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Fundamentals of pentlandite mineralogy and its effect on its electrochemical behaviour

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ABSTRACT

Pentlandite [$(Fe,Ni)_9S_8$] is the primary source of nickel and an important carrier of palladium and rhodium. Previous mineralogical investigations indicated compositional variations of natural pentlandite. However, the effect these mineralogical effects may have on the electrochemical behaviour of pentlandite is not clear. In this study, compositional variations of natural single pentlandite particles (~100 μm in size) sourced from the Bushveld Igneous Complex were shown. Experimental difficulties when measuring pentlandite microelectrodes are discussed. As a result only massive pentlandite samples were considered. The electrochemical investigations of the massive electrodes were carried out in an oxygen-free and air saturated 0.05 M borate solution using polarisation resistance, mixed potential, linear anodic voltammetry, electrochemical impedance spectroscopy and capacitance measurements.

Slight compositional variations of the massive pentlandite electrodes influenced the electrochemical behaviour. Iron-enriched pentlandites were less reactive after progressive oxidation. Electrochemical investigations established that as pentlandite oxidises, the oxides develop and grow at the surface decreasing the reactivity of the mineral. The decrease in reactivity of the electrodes was related to the mechanism of the reduction of oxygen at oxidised passive electrode surfaces. A variation in the electronic properties of the formed oxide film was observed. Effects of pentlandite Fe/Ni ratio and cobalt were evident.

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1. Introduction

The Bushveld Igneous Complex (BIC) is the major platinum-group element (PGE) resource in South Africa. In this resource, PGEs occur either as discrete platinum-group minerals (PGMs) or in solid solution in the base metal sulfides (BMSs) such as chalcopyrite, pentlandite, pyrrhotite and pyrite (Peyerl, 1983; Cabri, 1989; Jones, 1999). The Merensky reef is one of the PGE-rich layers of the Bushveld Igneous Complex. The majority of the platinum-group elements in the Merensky ore are associated with pentlandite [$(Fe,Ni)_9S_8$], occurring either in pentlandite grains or at the pentlandite–gangue grain boundaries (Peyerl, 1983; Jones, 1999). Palladium and rhodium are the PGEs contained mostly in pentlandite (Peyerl, 1983; Cabri, 1992; Godel et al., 2007).

Pentlandite [$(Fe,Ni)_9S_8$] is recovered by milling and flotation (Penberthy, 2001; Bradshaw et al., 2006). During flotation, oxidation depresses pentlandite resulting in poor grade-recovery performance due to the poor adsorption of collector on the mineral surface (Stamboliadis, 1976; Heiskanen et al., 1991; Kelebek et al., 2007). Stamboliadis (1976) investigated the effect of pH on the recovery performance of millerite, pyrrhotite and pentlandite minerals in the presence of dialkyl-dithiophosphate as a collector. In his study, he found that the maximum recovery of pentlandite, pyrrhotite and millerite occurs at a pH where the required maximum unilayers of dialkyl-dithiophosphate are adsorbed on the mineral surface. Pyrrhotite did not float above pH of 9 while pentlandite and millerite did not float above pH of 12 with few unilayers of collector adsorbed. This was found to be due to the insufficient adsorption of the collector on the mineral surface.

Pentlandite is one of the major nickel – hosting sulfide minerals. In sulfide flotation, the recovery of pentlandite is often associated with the recovery of nickel. Different nickel recoveries have been observed from various ores (Heiskanen et al., 1991) and, in some cases, from different areas of the same deposit. Besides other factors, such as mineralogical variations in the ores, dissolution of minerals, pH, aeration and the extent of oxidation, variation in the composition of pentlandite may also be a cause of differences in nickel recoveries. Previous research indicates compositional variation of a natural pentlandite (Brynard et al., 1976; Merkle and Von Gruenewaldt, 1986; Van Zyl, 1996; Harney and Merkle, 1991; Penberthy, 2001; and Godel et al., 2007). The variation seems to be independent of the reef and the deposit.

