L (about 20 times higher than typically required for leaching free-milling gold). The authors used an air-purged *C. violaceum* culture bottle for biological cyanide production and two NaOH traps to capture and accumulate the HCN produced in the culture bottle according to **Equation (3)**. The HCN is produced by the enzyme HCN-synthase that exists in *Pseudomonas* species and in *C. violaceum* (Blumer and Haas, 2000). The enzyme HCN-synthase produces HCN in the presence of amino acids such as glycine (Castric, 1977). The hypothetical pathway for the production of cyanide from glycine by bacteria is shown in **Equation (4)** (Wissing, 1974).

$$HCN + NaOH \rightarrow NaCN + H_2O \tag{3}$$

$$H_2N - CH_2 - COOH \xrightarrow[\text{flavoprotein}]{\text{(i) oxidation}} HN = CH - COOH \xrightarrow[\text{flavoprotein}]{\text{(ii) oxidation}} HCN + CO_2$$
$$(4)$$

5.3.3. Potential of biogenic cyanide in PGM leaching

Based on the findings by Mwase and co-workers (2014), with chemical cyanide, bioleaching of PGMs might have to be conducted over a period of not less than 21 days. Using biogenic cyanide, Shin and co-researchers (2015) found a pH ∼ 11.8 as optimum during the leaching of Pt from secondary sources. It is known that cyanide needs to be in an

environment of pH 10 or higher in order to avoid the production of HCN (Yopps and Baglin, 1991). Huang and co-researchers (2006) used a temperature of 160 °C, 10 g/l NaCN, pressure of 1.8 MPa and a solid-to-liquid ratio of 1:4 for the extraction of PGMs after removal of base metals with H$_2$SO$_4$, and achieved an overall recovery of 95% after 2 h. Chen and Huang (2006) also obtained the same recoveries after 1 h at the same temperature and solid-to-liquid ratio as those for Huang and co-workers (2006), but using a NaCN concentration of 6.25 g/l and pressure of 1.5 MPa. It can be deduced that Chen and Huang (2006) used less aggressive conditions than those by Huang and co-workers (2006). The effect of temperature on platinum recovery from spent industrial dehydrogenation catalyst using cyanide leaching is shown in Fig. 6 (Shams et al., 2004). It can be deduced from Fig. 6 that highest Pt recoveries (80%) were achieved at temperatures of about 140 °C, beyond which a general decrease was observed. Higher recoveries might be achievable at lower particle sizes, higher NaCN concentrations and longer leaching during durations.

Based on the effectiveness of chemical NaCN (Mwase et al., 2014; Yopps and Baglin, 1991; Chen and Huang, 2006; Huang et al., 2006; Shams et al., 2004), it is anticipated that biogenic NaCN that is produced from HCN should yield similar or greater PGM recoveries, as was observed by Shin and co-researchers (2015) on secondary materials. However, the approach used in PGM leaching plays an important role in the outcome of the cyanidation process. Three different possible approaches to bio-cyanidation, documented in literature, are discussed in Sections 5.3.3.1 to 5.3.3.4.

5.3.3.1. Single-Step process. In a single-step process, the bioleaching of PGMs would be achieved using cyanogenic bacteria in the presence of substrates and PGM concentrate. The cyanide generation by the cyanogenic bacteria and bioleaching of metals would then occur simultaneously. Under these conditions metals in the PGM concentrate would be caused to undergo dissolution hence, achieving metal extraction (Liu et al., 2016). The single step option is the simplest and straight forward in terms of its application. However, its applicability is limited due to toxic effect of metals ion which inhibits the microbial growth thereby reduces lixiviant production and metal dissolution efficiency (Natarajan and Ting, 2015).

One of the key factors that influence cyanide generation is initial pH (Rodgers and Knowles, 1978). The optimum pH for cyanogenic bacteria growth is in the range of 7–8 (Natarajan and Ting, 2015; Lawson et al., 1999). According to a study conducted by Lawson and co-researchers (1999), on the solubilisation of gold with the use of *C. violaceum*, at pH values above 8, bacterial growth was inhibited which in turn adversely affected cyanide generation. However, for PGM processing, an optimum pH of 11.8 was found to be the most effective for leaching (Shin and co-researchers, 2015). This is because the higher the pH, the higher the quantity of free cyanide available in solution for metal

complexation reactions. This, therefore, implies that two separate environments would be required, one for optimal growth of cyanogenic bacteria and generation of cyanide and the other for optimal cyanide leaching of PGMs. The single-step process is therefore not feasible for PGM bioleaching.

5.3.3.2. Two-Step process. The two step process has been widely used in recovering precious metals from secondary resources mainly electronic waste (Brandl et al., 2008; Natarajan and Ting, 2015; Pradhan and Kumar, 2012; Jujun et al. 2014; Sahni et al. 2016; Kumar et al., 2021). In the two-step process, the value PGM concentrate would only be added when microorganisms would have reached the maximum lixiviant production stage. The bioleaching for the two-step process can take up to 27 days after the addition of value-bearing material (Horeh et al., 2016).

The two-step leaching has been reported to result in improved recoveries compared to the one-step leaching method during the recovery of gold from e-waste (Natarajan and Ting, 2015). Work by Natarajan and Ting, (2015) showed that by first growing the microorganisms in the absence of electronic waste followed by the addition of different concentrations of electronic waste for metal mobilization after the attainment of maximum cell density and cyanide production, the metal extraction efficiency could be increased.

The two-step process ensures that toxic metals do not hinder in microbial growth (allow to attain maximum cell number so as to reach stationary phase of the growth) and thereby the lixiviant (biogenic cyanide) production. However, it is limited to those cases where the growth conditions are similar to the subsequent leaching conditions. As such, it would not be ideal for PGM leaching considering the difference in the best conditions for cyanide producing microorganisms from those for PGM cyanide leaching. Furthermore, it has been reported that metal toxicity also comes into play during the two-step leaching approach, although to a lesser extent than during the single-step process (Karim and Ting, 2022). It has also been reported that the presence of microorganisms leads to a decrease in CN$^-$ concentration with time due to biodegradation or reuse of CN$^-$ by the same microorganisms (Brandl et al., 2008). Karim and Ting (2022) investigated the efficacy of the two-step leaching process on the leaching of PGMs from spent autocatalysts, and found that it was not as effective as the spent-medium approach that will be discussed next.

5.3.3.3. Spent medium approach. The spent medium approach requires a complete separation between the microorganism culturing and cyanide generation vessel, and the cyanide leaching vessel. In spent medium leaching, microorganism cells are separated from the culture media after reaching maximum cell density and cyanide production. Only cell-free metabolites are used for leaching in a separate vessel (Cui and Zhang 2008). The separation is achieved by filtration and centrifugation techniques.

The spent medium has been proposed as a way of overcoming challenges such unsuitable pH, for bacterial growth, unsuitable leaching temperatures, too low pulp densities and the inability of the cyanide lixiviant to access the mineral surfaces blocked by cell biomass. In the leaching of valuable metals from spent lithium-ion mobile phone batteries, the spent medium bioleaching option resulted in more recovery than the two-step option due to the absence of metal toxicity on the fungi (Horeh et al., 2016).

Horeh and co-researchers (2016) reported that using the spent medium method allows for the possibility of optimizing acid production and bioleaching processes separately. The bioleaching of PGMs requires much higher temperatures than required during acid production. Furthermore, Sibrell and collaborators (1994) reported that high temperatures for PGM cyanide leaching resulted in very minimum co-extraction of base metals, most likely due to the relatively higher tendency of PGMs to complex with PGMs. Therefore, using the spent medium method for PGM bioleaching will allow for high temperatures and
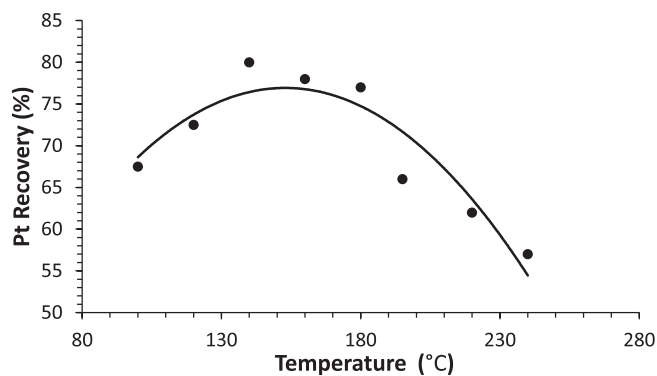
Fig. 6. Effect of temperature on platinum recovery (digestion time: 1 h, NaCN concentration: 1 wt.%, catalyst: coked, NaCN/catalyst wt. ratio of 4:1, average particle size: 2 mm, pH: 9) (Shams et al., 2004).

will ensure that any remaining base metals in the PGM-rich residue will not be co-extracted.

