

HEAP LEACHING FOR SUSTAINABLE DEVELOPMENT IN THE SOUTH AFRICAN PGM INDUSTRY

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ABSTRACT

The platinum group metal (PGM) industry is currently reliant on the crush-mill-float-smelt-refine route to process PGM ores. However, there are many instances where this route would not be feasible. An alternative process route has been developed which involves heap bioleaching to extract base metals followed by heap reclamation and a water wash step, leading into heap cyanide leaching to extract precious metals. This process was evaluated through test work on samples of Platreef ore using laboratory scale columns. After 304 days 75% Ni and 93% Cu were extracted in the bioleach experiment at 65°C, and after 60 days 58% Pt, 99% Pd and 90% Au in the follow-up cyanide leach experiment at 50°C. A preliminary process flow sheet has been developed around this. Analysis via a mineral liberation analyser showed that the remaining Pt was in the form of the mineral sperrylite, which appeared to be slow leaching in cyanide in comparison to the other mineral types. Analysis of cyanide effluent solution showed high levels of thiocyanate, which present an environmental risk for disposal and high consumption of cyanide. Further studies to develop the process for commercial application in the South African PGM industry are outlined.

KEYWORDS

Heap leaching, platinum group metals, base metals, cyanide, bioleaching, Platreef ore

INTRODUCTION

As much as 88% of all the world's primary platinum group metal (PGM) reserves can be found in the Republic of South Africa, mostly in the area known as the Bushveld Igneous Complex which consists of three unique ore bodies namely the Merensky Reef, the Upper Group 2 (UG2) and the Platreef (Schouwstra & Kinloch, 2000). Aside from the vast reserves of PGMs, these ore bodies house significant quantities of base metals (BMs), namely copper, nickel and cobalt, mostly in the form of sulphide minerals. The industry currently relies heavily on the conventional crush-mill-float-concentrate-smelt-refine route to obtain PGMs (Seymour & O'Farrelly, 2001). This in turn relies on the mineralogy of the ore being suitable for this process. The PGMs must deport to the copper and nickel sulphide minerals which are liberated by crushing and milling and recovered via flotation. The high grade concentrate can then be treated by a smelter for further concentration and the resulting matte refined by a series of pressure leach and purification stages to produce the BMs and PGMs. However there are many instances where this process may not be feasible.

The authors are currently developing and have patented a new two-stage heap leach process (WO 2012/114165 A1, 30 August 2012) that may serve as an alternative to the conventional process route. The process also boasts many features which can contribute to sustainable development in the PGM industry. Firstly, the choice of reactor is the heap which has lower capital and operating costs than the standard route. This allows for more flexibility in what is currently a capital intensive industry to operate in. Heap leaching also allows for effective water management and use of leaching reagents. The solid to liquid ratio is around 3:1, which is the opposite for tank leaching where it is 1:3 and the pregnant leach solution and spent liquors after recovery processes such as electrowinning and adsorption to carbon, can be recycled back to the heap several times over. It can be argued that because of this closed loop, heap leaching is relatively environmentally benign as waste effluent solution and solid waste are not constantly being discharged to the environment or tailings storage facility. Finally, because heap leaching requires low skilled labour as compared to the standard route, it creates opportunities to engage with local communities in rural areas where such an operation is likely to be situated.

Examining the process further, the first stage is a high temperature bioleach to extract base metals. The leaching mechanism consists of a microbially assisted ferric/ferrous couple. The sources of the ferric/ferrous ions are typically the minerals pyrite and pyrrhotite in the ore itself, and the microorganisms are naturally occurring and often indigenous to the mine sites. This reduces the cost of reagents for the process. The elevated temperature in the process is achieved by the exothermic reaction of sulphide mineral oxidation, assisted by mesophilic and thermophilic microorganisms (Tempel, 2003; Ream and Schlitt, 1997). The heat is maintained in the heap by regulating the flow of solution irrigation and aeration to the heap (Neale, 2012; Pradhan et al., 2008). The leachate from the heap can be treated by a number of methods, e.g. solvent extraction, or using ion exchange technology (Libenberg et al., 2013). The ore from the heap is then reclaimed and washed with water, which is re-used for solution make-up in the bioleach process. Then

