

# The use of oxidising agents for control of electrochemical potential in flotation



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## ABSTRACT

Relating flotation performance to the electrochemical characteristics of a pulp remains a complex issue both in fundamental research and in practice. For example, in the case of thiol collectors different Eh values can result in the formation of the dimer or the metal thiolate which may or may not enhance the hydrophobicity of the mineral. Reducing or oxidising conditions in a flotation system, viz. changing the Eh value, are usually manipulated to achieve an optimum flotation response by the control of pH and dissolved oxygen levels in the system. It is also possible to vary the potential by the addition of modifiers such as sodium hydrosulphide (NaHS), sodium hypochlorite (NaClO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The objective of the present study was to investigate the effect of the addition of the oxidising agents, NaClO and H<sub>2</sub>O<sub>2</sub>, on valuable mineral recoveries and grades in the flotation of sulphides from a PGM bearing Merensky ore. Batch flotation tests were conducted at pH 9.2, the natural pH of the system, in the absence and presence of a xanthate collector and Eh modifiers, viz. NaClO or H<sub>2</sub>O<sub>2</sub>. Most importantly in this way it was possible to vary Eh at constant pH and DO levels. The results indicate that in the absence or presence of xanthate the addition of H<sub>2</sub>O<sub>2</sub> reduced both the recovery and grade of copper and nickel. In the absence of xanthate, the addition of NaClO improved the recovery of copper slightly and both the recovery and grade of nickel significantly, but in the presence of xanthate NaClO addition resulted in unchanged copper recovery and grade, but those of nickel were reduced. Based on anecdotal evidence that the addition of trace amounts of a potential modifier could improve flotation performance further tests were conducted the results of which suggest improved flotation performance.

## 1. Introduction

In the Merensky Reef, platinum group minerals (PGM) are commonly associated with base metal sulphides (BMS) and this has an effect on the way in which these minerals can be concentrated by flotation (Vermaak et al., 2004; Wiese et al., 2005; Schouwstra et al., 2000). A major problem stemming from this association has been reported to be the loss of valuable minerals (PGM) associated with the loss of BMS (Wiese et al., 2005) during flotation. Shackleton (2007) suggested that PGM behave in a similar manner to sulphides during flotation. Therefore, in order to recover the PGM, base metals are targeted. There is thus a need to investigate ways to improve the flotation performance of the sulphide minerals. The electrochemistry of the flotation of sulphide minerals has been studied for over half a century and there is consensus that sulphide minerals float only under a suitable redox environment (Heyes and Trahar, 1979). This implies that reducing and oxidising conditions during flotation of ores such as Merensky can be manipulated/varied to achieve an optimum flotation response.

During flotation, sulphide minerals interact with thiol collectors in an electrochemical reaction to form hydrophobic species at the mineral surface (Finkelstein and Goold, 1972; Rand and Woods, 1984). The sulphide minerals are semiconductors and their interaction with collectors involves transfer of electrons. As such, a potential difference results which is responsible for driving electrons between reacting species (Fuerstenau et al., 2007). The magnitude of the potential difference affects the relative energies of charge carriers (electrons) at the mineral/solution interface hence controlling the direction and rate of charge transfer or rate of reaction (Bard and Faulkner, 2001). In a mixed mineral system the mineral/solution interface potentials account for the mixed potential which is critical to the process of flotation (Chander, 2003; Woods, 2003).

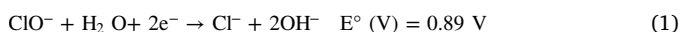
The use of potential as a parameter to control flotation has been widely proposed in literature (Woods, 2003; Smith et al., 2012; Chander, 2003; Javadi, 2013; Ross and Van Deventer, 1985; Allison et al., 1972; Gardner and Woods, 1979). There have, however, been significant contradictions and inconsistencies in potential range values

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where flotation recovery can be maximised (Guo and Yen, 2003). In addition, there are uncertainties around parameters such as oxidation-reduction potential (Eh), dissolved oxygen (DO) and pH during flotation of mixed sulphide mineral systems (Heyes and Trahar, 1979). It has been noted that it is difficult to accurately predict the effect on recovery of changing these parameters. These parameters affect the nature of oxidation-reduction reactions, the stability of the collector and the processes of precipitation and dissolution at either the mineral surface or in the pulp (Abramov and Avdohin, 1998).

In addition to the methods mentioned in the previous paragraph potential modifiers such as reducing agents to lower potential and oxidising agents to increase potential may be used (Rao, 2004). The flotation response of a complex ore e.g. Merensky ore when the redox potential has been controlled by means of chemicals has not been the subject of research. Most studies have focussed on single mineral systems and do not specifically provide information on the mechanism involved (Chanturiya and Vigdergauz, 2009). Potential modifiers such as sodium hydrosulphide (NaHS), sodium hypochlorite (NaClO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) can be used to alter the potential of flotation pulps. The following reaction shows the reduction of hypochlorite under the conditions investigated in this study, where the natural pH of the ore is generally around 9.



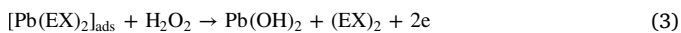
$E^\circ (\text{V})$  is the standard potential.