5.3.3.4. Decoupled approach. It is evident that cyanogenic microorganisms produce cyanide in form of HCN, which is a gas and is volatile in nature. Furthermore, when exposed to nutrient scarcity and highly toxic environments, cyanogenic microorganisms employ specialized enzymes to metabolize, break down, or neutralize cyanide. As a result, only minimal quantities of cyanide are produced. Growing the cells in a bioreactor and collecting/trapping the biologically produced HCN in another vessel (NaOH trap) avoids the gaseous emission of HCN at pH values less than 9. One such attempt has been made by Shin et al. (2015) in a batch and continuous culture system using *C. violaceum*.

The batch type system consisted of an aerated culture bottle connected to a NaOH trap. The continuous system was similar to the batch system, but had feed, drainage systems and pumps to ensure flow and drainage. The biogenic cyanide produced by Shin and co-workers (2015) had a cyanide concentration of 1000 mg/l and extractions of 92.1%, 99.5% and 96.5% of Pt, Pd, and Rh, respectively, were attained. Previous studies used chemical cyanide concentrations of 5.3 g CN/L (Desmond, 1991; Atkinson et al., 1992; Kuczynski et al., 1992; Shams et al., 2004) and 3.3 g CN/L (Chen and Huang, 2006). However, Shin and co-workers (2015) reported that excessive CN concentrations would be detrimental to leaching efficiencies as they would result in the challenges such as pH values much higher than those required for PGM leaching. The high pH values arise from the competition for metal sites between cyanide ions and oxygen. As such, Shin and co-workers (2015) limited the concentration of biogenic cyanide to 1000 mg CN/L although they had obtained concentrations of up to 6000 mg CN/L. The biogenic cyanide concentration was adjusted using 0.0001 N NaOH, to avoid the formation of HCN, and then 1 M H_2SO_4 was added to reduce the pH to 11.

The results by Shin and co-researchers (2015) were comparable to those from chemical cyanidation under the same operating conditions. Shin and co-researchers (2015) obtained leaching efficiencies of 100% Pt, 99.9% Pd and 100% Rh using chemical cyanidation at 150 °C. The slightly lower leaching efficiencies for biogenic cyanide as compared to chemical cyanide were attributed to the effect of sulphate anions or oxygen, since H_2SO_4 was used to adjust the pH of the biogenic cyanide solution from 14 to 11, in order to promote PGM cyanidation.

The high temperature required for PGM cyanidation is attributed to their strong metallic bonding (higher than that for gold) (Chen and Huang, 2006). Other researchers (Desmond, 1991; Bruckard et al., 1992; Shams et al., 2004) also reported the need for high temperatures to leach PGMs using cyanide. However, temperatures beyond 160 °C cause PGM leaching efficiencies to deteriorate (Desmond, 1991; Bruckard et al., 1992; Shams et al., 2004). The leaching efficiency is compromised by factors such as the hydrolysis of the CN⁻ species, decrease in dissolved oxygen and the thermal decomposition of PGM-cyanide complexes to metals (Habashi, 1997; Chen and Huang, 2006). The hydrolysis of cyanide occurs above 100 °C according to **Equation 5** (Sibrell et al., 1994). As CN is hydrolysed, the pH increases to levels not suitable for PGM leaching by cyanidation (Shin et al., 2015). Furthermore, the products of the hydrolysis reaction (HCOO⁻ and NH_3) might react with the PGMs in solution to form undesirable ligands and complexes. Sibrell and co-researchers (1994) found that cyanide hydrolysis can be avoided by adding cyanide to the autoclave after reaching the operating temperature. The other major effect of high temperatures is the associated decrease in dissolved oxygen which, compromises the leaching efficiency (Shin et al., 2015). The corresponding high oxygen pressure is also known to cause surface oxidation passivation (Chen and Huang, 2006). Therefore, bioleaching of PGMs should not be done at temperatures exceeding 160 °C.

$$CN + 2H_2O \rightarrow HCOO^- + NH_3 \quad (5).$$
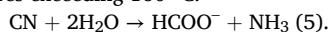
5.4. Challenges and opportunities of bioprocessing of PGMs

5.4.1. Challenges

Bioprocessing seems to be a more effective, economically meaningful, and environmentally friendly process for the separation of various minerals from their ores (Ilyas et al., 2018; Gherghe, 2017). However, mineral bioprocessing still has limitations in large-scale industrial applications. Commercial acceptance by the industry is biased towards conventional methods (Ilyas et al., 2018). Bioleaching of PGMs consists of three main stages: base metal removal, silicate decomposition and the subsequent recovery of PGMs. Each of these stages has its own unique challenges since different types of microorganisms are involved. Nevertheless, some challenges are common for the two stages. In this section, challenges with respect to base metal removal will be discussed first, followed by challenges associated with the subsequent recovery of PGMs. Common challenges to the two stages will be discussed at appropriate intervals.