the ore is stacked on a separate heap for the second stage which is a cyanide leach at elevated temperature, achieved by heating of cyanide solution via means of solar energy or other available natural sources such as geothermal heat. It is also proposed that the water used to wash the ore in between heap leaching stages be heated by the same energy sources. This will aid in conserving some of the heat from the bioleach process and thus the ore will not have to be re-heated for the cyanide leach stage. The cyanidation process operates under alkaline conditions, making it relatively selective to the valuable elements and having low solubility for gangue minerals which form the bulk of the ore. This allows a typical heap leach to operate with low cyanide solution concentrations in the range of 100-600 ppm. Separate studies within this project have shown that the precious metals can be efficiently recovered from cyanide leach solutions using adsorption to carbon and subsequent elution (Synders et al., 2013; Mpinga et al., 2013). While cementation is adequate for gold recovery it does not effectively recover PGMs (Mpinga et al., 2014). Despite common perceptions, cyanide is the most effective and environmentally friendly reagent from a short list of reagents (sodium bisulphide, thiosulphate, thiourea, hypochlorite, chloride and bromine/bromide solutions) that can be used for this application (Kappes 2002). Cyanide residues on tailings will naturally degrade in the presence of air and sunlight, and there are several technologies to treat waste solutions and recover value from them such as the SART[®], ASTER[™], EMS[®], INCO and Caro processes.

This paper presents some of the experimental data from test work conducted to develop the process using a flotation concentrate as well as assess the feasibility of the process from testing a whole ore sample, which had not been done previously. It discusses the strengths of the process and the challenges that still need to be met before the process can be commercialized and the implications it can have for the South African PGM industry.

EXPERIMENTAL

The authors conducted test work on both flotation concentrate and crushed ore originating from a Platreef ore body (Mwase et al., 2012a, 2014).

Flotation Concentrate

We took four 600 g samples of flotation concentrate and made them into slurry in a water to liquid ratio of approximately 3:5 and coated them onto granite pebbles (approximately 6 mm in size) in a concentrate to support media ratio of 1:7 by mass. We then packed the coated pebbles into cylindrical PVC columns with an internal diameter of 90 mm and height 0.6 m. This was done to simulate heap leaching. The columns were left overnight to partially dry and prevent wash out of concentrate once irrigation with feed solution commenced. Tables 1 and 2 show the average grade and general mineralogy of the concentrate. The concentrate was 83% passing 38 μm . We operated the columns at temperatures of 65, 70, 75 and 80°C and aerated the columns at a rate of 130 mL/min. We irrigated the columns with a solution containing 10 g/L of H₂SO₄, 2 g/L Fe and a pure culture of *Metallosphaera hakonensis*. We calculated the extractions of the BMs by

analysing the effluent solution through atomic absorption spectroscopy (AAS). Additionally, we set aside a sub-sample of residual concentrate from one of the columns for analysis via a mineral liberation analyser (MLA).

After the experiment we recovered the samples by washing the concentrate off the support with water, filtering and drying. We took two of the four samples and prepared and leached them in identical columns, in an identical manner as the bioleach experiment, except in this case we irrigated the columns with a 5 g/L solution of sodium cyanide. We operated the columns at a temperature of 50°C and aerated them at a rate of 150 mL/min. After the experiment we recovered the samples in the same manner as before and set aside a sub-sample of residual concentrate from one of the columns for analysis by MLA. We calculated the extractions of the PGMs by analysing the effluent solution through inductively coupled plasma mass spectrometry (ICP-MS).

Table 1 - PGM and BM grade of concentrate

Pt g/t	Pd g/t	Au g/t	Ni %	Cu %	Co %	S %
21	27	3.8	3.4	2.3	0.1	8

Table 2 - Major PGM, BM and gangue minerals grouped by relative abundance

Minerals/Mineral group	(Wt %)
PGMs (sulphides, tellurides & arsenides in equal amounts)	<1%
Chalcopyrite	4.9
Pentlandite	7.7
Pyrite	1.9
Pyrrhotite	5.3
Silicates	66.5
Others*	13.7

Coarse Crushed Ore

From a drill-core sample of Platreef ore that had been crushed with a high pressure grinding roll mill, we prepared two samples of ore by screening to size fractions -25 mm + 1 mm and -6 mm + 1 mm. The samples were bioleached using identical columns, microorganism and operating parameters as used with the flotation concentrate. However, in this case the extractions of BMs were determined by analysis of the effluent solution using inductively coupled plasma optical emission spectrometry (ICP-OES). Tables 3 and 4 show the grades and mineralogy of the ore samples respectively. In this case the PGMs were largely in the form of tellurides and arsenides, with a small contribution from the sulphides and Fe-alloys.

