# Role of Redox Potential in Flotation of Galena

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## Abstract

Flotation chemistry is fundamental to flotation recovery. The fact that part of the mechanism for hydrophobicity is electrochemical in nature suggests that redox (oxidation reduction) potential could be an indicator, and possibly an important driving force for flotation recovery. In this study the behaviour of the mineral galena has been studied in single mineral studies using micro-flotation and in batch flotation experiments of a galena sphalerite ore. Pulp and/or solution conditions were varied to influence the redox potential using nitrogen gas, dissolved salts, pH and the oxidising agent $H_2O_2$. A design of experiments approach was used to determine any correlations between independent variables and the responses recovery and Eh. The scope of variables considered facilitated a broad overview of the role of Eh and it has been concluded that the role of Eh cannot be considered in isolation of chemical processes such as precipitation and mineral surface oxidation.

## 1.0 Introduction

The role of Eh has been a topic of interest for flotation chemistry investigators since the adsorption mechanism of xanthate was determined to be electrochemical. Hydrophobicity is known to occur on sulphide minerals through some combination of reduction and oxidation reactions. It follows therefore that redox potential (Eh) should be a significant parameter when identifying hydrophobic mineral surfaces in flotation chemistry. To contextualise the role of Eh it is necessary to understand the chemical processes with which it influences. Following much debate on the mechanisms of xanthate adsorption Nixon (1957) settled the matter with the proposal that all chemical reactions involved during xanthate adsorption involve an electrochemical process. In summary collector adsorption processes can be described as being either (Yoon & Basilio 1993); chemisorption of a thiolate ion on the mineral surface which would require the release of an electron to maintain neutral charge, 2) oxidation of mineral surfaces to form metal cations which chemically react with thiolate ions through electrostatic interactions and finally 3) the participation of a mineral surface as a catalytic pathway for the loss of an electron from the thiolate ion to form dixanthogen. In all possible scenarios, the electron acceptor has been determined to be oxygen through the following chemical reaction (Biegler et al. 1975a; Biegler et al. 1975b);

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^o = 0.4\ V \qquad (1)$$

The main implications on this system of reactions are that; hydrophobicity and therefore recovery are related to the redox potential based on chemistry alone. It has been shown to be so in many instances in the flotation literature and yet it has been observed that this is not the case in all instances (Woods 2003; Ralston 1991; Woods 2010).

### 1.1 Oxidation Reduction Potentials

The question that must be considered if redox potential is to be a significant parameter in flotation chemistry is that of which potential to consider. There are two potentials which can be measured in the flotation system; mineral solution interface potential and solution potential. The former has been referred to as the 'rest potential' of a mineral or the mixed potential of a mineral and the latter is often referred to as Eh. Some researchers interchange the two terms but for the purposes of this paper Eh will refer to the potential measured by a noble metal electrode such as platinum.

Rest potential or mixed potential is referred to as such because it is an indicator that the potential being measured is due to multiple reactions occurring at the mineral surface with the resulting potential arising across the mineral solution boundary being a non-equilibrium potential. The mixed potential of a mineral is therefore kinetically driven. In an aqueous solution this potential would be a result of oxidation of the mineral coupled with an electron accepting process such as reduction of oxygen (Woods 1971; Allison et al. 1972). Potential measured by a noble mineral electrode is also a mixed potential, however this potential refers to chemical species in solution being oxidised or reduced at a noble metal electrode surface. This potential gives an indication of the capacity of the solution surrounding the mineral to accept electrons or give up electrons. The two potentials can thus be differentiated as the electron accepting or donating properties of the mineral and the solution respectively. The clear advantage of the former is that it enables prediction of the reactions occurring at a specific mineral surface whilst the latter enables prediction for a mixed mineral system from a single measurement.

The three dominant chemical processes resulting in hydrophobicity on sulphide minerals are driven by conditions which facilitate the loss of electrons i.e. an oxidising environment. Loss of electrons is required for metal surface oxidation and collector oxidation is favoured by an electron deficient environment i.e. high Eh. Low Eh is a condition which should not favour the oxidation of the mineral surface or collector. This reasoning however excludes the catalytic capability of sulphide mineral surfaces and as a result the rest potential of a mineral within the pulp should perhaps be a non-negotiable parameter to consider. Kocabağ and Güler (2008) have shown the difference between the Eh and the rest potential of several sulphide minerals, including galena, and noted that the two measurements are very different and that the difference between the two measurements was mineral specific. Kocabağ and Güler (2008) also showed that galena as a mineral showed the least deviation compared to platinum electrodes than chalcopyrite and pyrite.

### 1.2 Control of Potential

Promotion of collector adsorption is the primary objective of potential control. Likewise, monitoring of potential should provide an indicator of the processes occurring on mineral surfaces to yield hydrophobicity. The challenge, however, is determining the relationship between potential and recovery of valuable minerals from a flotation cell (Ralston 1991).