To date, most of the work on bioleaching of base metals utilises mesophilic bacteria. However, one of the challenges associated with mesophilic bacteria is that of poor leaching kinetics. Donati and co-researchers (2016) highlighted that the poor leaching kinetics associated with base metal removal have led to poor implementation of the bioleaching technique at a large scale. Poor leaching kinetics imply high residence times. To compensate for the high residence times, base metal removal especially with mesophilic bacteria requires large reactor volumes. Although capital and maintenance costs are lower for large reactors, the main challenge is that the impact (on production) of shutting down a single unit is much more than when having multiple smaller sized vessels. Larger reactor volumes are associated with less flexibility and lower metallurgical performance (Wills, 2015).

Base metal removal with mesophiles is also a challenge in the presence of chalcopyrite. It is known that chalcopyrite is the only sulphide mineral that does not respond to mesophiles (Mehta and Murr, 1982). Chalcopyrite tends to passivate in the presence of mesophiles due to the high solution potentials associated with these microorganisms (Kamenati and Aoki, 1985; Hackl et al., 1995). Another issue with chalcopyrite leaching is that a large amount of copper ions is toxic to *A. ferrooxidans* (Pecina-Trevino et al., 2012). Furthermore, exothermic reactions during base metal extraction have been reported to generate too much heat to the detriment of the growth of the mesophilic microorganisms (Donati et al., 2016). Conversely, in cases where the base metal sulphide content is very low, heap leaching with mesophilic organisms might result in too little heat generation (Petersen et al., 2002), and that might consequently compromise the leaching kinetics. It is also likely that base metal removal using heap leaching might be affected by factors such as poor distribution of air and solution, as well as mineral occlusion in larger particles, as reported by Petersen and collaborators (2002). Another challenge with most acidophilic microorganisms is their strict need for an environment-intracellular pH gradient for them to be effective in the production of a lixiviant (Baker-Austin and Dopson, 2007).

As an alternative to mesophilic microorganisms, the use of thermophilic microorganisms has been investigated in order to improve on the bioleaching kinetics in the removal of base metals. Mwase and co-researchers (2012 a and b) found better base metal recovery with thermophilic microorganisms than with the mesophilic species. However, the use of thermophilic microorganisms has got its own set of challenges. It has been reported that in the culturing and isolation of the extreme thermophilic microorganisms, it is very difficult to establish their optimum conditions for growth (Donati et al., 2016). Furthermore, the slow growth of thermophiles increases chances of contamination or deterioration of the culture medium (Donati et al., 2016). The deterioration of thermophilic culture medium may be attributed to the difficulty in maintaining enzymes created at high temperatures (Donati et al., 2016). The difficulties surrounding the culturing and growth of thermophilic microorganisms will have a significant adverse impact on

the removal of base metals from PGM ores.

Thermophilic archaea *Sulfolobus acidocaldurius, Sulfolobus metallicus, Metallosphaera caldula* and *Acidianus brierelyi* are very sensitive to hydrodynamic conditions (Escobar et al., 1993; Torres et al., 1995; Clark and Norris, 1996). Norris and co-researchers (2013) also reported on the sensitivity of thermophilic archae to agitation in the presence of high pulp densities. Jones and co-workers (2013) further emphasised the need for optimal solids concentration when bioleaching with thermophilic archae. The efficiency of thermophiles is only up to pulp densities of 10 – 12 % (w/v). The sensitivity to agitation at high pulp densities is attributed to the increased fluidity of cellular membranes at the high temperatures associated with thermophilic leaching (Kelly and Deming, 1988). The sensitivity of thermophiles to hydrodynamic conditions implies that it might be difficult to employ thermophiles for base metal removal using stirred tank reactors. Furthermore, it is also known that thermophilic bacteria are not effective for the bioleaching of chalcopyrite in saline environments (Watling et al., 2016). Jones and co-workers (2013) also found that in the presence of pyrite, thermophilic microorganisms are likely to suffer from oxidative stress since high Fe^{2+} concentrations promote the generation of reactive oxygen species (ROS). Since pyrite is sometimes found in PGM ores, the oxidative stress on thermophilic microorganisms might impede base metal removal.