After the experiment we recovered the two samples, washed them with water and packed them in identical PVC columns and leached them with cyanide in an identical

manner to the flotation concentrate and analysed the effluent solution in the same manner. Further to this, we analysed the effluent using high pressure liquid chromatography to measure the levels of thiocyanate present and used the Cynoprobe® instrument to measure free cyanide to determine cyanide consumption. After the experiment we obtained a sub-sample from one of the columns and had it analysed via MLA.

Table 3 - PGM and BM grade of the coarse ore samples

	Pt g/t	Pd g/t	Au g/t	Cu %	Ni %	S %
-25 mm + 1 mm	1.6	2.0	0.3	0.1	0.4	0.8
-6 mm + 1 mm	1.6	2.0	0.3	0.1	0.4	0.8

Table 4 - Mineralogy of coarse ore samples

Mineral	Weight %
Pyrrhotite	1.8
Pentlandite	1.7
Chalcopyrite	0.8
Pyrite	0.1
Olivine & Orthopyroxene	36.0
Serpentine	22.7
Chlorite	3.2
Talc	5.7
Clinopyroxene	13.0
Magnetite	6.6
Chromite	0.8

RESULTS AND DISCUSSION

The results for the experiments can be seen in table 5 for flotation concentrate and table 6 for ore.

Table 5 - Results of bioleach and cyanide leach experiments on flotation concentrate

Columns	Bioleach		Extraction			Cyanide Leach		Extraction		
	Temp. °C	Period days	Ni %	Cu %	Co %	Temp. °C	Period days	Pt %	Pd %	Au %
1	65	88	98	91	84	50	45	34	97	63
2	70	88	97	66	86	-	-	-	-	-
3	75	88	98	85	83	50	45	32	93	98
4	80	88	93	57	77	-	-	-	-	-

Table 6 - Results of bioleach and cyanide leach experiments on coarse crushed ore

Samples	Bioleach		Extraction		Cyanide Leach		Extraction		
	Temp. °C	Period days	Ni %	Cu %	Temp. °C	Period days	Pt %	Pd %	Au %
-25 mm	65	304	67	82	50	60	50	80	83
-6 mm	65	304	75	93	50	60	58	99	90

Tables 5 and 6 show that significant extraction levels of Cu, Ni and Co were achievable, at laboratory scale, using the bioleach process, for both crushed whole ore and concentrate. It was further observed that in the temperature range of 65-80°C, 65°C was the optimal operating temperature. Analysis of the residual materials indicated that there was no change in the PGM mineralogy after the bioleach process. The tables also show that high levels of Pd and Au extraction are achievable from both ore and concentrate, but the highest extraction achieved for Pt was 58% in a similar space of time as the Pd and Au (45 days for concentrate and 60 days for ore). However it was noted that the Pt had not stopped leaching completely after the 45 and 60 day periods, but that at a certain point the rate decreased significantly (see Figure 1). MLA analysis on residual ore and concentrate showed that 79% of the remaining PGMs were in the form the mineral sperrylite (PtAs₂). The analysis also indicated that the mineral was liberated and had sufficient contact with cyanide solution, proving that it was leaching slowly in cyanide, and the process was not reagent limited.

