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The value and limitations of electrochemical measurements in flotation of precious metal ores

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Abstract

Electrochemical measurements have successfully been used to interpret flotation behaviour of sulphide ores as their flotation performance is considerably affected by the oxidation state and amount of different minerals in the ore, the galvanic interactions between grinding media/sulphide minerals and sulphide minerals with different rest potentials, chemicals and dissolved ions in the pulp. However, although the Merensky ore obtained from Bushveld Igneous can be considered as a complex sulphide ore in terms of variety of the sulphide minerals, the total sulphide mineral content is less than 1%. Therefore, the usefulness of the electrochemical measurements in flotation of Merensky ore was discussed based on the mineral potential measurements taken from the experiments performed with different types of milling media in the presence and absence of copper sulphate. The results revealed that it could be misleading to relate flotation behaviour of the sulphide minerals in Merensky ore directly with the electrode potentials, presumably due to presence of very low content of sulphide minerals and the influence of other factors such as froth stability which changed depending on the type of milling media and copper sulphate addition.

Keywords: Precious metal ores; Redox reactions; Grinding; Froth flotation

1. Introduction

In flotation, the separation of valuable minerals from unwanted gangue is made on the basis of differences in mineral surface hydrophobicity. In sulphide flotation, thiol collectors are added to render the sulphide mineral surfaces hydrophobic. This is achieved by the collector—mineral reactions resulting in the formation of hydrophobic surface species such as elemental sulphur, a metal-deficient sulphur layer, metal–xanthate or dixanthogen formation at the surface. These reactions have been shown to be electrochemical in nature (Toperi and Tolun, 1969; Allison et al., 1972; Finkelstein and Poling, 1977; Woods, 1984) and their occurrence is influenced by process conditions such as the amount of different sulphide minerals, the oxidation state of the minerals and their galvanic interactions, as well as chemicals and dissolved ions present in the flotation pulp.

It is therefore expected that it would be possible to optimize flotation performance, both bulk recovery and selectivity, by the control of the oxidation–reduction or redox potential (E_h) as measured in the flotation pulp. However, it has not been possible to generalize the relationship between the electrochemical measurements in the pulp (such as E_h and dissolved oxygen concentration (DO)) and the flotation behaviour of sulphide minerals from different deposits due to the differences in the mineralogy and electrochemical reactivity of the sulphide minerals (Labonte and Fich, 1988; Hintika and

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Leppinen, 1995; Leppinen et al., 1998; Bradshaw et al., 1999; Buswell et al., 2002). The mineralogy of sulphide ores from different deposits, and even from the same deposit, may change drastically. Besides the degree of liberation, the changes in mineralogical composition of the feed to a flotation process affect the chemical, electrochemical and galvanic reactions and their kinetics in the flotation pulp.

In the present study, the value and limitations of E_h and DO measurements in a Merensky PGM ore flotation were discussed based on the measurements of redox potential of sulphide mineral electrodes present in the ore and a platinum electrode. In addition to that the effect of different grinding media on pulp chemistry and froth stability were also investigated by using stainless steel and mild steel milling media.

2. Experimental details

2.1. Materials

Merensky ore sample, obtained from the Bushveld Igneous Complex in South Africa, was used in this investigation. The sulphide grade was about 1% and was made up of 0.3% iron sulphides [approx. 0.06% pyrite (FeS_2) and 0.24% pyrrhotite ($Fe_{1.13}S$)], 0.4% pentlandite ($Ni_{0.5}Fe_{0.5}S$) and 0.2% chalcopyrite ($CuFeS_2$). The remaining 99% of the ore consisted of non-sulphide gangue minerals, such as talc, quartz, pyroxene and feldspar.

2.2. Pulp chemistry

Stationary chalcopyrite and pyrrhotite electrodes were made with pure mineral samples from Wards Natural Science Institute and a similar electrode was made with synthetic pentlandite from Johnson–Matthey (Buswell et al., 1988). Mineral potentials were measured relative to Ag/AgCl electrode (+0.207 V vs. SHE) and were logged continuously throughout the pulp conditioning stages. Mineral electrodes were removed during the flotation stage. All potentials reported in this paper have been converted to the standard hydrogen electrode (SHE) scale. Dissolved oxygen (DO), (YSI membrane electrode), pulp potential (E_{Pt}), (Pt–Ag/AgCl electrode), pH (Glass combination electrode) and temperature were logged continuously with a TPS meter throughout the conditioning and flotation stages. The pulp temperature, approximately 24 °C, was similar in all flotation tests.

2.3. Flotation experiments

For each test, 1.1 kg ore sample was milled in a Sala laboratory rod mill at 60% solids to obtained a particle size distribution of 45% passing 75 μm and transferred to a 3 L modified Leeds cell with water added to adjust the pulp density to 30% w/w. Stainless steel and mild steel grinding media were used in separate tests to change the pulp potential and to investigate the effect of milling media and galvanic interaction on the flotation performance. The pH was not modified but was recorded continuously and was constant at pH = 9 due to natural buffering effect of the ore. Where included in the reagent suit, 50 g/t copper sulphate was added and conditioned for 5 min. 30 g/t each of sodium isobutyl xanthate (SIBX) and SK5 (a dithiophosphate collector) were added as collectors together with 15 g/t SF7000 as frother and conditioned for 5 min. These reagents were supplied by Senmin Mining Chemicals and were used as received. Ten millilitres of a 1% solution (100 g/t) of IMP4, a modified guar depressant supplied by Trohall, was the last reagent added for depression of talc and conditioned for 1 min. Five flotation concentrates were collected after 1, 3, 5, 10 and 20 min and the mass and water recovery data collected. The measurements of water recovery and mass yield were used as indicators of the nature of the froth zone. An increase in the water recovery and mass yield indicates an increase in the stability of the froth. The reproducibility of the tests was deemed within acceptable limits for batch flotation test work. All recovery results presented are an average of duplicate experiments.

Analysis of the flotation samples for copper and nickel was performed by digestion and AA analysis and Leco was used for sulphur analysis. The grade and recovery for chalcopyrite and pentlandite are given in terms of Cu and Ni assays. Since there were minerals other than pyrrhotite ($FeS_{1.13}$) and pyrite (FeS_2) containing iron, the iron sulphides were calculated from the residual sulphur remaining after subtracting sulphur in chalcopyrite ($CuFeS_2$) and pentlandite ($Ni_{0.5}Fe_{0.5}S$) from the total sulphur assayed.

3. Results and discussion

Two types of milling media (stainless steel (SS) and mild steel (MS)) were employed to investigate the effect of E_h and DO in flotation of Merensky ore. The dissolved oxygen (DO) measurements in Fig. 1 shows that the effect of milling in mild steel is to remove almost all the DO from the flotation pulp. It can be seen that once the air is turned on at the start of flotation, DO levels are similar for both milling media. The addition of copper sulphate as an activator for iron sulphides and particularly SIBX as collector decreased DO slightly with SS milling condition. This was mainly considered to be due to the following two half reactions occurring simultaneously.

Anodic oxidation of xanthate which may take place in the following forms: