



An investigation of the leaching of Pt and Pd from cooperite, sperrylite and column bioleached concentrates in thiocyanate-cyanide systems



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ABSTRACT

This study investigates the effectiveness of a combined thiocyanate-cyanide leach system in Pt and Pd containing minerals with a view to simplifying the traditional smelt-matte-refine process for PGE recovery by providing a route that is potentially more economical and environmentally more sustainable. Initial studies performed on the key Pt minerals, cooperite (PtS₂) and sperrylite (PtAs₂) in batch stirred tank reactors explored the effect of lixiviant concentration, temperature, pH, oxidants and the influence of a mixed lixiviant system on Pt extraction and compared this to individual systems. Overall, cooperite demonstrated improved Pt extraction in the mixed (SCN⁻/CN⁻/[Fe(CN)₆]³⁻) and SCN⁻/CN⁻ systems, obtaining 54% and 56% Pt extraction, respectively. Sperrylite did not leach well but showed enhanced Pt extractions in the CN⁻/[Fe(CN)₆]³⁻ and the mixed (SCN⁻/CN⁻/[Fe(CN)₆]³⁻) system achieving, 5.9% and 8.1% extraction, respectively.

Subsequent column leach tests conducted on a low grade Merensky concentrate, revealed that a mixed lixiviant system comprising of SCN⁻, CN⁻ and [Fe(CN)₆]³⁻ again displayed enhanced extraction relative to a system consisting of either SCN⁻/CN⁻ or CN⁻/[Fe(CN)₆]³⁻; achieving 47% Pt extraction over a 55 day period and close to 100% Pd extraction over 30 days. It is concluded that ferricyanide acts as an oxidant promoting the dissolution of Pt and Pd, whereas the formation of heterogeneous (mixed) ligand complexes containing both thiocyanate and cyanide ligands, is postulated to ensure enhanced stability of the Pt and Pd in the leach solution.

1. Introduction

The Platinum Group Elements (PGEs) consist of platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os). These metals are often concentrated together geologically due to their similar geochemical characteristics (Jones, 2005). The PGEs are categorised as noble metals owing to them being chemically inert to various substances, as well as their high resistance to oxidation and corrosion. Thus they are valuable commodities that are used in important applications such as industrial catalysts in chemical processes and catalytic converters in the automotive industry. The aesthetic quality of platinum makes it ideal also for the production of jewelry as well as an investment metal (Rao and Reddi, 2000).

> 75% of the world's platinum and 35% of palladium are produced in South Africa, originating from ore bodies in the Bushveld Igneous Complex. The primary platinum ores mined are from the Merensky reef, Upper Group 2 (UG2) reef and Platreef (Jones, 2005). These three ore bodies are differentiated by their distinct mineralogical characteristics.

The South African in situ ores comprise of 7–10 g/t total PGE concentration (Crundwell et al., 2011). Both the Merensky reef and Platreef

have PGE containing minerals associated with base metal sulphides, with Platreef having a relatively high content of base metal sulphides and comparatively lower ratio of Pt to Pd of 1:1.1 (Table 1). The UG2 chromitite layer possesses a high concentration of chromitite in conjunction with low quantities of base metal sulphides, < 1% (Jones, 1999).

PGMs occur mainly in the form of sulphides (cooperite and braggite), arsenides (sperrylite and stillwaterite), tellurides (moncheite, kotulskite and merenskyite) and metallic ferroalloys (isoferroplatinum) in the ores of the Bushveld igneous complex, Table 2.

The traditional route utilised for the recovery of PGEs in South Africa encompasses the concentration of PGM (Platinum Group Minerals) ore by milling and flotation, followed by smelting to produce a PGM rich matte, which is then digested by various hydro-metallurgically routes to solubilise base metals and PGEs (Crundwell et al., 2011). The PGM dissolution is usually by aggressive aqua regia or Cl₂/HCl systems; this process is associated with high operating costs as well as environmental concerns (Mpinga et al., 2014). Furthermore, the complex concentration and smelting processes are energy/capital intensive, adding substantially to the production cost of PGEs. There is,

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Table 1
Average in situ concentrations of PGE in ore bodies of the BIC (Crundwell et al., 2011).

PGEs	Merensky	UG2	Platreef
	g/t	g/t	g/t
Pt	3.3	2.5	1.3
Pd	1.4	2.0	1.4
Rh	0.2	0.5	0.09
Ru	0.4	0.7	0.12
Ir	0.1	0.1	0.02
Au	0.2	0.02	0.1

Table 2
Selection of Platinum Group Minerals (Cabri, 2002).

Groups	Mineral	Formula
Sulphides	Cooperite	PtS
	Braggite	(Pt,Pd)S
Arsenides	Sperrylite	PtAs ₂
	Stillwaterite	Pd ₆ As ₃
Tellurides	Moncheite	(Pt,Pd)(Te,Bi) ₂
	Kotulskite	PdTe
	Merenskyite	(Pd,Pt)(Te,Bi) ₂
Alloys	Isoferroplatinum	Pt ₃ Fe

therefore, a need to investigate new methods of devising more economical processes for metal extraction. Recently, several studies (Mwase et al., 2012a; Mwase et al., 2012b; Mwase et al., 2014) have focused on the extraction of PGMs from different low-grade concentrates (28 g/t and 56 g/t) and Platreef ore (4.5 g/t) by adopting a purely hydrometallurgical route.