Both thermophilic and mesophilic microorganisms can be affected by the formation of precipitates such as jarosite. Such precipitates tend to block the surfaces of mineral particles thereby reducing the available surface contact area for lixiviant action (Murr and Mehta, 1982). Another common challenge for the mesophilic and thermophilic microorganisms is with respect to cultivation of single microbial colonies. Donati and co-workers (2016) reported that to obtain single microbial colonies, the mesophiles and thermophiles should be cultivated in solid media. Cultivating microorganisms in solid media is difficult due to their melting at thermophilic temperatures, and in the case of mesophiles, they are adversely affected by the hydrolysis products of the solid media (agar plates) (Donati et al., 2016). This challenge will impact negatively on the base metal removal stage that depends on continuous cultivation of either mesophiles or thermophiles.

The extraction of PGMs using cyanogenic microorganisms also has its own challenges. The first challenge is the need to deal with pH swings associated with the transition from the low pH values required during the pretreatment stage to the high pH values associated with the cyanidation process. This might pose a high demand on the use of environmentally unfriendly chemicals such as NaOH. The other challenge is the low concentrations of cyanide (3 – 15 mg/L) produced by cyanogenic microorganisms (Wissing, 1974; Tran et al., 2011). The low cyanide concentrations have a potential to negatively impact on the efficiency of the PGM extraction process that relies heavily on the cyanide concentration. In addition, the use of expensive glycine for microbial conversion to cyanide poses an economic challenge that is aggravated by the associated low glycine conversion. Another disadvantage associated with cyanide-producing bacteria is that the pH for bacterial culturing is different from that required for cyanidation (Rees and Van Deventer, 1999; Shams et al., 2004). The difference in the pH for culturing and that for cyanidation implies that different reactors will be needed for the PGM bioleaching process, increasing capital costs associated with this spent media approach. Shin and co-researchers (2015) also reported that biofilms and extracellular polymeric substances associated with cyanogenic microorganisms tend to block the mineral surfaces, in one-step and two-step bioleaching, compromising the leaching efficiency. The leaching of PGMs is controlled by a surface chemical reaction (Chen and Huang, 2006), as such there is need to ensure sufficient filtration to avoid the polymeric substances hindering the extraction process.

One of the challenges related to PGM bioleaching is the influence of mineralogy. Different PGM deposits exhibit distinct mineral compositions. For instance, unlike the Merensky Reef, the Platreef and UG2 ores contain significant amounts of refractory sperrylite ($PtAs_2$), that does not respond well to cyanidation (Mwase and Petersen, 2017). As a result, the implementation of more intensive methods such as sulfation-roast-water leach (Mpinga et al., 2017) and the single-stage molten salts chlorination roast-leach process (Mpinga et al., 2018) becomes imperative, leading to a rise in processing expenses. The use of oxidants like ferricyanide has been reported to aid in Pt leaching in sperrylite rich ores (Mwase and Petersen, 2017). However, implementing such methods would lead to higher operational expenses and raise environmental concerns. Additionally, UG2 ores are known to have a high chromite content with low sulphide levels (Mpinga et al., 2018). The low sulphide content negatively impacts the effectiveness of S oxidising microorganisms employed for the removal of interfering elements before PGM leaching, necessitating an additional sulphide source. Furthermore, the intricate mineralogy of ores like the Platreef can adversely affect the overall control of the bioleaching process.

Efficient bioleaching of PGMs might require temperatures of up to 150 °C (Shin et al., 2015). The high temperature dependency of PGM bioleaching implies high-energy costs and the need for costly equipment such as autoclaves. The high temperatures associated with PGM bioleaching cause PGM-cyanide complexes to thermally decompose (Chen and Huang, 2006), and this compromises the leaching efficiency. Furthermore, at these high temperatures microorganisms cannot survive, thus making it impossible to use the less capital intensive and more straight forward one-step bioleaching approach in the extraction of PGMs. As temperature increases above 100 °C, the hydrolysis of cyanide also increases (Sibrell et al., 1994), further compromising the leaching efficiency. Another factor that reduces leaching efficiency with increasing temperature is the loss of oxygen from solution (Habashi, 1997). Oxygen plays an important role in the formation of PGM cyanide complexes, such that, any decrease in concentration has an adverse impact on the leaching efficiency. In addition to high temperatures, high oxygen pressures for PGM bioleaching tend to passivate the mineral surfaces (Chen and Huang, 2006), and this in turn has an adverse effect on the overall leaching kinetics. Furthermore, PGM mineralisation might necessitate energy intensive techniques such as roasting prior to leaching of refractory ores.

