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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_2O_2). The objective of the present study was to investigate the effect of the addition of the oxidising agents, NaClO and H_2O_2, 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_2O_2. 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_2O_2 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_2O_2) 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.

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad E^\circ\,(V) = 0.89\ V \tag{1}$$

E° (V) is the standard potential.

Reaction (1) is stable around pH 9 judging by the positivity of its standard potential, E° (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).

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

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_3AsS_4). 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 chalcopyrite ($CuFeS_2$) from galena (PbS) by control of the redox potential measured. High recoveries of chalcopyrite 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_2O_2 as a chemical modifier of pulp potential, Wang (1992) has shown that H_2O_2 can significantly influence the relative floatability of chalcopyrite and galena. At potentials in the range 400–700 mV the recovery of chalcopyrite was about 90% whereas the recovery of galena decreased rapidly as the potential increased in the same range. The most favourable concentrations of H_2O_2 for chalcopyrite recovery were in the range of 10^{-4}–10^{-3} mol/l. The depression of galena is ascribed to the formation of lead oxide caused by the presence of the strongly oxidising H_2O_2. The reaction proposed is:

$$[Pb(EX)_2]_{ads} + H_2O_2 \rightarrow Pb(OH)_2 + (EX)_2 + 2e \tag{3}$$

It is also proposed that under those conditions dixanthogen present on the chalcopyrite surface remains stable rendering the mineral hydrophobic. Recently it has been claimed that the use of small quantities of H_2O_2 can significantly increase the recovery of chalcopyrite 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_2O_2 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_2O_2), 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 chalcopyrite 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 chalcopyrite, 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
Chalcopyrite	0.36
Pyrrhotite	0.43
Pyrite	0.06
Olivine	0.28
Biotite	0.40
Chlorite	3.77
Chromite	0.26
Diopside	6.93
Horneblende	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

dosage of 40 g/t was used as the frother in its concentrated form. Two different reagents were used for potential (Eh) control; sodium hypochlorite (NaClO), supplied by Kimix and hydrogen peroxide (H_2O_2) supplied by Merck. 0.1 M and 0.001 M solutions of NaClO and H_2O_2 were prepared using distilled water for addition to the flotation tests.

2.3. Batch flotation tests

A 1 kg sample of the ore (± 3 mm) was milled using synthetic plant water in a laboratory scale rod mill using stainless steel rods to the required particle size of 60% passing 75 μm. After milling, the slurry was transferred to a 3 L Barker flotation cell and made up to a pulp density of 35% by addition of synthetic plant water (Wiese et al., 2005). The NaClO or H_2O_2 were added for conditioning into the flotation cell. The collector was always added to the mill. A YSI multiprobe was used for the measurement of Eh and pH during the conditioning stage only of the batch flotation tests. The impeller speed of the flotation cell was set to 1200 rpm and an airflow rate of 7 L/min was used in all tests. A total of four concentrates were collected by scraping froth into a collection tray every 15 s over a total flotation time of 20 min. A froth height of 2 cm was maintained throughout each test by the addition of synthetic plant water. The feed, concentrate and tails samples from all tests were filtered, dried and weighed before being assayed for copper and nickel using a Bruker S4 Explorer XRF. All experiments were conducted in duplicate. Error bars on figures show standard error between duplicate tests. All Eh values are reported versus the standard hydrogen electrode (SHE).

2.4. EDTA extraction

Pure chalcopyrite supplied by Wards was used in Ethylene Diamine Tetra-acetic Acid (EDTA) extraction tests. 5 g samples of chalcopyrite, which were prepared to a particle size of −106 + 38 μm in a Sieb mill, were contacted in deionised water and synthetic plant water, as well as in solutions of NaClO and H_2O_2 for 5 min. A 25 ml aliquot from each solution was injected into a 400 ml glass beaker containing 250 ml of a 3% (w/w) solution of EDTA. The pH of the solution was adjusted to 7.5 using NaOH. The solution was stirred for 5 min before being filtered using a 0.2 μm Millipore filter. The filtrate was analysed for iron (Fe) using of Atomic Adsorption Spectroscopy (AAS).

3. Results and discussion

Rest potential measurements were carried out on chalcopyrite, pentlandite, pyrite and pyrrhotite at pH 9 and 11 both before and after the addition of SEX as well as after the addition of NaClO followed by SEX addition or after addition of SEX followed by NaClO addition. In all cases the potential was greater than 150 mV which is the potential above which dixanthogen is expected to form. In the case of pyrrhotite the potentials measured were very close to the value of 150 mV.

The results shown in Fig. 1 were obtained in order to determine whether the potential could be adjusted by addition of NaClO without any major effect on pH. The NaClO was prepared as a 1% solution which equates to 0.1 M. Fig. 1 shows the way in which Eh changed upon the addition of NaClO at pH ~9 and 11. At pH 9, the natural Eh of the slurry was between 100 and 200 mV. The NaClO was added dropwise and the Eh monitored after successive additions until it attained a value between 500 and 600 mV after which addition of NaClO did not result in any further increase in the potential. Most significantly the increase in Eh did not result in any significant change of pH. These results were obtained irrespective of whether distilled or synthetic plant water was used. When the pH was adjusted to pH 11 by the addition of NaOH, the natural Eh decreased to a region between 0 and −100 mV. Similarly, when NaClO was added at pH 11 the Eh increased to ~250 mV as shown by the squares in Fig. 1. It can therefore be deduced that Eh is independent of pH under the conditions tested. The dashed line in Fig. 1 represents the Eh above which xanthate will dimerize to dixanthogen viz. 150 mV. No similar tests were carried out using H_2O_2.

