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Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques

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ABSTRACT

The fast depletion of sulfide PGM-bearing minerals and the deteriorating socio-political environments in most primary PGM producing countries have triggered interest in exploring the recovery of these metals from high-chromium PGM-bearing oxidized ores – sometimes contain relatively high marketable PGM values – which have proven to be more difficult to process by conventional metallurgical practice which involves grinding, milling, froth flotation into a sulfide concentrate, smelting and matte production and chemical refining.

This paper reports the results of an extensive evaluation campaign performed in both acidic sulfuric and chloride media. Leach tests were conducted in either a single-stage or a two-stage process and the results are compared and contrasted. Using a high-chromium PGM oxidized mineralized ore, the hybrid pyro-hydro-metallurgical and low-temperature single-stage salt chlorination process proved successful for simultaneously and efficiently leaching Cu, Ni, Pt and Pd without the need and/or addition of further oxidizing agents. The technique is expected to be a direct treatment route from flotation concentrate to PGM refinery feed.

Various chlorinating agents, including $CaCl_2$, $MgCl_2$, $SnCl_2$ and $AlCl_3$, were tested. A $CaCl_2$ and $MgCl_2$ mixture acted synergistically for simultaneous dissolution of both Pt and Pd, achieving 99.7% Pt and 100% Pd recovery when thermally calcined at 650 °C, at a heating rate of 5.42 °C/minute for 6 h, and then leached at 90 °C for a minimum of 3 h in 6 M HCl. Copper and nickel extraction were lower but had not plateaued even after 24 h reaching 75.4 and 90.9% extraction respectively.

It was also observed that when $MgCl_2$ was used on its own, it dissolves more platinum than palladium, while the opposite was true using $CaCl_2$. The leaching process was controlled by surface chemical reactions with a determined activation energy of 46 kJ/mol. The dissolution rate was limited by the ratio of HCl volume-to-solid content. The recovery mechanism of Pt from $PtAs_2$ and some recommendations for future prospects have been suggested.

1. Introduction

The fast depletion of sulfide PGM-bearing minerals and the deteriorating socio-political environments in most primary PGM producing countries have triggered interest in exploring the recovery of these metals from high-chromium PGM-bearing oxidized ores – sometimes contain relatively high marketable PGM values – which have proven to be more difficult to process by conventional metallurgical practice which involves grinding, milling, froth flotation into a sulfide concentrate, smelting and matte production and chemical refining (Sefako et al., 2017; Kraemer et al., 2015; Bulatovic, 2003).

In general, the processing of high-chromium oxidized ores by conventional flotation techniques typically results in very poor concentrate grade and PGM recoveries (Becker et al., 2014; Lewins and Greenaway, 2004; Bulatovic, 2003). Previous attempts to extract PGMs from such ore type have proved uneconomic due to low recoveries (≪50%) achieved by conventional metallurgical methods (Oberthür et al., 2013). Hence if an oxide ore cannot be preconcentrated, the method of treatment will have to accommodate large volumes of relatively low-grade material containing PGMs in a wide variety of mineral forms (Evans, 2002) that cause hydrometallurgical processes to be inappropriate. At present, oxide ores are either left *in-situ*, stockpiled or discarded as waste (Oberthür et al., 2013).

There has been some considerable research aimed at improving flotation recoveries of oxidized PGM ores by employing techniques such as (1) controlled potential sulfidization prior to flotation (Kalichini et al., 2017; Becker et al., 2014; Lee et al., 2009; Newell et al., 2006), (2) acid pretreatment of ores before flotation (Luszczkiewicz and Chmielewski, 2008) and (3) the use of various flotation reagent schemes (Becker et al., 2014; Lee et al., 2009; Bulatovic, 2003; Lee

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et al., 1998; Assis et al., 1996). Besides these techniques, direct leaching approaches have also been tested, where sperrylite has been found to be the main residual platinum bearing mineral remaining undissolved (Mpinga et al., 2017; Sefako et al., 2017; Mwase and Petersen, 2017; Kraemer et al., 2015).