The effect these variations may have on the electrochemical oxidation of pentlandite is poorly understood. Pentlandite is a metallic conductor (Vaughan and Craig, 1978). The reactions occurring at pentlandite surface in aqueous media in the presence and absence of oxygen are electrochemical in nature and can be studied using electrochemical techniques (Trahar, 1984; Woods, 1984). Legrand et al. (2005) and Buckley and Woods (1991) investigated the oxidation of a natural pentlandite. Based on their work, it appears that oxidation products are independent of pentlandite composition; both the iron-rich and nickel-rich pentlandite resulted in similar oxidation products. However, the effect these products may have on the progressive oxidation behaviour of pentlandite is not clear. Chander (1984) proposed that the properties of the oxide films are responsible for the reactivity of sulfide minerals in the flotation systems. Previous electrochemical techniques employed, characterised the electrochemical behaviour of pentlandite with potential (Buckley and Woods, 1991; Khan and Kelebek, 2004). The extend of oxidation impairs the effective interaction of mineral surface with the flotation reagents. It was therefore of utmost interest to investigate the behaviour of pentlandite in deaerated and aerated solutions using the linear anodic voltammetry, polarisation resistance and mixed potential techniques. Polarisation resistance is one of the few techniques available to characterise progressive oxidation behaviour of electrodes with time in the presence of oxygen (Tolley et al., 1996; Jones, 2005). Polarisation resistance is one of the circuit elements the electrochemical impedance technique employs to model the electrode–electrolyte interphase. This method has been previously used to study the oxidation kinetics of various sulfide minerals (Tolley et al., 1996; Mendiratta, 2000). For freshly cleaved chlorite, chalcopyrite and pyrite, oxidation increased the polarisation resistance in aerated borate solution (Tolley et al., 1996). The increase was attributed to the formation of increasing iron hydroxide amounts at the surface. Extended oxidation periods, resulted in a further increase in the polarisation resistance values, indicating reduced reactivity of the electrode.

The aim of the study was to investigate whether there is any compositional variation of pentlandite particles from the flotation concentrate samples and selected massive ore bodies. The aim was to use these techniques to determine the electrochemical response of various pentlandite electrodes. The measurement of polarisation resistance with time provided insight into the progressive oxidation behaviour of pentlandite in an oxygen-rich environment.

2. Experimental procedures

2.1. Electrode preparation

Pentlandite electrodes were prepared from natural pentlandite particles and massive samples. Natural pentlandite particles (±100 μm in size) were sourced from actual flotation operations (i.e. Lebowa Merensky, Lebowa UG-2, Nkomati Mine, Sheba's ridge and Platreef flotation concentrate in South Africa) while massive pentlandite samples were sourced from the Pechenga deposit in Kola Peninsula (Russia) and Phoenix deposit (Botswana). The synthetic pentlandite originated from ARC (AngloPlatinum Research Centre) and it was synthesised according to well established procedures (Richardson and Vaughan, 1989). Only massive pentlandite grains with a minimal pyrrhotite phase were used. Energy dispersive spectrometer (i.e. EDS) analysis of the scanning electron microscope was employed to identify if the massive samples and pentlandite particles are Fe–Ni–S minerals. An electrical contact with a single pentlandite particle was achieved with a wire assembly consisting of a 50 μm tungsten wire and 0.5 mm copper wire. Tungsten wire was cemented onto a copper wire using silver paint (Acheson silver dag 11415 M supplied by Agar Scientific). The tip of 50 μm tungsten wire was dipped in a conductive epoxy supplied by RS Components and slowly brought into contact with a single pentlandite particle placed on a glass slide using a 152 Micromanipulator, fitted to an optical microscope. The preparation of the microelectrode and further discussions on the technique are given in detail elsewhere (Vermaak et al., 2006). The tungsten wire was supplied by Good Fellow. However, an electrical contact with the massive pentlandite grain was obtained using 0.5 mm copper wire and conductive epoxy only instead of 50 μm tungsten wire, 0.5 mm copper wire and conductive epoxy.

2.2. Electron microprobe analyses

The various compositions of pentlandite microelectrodes and massive electrodes were determined using an electron microprobe. For quantitative analysis, the surface of each pentlandite electrode was polished to a flat smooth surface – this surface was obtained using Aka-daran and MDNap polishing cloths (see Fig. 1 for backscattered electron image of a pentlandite particle). Electron microprobe analyses were carried out with a Cameca SX-100 electron microprobe at the University of Pretoria in South Africa. Pentlandite grains were analysed for Fe, Ni, Co, Cu and S. The following standards were used: troilite for S and Fe, nickel oxide for Ni, cobalt metal for Co and chalcopyrite for Cu. The electron microprobe