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Platinum, palladium and gold leaching from magnetite ore, with concentrated chloride solutions and ozone

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ABSTRACT

A leaching process for platinum contained in a magnetite ore was studied, as an alternative process to cyanidation and aqua regia digestion. The proposed process employs concentrated chloride solutions and ozone gas injection during the entire leaching process. The effect of pH, chloride concentration and temperature was analyzed. Under atmospheric pressure at a temperature below 30 °C, after 3 h of leaching, metal extraction >90, 70 and 50% was attained for Pt, Pd and Au, respectively. The apparent activation energies for Pt, Pd and Au were found to be 44, 39 and 23 kJ/mol, respectively. The magnetite mineral matrix was not attacked during the leaching of platinum group metals.

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1. Introduction

Since ancient times, precious metals have caught the curiosity of humankind at all levels, from those who used them as ornamental objects, to those who flaunt them as an economic power symbol to the scientist that marvels at their unique and sometimes disconcerting properties. Among the precious metals are included metals of the platinum group (PGM), which in recent decades have become very important in areas such as catalysis, bio-engineering and nano-science. The main sources of these metals are mineral reserves, although recently their recovery from recycling, mainly of catalytic converters, has become important.

Most commercial processes for treating ores containing PGM (in this paper gold is considered part of this group) include in this processing routes beneficiation, pretreatments and hydrometallurgical recovery. The first stage is commonly known as the “MF2 cycle” and was developed for the South African deposits; the name implies the use of Milling and Flotation units in series, which require at least two cycles. The second stage includes different processes where calcination, smelting and refining are combined. However, there are no uniform plant routes and each producer has his/her own processing methodologies (Cole and Ferron, 2002; Mwase et al., 2012, 2014).

Currently, the main (or at least the most common) industrial path includes in one of its stages pyrometallurgical processes, that is the smelting of the materials at temperatures above 1500 °C (Lake and Noble, 1978; Saville, 1981, 1987), combined with subsequent hydrometallurgical treatment. These industrial processes at extremely high temperatures, with the consequently elevated energy consumption are extremely inefficient; additionally, they generate large amounts of waste and atmospheric emissions. Furthermore, this corresponds only to the initial stage of processing for the PGM.

The final recovery step combines the most advanced hydrometallurgical processes in complex circuits which may include pressure leaching and high temperatures. Most involve up to three leaching-washing cycles of the mineral slurries. Although each plant is designed according to the mineralogy of the reserves (Kyriakakis, 2005), the majority of the processes have in common the use of aqua regia, a reagent that destroys the structure and dissolves almost all elements in the ore. These industrial processes use non-selective reagents and consequently both the mineral matrix and the metals of interest are dissolved in the process. Liquors obtained usually contain a large amount of metal ions, which involves multiple subsequent stages of chemical purification. Furthermore, the aggressiveness of the reagents employed obliges the use of corrosion-resistant facilities. Cyanidation also has been employed to process PGM, although not from magnetite containing ores (Chen and Huang, 2006). Finally, because of the chemical characteristics of these methods, it is difficult to reuse the reagents, leading to their excessive consumption thereof.

In the past forty years there have been numerous attempts to develop new technologies for the recovery of PGM; most are protected by patents and some are currently in use in the metallurgical industry. These alternative processes have sought out other chemical systems:

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employing ozone, chlorides and mixtures of inorganic acids; some use aqueous solutions of sodium chloride and mineral suspensions to extract gold (Schenider and Lindstrom, 1973). Others use mixtures of nitric, hydrochloric acid and sodium chloride at 90 °C (Cronjäer, 1975). Included are methodologies with the injection of ozone as a pretreatment and subsequent cyanide, hypochlorite and/or thiocarbamate PGM leaching (Van Antwerp and Lincoln, 1987). In some cases, preliminary roasting is followed by PGM leaching with sulfuric acid and bromide mixtures (Duyvesteyn et al., 1994). Other processes use PGM leaching by sparging ozone into sulfuric and hydrochloric acids mixtures (Vinyals et al., 2003). Similarly, autoclave leaching has been used at temperatures above 170 °C, with oxygen injection to the leaching system in order to achieve pressures above 1 atm (Fleming et al., 2003). Another process employs solutions containing hydrogen peroxide and applies an electric current between three to six hours at room temperature (Pearce and Pearce, 2009). Some methods also pursue electrochemical dissolution by imposing potentials to chloride solutions in contact with PGM (Lillkung et al., 2012). Recently, gaseous chlorine (Chlorination at 850 °C) has been injected during leaching into solutions of 1.5 M hydrochloric acid (De Villiers and Chennells, 2014). All of the above techniques, employ either highly acidic or elevated temperatures, which are non-selective, or imply multistage processes.

In the last decades, ozone has become an alternative oxidizing agent in hydrometallurgical processing. The advantages stem from the fact that its production is relatively easy, it can be added to the aqueous solution by direct injection, it also has high oxidizing power (2070 mV) and the solution potential is controlled by modifying the ozone flow to the solution. However, the disadvantage is its low solubility in aqueous solutions (14 mmol/L, at 20 °C) (Eriksson, 2005).