This study follows on from earlier work by the same authors (Mpinga et al., 2017; Mpinga et al., 2015) where the investigation focus was to optimise the recovery of copper, nickel, platinum and palladium from a complex, chromite-rich Ni-Cu-PGM oxidized mineralized ore. This paper presents the results of exploratory research aimed at extracting these metals through either a single or a two-stage leach process. The results of sulfation roast as well as a salt chlorination roast are presented, followed by various aqueous processing options. Most of the emphasis was on the atmospheric pressure chlorination roast pretreatment followed by an acid chloride leach of the oxidized ore as it proved most effective. Emphasis was also placed on platinum (mineralized as sperrylite) due to its reputation of being more refractory towards oxidation/dissolution in comparison with other precious metals (minerals).

2. Theoretical background

2.1. Base metals beneficiation for exposing refractory PGMs

Base metals beneficiation associated with PGM ores in oxidized mineralization has been extensively reviewed by Mpinga et al. (2017). These authors outlined the significance of H_2SO_4 concentration on sulfation roast process prior to water leach. Their results revealed that most of the leaching occurred in the first 60 min (first data point) achieving 86% overall Ni extraction. A small increase of 4% was attained after 24 h and the curve plateaued at approximately 90%. In addition, only a low percentage of chromium and iron (10.40 and 13.60% in the ore, respectively) accompanies copper and nickel as water-soluble sulfates (0.80 and 1.46%, respectively).

However, the mineralogical characterization unfortunately still identified the presence of sperrylite in the water leach residues following the roast at 550 °C. To the best knowledge of the authors, chlorine gas is required to improve the extraction in a two-stage leach process (Liddell and Adams, 2012; Tatarnikov et al., 2004). PGM-bearing concentrates are leached under aggressive conditions in a HCl/Cl_2 medium (Sole et al., 2005). The HCl/Cl_2 leach approach is not suitable for low-grade ores or concentrates, but rather highly concentrated PGM feedstocks as found in PGM refineries. Therefore, the dissolution efficiency of refractory PGM minerals such as $PtAs_2$ might only be improved by thermal pretreatment processes supposed to influence the oxidation state of arsenic in the sulfide melt.

Hence instead of sulfation bake, a molten salt chlorination bake process performed at 650 °C, which lies just below the temperatures at which copper and nickel ferrites form (670 and 764 °C, respectively) and just above the temperatures (500–600 °C) at which $PtAs_2$ starts to decompose (Muir and Ariti, 1991; Okamoto, 1990) would be appropriate to volatilize and remove arsenic in the off-gas stream or as a calcium arsenate $Ca_3(AsO_4)_2$ compound. The sublimation point of arsenic is 613 °C (Dunn et al., 1995).

2.2. Thermodynamic considerations – minimum concentration of HCl as lixiviant

The Eh-pCl diagram (pCl being the negative logarithm of the Cl concentration) in Fig. 1 presents the stability regions of platinum chlorocomplexes. Their domain exists below the oxygen line and hence, from a thermodynamic viewpoint, the leaching of platinum metal is possible in chloride solutions containing oxygen. The diagram also shows that under high chemical potential of chloride ions, i.e. in the low pCl region, the complex ions $PtCl_6^{2-}$ and $PtCl_4^{2-}$ are more stable than Pt chlorides and Pt oxides (Horike et al., 2012). $PtCl_6^{2-}$ predominates at a wide area of acidic and high potential regions. This implies that chlorinated platinum can be dissolved in acidic chloride-ion-containing solutions without requiring a strong oxidant, as it is already present in an oxidized valent state.