Fig. 2 shows the final solids and water recovered to the concentrate obtained from batch flotation tests conducted using 0.1 M solutions of H_2O_2 and NaClO as potential modifiers in both the presence and absence of SEX. The Eh values attained are shown in the Figure. The amount of water recovered is the mass of water recovered from the flotation cell to the concentrate as part of the froth and was calculated by subtracting the mass of solids and wash water from the mass of the total concentrate material to provide the mass of the water present in the froth as free water surrounding the bubbles. Results for baseline tests i.e. without the addition of potential modifier are also shown. For tests conducted in a potential range of 100–200 mV in the absence of SEX and oxidising agents or in the presence of SEX alone, the mass of solids and water recovered to the concentrate was almost identical demonstrating that in this potential range the absence or presence of SEX did not affect the amount of solids and water recovered to the concentrate at all. Obviously xanthate would have increased the recovery of the sulphides but in terms of overall mass recovery this was not significant. When either H_2O_2 or NaClO were added in the absence or presence of SEX the potential of the pulp increased to 300–400 mV for H_2O_2 and 500–600 mV for NaClO both of which are greater than the critical potential for dixanthogen formation viz. 150 mV. This increase in the potential was accompanied by an increase in both solids and water recovered to the concentrate above those obtained from the baseline tests with results obtained in the presence of SEX being higher than in its absence. The use of H_2O_2 resulted in significantly higher solids and water recovered to the concentrate than those obtained for NaClO. In this case the very significant increase in the amount of water recovered and the resultant increase in the amount of solids recovered may also be an indication that the stability of the froth had increased. An increase in solids recovered can be due to either true flotation or entrainment or both (Wiese, 2009). In the case of the NaClO there was an increase in water and solids recovered to the concentrate compared to the relevant base cases. However, these increases were much less than for H_2O_2 where the amount of water recovered to the concentrate more than doubled for both the case of no xanthate or xanthate present.

Fig. 3 presents the final copper recoveries and grades, respectively, obtained from batch flotation tests conducted using 0.1 M solutions of H_2O_2 and NaClO as potential modifiers in both the presence and absence of SEX. The number of moles of each modifier added in the respective tests was held constant at 0.0135. The addition of H_2O_2 resulted in the potential increasing to a range between 300 and 400 mV which was lower than that obtained in the case of NaClO viz. 500–600 mV. It is expected that dixanthogen will be formed on the mineral surface in both potential regions as they are greater than the critical potential for dixanthogen formation viz. 150 mV. The results show that, in the absence of xanthate, after H_2O_2 addition, the recoveries and grades of copper decreased significantly compared to the base case. For the same conditions addition of H_2O_2 had resulted in significantly greater amounts of solids and water being recovered to the concentrate (Fig. 2). The decrease in grade is easily ascribed to the greater recovery of solids to the concentrate which will be mainly gangue minerals, which is consistent with the greater amount of water recovered to the concentrate since such minerals will be mainly recovered through entrainment. However, the decrease in chalcopyrite recovery can only be ascribed to the possibility of significant oxidation of the sulphide mineral. In the absence of xanthate the surface may be affected by the formation of hydroxides which would render the mineral hydrophilic. In the presence of xanthate this effect is mitigated since the xanthate was added in the mill and the H_2O_2 in the flotation cell thus allowing the xanthate the opportunity to render the mineral hydrophobic before being exposed to the peroxide. It is possible that the presence of H_2O_2 results in the release of oxygen as per Eq. (4), which