Various methods have been applied for influencing the potential within a flotation cell. The least obstructive in terms of the chemistry of the process is the alteration of dissolved oxygen content through aeration or injection of dissolved oxygen (Grano et al. 1990; J. Ralston 1994). Increase in oxygen content promotes oxidising conditions within the pulp (high Eh) and simultaneously provides excess oxygen for the promotion of the oxidation of collector which has been determined to be necessary for these reactions to take place. It should be noted that literature has demonstrated that in the absence of oxygen but under oxidising conditions collector is oxidised and hydrophobicity achieved which is an

important result (Woods 2010). An increased concentration of oxygen in the solution provides an electron acceptor (Dissolved $O_2$) in excess. The challenge with promotion of oxidation within the pulp is that the process is non selective and is purely driven by thermodynamics. Mineral oxidation is well known to be detrimental to recovery and more so for minerals containing iron such as chalcopyrite and pyrite (Hayes & Ralston 1988; Woods 2003).

Chemical control of potential has been the most investigated method of potential control and probably the most practical. Potential controlled sulphidisation has been very successful and this involves reduction of sulphide species e.g. $HS^-$ to sulphur species on mineral surfaces to increase the sulphide behaviour of minerals. Sulphidisation occurs under reducing conditions and is achieved using reagents such as NaHS and $NaS_2O_3$. Sodium hypochlorite and hydrogen peroxide have perhaps received the most attention as possible oxidising agents. Both are used in water purification for their high oxidising capacity and non-deleterious effect on water quality. Such is the case in flotation systems. The challenge with oxidising agents, however, is their non-selectivity and potential to have a depressing rather than activating effect on minerals (Trahar et al. 1994; Hayes & Ralston 1988; Heyes & Trahar 1979).

Hydrogen peroxide which is used in this study acts as an oxidising agent in alkaline solutions and is such a powerful agent that it is used to promote leaching/dissolution of minerals. It has been reported that $H_2O_2$ at high concentrations is detrimental to recovery (Javadi Nooshabadi & Hanumantha Rao 2014), however more recently it has been demonstrated that at low concentrations of the oxidant an increase in recovery can be achieved (Chimonyo *et al.*, 2017a; Chimonyo *et al.*, 2017b). Iron bearing minerals are particularly negatively affected by the presence of hydrogen peroxide due to the relative ease of oxidation of Fe and $Fe^{2+}$. In addition to this studies have shown that sulphide minerals have the capacity to catalyse the generation of peroxide through oxidation of water and further supports the conclusion that positive effects of peroxide on recovery can only be realised at low concentrations of the oxidant.

In this paper, the responses of galena to changes in the oxidising environment are discussed based on some experimental data either on pure mineral samples or on ores. The proposed hypothesis is that positive potentials drive collector oxidation leading to increased hydrophobicity regardless of how potential values are achieved. The sub-processes that accompany an increase in oxidation conditions will be identified with the aim of establishing the boundaries in which the different processes contribute to an increased understanding of the influence of Eh on recovery.

## 2.0 Experimental Methods

### 2.1 Reagents and Materials

Sodium di-isobutyl xanthate (SIBX) obtained from Senmin at 99.0 % purity was used as collector. Senfroth 516 was used as frother and obtained from Senmin at high purity. Hydrogen peroxide was an aqueous solution of 30 wt % $H_2O_2$ used as supplied from Merck. All other reagents used were of technical grade.

For micro-flotation tests pure galena was obtained from WARDS Scientific in a 1kg bulk sample. The sample was broken down into chunks using a hammer. It was then transferred to a Sieb mill to be pulverised for 10s. The size fraction used for flotation tests was 38 µm – 106 µm, which was purged with nitrogen and stored at temperatures below – 30 $^oC$ in order to retard oxidation. All flotation samples were used within 24 hrs of preparation for flotation.

A South African lead bearing ore was used for batch flotation tests. The ore was milled to a grind size of 60 % passing 75 μm in a laboratory rod mill and contained an average lead content of 2.19 % determined by x-ray fluorescence (XRF) using a Bruker S4 Explorer XRF Spectrometer. The quantitative x-ray diffraction (QXRD) was performed using a PANalytical X'Pert Pro diffractometer and the results have been classified according to the following criterion; major (>30%), moderate (10-30%), minor (2-10%) and trace (<2%) in Table 1.