The stability of PGM chlorocomplexes increases at higher chloride ion concentrations in solution, and this also increases their dissolution efficiency (Horike et al., 2012; Mahmoud, 2003). Baglin et al. (1985) emphasized that half reactions for their dissolution in chloride media are not dependent upon solution pH, but are strongly dependent on chloride concentration (Eqs. (1) and (2)). Dawson and Kelsall (2007) stated that it is usual practice when dissolving PGMs in acidic chloride media to use chloride concentrations of > 3 M, in order to increase their product solubilities and depress their equilibrium potentials.

$$Pt_{(s)} + 4Cl^-_{(aq)} \rightarrow PtCl^{2-}_{4(aq)} + 2e^- \quad E^\circ = -730\ mV_{SHE} \tag{1}$$

$$PtCl^{2-}_{4(aq)} + 2Cl^-_{(aq)} \rightarrow PtCl^{2-}_{6(aq)} + 2e^- \quad E^\circ = -744\ mV_{SHE} \tag{2}$$

Industrial leach liquors generally contain up to 6 M HCl (Malik and Paiva, 2010). In this context, Nikoloski and Ang (2014) have observed that $PtCl_6^{2-}$ predominates in acidic solutions when HCl is ≥ 3 M, while $PdCl_4^{2-}$ dominates for concentrations of ≥ 0.1 M, and $RhCl_6^{3-}$ is the prevailing species when HCl is ≥ 6 M. Although a standard potential higher than 730 mV_{SHE} (Eq. (1)) is required to oxidize $Pt_{(s)}$, the rate of this reaction is far too slow for practical purposes (Benke and Gnot, 2002).

2.3. Molten salt chlorination roasting

It has been stated that following a salt fusion, platinum metals cannot be brought into solution, or can only be brought into solution with unsatisfactory yields without special measures (Schlecht, 1958). Among those measures, a requisite quantity of water may be added to facilitate increased physical contact between reactants in the roasting process (Han and Kim, 2006). Water is added such that the resulting mixture forms into a paste-like consistency (Mpinga et al., 2017; Han and Kim, 2006).

Molten salt chlorination roasts are typically carried out in the presence of moisture and in mildly reducing atmospheres. Moisture has been considered to be an essential component in the process for the production of HCl and/or Cl_2 (Eqs. (3)–(6)) by pyrohydrolysis of chloride salts under the catalysis of silica (Zhou et al., 2016). Chloride salts – preferably $CaCl_2$ or $MgCl_2$ – are chosen based on their low melting points and low vapour pressures as compared to the temperature (650 °C in this study) and the nature of the roasting reactor to be used.

$$MgCl_{2(s)} + SiO_{2(s)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + MgO{\cdot}SiO_{2(s)} \tag{3}$$

$$CaCl_{2(s)} + SiO_{2(s)} + H_2O_{(g)} \rightarrow 2HCl_{(g)} + CaO{\cdot}SiO_{2(s)} \tag{4}$$

$$2HCl_{(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)} + Cl_{2(g)} \tag{5}$$

$$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)} \tag{6}$$

The melting point of chloride salts varies significantly depending on their degree of hydration. It is as low as 30 °C for $CaCl_2{\cdot}6H_2O$, while 772 °C for anhydrous $CaCl_2$; likewise $MgCl_2{\cdot}6H_2O$ is 117 °C and 714 °C for anhydrous $MgCl_2$. At molar ratio of 1:1, Venkatesh et al. (2016) found that $MgCl_2/CaCl_2$ eutectic melting occurs at 625 °C. Hence base and precious metals chlorination may occur through $MgCl_2/CaCl_2$ eutectic melt in the reaction product layers. According to Doná et al. (2009), Cl_2 is able to attack Pt surface to form $PtCl_4$ (Eq. (7)). Platinum chloride ($PtCl_4$) is the only chloride of platinum species that is soluble in water (Renner et al., 2001; Gee, 1920). Other PGM chlorides that could form during the roasting stage may include: $PtCl_2$, $PtCl_3$, $PtCl_4$ and $PdCI_2$ (Chusova and Semenova, 2008).

$$Pt + 2\ Cl_2 \rightarrow PtCl_4 \tag{7}$$