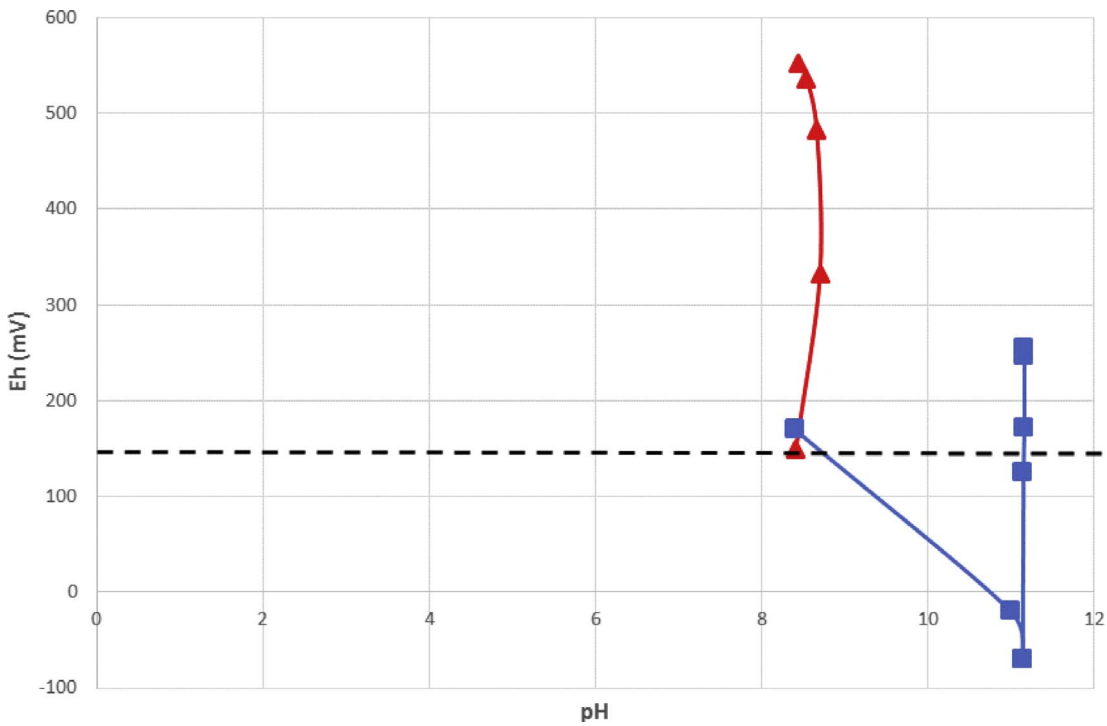

Fig. 1. Change in Eh as a function of pH using NaClO as a potential modifier. Dashed line represents Eh above which dixanthogen formation is favoured. Triangles represent Eh values at pH 9, and squares those obtained at pH 11.

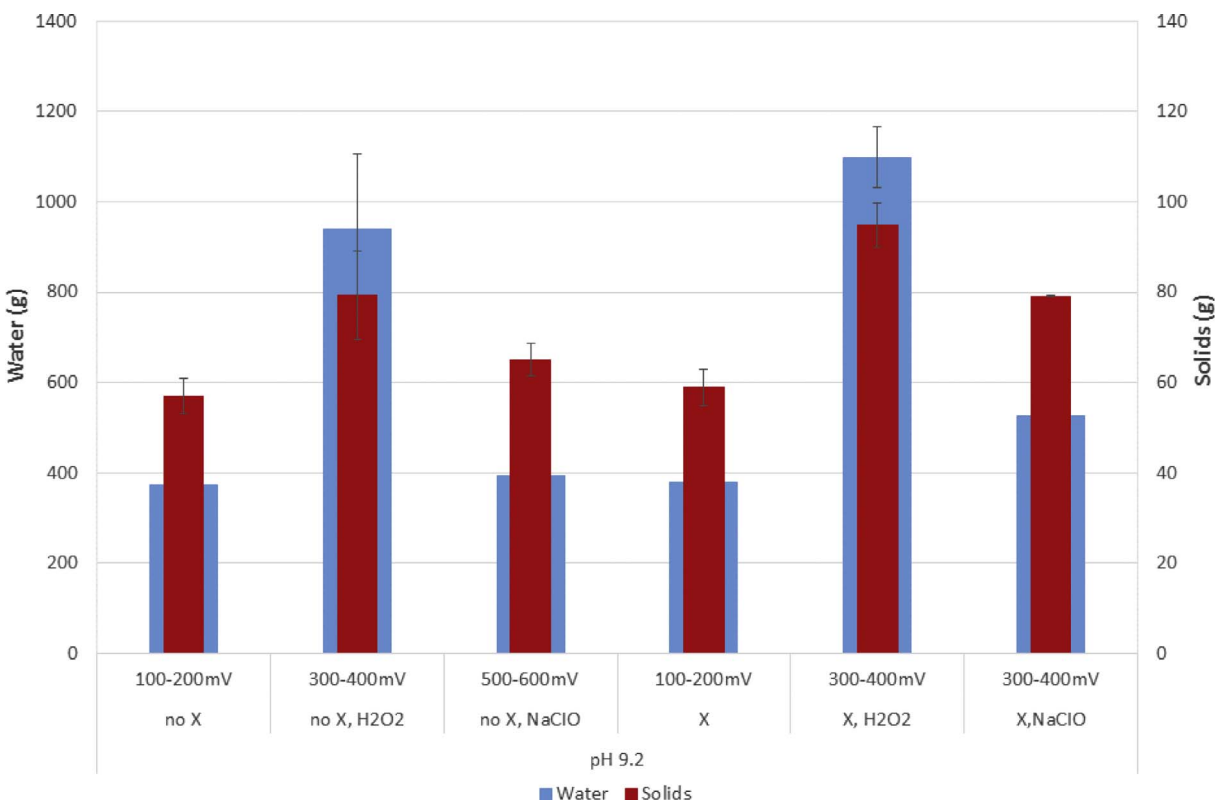

Fig. 2. Final solids and water recovered to the concentrate from batch flotation tests using 0.1 M concentrations of H_2O_2 and NaClO as potential modifiers. X refers to xanthate.

then undergoes reduction (Eq. (5)) forming OH^- ions (Mielczarski et al., 1998). The OH^- ions are possibly responsible for depressing the floatability of the chalcopyrite mineral as shown in Eq. (6) through formation of hydroxides.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (4)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \quad (5)$$

$$CuFeS_2 + 5OH^- \rightarrow Cu(OH)_2 + Fe(OH)_3 + 2S^{2-} \quad (6)$$

It is important to note that across all Eh ranges in this study, viz. 100–600 mV the recovery of chalcopyrite was always in the region of 80% in the presence of xanthate. This indicates that the low recoveries