**Table 1. QXRD classification of ore**

| **Mineral** | **Abundance %** |
|---|---|
| Magnetite | Major |
| Quartz | Major |
| Calcite | Minor |
| Actinolite | Minor |
| Muscovite | Minor |
| Galena | Trace |
| Chalcopyrite | Trace |
| Dolomite | Trace |
| Sphalerite | Trace |

The process water used in all experiments had variable ionic strength which was achieved by varying the concentrations of ions in solution. Two levels of ionic strength were investigated are indicated in Table 2, which shows the molar concentration of ions and the ionic strength calculated using the Debye-Huckel model;

**Table 2. Solution compositions and concentrations of ions determining synthetic plant water**

| | **1SPW** | **5SPW** |
|---|---|---|
| $MgSO_4.7H_2O$ | 0.00250M | 0.01248M |
| $Mg(NO_3)_2.6H_2O$ | 0.00042M | 0.00209M |
| $Ca(NO_3)_2.6H_20$ | 0.00868M | 0.04341M |
| $CaCl_2.2H_2O$ | 0.00100M | 0.00500M |
| NaCl | 0.00609M | 0.03046M |
| $Na_2CO_3$ | 0.00028M | 0.00142M |
| (Debye-Huckel) Ionic Strength | **0.11 M** | **0.55 M** |

### 2.2 Micro-flotation Tests

Mineral surface area was determined using BET measurements of which the BET surface area of the sample was found to be 0.0692 ± 0.0002 m²/g. SIBX was added based on a calculation of 50 % coverage of the mineral surface.

3 g of pure galena was used for micro-flotation. The sample was cleaned for 5 minutes in an ultra-sonic bath prior to flotation. Collector conditioning time was allowed for 5 minutes was allowed for conditioning with collector, concentrate samples were collected after 2, 6, 12 and 20 minutes. Further details about the micro-flotation instrument can be found in Bradshaw and O'Connor, (1994). pH, Eh and dissolved oxygen concentration (DO) were measured before and after each experiment using a TPS benchtop meter (90-FL series). Dissolved oxygen concentration was varied from a high value to a low

value by purging the system with nitrogen. A low dissolved oxygen concentration of 1.4 ppm was achieved under these conditions. Air flow rate into the micro-flotation cell was maintained at 6.5 ml/min. Concentrates for each float were filtered, dried and weighed, recovery was determined by mass balance.

A design of experiments approach was taken for micro-flotation tests in which a $2^3$ full factorial design was implemented. Recovery and Eh were recorded as independent responses to the variables, pH, ionic strength and DO. A summary of the factors and levels investigated is presented in Table 3. All statistical analysis was conducted using Statsoft (Statistica) 12 (Soft 2013).

**Table 3. Factors and levels investigated in micro-flotation tests.**

| Factor | Low | High |
|---|---|---|
| **pH** | 9.2 | 11.8 |
| **IS** | 0.11 M | 0.55 M |
| **DO** | 1.4 ppm | 8.0 ppm |

### 2.3 Batch Flotation Tests

Batch flotation experiments were conducted in a 3L modified Leeds cell. The milled ore was transferred to the cell and topped up with water to achieve a flotation pulp of 33 % solids by weight. SIBX (120g/t) was added to the pulp and conditioned for 2 minutes before frother addition 40 (g/t) and a further 1 minute of conditioning. Air was introduced into the cell at an air flowrate of 6 L/min and an agitation speed of 1500 rpm was maintained. Froth height was manually controlled at a level of 3 cm. Four concentrates were collected after 2, 6, 12 and 20 minutes respectively in order to evaluate flotation kinetics. A feed sample was collector prior to flotation and two tails samples were collected after flotation. Water was also accounted for by monitoring all external addition of liquid by mass. Water and mass balances were calculated from these samples. All concentrates obtained were analysed for Pb and Zn assay using XRF s described above. Eh and pH were measured before and after each experiment and the average values are those reported in this paper.

A design of experiments approach was once again adopted for this set of experiments. A 3 factor 2 level design was investigated with pH, IS and oxidising conditions (OC) being investigated as independent variables and recovery and Eh being measured as dependent/response variables.

**Table 4. Factors and levels investigated in batch flotation tests.**

| Factor | Low | High |
|---|---|---|
| **pH** | 9.2 | 11.8 |
| **IS** | 0.11 M | 0.55 M |
| **[$H_2O_2$]** | 0M | 0.044 M |

Hydrogen peroxide was used to alter DO levels within the pulp and this concentration was kept constant at 0.044M in order to ensure that the effect of hydrogen peroxide was comparable. pH was modified using lime and was varied between pH 8 and pH 11. The ionic strength was varied between 0.11 M and 0.55 M. Eh and recovery were the responses for this experimental design. All statistical analysis was conducted using Statsoft (Statistica) 12 (Soft 2013). All statistical calculations, analysis of variance ANOVA, F-Test and multiple regression were conducted through statisitica.

### 3.0 Results and Discussion

The objective of this study was to investigate whether a relationship existed between Eh and recovery and the boundaries on which this relationship would exist or fail to exist. The two studies investigated, micro-flotation and batch flotation were designed independently and the results used to provide alternative perspectives on the flotation of galena under different oxidising environments.

