Minerals Engineering 70 (2015) 148–155

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

# An investigation into electrochemical interactions between platinum group minerals and xanthate: Voltammetric study

M. Tadie [a], K.C. Corin [a,*], J.G. Wiese [a], M. Nicol [b], C.T. O'Connor [a]

[a] Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch 7701, South Africa
[b] School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia

ARTICLE INFO

*Article history:*
Received 9 June 2014
Accepted 26 August 2014
Available online 6 October 2014

*Keywords:*
Electrochemistry
Cyclic voltammetry
PGM

## ABSTRACT

In the flotation of platinum group minerals (PGMs) containing significant amounts of tellurides and arsenides it is generally assumed that these minerals will respond in the same way as sulphides to collectors such as xanthates which are typically used in sulphide flotation. This paper presents the results of a fundamental study which has been conducted to provide a greater insight into the comparative interactions between synthetic moncheite ($PtTe_2$) and cooperite (PtS) with sodium ethyl xanthate (SEX). Cyclic voltammetry has been used to investigate these interactions in the absence and presence of sodium ethyl xanthate (SEX) in aerated and de-aerated solutions. Reduction potentials of the SEX/dixanthogen couple have been measured and compared to published data. Reduction potentials of possible reactions of the minerals have been predicted from thermodynamic calculations and used to attempt to interpret the potentials measured in the cyclic voltammetry investigations. Results have shown differences in the oxidation behaviour of the minerals as well as in the SEX interaction with the minerals. The effect of pH was investigated in the case of the Pt minerals and fractional surface coverages were calculated with a view to ultimately correlate these results with flotation behaviour. Proposals are made with respect to the various reactions occurring under the conditions studied.

## 1. Introduction

The distribution of platinum group minerals (PGMs) in the Platreef is variable. It has been found that the majority of the platinum group minerals belong to the telluride group which is unlike the distribution of PGMs in the other PGM bearing reefs (Merensky and UG-2) where the majority have been found to belong to the sulphide group (Shamaila and O'Connor, 2008; Viljoen and Schurmann, 1998). In certain areas of the Platreef the mineralogy indicates that the reef is almost barren of sulphide minerals (Viljoen and Schurmann, 1998). Since reagent suites for flotation of the ore from this reef are based on those typically used in the flotation of sulphide minerals, the study of the telluride minerals is of significance since it is important to understand whether there are any differences between these minerals in their interactions with the reagents being used. Vermaak et al. (2004, 2005, 2007a,b) conducted studies using platinum (Pt) and palladium (Pd) tellurides and bismutho-tellurides. In their work, electrochemistry coupled with Raman Spectra and F-TIR was used to identify species present on the mineral surfaces and to determine the reactivities of these minerals with sodium ethyl xanthate (SEX). They found that there was interaction between SEX and the mineral surfaces.

Ethyl xanthate (EX) is one of the most studied of all thiol collectors. This is considered to be a bulk collector in that it has strong collecting properties and renders a wide range of minerals hydrophobic (Bulatovic, 2007). Studies have shown that the mechanism of interaction of this collector with minerals is via an electrochemical oxidation (Yoon and Basilio, 1993; Nagaraj, 1988; Somusandaran and Nagaraj, 1984). This mechanism involves anodic oxidation of the collector coupled to cathodic reduction of oxygen resulting in an oxidised SEX species being present on the mineral surface. The oxidation reactions are represented by Reactions (1)–(3) below for a divalent metal ion, in which Th refers to a thiol species;

$$Th^{-} \rightarrow Th_{ads} + e^{-} \qquad (1)$$

$$M^{2+} + 2Th^{-} \rightarrow MTh_2 \qquad (2)$$

$$2Th^{-} \rightarrow Th_2 + 2e^{-} \qquad (3)$$

The corresponding reduction reaction is represented by Eq. (4);

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (4)$$

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* Corresponding author. Tel.: +27 21 6502018.
*E-mail address:* Kirsten.Corin@uct.ac.za (K.C. Corin).

http://dx.doi.org/10.1016/j.mineng.2014.08.022
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Adsorption of the SEX species on the mineral surface can be through physisorption or chemisorption. Reaction (1) which represents the adsorption of the thiol species on the mineral surface can occur through the formation of covalent bonds between the thiol and the mineral surface. This chemisorption reaction is dependent on a metal atom being accessible at the surface. Reaction (3) is believed to produce the most hydrophobic surface mainly due to the increased hydrophobicity resulting from the physisorption of the $Th_2$ species. Reaction (2) on the other hand occurs after the oxidation of the mineral to release metal ions which ionically bond with the SEX to form the insoluble species $MTh_2$. Hydrophobicity is therefore determined by the solubility of the species adsorbed as well as oxidation of the mineral resulting in the release of the metal ions.

All these reaction mechanisms are to an extent dependent on the reactivity of the mineral which is determined by the nature of the mineral and its crystal structure (Persson, 1994; Hu et al., 2009). The telluride minerals studied in this work are ditellurides, belonging to the melonite crystal structure group. This structure consists of $MX_6$ octahedron forming sheets that are held together by Van der Waals forces (Fig. 1a). The sulphide minerals on the other hand consist of edge and corner sharing square planar $(Pt,Pd)S_4$ (Fig. 1b) structures with the sulphur atoms tetrahedrally coordinated by metal atoms (Strunz and Nickel, 2001). It is expected that the differences between the octahedron and tetrahedron structures will affect the reactions that take place on these mineral surfaces, particularly with reference to the availability of metal atoms on the surface.