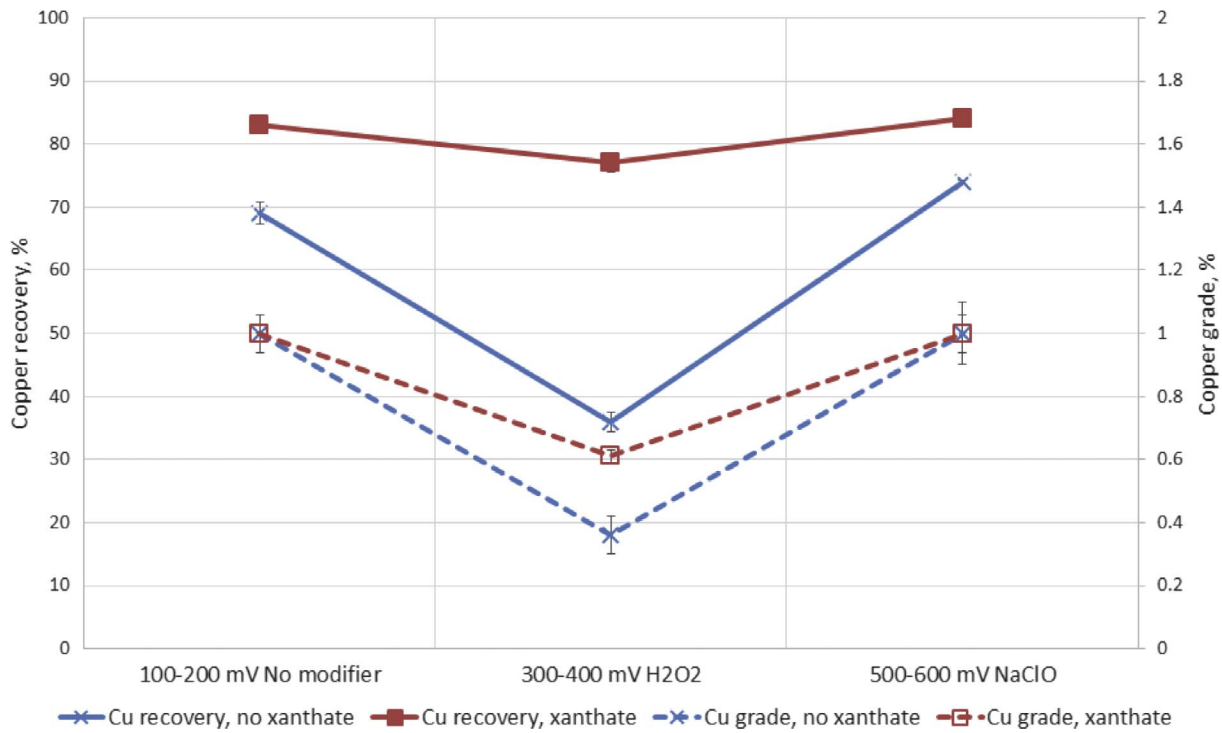

Fig. 3. Final copper recoveries and grades obtained from batch flotation tests using 0.1 M concentrations of H_2O_2 and NaClO as potential modifiers in the absence and presence of xanthate as a collector.

obtained when H_2O_2 was used in the absence of xanthate was not due to any change in Eh but rather probably due to a chemical effect which reduces recovery by rendering the particles more hydrophilic (Hu et al., 2009). It should also be noted that at the Eh-pH resulting from the use of H_2O_2 the Pourbaix diagram (Debernardi and Carlesi, 2011) indicates that the dominant phase is Cu_2O whereas after NaClO addition it is predominantly CuO but it is not clear if this could explain the differences observed between the results obtained for the two modifiers.

In the case of NaClO addition in the absence and presence, respectively, of xanthate the recoveries were marginally higher compared to the base case. With respect to the grades these were the same as when no modifier was added both in the absence and presence of xanthate. This is surprising since Fig. 2 showed that when NaClO was added, especially in the presence of xanthate, the solids and water recovered to the concentrate increased significantly compared to the case of no xanthate being present. This can only be ascribed to the possibility that the increased recovery in the presence of xanthate compensated for the increased gangue recovery resulting in similar grades. The relatively high recovery of chalcopyrite observed in collectorless flotation is consistent with findings of other researchers (Ross and Van Deventer, 1985; Hayes et al., 1987).

Fig. 4 shows a similar set of results for nickel. The low recovery of nickel in the absence of xanthate may be attributed to the possible formation of various hydroxides at the pentlandite mineral surface. These oxidation products are hydrophilic and would result in the low recovery of nickel in the absence of collector (Hodgson and Agar, 1989). In the absence of xanthate, NaClO resulted in an almost threefold increase in nickel recoveries and grades. In the light of the results shown in Fig. 2, which showed that under these conditions there was a slight increase in solids recovered to the concentrate, this seems to indicate that NaClO may be playing a selective role in increasing the hydrophobicity and hence recovery of pentlandite. H_2O_2 addition hardly changed the recoveries or grades from their low values in the absence of xanthate. The presence of xanthate increased recoveries greatly but this increase was less than when H_2O_2 was present compared to the base case. Xanthate addition also resulted in higher grades but again relatively less when H_2O_2 was present. Again, as in the case of chalcopyrite the changes in Eh caused by the addition of H_2O_2 was not conducive to improved flotation performance and hence it may again be deduced that the H_2O_2 was having a chemical effect such as oxidising the surfaces and reducing recoveries. Delgado (2001) has stated that the flotation of chalcopyrite can be completely suppressed by the heavy oxidation of strong oxidants such as H_2O_2 and that would be consistent with the results shown in Fig. 3.