### 3.1 Micro-flotation Results

Micro-flotation of pure galena was conducted to determine the hydrophobic behaviour of the mineral under different oxidising conditions. By following the same treatment for each experiment the same degree of oxidation of the mineral prior to flotation was assumed such that the results presented in Figure 1 are comparable. The largest standard deviation in the experiments is observed for the condition of 0.11 M and 8.0 ppm at pH 9.2, but lies within 10 % of the measurement. Figure 1 shows the results of these tests along with the respective Eh values for each experiment.

The Eh responses to changing chemical conditions in the pulp are as follows; apart from the condition where IS was 0.55 M, pH 11.8 and DO 1.4 ppm, an increase in Eh was observed as ionic strength increased in solution, however the most notable change was a drop in Eh as pH increased. The relationship between IS and Eh can be accounted to mechanism involving the reduction of negatively charged ions such as $HOCl^-$ from $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ in decreasing order of influence. The cations within the system are stable within this potential region and cannot be concluded to be contributing significantly to the redox potential. The analysis of variance on the experiments for the Eh response, which is presented in Table 5, indicates that all three factors as expected are significant with p=0.000 for pH, p= 0.00018 for IS and p=0.000 for DO indicating their significance. The most significant interactions were pH and IS (p=0.00076) and pH and DO (p=0.000001).

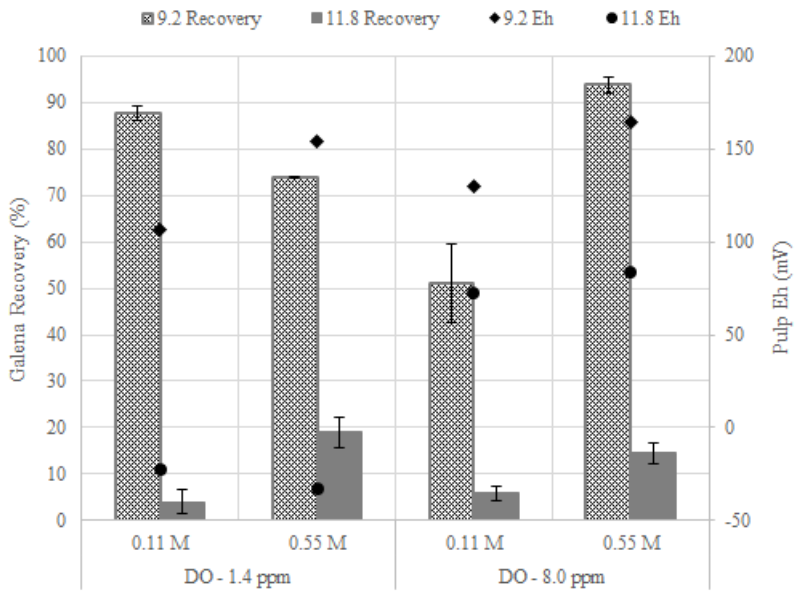



**Figure 1. Results from micro-flotation tests for galena under varying oxidising conditions**

**Table 5. Analysis of variance on 3 factor 2 level factorial design for Eh in micro-flotation experiments**

| Factor | SS | df | MS | F | p |
|---|---|---|---|---|---|
| pH | ***54098.89*** | ***1*** | ***54098.89*** | ***893.233*** | ***0.000000*** |
| IS | ***2252.14*** | ***1*** | ***2252.14*** | ***37.185*** | ***0.000180*** |
| DO | ***15772.01*** | ***1*** | ***15772.01*** | ***260.413*** | ***0.000000*** |
| pH & IS | ***1501.05*** | ***1*** | ***1501.05*** | ***24.784*** | ***0.000761*** |
| pH by DO | ***8304.07*** | ***1*** | ***8304.07*** | ***137.109*** | ***0.000001*** |
| IS by DO | 5.80 | 1 | 5.80 | 0.096 | 0.764017 |
| Error | 545.09 | 9 | 60.57 | | |
| Total SS | 82479.04 | 15 | | | |
| $R^2$=0.99339 | | | | | |

Due to Eh and recovery being independent responses to the variables studied it was the intended to compare trends of increasing Eh to those of increasing recovery and conclude from flotation chemistry fundamentals. The expected influence of Eh was that an increase in Eh would result in a corresponding increase in recovery due to the generation of collector oxidising conditions. It is clear from Figure 1 that this hypothesis is not supported. The analysis of variance (Table 6) provides greater insight to mechanisms which would be more dominant than that of collector oxidation at the mineral surface within this flotation system. Table 6 shows that pH has an effect on galena recovery (p=0.000001) and that the interaction between pH and IS had an effect on recovery (p = 0.031473). All other variables and interactions were not statistically significant.