The need for high temperatures for both bioleaching with thermophilic microorganisms and bioleaching with cyanide-producing microorganisms imply that the reactors will require expensive corrosion resistant materials such as ceramics or special stainless steel. In addition, special designs will be required in order to minimise evaporation (Donati et al., 2016), for both base metal extraction (if extreme thermophiles are employed) and for the subsequent PGM extraction.

The need to control particle size is applicable for both base metal removal and PGM extraction. It is known that bioleaching is adversely affected when particles get smaller beyond a certain critical level (Nemati et al., 2000; Norris et al., 2013). Nemati and co-workers (2000) found that very fine particles damage microorganisms by attrition. Jones and collaborators (2013) also reported that microorganisms do not attach easily to very fine particles. The inevitable presence of very fine particles is therefore likely to compromise leaching efficiencies for both base metal removal and PGM extraction. Another factor that might affect the two bioleaching stages for PGM extraction is that generally, there is a huge variation for bioprocesses, between optimal laboratory parameters and those for plant operations (Norris et al., 2013). Therefore, even after successfully optimising the bio-recovery of PGMs at laboratory scale, upgrading of the techniques is another hurdle that needs overcoming.

5.4.2. Opportunities

Amid the above-mentioned challenges, there is immense potential for the bio-recovery of PGMs using the spent medium approach on base metal-free PGM residues. As mentioned earlier, following base metal removal from a PGM concentrate, Mwase and co-researchers (2012b) used cyanide solution at 23 °C to extract 20.3% Pt, 87% Pd and 46% Rh after 21 days. The authors recovered 57.8% Pt and 99.7% Pd using

cyanide solution at 50 °C for 60 days. In both cases, Pt recoveries were low since most of the Pt existed as sperrylite ($PtAs_2$) which is resistant to cyanide leaching (Mwase et al., 2014; Mwase et al., 2017). However, with the use of autoclaves and temperatures of up to 150 °C, as in the work of Shin and collaborators (2015) on autocatalytic convertors, it is likely that Pt recoveries might be increased. It can be deduced from the results of Mwase and co-workers (2012b) and Mwase and co-workers (2014), that higher Pt recoveries are associated with higher leaching temperatures. Although Mwase and co-workers (2014), Mwase and co-workers (2012b) and Eksteen and collaborators (2014) used chemical cyanide, the results by Shin and co-researchers (2015) showed that biogenic cyanidation achieves comparable results. The heat released from the exothermic reactions during base metal sulphide leaching may be harvested towards the high temperature demands of PGM leaching. Furthermore, as mentioned earlier, the incorporation of complexing agents such as SCN^- and oxidants such as $[Fe(CN)6]^{3-}$ might help to increase the PGM extraction.

Shin and co-researchers (2015) managed to overcome the challenge of low CN concentrations associated with cyanogenic microorganisms by using a system that allows for gradual accumulation of biogenic cyanide that would then be used for bioleaching in a separate vessel. This decoupled approach by Shin and co-researchers (2015) also helps to overcome the challenge of the need for a different pH for bacterial growth and for the bioleaching of PGMs. Natarajan and co-researchers (2015) reported that metabolically engineered *C. violaceum* strains doubled the production of CN. Therefore, using metabolically engineered *C. violaceum* strains Natarajan and co-researchers (2015) in the two-step process (Shin et al., 2015) might strongly enhance the feasibility of large scale bioleaching of PGMs.

The BioHeap™ technology that uses cultures grown on hypersaline and high temperatures to recover heavy metals (Zhuang et al., 2015) could be extended to PGM extraction. The BioHeap™ technology is based on the use of ligands produced by microorganisms to solubilise metals. Zhuang and co-workers (2015) argued that the high value of PGMs would compensate for the use of expensive organic ligands associated with the technology. An example of a ligand produced by microorganisms, citric acid, has been successfully used for the efficient recovery of heavy metals (Deng et al., 2013), and as such has been proposed for the heterotrophic bioleaching of PGMs (Zhuang et al., 2015).