In the case of pentlandite, Pourbaix diagrams indicate that at the Eh-pH conditions used in this study the predominant phases present are NiO and Fe_2O_3 after H_2O_2 addition (Eh = 300–400 mV) whereas at the conditions resulting from NaClO addition (Eh = ~50 mV), the predominant phase is Ni_3O_4 (Warner et al., 1996). There appears to be no readily available literature on the effect of Eh on pentlandite recovery and hence it can only be surmised that the Fe_2O_3 may be playing a role in the fact that the addition of xanthate has no beneficial effect on recovery. It is well known that iron hydroxides which would form from the Fe_2O_3 would render the surface hydrophilic. This situation may be exacerbated by the presence of H_2O_2. The absence of the iron oxide species at the higher Eh resulting from the addition of NaClO may explain the different behaviour of the H_2O_2 and the NaClO and hence in the latter case the major effect is to modify Eh values rather than alter the chemistry.

The question of the effect of dosage of potential modifiers has been referred to briefly in the literature. With respect to NaClO, Chanturiya and Vigdergauz (2009) have proposed that if the concentration were excessive it could lead to the decomposition of dixanthogen and hence poor valuable mineral recovery. However, this did not appear to be the case in the present study. With respect to H_2O_2 it has recently been reported that very small dosages when added to the flotation pulp can significantly increase the recoveries of chalcopyrite (E & MJ, 2015). In order to investigate the effect of the dosage of the modifier, tests were therefore conducted in which the concentration of NaClO and H_2O_2 was reduced by two orders of magnitude (i.e. changed from 0.1 M to 0.001 M) and the effect on the flotation variables analysed. The results obtained were compared to those obtained in the absence of potential modifiers and in the presence of H_2O_2 and NaClO at 0.1 M concentra-

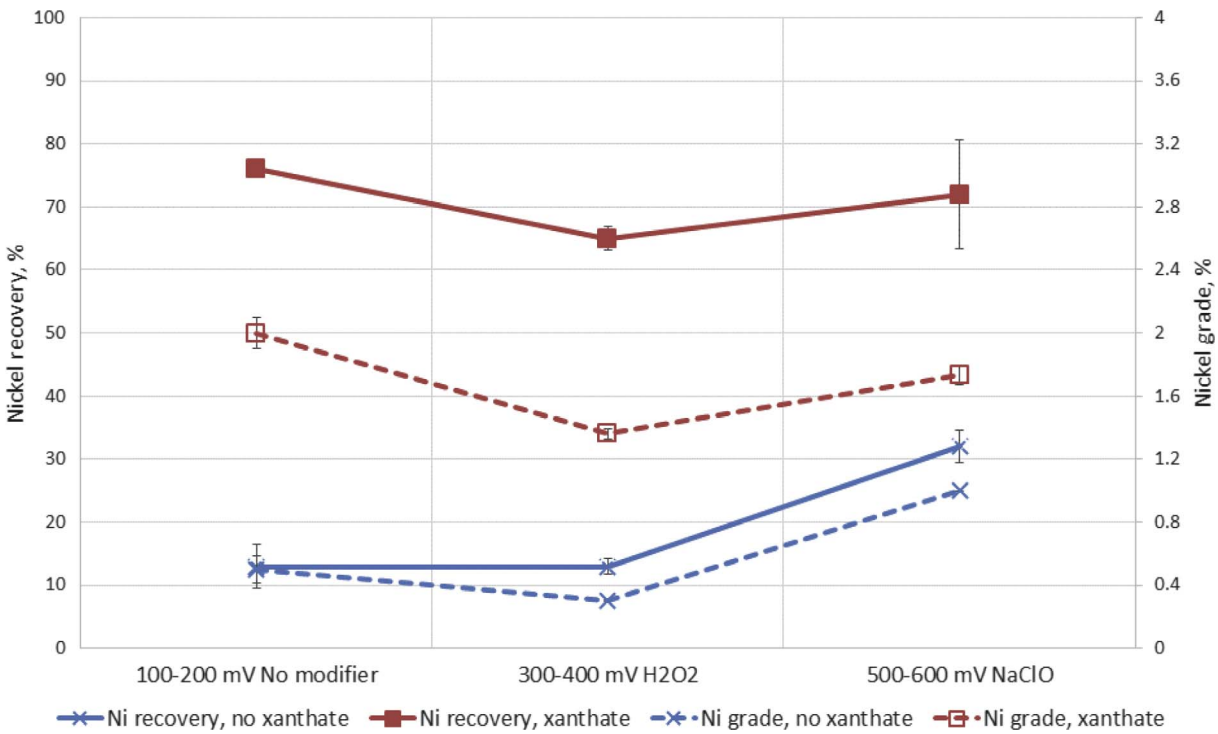

Fig. 4. Final nickel recoveries and grades obtained from batch flotation tests using 0.1 M concentrations of H_2O_2 and NaClO as potential modifiers in the absence and presence of xanthate as a collector.