Galena recovery at pH levels above pH 11 is reduced due to the formation of lead hydroxide species (Ralston 1994). The decrease in galena recovery can also be attributed to the interaction of pH and IS because the pH of the solution plays a major role in determining the amount and type of dissolved ions in solution. At high pH values precipitation is a dominant mechanism which within the solution conditions investigated, the precipitation of $Mg(OH)_2$, $CaCO_3$ and $MgCO_3$ are most significantly affect. Negligible recovery is observed at pH levels that are very high and at high IS as expected, the recovery observed is more likely to be due to entrainment rather than true flotation.

**Table 6. Analysis of variance on 3 factor 2 level factorial design for galena recovery in micro-flotation experiments**

| **Factor** | **SS** | **df** | **MS** | **F** | **p** |
|---|---|---|---|---|---|
| pH | ***17582.76*** | ***1*** | ***17582.76*** | ***138.989*** | ***0.000001*** |
| IS | 512.57 | 1 | 512.57 | 4.052 | 0.074976 |
| DO | 102.41 | 1 | 102.41 | 0.810 | 0.391686 |
| pH & IS | 23.43 | 1 | 23.43 | 0.185 | 0.677083 |
| pH by DO | 67.24 | 1 | 67.24 | 0.532 | 0.484507 |
| IS by DO | ***819.10*** | ***1*** | ***819.10*** | ***6.475*** | ***0.031473*** |
| Error | 1138.54 | 9 | 126.50 | | |
| Total SS | 20246.06 | 15 | | | |
| **$R^2$ = 0.94376** | | | | | |

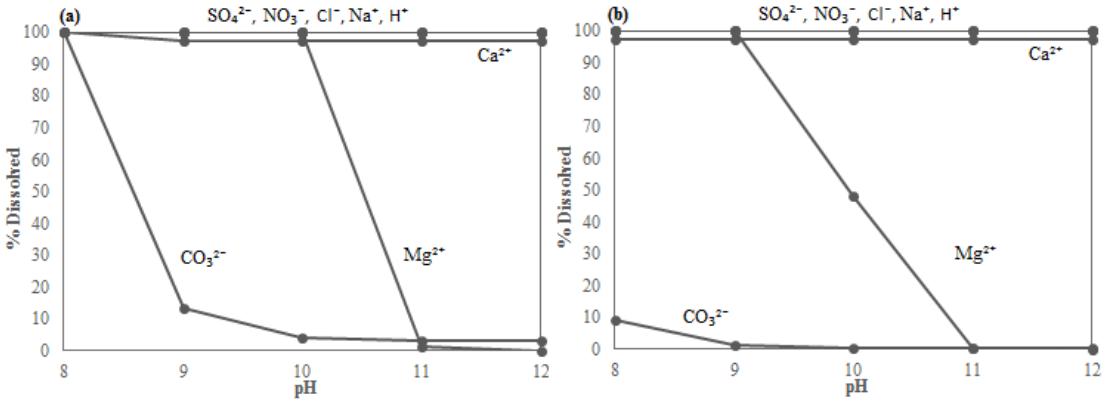



**Figure 3. Calculated solubility profiles for the ions present in solution a) at 0.11 M ionic strength and b) 0.55 M ionic strength. Calculation using Visual Minteq 3.0** (Gustafsson 2011)

Micro-flotation results presented suggest that there might be a correlation between Eh and recovery at a pH that does not favour precipitation.

### 3.2 Batch Flotation Results

Batch flotation tests were conducted to investigate the influence of Eh and oxidation on the recovery of Pb in a galena bearing ore. The following results will focus solely on the flotation of Pb. Oxidising conditions were altered using IS, pH and hydrogen peroxide concentration. Hydrogen peroxide addition was constant for all experiments which included the oxidising agent. The choice of hydrogen peroxide as an oxidising agent follows recent studies which have considered its use in flotation as flotation booster and as a means of increasing selectivity between minerals (Chimonyo et al. 2017; Owusu et al. 2015; Hirajima et al. 2017).

#### 3.2.1 Oxidising conditions and Solids Recovery

The oxidation potential for the conversion of SIBX to dixanthogen was calculated to be 0.0586 V using the Nernst Equation for the conditions of this study using a standard reduction potential value of -0.128 V (Buswell 1998). Hydrogen peroxide addition was chosen in order to induce Eh values greater than 0.0586 V. The addition of 0.044 M hydrogen peroxide resulted in Eh values between 2.75 mV and 135 mV, shown in Figure 3. The natural Eh of the pulp was observed to be highly reducing with the Eh values lying between -350 mV and -440 mV (Figure 3).