This paper presents a study of PGM extraction from a magnetite ore by leaching at near room temperatures, using gaseous ozone as oxidant in contact with concentrated chloride solutions. This system and conditions were chosen on the basis of their selectivity for the precious and PGM.

2. Materials and methods

All experiments were performed with a 20 kg representative sample of previously magnetically concentrated mineral, classified by size using conventional techniques. The metallic contents were determined from a number of digestions with aqua regia until complete dissolution of the sample (excluding silica). The filtered solutions were analyzed by atomic absorption spectrometry (Varian, SpectrAA220fs) with the standard addition method.

The source of chloride ions for the leaching tests was analytical grade sodium chloride (J.T. Baker). The pH of the solutions was adjusted with a dilute solution of hydrochloric acid (J.T. Baker). In this paper, the terms brine or leaching solution are used indistinctly to refer to the aqueous chloride mixture. All aqueous solutions and calibration standards were elaborated using deionized water (Millipore, Milli-Q).

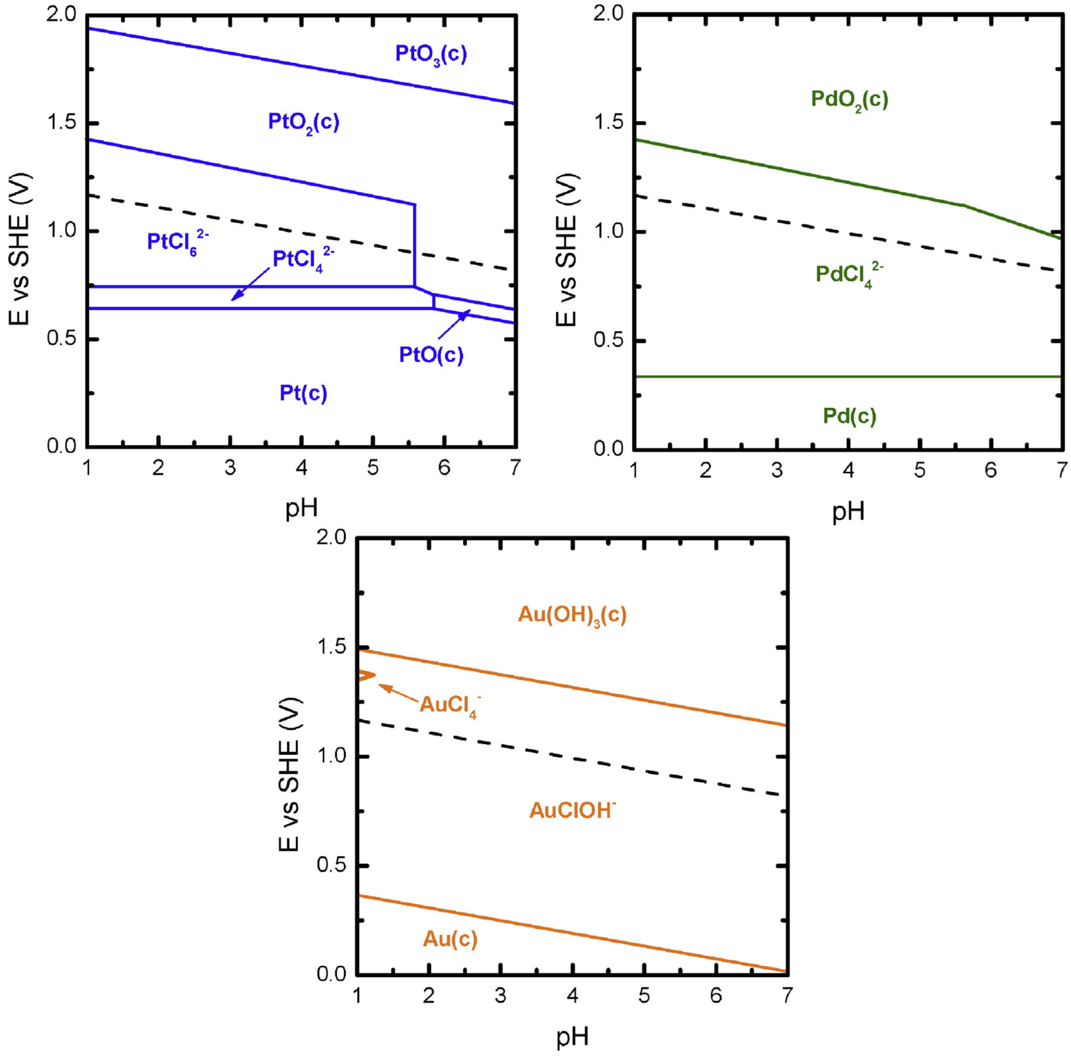

Fig. 1. Predominance diagrams for 0.001 M Pt, Pd or Au and 1 M Cl^-. Designed with MEDUSA© software.

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