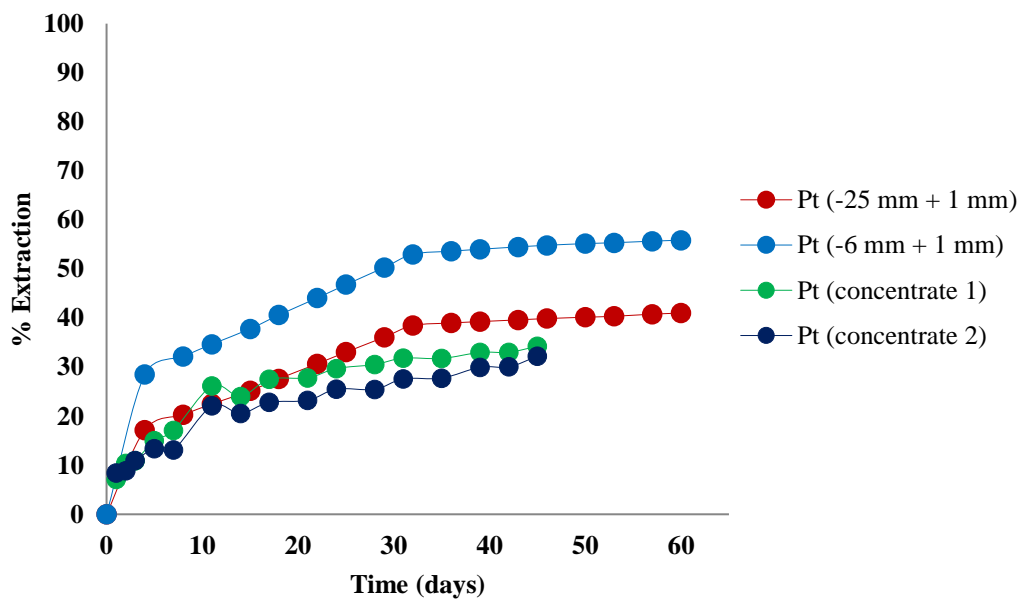


Figure 1-Percentage extractions achieved in cyanide leaching experiments of concentrate and coarse ore particles

High levels of thiocyanate, in the ranges of 1000 to 5000 ppm, were detected in the cyanide effluent solution initially (first 18 days) in both ore and concentrate experiments. This was taken as an indication of the presence of reduced sulphur compounds in the concentrate and ore, which reacted with cyanide to form thiocyanate. Analysis via MLA on the bioleached residual solids indicated the absence of elemental sulphur and only minor traces of undissolved sulphide minerals, but these could not account for the quantities of total sulphur indicated by a LECO combustion test on the residual concentrate and ore. It is suggested that these sulphur species are the result of incomplete sulphur oxidation in the bioleach stage. The sulphur compounds formed are most likely to be polysulphides or polythionates which precipitated to a solid form and migrated with the residual concentrate and ore to the cyanide leach stage. These sulphur species are known to be very reactive with cyanide and form thiocyanate (Luthy and Bruce, 1979), but were not detectable by the MLA due to their physical structures, low concentration and possible association with Fe hydroxide phases. The presence of thiocyanate in cyanide effluent solution is typical of operations in which concentrate material has been subjected to bacterial pre-oxidation prior to cyanidation (Aswegen et al., 2007; Miller and Brown, 2005). This represents problems through both a high amount of cyanide consumption and increased environmental risk, as thiocyanate is one of the most stable cyanide complexes. The test work was run with a solution concentration of 5 g/L of sodium cyanide (NaCN) but analysis on the effluent indicated that only half of the available cyanide was used, indicating the process could occur with a concentration of 2.5 g/L. Cyanide consumption was overall very high at 28 kg/t of ore, but this was because the test work was conducted at high cyanide concentrations (5 g/L). This needs to be explored further to bring consumption closer to that of typical gold heap leach operations which consume 0.1-2.5 kg/t (Roxburgh, 2011; Marsden and House, 2006; Kappes, 2002;).

FUTURE WORK

Given that the majority of the remaining Pt rests in sperrylite, finding a route to increase the rate of leaching of sperrylite in cyanide is the key to make the process more commercially attractive. There is no literature on the chemistry of sperrylite in cyanide or any common leach solution, and the same can be said about most PGM minerals of significance. This is because PGMs are traditionally obtained hydrometallurgically from metallic sources, specifically alloys, after ore concentrates have undergone smelting which converts the PGMs from minerals to a mixed mass of metallics/alloys. To a much smaller but noticeable extent they are also obtained from spent catalysts, where they are also in metallic form. In this form they require extreme conditions of temperature, pressure and high concentration of aggressive reagents to be dissolved for recovery. However tables 5 and 6 shows that in mineral form they can be potentially leached using process conditions more conducive to a heap leach environment. Future studies in this project will investigate the fundamental science behind the sperrylite leaching mechanism in cyanide. In the broader context, this study may serve as basis for investigating direct hydrometallurgical extraction of PGMs, circumventing smelting, from other ore bodies on the basis of ore mineralogy.