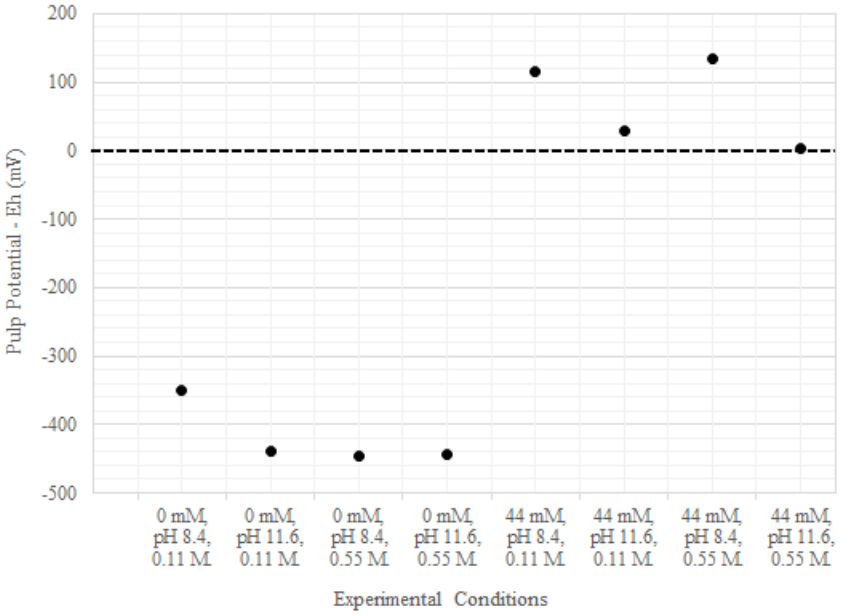



**Figure 3. Eh values of each experiment relative to the oxidation potential of SIBX (0.0586 V).**

The flotation response of the ore due to variable oxidising conditions is shown in Figure 4 which shows solids recovery for each flotation condition investigated along with the corresponding Eh values for each experiment. Whilst a direct comparison between micro-flotation and batch flotation can certainly not be drawn it is noted that under aerated conditions within a micro-flotation cell the effect of Eh showed a positive influence on recovery which translates to hydrophobicity at pH 9.2. In the more complex batch flotation system it was expected that a direct relationship between Eh and recovery may be observed. The results in Figure 4 show that there is higher recovery under more reducing conditions than the oxidising conditions which is contrary to the hypothesis that oxidising conditions will favour the oxidation of collector at these conditions and for this particular ore. Due to an ore specific response, it will not be claimed that Eh plays no role on recovery since there is insufficient evidence to support this.

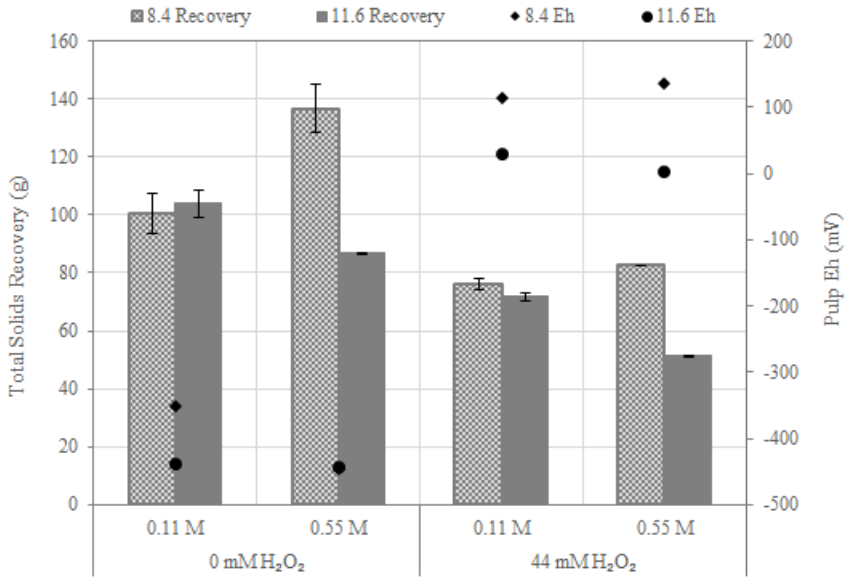



**Figure 4. Total solids recovered in batch flotation tests under various oxidising conditions.**

The natural pH of the ore was found to be 8.4. At this pH the influence of ionic strength is observed to increase the recovery of solids whether in the absence or presence of hydrogen peroxide. A decrease in solids recovered is noted with an increase in pH and corresponding increase in IS, at both low and highly oxidising conditions. This observation suggests an interaction between pH and IS which is consistent with statistical analysis of the factorial design (Table 7), where a pH and IS interaction is found to be significant (p=0.000912). The variables pH (p=0.0008) and hydrogen peroxide concentration (p=0.000008) are found to be the significant variables influencing recovery.