In this section we looked at the various possible approaches for the bio-recovery of PGMs. Considering the depletion of high-grade PGMs ores, environmental concerns and the increasing demand for PGMs, it is worthwhile looking into some of these approaches. The various approaches presented in this section suggest that there is immense potential for commercial bioprocessing of PGMs. For a start, the bioleached PGMs can be further recovered using conventional approaches such as the carbon in pulp process. However, biotechnology has the potential to be extended to the downstream process techniques such as bio-sorption. It is known that there are naturally occurring microorganisms with high binding capacities on a variety of PGMs (Vijayaraghavan and Yun, 2008; Gadd, 2009; Moriwaki and Yamamoto, 2013). It might therefore be necessary to consider bio-sorption in the subsequent PGM extraction stages towards a complete shift to bioprocesses.

5.5. Proposed process flow sheet for the bioleaching of PGMs

A proposed process flow diagram for the bioleaching of PGMs is shown in Fig. 7. The process flow diagram is an integration of the proposed routes by Mwase and co-researchers (2012a) and Shin and co-workers (2015) and based on information from literature. Base metal removal may be done using heap leaching for the process to be cost effective. However, PGM bioleaching should be done in an autoclave for the attainment of optimum conditions. As highlighted above, PGM mineralisation plays a role in PGM extraction. For example, Mwase and co-researchers (2012a) found that most Pt was in the form of sperrylite, and could not be leached with cyanide. Thus, some form of pretreatment such as calcination or roasting might be necessary to transform refractory elements to a leachable form. The use of an oxidant such as $[Fe(CN)6]^{3-}$ might also promote sperrylite leaching as reported by Mwase et al., 2017.

In the process flow diagram (Fig. 7) the use of thermophilic microorganisms is proposed for fast kinetics of base metal removal. The heat generated during base metal sulphide bioleaching can be harvested and used for PGM extraction, which requires temperatures of up to 150 °C. It is important to pre-heat raffinate streams to appropriate bioleaching temperatures before feeding them into the leaching tanks to maintain temperatures so that leaching kinetics might not be affected. The base
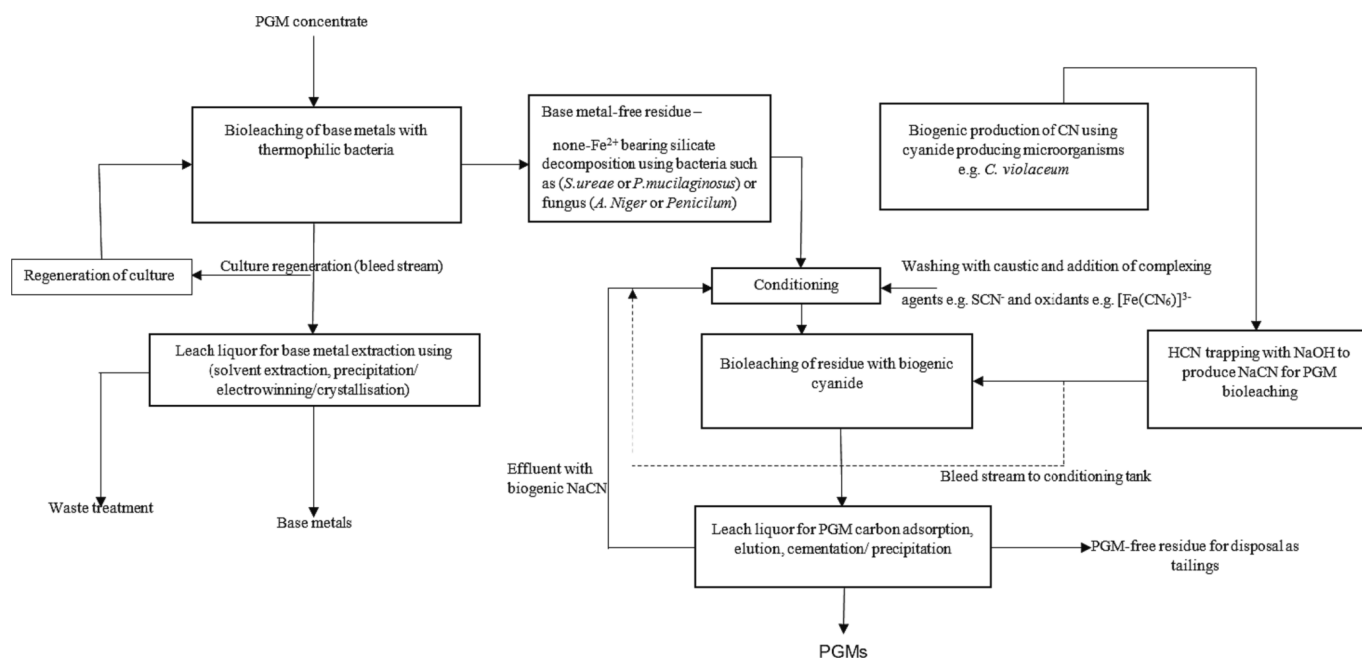