With regards to the significant presence of thiocyanate, it is proposed that future experiments will use additional sulphur-oxidising microorganisms together with the current species of *Metallosphaera hakonensis* in the bioleach stage. This may help to oxidise more of the sulphur species in the ore, minimising the presence of intermediate sulphur compounds that would otherwise migrate to the cyanide leach stage. Current literature (Aswegen et al., 2007) supports this method in cyanide tank leaching of concentrates that have undergone biooxidation, but the effectiveness of this method has not been sufficiently quantified and studied in a heap leach scenario. Chemical treatments such as HCl, HNO₃, NaOH or SO₃²⁻ at temperatures of 50-95°C are most likely to be effective in completely oxidising the sulphur, but are not economically viable and not environmentally friendly for the scale at which a whole ore heap leach operates. Finally the reduction of the high cyanide consumption will also be further investigated. An actual gold heap operation uses only 40-65% of the cyanide used in column test work (Roxburgh, 2011). In addition, certain gold minerals have exhibited a higher affinity for cyanide in environments with high Cu and sulphur content, resulting in preferential leaching of the gold (Stewart and Kappes, 2011), thus eliminating the need for high concentrations of cyanide solution and pre-treatment. Furthermore, Pt, Pd and Au form stronger complexes with cyanide than most elements. This all supports the need to determine if the PGM minerals in the bioleached residues of Platreef ore also exhibit preferential leaching characteristics in low concentrations of cyanide solution (0.2-0.6 g/L).

POTENTIAL APPLICATIONS FOR THE PROCESS

Although only preliminary bench-scale test work has been conducted on the process, the results are still promising and potential applications for the process can be conceptualized. The process was originally developed to treat ore from the Platreef ore body, which is currently largely untapped despite its rich mineral reserves. The Platreef is distinguishable from the Merensky Reef and UG2 in mineralogy in that a significant quantity of PGMs deport to silicate minerals rather than sulphides (Mogosetsi, 2006), which makes recovery by flotation and smelting uneconomical. The application of the conventional process route is only feasible if Platreef concentrates are blended with higher-grade Merensky or UG2 concentrates, or through the use of ultra-fine grinding or high mass pulls during flotation to achieve acceptable PGM recoveries (Newell, 2008). The results from the test work have shown that the process may be an alternative route to treat Platreef ore.

The test work on Platreef ore also suggests that ore bodies such as Merensky and UG2, where tellurides and sulphides are more prevalent than arsenides, may produce higher extractions of platinum. This presents an alternative route for current platinum producers in the face of rising smelter costs and may allow entry into the PGM industry, of smaller platinum producers that do not have the capital for the standard route. Despite being effective on Merensky and UG2 ore, the conventional process is not 100% efficient. As much as 5% of the PGMs report to tailings and secondary concentrates (Mwase et al., 2012b). The value of these metals accumulates annually, but because of the low-grade and high through-put of these materials the conventional process cannot be used. However

some value may still be recovered by coating these materials onto support rock and heap leaching them using the alternative process.

Finally, the various PGM ore bodies outcrop to surface and as a result, the ores become weathered and oxidised. These ores report poor PGM recoveries from flotation (Becker et al., 2011) as the sulphides have been converted to oxides or been passivated with an oxide layer. However such deposits are economically important as they eliminate the cost of deep shaft mining. These ores may potentially be processed by direct cyanide heap leaching.

Unlike the copper and gold industry that have developed various percolation leaching technologies (heap, dump and vat leaching) to treat ores that cannot be concentrated or smelted, no such technologies are widely applied in the PGM industry. For this reason a number of opportunities for further development in the industry are left unexploited. Despite having the majority of the worlds' PGM reserves, there are only 13 PGM producers, of which only 4 have the ability to smelt ore, in South Africa (Department: Minerals and Energy). This is because the current methods of processing ore are capital intensive, restricting entry by smaller entities. The two-stage heap leach process may be a means to allow more participants into this industry and extend to localities of processing operations to remote locations without easy access to smelters.

CONCLUSIONS

A two-stage sequential heap leach process combining bioleaching and cyanide leaching, was tested at laboratory scale and has shown promising results as an alternative process route to concentrating and smelting PGM ores. The process may find a wide range of applications in the South African PGM industry amongst different size organizations, processing different ore types with varying grades. The process should be considered for pilot testing.

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