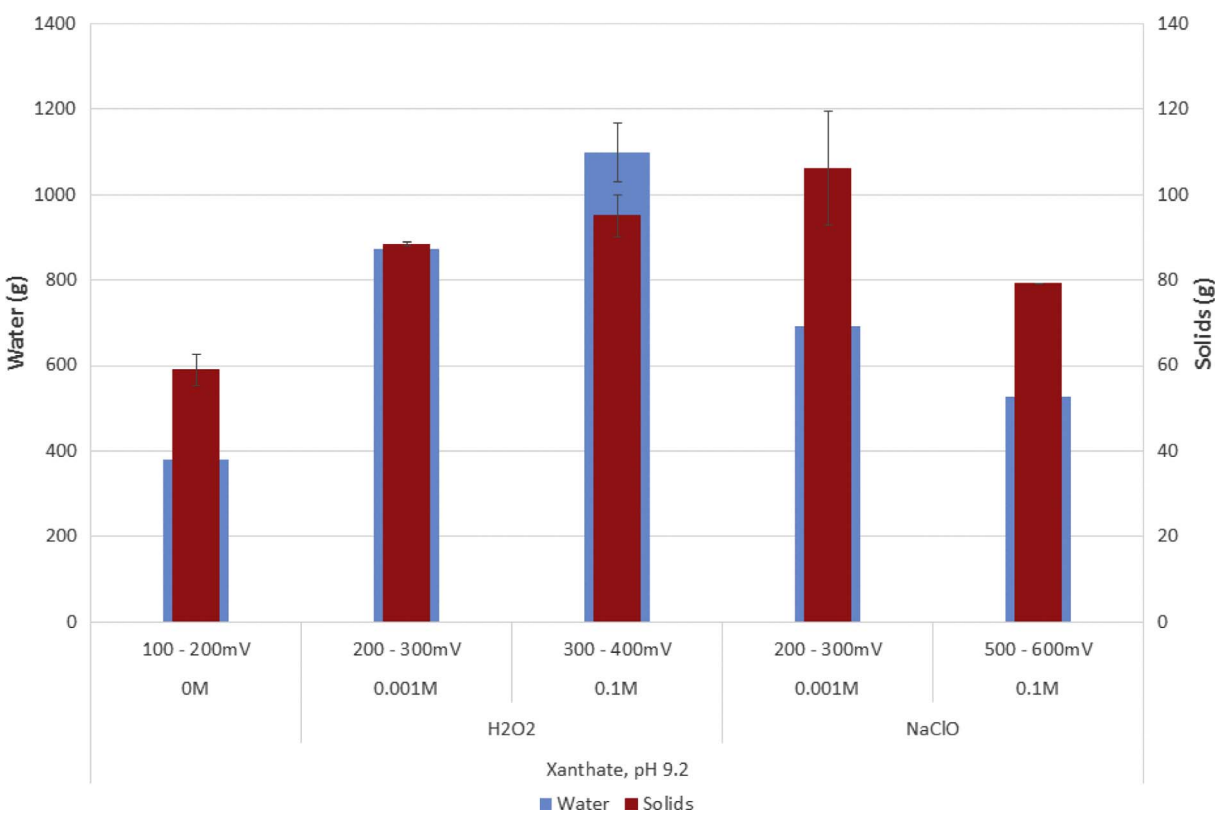

Fig. 5. Final solids and water recovered to the concentrate obtained from batch flotation tests using H_2O_2 and NaClO as potential modifiers at concentrations of 0.1 M and 0.001 M.

tion. At the lower concentration, both potential modifiers resulted in pulp potential in the range 200–300 mV, which is greater than the critical potential for dixanthogen formation viz. 150 mV. The results obtained for solids and water recovered to the concentrate are shown in Fig. 5. In the case of H_2O_2 the amount of solids recovered was between that obtained in the absence of modifiers and that obtained for the higher dosage. For NaClO the solids recovered was highest at the low dosage. The same trends were observed in the case of water.

The results for copper recoveries and grades obtained from batch flotation tests conducted using concentrations of 0.001 M of H_2O_2 and NaClO as potential modifiers in the presence of SEX are shown in Fig. 6 together with the results obtained when 0.1 M concentration of the