Mwase et al. (2014) investigated a two-stage heap leach process using a thermophilic heap bioleach to extract base metals from a Platreef type ore, followed by cyanidation heap leaching to extract PGEs from the residue. Cyanidation has been used for the recovery of gold from mineral resources for over a century (Habashi, 1999). Cyanide has a strong affinity for metals in solution, making it an ideal leaching reagent. It is capable of complexing with virtually any heavy metal at low concentrations (Young and Jordan, 2001). Platinum(II) and palladium(II) form relatively stable complexes with cyanide (Table 3), specifically [Pt(CN)₄]²⁻ and [Pd(CN)₄]²⁻ presented in Eqs. (1) and (2) (Kabesova and Gazo, 1980).

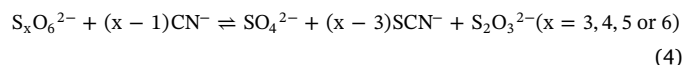


During the cyanidation process, cyanide is well known to react with several other scavenging constituents in the ore, specifically partially oxidised sulphide species, forming thiocyanate (Eq. (3)–(5)). Mwase et al. (2014) found during their experiments that 39% of the cyanide was consumed for non-leaching purposes, as analysis of the cyanide leachate revealed high levels of thiocyanate. The formation of thiocyanate is possible through the reaction of cyanide with the oxidised sulphur species thiosulphate (S₂O₃²⁻), polythionate (S_xO₆²⁻) and polysulphide (S_xS²⁻) (Luthy and Bruce, 1979) which are potentially produced during the bioleaching stage.

Table 3
Stability constants for Pt and Pd complexes at 25 °C.

Ligand (n)	log β _n (Pt ²⁺)					log β _n (Pd ²⁺)				
	1	2	3	4	Reference	1	2	3	4	Reference
Cl ⁻	4.97	8.97	11.89	13.99	1	4.47	7.76	10.17	11.54	1
SCN ⁻	–	–	–	33.6	1	814	15.46	21.94	27.42	2
CN ⁻	–	–	–	41	3	–	–	–	63	1

References: 1 – Mountain and Wood (1988); 2 – Le Roux et al. (2014); 3 – Muir and Ariti (1991).



Similarly, the reactions between cyanide and pure sulphide minerals, pyrite (FeS₂), pyrrhotite (Fe₉S₉) and chalcopyrite (CuFeS₂), pose another possible route in generating thiocyanate which was studied by Wilmot (1997). However, based on the reaction kinetics it is believed that polysulphides and thiosulphate are key species responsible for thiocyanate formation (Luthy and Bruce, 1979; Wilmot, 1997). Mwase et al. (2014) made a further key observation during the two-stage heap leach test work, in that there was an apparent connection between high levels of thiocyanate formation and elevated levels of platinum extraction over the first 4 days of leaching, suggesting that thiocyanate may have promoted its dissolution.

The thiocyanate ion consists of a linear structure with a carbon atom positioned in the centre; it is able to complex via both the S and N terminal (Kononova, 2005). Thus the chemistry of thiocyanate complexation is made more challenging owing to its ambidentate nature. Hamacek and Havel (1999) identified thiocyanate to form extractable complexes with both platinum and palladium which displayed increased stability (Table 3), when compared to chloro complexes (Hancock et al., 1977; Le Roux et al., 2014). Both platinum(IV) and palladium(II) form complexes coordinating with the sulphur atom, leading to Pt(SCN)₆²⁻ and Pd(SCN)₄²⁻ complexes (Eqs. (6) and (7)). The rate of complexation for Pd is faster by a factor of 10⁵–10⁶ relative to Pt. However, the rate of complexation between Pt and thiocyanate is greatly dependant on thiocyanate concentrations, and it can be accelerated by heating or exposing to light (Oleschuk and Chow, 1998). A recent study by Le Roux et al., 2014 has shown that palladium(II) complexation with thiocyanate exists in 5 different modes. These complexes are generally accepted to be square planar. However, the addition of the 5th ligand leans towards square pyramidal geometry with enhanced stability obtaining a cumulative formation constant of log β₅ = 31.94 for the [Pd(SCN)₅]³⁻ complex.



Work by Kriek (2008) has shown pronounced recoveries during thiocyanate leaching of PGEs from virgin automotive catalytic converters, ranging from 80 to 90% Pt, 90–100% Pd and 29–32% Rh when leaching was conducted with a solution of 0.3 M, sodium thiocyanate and 0.25 M ferric sulphate at pH 1.28 and 50 °C for a period of 24 h. Extensive research has been carried out on thiocyanate dissolution of gold which can serve as a reference, as the coordination chemistry of PGEs closely mirrors that of gold. Previous researchers (Broadhurst, 1987; Kholmogorov et al., 2002; Li et al., 2012b) have investigated the speciation and kinetics of gold leaching in thiocyanate solutions. Li et al. (2012a) also established the chemistry and thermodynamics involved in metal-thiocyanate systems; they present E_h/pH diagrams for the SCN–H₂O, Au–SCN–H₂O, Cu–SCN–H₂O, and Fe–SCN–H₂O systems. However, the majority of the studies have focussed on metallic gold,

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