**Table 7. Analysis of variance on 3 factor 2 level factorial design for galena recovery in batch flotation experiments**

| **Factor** | **SS** | **df** | **MS** | **F** | **p** |
|---|---|---|---|---|---|
| IS | 24.950 | 1 | 24.950 | 0.41202 | 0.536949 |
| pH | ***1479.172*** | ***1*** | ***1479.172*** | ***24.42688*** | ***0.000800*** |
| $[H_2O_2]$ | ***4966.726*** | ***1*** | ***4966.726*** | ***82.01995*** | ***0.000008*** |
| pH & IS | ***1422.798*** | ***1*** | ***1422.798*** | ***23.49593*** | ***0.000912*** |
| IS & $[H_2O_2]$ | 196.701 | 1 | 196.701 | 3.24829 | 0.105007 |
| pH & $[H_2O_2]$ | 61.309 | 1 | 61.309 | 1.01245 | 0.340602 |
| Error | 544.996 | 9 | 60.555 | | |
| Total SS | 8696.651 | 15 | | | |
| **$R^2$ = 0.93733** | | | | | |

At low pH values the increase in solids recovery is very indicative of the froth stabilising effect of ions in solution as reported in literature (Farrokhpay & Zanin 2012). This effect however is overpowered by the more significant influence of pH and IS interaction on recovery. This interaction is a negative influence due to formation of hydrophilic precipitates such as $Mg(OH)_2$ and $CaCO_3$ on already hydrophobic surfaces or non-altered mineral surfaces within the pulp (Figure 3). This coating of hydrophilic species is not expected to be a competitive process to collector adsorption but an independent coating of all surfaces and would result in depression of hydrophobic material.

### 3.2.2 Pb Recovery and Grade

The influence of chemical conditions on recovery of Pb can be seen from Figure 5. The results indicate an inverse relationship between Eh and recovery of Pb which on further analysis can be related to hydrogen peroxide reactions at the surface rather than the value of Eh. Highest recoveries are observed at pH 8.3 in the absence of hydrogen peroxide and these are followed by those at pH 11.6 at both conditions of ionic strength. Decreased recovery at pH 11.6 is consistent with the observations of decreased recoveries above a pH of 11.6 for galena (Ralston 1994; Guy & Trahar 1984). Recoveries of Pb are reduced even further in the presence of hydrogen peroxide by as much as a 20 % decrease in recovery. It should be noted that all recoveries are found to be greater than 50 %, however. Negligible differences are observed on Pb recovery for the conditions which include hydrogen peroxide.

At pH 11.6 it was observed in Figure 4 that total solids recovery was reduced for high ionic strength concentration, however the recovery of Pb is comparable to that of experiments conducted at pH 8.3. Guy and Trahar, (1984) reported galena flotation at pH 11 under Eh conditions reaching up to 70 mV which is in agreement with the data presented in this work. The Eh conditions at pH 11.6 where hydrogen peroxide was used to oxidise the pulp were 29.1 mV and 2.75 mV which are considered to be sufficiently oxidising conditions for galena flotation.

In the absence of hydrogen peroxide the Eh of the pulp was found to be highly reducing. Guy and Trahar (1984) and Grano et al., (1990) have all shown that galena flotation can occur under reducing conditions with the former showing recoveries at Eh values as low as -300 mV which is consistent with the results presented here. Both papers propose that the mechanism of collector oxidation is driven by the reduction of PbS which is formed within the mill according to reaction (2), where X denotes a xanthate ion. The mill used in this work was a steel rod mill, which might account for the low reduction potentials within the pulp.

$$PbS + 2X^- \leftrightarrow PbX_2 + S + 2e^- \qquad E^o = -0.124\ V \qquad (2)$$

Since their work it has been shown that flotation can be induced through 'under-potential deposition' of xanthates (Buckley & Woods 1994).