Pt has good catalytic properties due to the presence of d orbitals that are available for bonding. Sulphur (S) and Tellurium (Te) are both group 6 elements. S is more electronegative than Te and therefore in single bonds it forms stronger bonds with Pt than Te (Livingstone, 1965). Sulphide minerals are proposed to form elemental S under acidic conditions and oxidise to form sulphate or sulphite under alkaline conditions (Pourbaix, 1974). Telluride minerals have also been shown to be very reactive in solution (Vermaak et al., 2005; Vermaak et al., 2007a, 2007b). They found the order of reactivity to be BiTe > Te. It is proposed that in alkaline solutions the oxidation of the mineral could result in the formation of a tellurite ($TeO_3^{2-}$) ion which is soluble in solution (Vermaak et al., 2007a, 2007b).

In this study the electrochemical interactions between Pt and Pd sulphides and tellurides with sodium ethyl xanthate (SEX) are compared using cyclic voltammetry. The potentials for the different reactions that may be occurring are predicted thermodynamically and these values are then compared to the results obtained from the voltammogram studies in order to propose possible mechanisms for the adsorption of the SEX onto the minerals. $PtTe_2$, $PdTe_2$, PtS and PdS are studied together with the pure metals Pt and Pd for comparison. These results will serve to gain a greater understanding of the role which SEX may be playing in the flotation of these minerals in industrial circuits from a surface chemistry perspective.

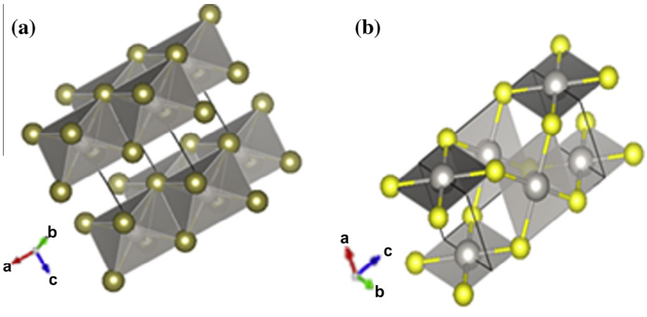

**Fig. 1.** (a) moncheite crystal structure projection and (b) cooperite crystal structure projection.

## 2. Experimental

### 2.1. Materials

Sodium ethyl xanthate (SEX) with purity greater than 99% was obtained from Senmin. Other reagents, viz. sodium tetraborate (buffer) and sodium sulphate, were sourced as AR grade from Merck and Associated Chemical Enterprises respectively. The PGM minerals were synthesised from their pure elements and the procedure is described elsewhere (Shackleton et al., 2007). The mineral samples were fabricated into cylindrically shaped electrodes using silver epoxy as the contact between the mineral and a stainless steel stud both of which were encased in epoxy resin to produce a cylindrical probe with the bottom face exposed. The electrodes were manufactured to fit into a conducting holder that was made of copper rod embedded in an epoxy casing.

#### 2.1.1. Electrochemical measurements

The electrolyte used was made from deionised water (conductivity of 10 MΩ cm) and 0.1 M sodium sulphate. A buffer of 0.05 M sodium tetraborate was used to achieve pH 9.2 and 1 M NaOH was used to adjust the pH to 11.2. 0.1 M Potassium dihydrogen orthophosphate was used as a buffer for pH values of 7 and 5.2, 0.1 M NaOH was used in each case to adjust pH to the desired value. In each experiment the volume of buffered electrolyte used was 0.45 l. Temperature was maintained at 298 K by conducting measurements in glass jacketed vessels which had water circulation from a water bath attached to a temperature controller. The mineral electrode was prepared prior to each experiment by grinding with 600 grit emery paper and then successively polishing with 1 μm, 0.3 μm and 0.05 μm alumina powders. The electrode surface was washed with deionised water to clean the surface before immersion into the electrolyte. Measurements were made in solutions saturated with air or nitrogen. In the case of nitrogen the gas was bubbled through the solution for 30 min prior to measurements being taken. This was the time determined to reach dissolved oxygen levels of below 0.5 ppm. No stirring was applied during measurements except to mix the SEX into the electrolyte. A three electrode system comprising of a working electrode (mineral), a reference electrode and a counter electrode (platinum wire) was used for the cyclic voltammetry measurements. The reference electrode used was a Ag/AgCl reference electrode filled with 3 M KCl solution having a potential of +0.207 V versus the standard hydrogen electrode (SHE). All measurements were made using a Gamry 600 potentiostat and Gamry PHE200 software to control the cyclic voltammetry measurements. Voltammetry measurements were made in the presence and absence of SEX. Sweep rates were kept constant at 10 mV/s and the sweep direction was alternated between positive and negative. Voltammograms were measured in duplicate in fresh solution for reproducibility. All potentials are shown versus SHE.

It is important to define clearly the conventions used in this paper. To that end it should be noted that:

- Reactions are presented as either oxidation or reduction reactions while the potentials are shown as equilibrium reduction potentials.
- Potential sweep directions are indicated as positive and negative.
- Positive currents are referred to as anodic.
- Negative currents are referred to as cathodic.