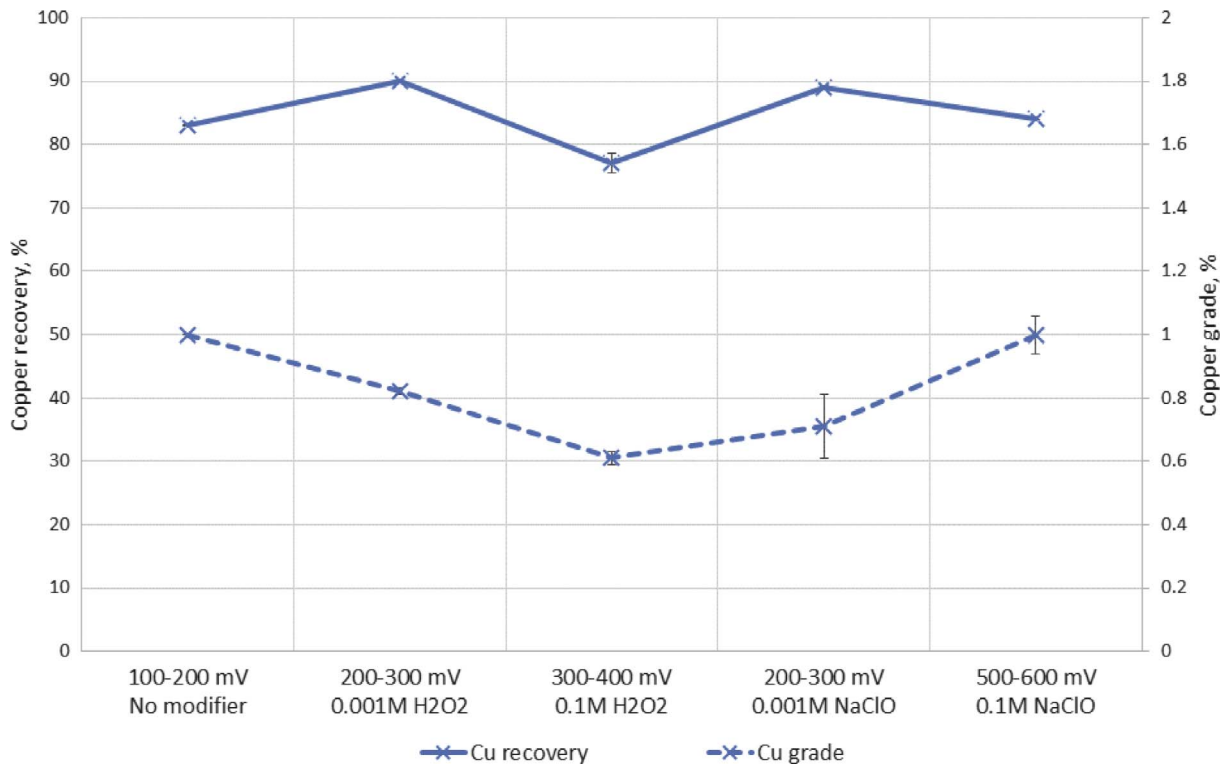

Fig. 6. Final copper recoveries and grades obtained from batch flotation tests using two different concentrations of H_2O_2 and NaClO as potential modifiers in the presence of xanthate as a collector.

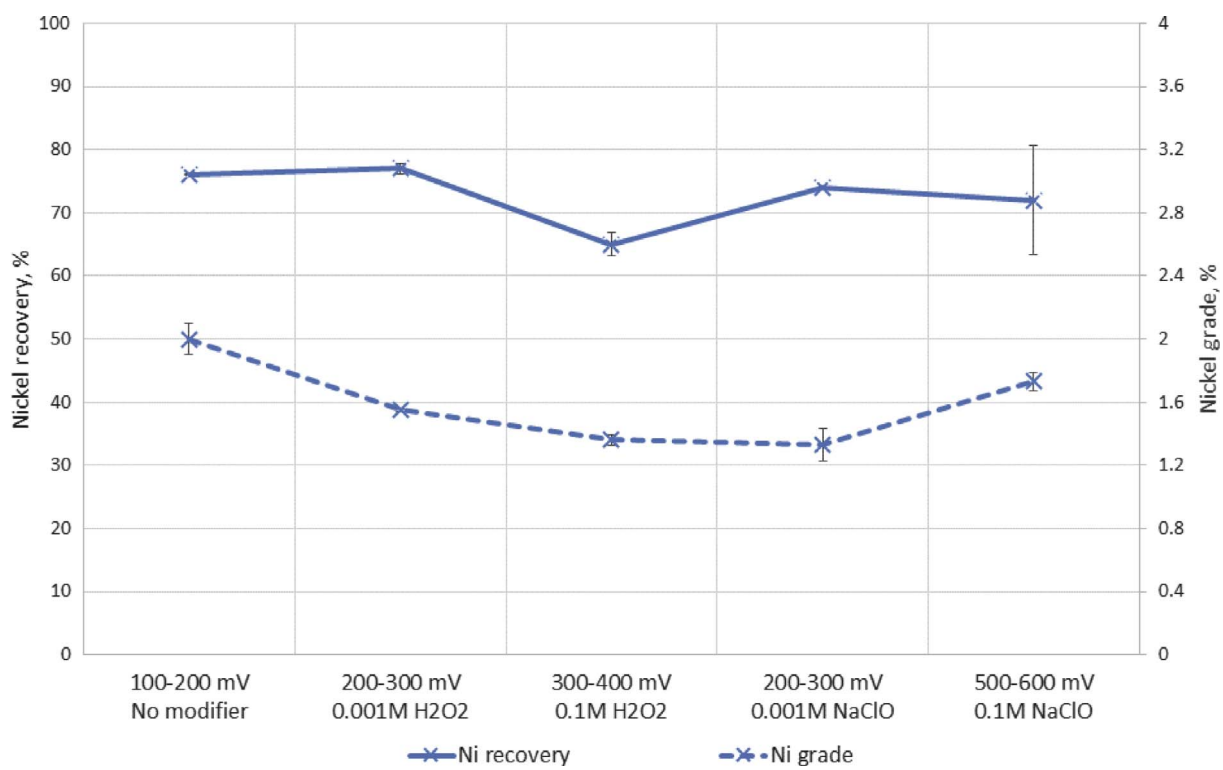

Fig. 7. Final nickel recoveries and grades obtained from batch flotation tests using two different concentrations of H_2O_2 and NaClO as potential modifiers in the presence of xanthate as a collector.