Fig. 7. Potential processing route for the bioleaching of PGMs.

metals bioleached into solution can be recovered downstream using techniques such as solvent extraction, precipitation, electrowinning or crystallisation. The additional advantage of recovering base metals is that their value will contribute positively to the overall economic feasibility of PGM processing. The washing of the leach residue after base metal removal helps to increase the pH to levels required for PGM cyanidation, as discussed in the previous sections (Mwase et al., 2012a).

After removal of base metals, a two-stage process is required for the removal of PGMs from the leach residue. The advantages of the two-stage approach were discussed in previous sections. It is known that cyanogenic bacteria produce biogenic cyanide in the form of HCN which is a gas (Shin et al., 2015). It is therefore important to trap the HCN produced using NaOH, to produce additional CN^- for the PGM cyanidation process.

The PGMs in the leach liquor can be recovered by techniques such as precipitation and electrowinning. Carbon adsorption may be employed to enhance the PGM leach liquor concentration prior to recovery. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions has already been reported (Snyders et al, 2013; 2014; Mpinga et al., 2014). >90% recoveries were attained for Pt and Pd, as well as Au, after 2 h of carbon adsorption. However, no significant adsorption of Rh was observed. The adsorption of Pt and Pd was reported to be largely a function of temperature, free cyanide concentration and base metals. Although higher temperatures favoured adsorption rate, they promoted the adverse effects of free cyanide, resulting in decreased PGM adsorption. Among the interfering elements, only Ni was found to compete to have the most negative effect on adsorption.

The potential for using strong base anion exchange resins to also extract PGMs from cyanide solutions was demonstrated (Schoeman et al., 2017a; 2017b). Adsorption was favoured by Pt and Pt cyanide concentrations as well as temperature, whereas the solution pH, and Zn/Ni cyanide concentrations did not have an effect. Elution studies were also done on both loaded activated carbon (Snyders et al, 2015a; 2015b) and base anion exchange resins (Schoeman et al., 2017a). Elution of Pt and Pd from activated carbon was favoured by temperature and cyanide pretreatment concentration, but was negatively affected by the concentration of Na^+ ions. Elution of Pt and Pd from base anion exchange resins was promoted by the concentration of potassium thiocyanate or zinc cyanide as eluting agents. There is therefore, potential to leach and recover PGMs, leaving behind a PGM-free siliceous residue that may be used for back-filling open pit mines or to make silica-based ceramic products.

6. Conclusions

It can be deduced from this paper that there is immense potential for bioleaching of PGMs. The three main stages proposed for the extraction of PGMs are base metal removal using acidophilic microorganisms, decomposition of silicates from the base metal-free residue and the bioleaching of PGMs using biogenic cyanide. Bioleaching of base metals from sulphide minerals has already been done successfully. It is known that by using mesophilic or thermophilic microorganisms, it is possible to remove the base metals associated with PGMs. Mixed bioleaching cultures have been found to be more effective than single cultures in the bioleaching of base metals. For faster kinetics, the use of mixed thermophilic cultures is being proposed in this review.

Bioleaching of PGMs from the base metal-free PGM-rich residue using inorganic cyanide (among other lixiviants) has already been done successfully on secondary materials. It is possible to generate biogenic cyanide either with the metabolically engineered cyanide-producing microbes or with natural species such as *C. violaceum*. The ability to leach PGMs from secondary sources using biogenic cyanide has also been demonstrated. Hence, it is reasonable to postulate the possibility of bioleaching of PGMs using biogenic cyanide. However, it is worth noting that mineralogy of PGMs is critical since some PGM species are resistant

to cyanidation, and might need further pretreatment using techniques such as roasting. The use of oxidants and complexing agents during PGM bioleaching might be required to aid biogenic cyanidation of refractory species.

In conclusion, researchers should explore the potential of bioleaching techniques for extracting PGMs from primary ores and concentrates due to the significant economic and environmental benefits they offer. While there are challenges associated with this proposed extraction route, the advantages outweigh them. Many of the challenges can be overcome through the solutions discussed in this paper. Therefore, it is worthwhile to investigate and further develop bioleaching as a viable method for PGM extraction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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