Reaction (1) is stable around pH 9 judging by the positivity of its standard potential,  $E^\circ (\text{V})$  of 0.89 V. The more positive the potential the higher the likelihood of the reaction to be thermodynamically stable. The value of the potential in a system can be calculated using the Nernst Equation shown below and depends on the activity of the available species (Mendiratta, 2000).

$$E = E^\circ - \left( \frac{0.05916}{z} \right) \log \left( \frac{[\text{Cl}^-][\text{OH}^-]}{[\text{ClO}^-]} \right) \quad (2)$$

NaClO has been proposed to be a suitable redox agent for potential control by various authors (Woods, 2003; Guo and Yen, 2003; Smith et al., 2012; Plackowski et al., 2013; Senior et al., 2009). Little information is available on how NaClO performs during bulk sulphide flotation. Plackowski et al. (2014) investigated the effect of increasing potential to +500 mV, using NaClO, in the flotation of enargite (Cu<sub>3</sub>AsS<sub>4</sub>). They found a high recovery of 82% at +500 mV compared to recoveries of 52% at a potential of +100 mV. Senior et al. (2009) studied the use of NaClO as Eh modifier in the flotation of gersdorffite in sulphide nickel systems and observed that the mineral did not float at potentials below -230 mV. It was also found by Woods (2003) that it is possible to float chalcocopyrite (CuFeS<sub>2</sub>) from galena (PbS) by control of the redox potential measured. High recoveries of chalcocopyrite at a potential of 450 mV and low recoveries of galena at the same potential were observed. Conversely galena was found to float effectively at a potential of -150 mV. Other studies have shown that NaClO is effective as a depressant of pyrite, arsenopyrite and galena (Beattie and Poling, 1988).

With respect to the use of H<sub>2</sub>O<sub>2</sub> as a chemical modifier of pulp potential, Wang (1992) has shown that H<sub>2</sub>O<sub>2</sub> can significantly influence the relative floatability of chalcocopyrite and galena. At potentials in the range 400–700 mV the recovery of chalcocopyrite was about 90% whereas the recovery of galena decreased rapidly as the potential increased in the same range. The most favourable concentrations of H<sub>2</sub>O<sub>2</sub> for chalcocopyrite recovery were in the range of 10<sup>-4</sup>–10<sup>-3</sup> mol/l. The depression of galena is ascribed to the formation of lead oxide caused by the presence of the strongly oxidising H<sub>2</sub>O<sub>2</sub>. The reaction proposed is:



It is also proposed that under those conditions dixanthogen present on the chalcocopyrite surface remains stable rendering the mineral

hydrophobic. Recently it has been claimed that the use of small quantities of H<sub>2</sub>O<sub>2</sub> can significantly increase the recovery of chalcocopyrite by flotation as well as reducing the amount of pyrite reporting to the concentrate (E & MJ, 2015). It is of interest to note that it has been shown that H<sub>2</sub>O<sub>2</sub> is formed during the grinding of a complex sulphide ore but these studies have not commented on the possible effect which this may have on flotation performance (Ikumapayi et al., 2012).

The aim of the present paper was to investigate the effect of using the potential modifiers, sodium hypochlorite (NaClO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), on recoveries and grades in the flotation of a PGM bearing Merensky ore. It is common practice to use the recovery of copper and nickel as proxies for the recovery of PGMs in the Merensky reef (e.g. Wiese et al., 2005). Solids and water recovered to the concentrate are also monitored to evaluate the effect which the presence of these modifiers may have on the froth behaviour. In general higher solids and water recovered to the concentrate are indicative of greater froth stability, whereas lower solids and water recovered to the concentrate are indicative of a less stable froth which has increased bubble coalescence and greater drainage of solids and water from the froth phase back to the pulp phase (Tao et al., 2000; McFadzean et al., 2016).

## 2. Experimental

### 2.1. Ore

The ore used in this study was a PGM bearing ore from the Merensky Reef in the Bushveld Igneous Complex. The copper mineral present in the ore was chalcocopyrite and that of nickel was pentlandite. A quantitative analysis of the ore was determined using X-ray Diffraction (XRD) and the results are shown in Table 1.

As shown in this table the major sulphide minerals present were chalcocopyrite, pyrrhotite and pentlandite and the major gangue minerals were bytownite which is a calcium rich feldspar mineral and enstatite which is a magnesium rich pyroxene silicate.

### 2.2. Reagents

The collector used in the batch flotation tests was sodium ethyl xanthate (SEX) at a dosage of 100 g/t. SEX was supplied in powder form by Senmin at close to 100% purity and was prepared for use in the batch flotation tests as a 1% solution using distilled water. 0.1 M sodium hydroxide (NaOH) solution was used to adjust the pH of the slurry in the flotation cell. DOW 200, supplied by BetaChem, at a

**Table 1**  
Minerals (sulphide and gangue) present in the ore as determined using XRD.

Mineral	wt%
Pentlandite	0.10
Chalcocopyrite	0.36
Pyrrhotite	0.43
Pyrite	0.06
Olivine	0.28
Biotite	0.40
Chlorite	3.77
Chromite	0.26
Diopside	6.93
Hornblende	3.23
Bytownite	42.41
Orthopyroxene	0.57
Talc	2.03
Enstatite	37.19
Epidote	0.63
Calcite	0.75
Quartz	0.60
Total	100.00

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