Electrochemical interactions of platinum group minerals with copper sulphate

M. Tadie*, K.C. Corin, J.G. Wiese, C.T. O'Connor

Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch 7701, South Africa

ARTICLE INFO

ABSTRACT

Activation of sulphide minerals by copper sulphate is common practice on platinum group mineral (PGM) concentrators. However, the role of copper sulphate in the flotation of PGMs is still unclear especially in the case of those PGM ores which contain relatively low concentrations of sulphides. This study was conducted to determine, using electrochemical techniques, the effect which the presence of copper sulphate has on the surface reactions occurring between xanthate collectors and minerals which are representative of those treated in PGM concentrators. Specifically rest potential and cyclic voltammetry measurements were conducted on the minerals moncheite ($PtTe_2$) and cooperite (PtS) at pH 6, 8 and 10. The results were interpreted by relating them to previous reports using the same minerals which included micro-flotation and X-ray photoelectron spectroscopy (XPS) studies. Electrochemical interactions between cooperite and $CuSO_4$ were observed to be occurring at all the pHs considered, whereas no significant interactions were seen in the case of moncheite. In the presence of SEX as a collector, $CuSO_4$ was shown to inhibit the electrochemical interactions of xanthate with both the sulphide and telluride mineral surfaces and this is consistent with the observations reported previously on the negative effect of copper sulphate on the flotation of these minerals.

1. Introduction

Copper sulphate has been used as an activator on industrial flotation operations for many years and has been proven to lead to a significant improvement of valuable mineral recovery. $CuSO_4$ is mostly used in the flotation of base metal sulphides. Much of the literature relating to the mechanisms of $CuSO_4$ activation is focused on sphalerite and pyrite flotation. The mechanisms which have been proposed however suggest that the use of $CuSO_4$ as an activator is not only applicable to galena and sphalerite (primary lead and zinc bearing minerals) but to all sulphide minerals (Finkelstein and Allison, 1976). In the flotation of platinum group minerals (PGMs) in South Africa, $CuSO_4$ is used as an activator. The Bushveld Complex mineralogy is such that PGMs are frequently closely associated with base metals such as chalcopyrite, pyrrhotite and pentlandite (Schouwstra and Kinloch, 2000) and hence $CuSO_4$ is used as an activator in these operations. In the Platreef ore body, which is hosted in the Northern Limb of the Bushveld Complex, the mineralogy differs from that of the Merensky and UG-2 ore bodies and PGM occurrences in this reef are more commonly found on grain boundaries or locked within silicate gangue minerals. Liberation also yields discrete PGM grains. Furthermore the distribution of PGMs as sulphides in comparison to tellurides and arsenides is significantly

lower (Barnes and Maier, 2002; Schouwstra and Kinloch, 2000). It has been proposed that in the treatment of such ores copper sulphate is of limited value (Shackleton et al., 2007a) and it has even been shown in micro-flotation studies that the recoveries of some synthetic platinum group minerals ($PtTe_2$, PtS, PdS and $PdTe_2$) are in fact reduced in the presence of $CuSO_4$ (Shackleton et al., 2007a).

Significant research has been reported on the mechanisms of copper activation with, as mentioned above much of the literature being based on sphalerite and pyrite flotation (Chandra and Gerson, 2009; Finkelstein and Allison, 1976; Finkelstein, 1997; Wang et al., 1989a,b). The literature indicates that pH has a significant effect on activation and that the mechanism of activation is a combination of effects due to species precipitation and electrochemical reactions.

Activation under acidic conditions is proposed to result in the formation of a CuS species at mineral surfaces. The mechanism of CuS formation has been suggested to occur via (Wang et al., 1989a):

(i) a precipitation reaction in which cupric ions combine with sulphur and precipitate at the mineral surface
(ii) an ion exchange reaction in which cupric ions replace metal cations within the crystal lattice of the sulphide mineral
(iii) an electrochemical reaction in which sulphur species are reduced

---

and combined with cupric ions to form the CuS species.

Each mechanism has its limitations and these are discussed in the same paper. Attempts at analysis of the activation products have indicated the presence of Cu(I) at the mineral surface which implies the presence of, for example, Cu_2S rather than CuS at the mineral surface. Electrochemical and spectroscopic studies have suggested that there is a two-step activation mechanism in which CuS is precipitated and then electrochemically reduced to form Cu_2S in the second step (Finkelstein, 1997).

Electrochemical experiments which include rest potential measurements and voltammetry experiments can provide useful information regarding the species present at mineral surfaces during activation. For example (Chen and Yoon, 2000) conducted rest potential measurements on sphalerite and found the resulting potential of sphalerite to be similar to that of a CuS surface thereby possibly confirming the formation of a CuS species on the mineral surface. In general the response of a mineral electrode has been found to increase in potential value in the presence of $CuSO_4$ which is attributed to the reduction of CuS to Cu_2S (Finkelstein, 1997; Wang et al., 1989a). In the case of sphalerite this is attributed to the formation of a CuS surface which has a higher rest potential than sphalerite (Chen and Yoon, 2000).

The mechanism described above is dependent on the availability of Cu^{2+} ions in solution and therefore acidic conditions. pH is therefore a significant factor in the activation process in regard to the species of copper available at activation. At alkaline pH conditions (pH 8 and above), hydrolysis of copper ions occurs thereby complicating the chemical environment and the nature of the resulting activation reactions which occur. Copper hydroxyl species at alkaline conditions are hydrophilic and their precipitation at sulphide mineral surfaces will result in a reduction in mineral hydrophobicity. Speciation diagrams for copper species in solution at a concentration of 1×10^{-4} M $CuSO_4$ (cf. Fig. 1, generated using Visual Minteq 3.0) show that the dominant copper species at acidic, neutral and alkaline conditions are as follows (Gustafsson, 2011):

- Below pH 6 the dominant copper species is Cu^{2+}
- Between pH 7 and pH 8 the dominant copper species are $Cu(OH)_{2aq}$, $Cu(OH)_{aq}^+$, $(Cu)_2(OH)_{2aq}^+$ and $Cu(OH)_{2s}$
- Above pH 10 the dominant copper species are $Cu(OH)_{2s}$ with some $Cu(OH)_{2aq}$.

Zeta potential studies have indicated that intermediate pH conditions result in the formation of negatively charged surfaces due to the adsorption of soluble hydroxyl species such as those shown in Fig. 1 and a corresponding decrease in the floatability of sulphide minerals rather than activation (Chandra and Gerson, 2009; Wang et al., 1989b).

Studies on the activation by $CuSO_4$ of base metal sulphides in the presence of xanthate collectors have indicated that the formation of a CuX_2 species results in sufficiently hydrophobic surfaces to enhance flotation. In the case of sphalerite a CuX_2 species is less soluble than ZnX_2 species and is therefore considered to impart a greater degree of hydrophobicity and hence the recovery of sphalerite is enhanced. (Finkelstein and Allison, 1976). Formation of this copper xanthate species occurs through different mechanisms which are dependent on pH. In acidic medium where Cu^{2+} ions are present, copper xanthate is formed directly from cupric ions. The ensuing reactions include the reduction of CuX_2 and to form Cu (I) and dixanthogen (X_2) according to the following mechanism;

$$Cu^{2+} + 2X^- \rightarrow CuX_2 \tag{1}$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{2}$$

$$2X^- \rightarrow X_2 + e^- \tag{3}$$

The overall reaction is often reported as (Chandra and Gerson, 2009);

$$Cu^{2+} + 2X^- \rightarrow CuX_2 \rightarrow CuX + X_2 \tag{4}$$

Reaction (4) which could occur according to the mechanism described through reactions 1, 2 and 3 occurs after sequential addition of activator and collector in that order.

In alkaline medium $Cu(OH)_{2(s)}$ is the dominant species present as the copper species. In the absence of collector, colloidal coverage of minerals surfaces by $Cu(OH)_2$ is attributed to causing low recoveries of PGMs (Shackleton et al., 2007a). Different theories have been proposed to support the presence of Cu(I) on sphalerite mineral surfaces at alkaline conditions. Chandra and Gerson (2009) and Finkelstein (1997) agree that at alkaline conditions $Cu(OH)_2$ is adsorbed at the mineral surface of sphalerite and converted to a CuS_2 species through ion exchange at the mineral surface. Evidence of the presence of Cu(I) species points to the suggestion that the full reaction mechanism follows that of Eq. (4). At intermediate pH values Wang et al. (1989b) suggest that ternary Cu-OH-X species are formed at sphalerite mineral surfaces and these are responsible for the resultant hydrophobicity.

X-ray photo-electron spectroscopy (XPS) and Time of Flight secondary ion mass spectrometry (ToF-SIMS) were used to determine the nature of the adsorbed species after $CuSO_4$ addition to $PtTe_2$ and PtS (Shackleton, 2007). These results are summarised in Table 1. It is important to note however that XPS and ToF-SIMS are ex-situ techniques meaning that the samples will usually be exposed to external ambient conditions prior to measurement. These ex-situ techniques can be combined with electrochemical techniques which are real-time in-situ
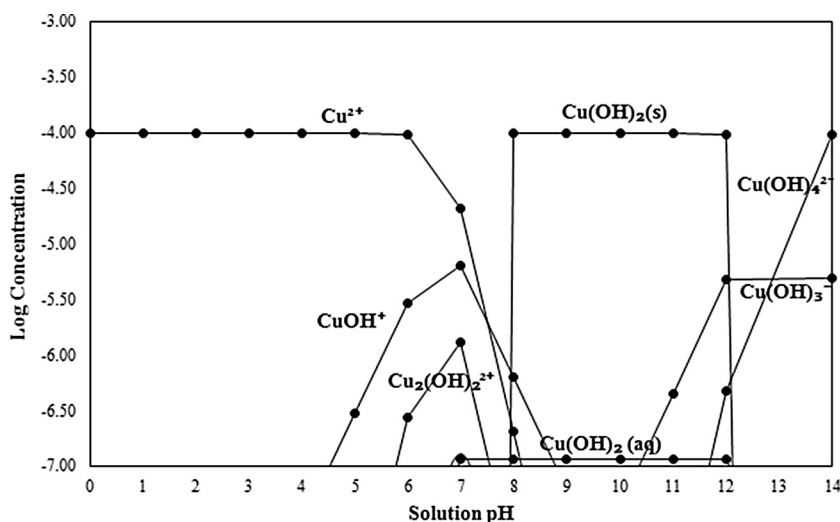

Fig. 1. Speciation diagram for copper species in solution at a concentration of 1×10^{-4} M $CuSO_4$ (Gustafsson, 2011).