potential modifiers were used. The equivalent results for nickel are shown in Fig. 7. Clearly the lower dosage resulted in the highest recovery of copper in the case of both modifiers. At the same time grades were reduced which is consistent with the results shown in Fig. 5. The grades obtained in the case of H_2O_2 were slightly higher than for NaClO which is consistent with the fact that in the latter case the solids recovered were greater. Similarly Fig. 7 shows that reducing the dosage resulted in slightly higher recoveries although this was marginal in the case of NaClO. Again the nickel grades decreased which is consistent with the amount of solids recovered. This is possibly due to

Table 2
Amount of EDTA extractable ions present in a chalcopyrite slurry before and after treatment with 0.001 M H_2O_2 and 0.001 M NaClO.

EDTA Extractable ions (mg/g), no reagent (deionised water)	EDTA Extractable ions (mg/g), no reagent (plant water)	EDTA Extractable ions (mg/g) after H_2O_2 addition	EDTA Extractable ions (mg/g) after NaClO addition
0.074	0.094	0.26	0.37

the large increases in solids and water recovered to the concentrate obtained when low concentrations of NaClO and H_2O_2 were used in comparison to the baseline test as shown in Fig. 5. The increases in solids recovered can be due to either true flotation or entrainment or a combination of these two mechanisms. It is also likely that the use of the potential modifiers activated the flotation of gangue minerals which would contribute to the increased amount of solids recovered thus diluting the grade. The large increases in solids recovered to the concentrate, from 59 g for the baseline test to between ± 90 and 105 g cannot be attributed to the recovery of valuable BMS alone as the concentration of BMS in the ore is only in the region of 1% which equates to 10 g for the 1 kg of ore used in each batch flotation test.

The results obtained from this study illustrate that very low concentrations of the modifiers used in this study resulted in increased copper recovery whereas relatively higher concentrations had a detrimental effect on the flotation performance of the Merensky ore used. The question arises as to what role these modifiers are playing which result in a greater recovery of chalcopyrite and pentlandite. The results are surprising since H_2O_2 in particular is known to be a strong oxidising agent and theoretically this should result in a reduced recovery. The relatively large amount of pyrrhotite in the ore would result in significant concentrations of Fe^{2+} in the pulp since at the Eh-pH of the system the Pourbaix diagram for pyrrhotite shows that there will be a significant amount of these ions in solution (Kalinkin et al., 2000). Hence it may be speculated that the H_2O_2 and the NaClO may play a role in cleaning the surface of the mineral thus making it more amenable to collector adsorption and consequently flotation. Exploratory tests were carried out using pure chalcopyrite which in which the amount of EDTA extractable ions was determined both before and after treatment with H_2O_2 and NaClO. These results are shown in Table 2. The dosages of the reagents were in each case 0.001 M which was the dosage which led to enhanced recoveries.

Table 2 shows that in the case of both H_2O_2 and NaClO the addition of these reagents resulted in significant increases in amount of EDTA extractable ions in the solution. It is only possible to speculate on what reactions may be occurring. It is known that H_2O_2 promotes the leaching of copper from chalcopyrite (Mahajan et al., 2007) and hence, although traditionally EDTA titrations are used to investigate the presence of iron species in solution, in the present instance it is likely that the EDTA is complexing with leached copper ions. The results in this table also appear to indicate that the NaClO may also leach copper from the chalcopyrite. Even though it may be speculated that in real operations the use of mild steel grinding media may result in iron hydroxides coating the surface of the sulphides and thus reducing their recoveries, in the tests done to produce the results in Table 2 relatively pure chalcopyrite samples were used and thus it is unlikely that there is any significant amount of iron hydroxides on the surface. However it remains unclear how these reactions could influence the recoveries of chalcopyrite and pentlandite as observed in the flotation tests carried out in this study. Further studies, probably involving surface chemical techniques, may shed more light on this phenomenon.

4. Conclusions

Changing dissolved oxygen concentration and pH is a common method to vary the Eh in a pulp. In this study NaClO and H_2O_2 were used as the potential modifiers, and it was found that it was possible to change Eh while holding the pH fixed. It was shown that there was no significant increase in the recovery of copper and nickel when changing the Eh to a higher value using 0.1 M concentrations of either potential modifier. The use of H_2O_2 in the same amount as NaClO was shown to reduce recoveries of sulphide minerals. At very low concentrations of H_2O_2 and NaClO (0.001 M) the recoveries of copper increased significantly and a slight increase of nickel recovery was observed. These results appear to indicate that careful control of the concentration of H_2O_2 and NaClO to appropriately low levels can increase the recoveries of sulphide minerals.

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