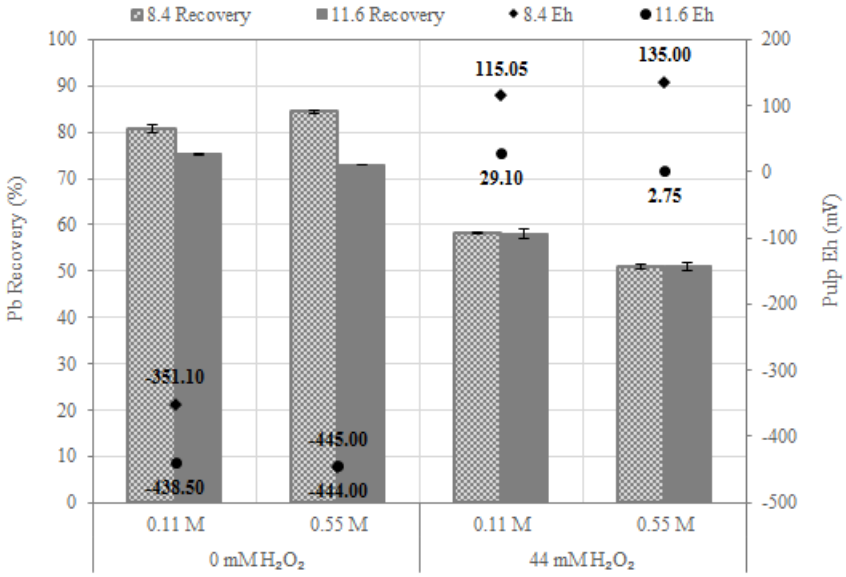



**Figure 5. Pb recovery under varying oxidising conditions**

The reduced total solids recovery and the reduced recovery of Pb in this ore is of particular interest because this is contradictory to the behaviour reported in the literature which clearly shows an increase in recovery with increasing Eh (Grano et al. 1990; J. Ralston 1994). The observed reduction in recovery can therefore be attributed to oxidation of the ore by hydrogen peroxide, observations which have also been reported in the literature (Javadi Nooshabadi & Hanumantha Rao 2014). Chimonyo et al. (2017) have shown that improved recovery of chalcopyrite is more a function of peroxide concentration than Eh. They found that below 1 % chalcopyrite recovery was improved. It is notable that at a concentration of 0.044 M which is just above 1%, recovery is not improved but reduced. The use of hydrogen peroxide can be controversial due to the highly oxidising conditions which may arise and produce detrimental effects on mineral recovery via over oxidation of the mineral surface. Over oxidation of minerals is reported more for Fe bearing minerals such as pyrite and chalcopyrite. It suggests that the influence of hydrogen peroxide on flotation of this more had a significant effect on the bulk mineral magnetite which is present within this ore.

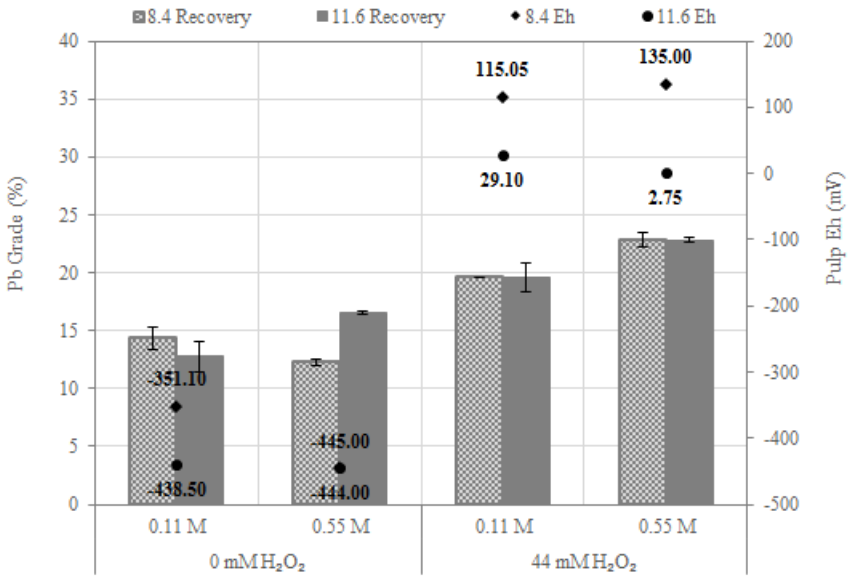



**Figure 6. Pb grade under varying oxidising conditions**

From Figure 6 it is apparent that there are marginal variations in grade between the experiments. Despite low grades being measured it is apparent that there is a slight increase in grade at the conditions where hydrogen peroxide is present. The relationship between Pb recovery and grade takes the following trend; high Pb recovery low Pb grade and low Pb recovery high Pb grade. The comparison of grade to solids recovery also follows that of metal recovery.

The increase in grade at low solids recovery also points to the possibility of an interaction between hydrogen peroxide and the Fe bearing minerals (e.g. magnetite) contained in the ore resulting in preferential oxidation of the gangue mineral magnetite which is contained in the ore to form Fe hydroxides. The chemistry of hydrogen peroxide which has also been reported in other mineral systems and studies supports this theory.

Hydrogen peroxide which is a strong oxidising agent is catalysed to form more strongly oxidising species such as hydroxyl radicals by $Fe^{2+}$ and $Fe^{3+}$ in the Fenton reactions;

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-} \quad (2)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HOO^{\cdot} + H^{+} \quad (3)$$

Javadi Nooshabadi and Rao, (2016) have also shown that iron bearing sulphide minerals generate hydrogen peroxide at the mineral surface in the presence of dissolved oxygen. They have shown that galena shows lower capacity for the formation of peroxide than pyrite, chalcopyrite and sphalerite in decreasing order. It can thus be concluded that the greatest influence on grade is the response of magnetite on increased oxidising conditions compared to any other chemical processes occurring in solution.

## 4.0 Conclusions

An investigation was conducted to observe the responses of galena recovery and Eh in a micro-flotation cell in response to three variable which would alter the Eh. Micro-flotation tests were conducted under

varying dissolved oxygen concentration, ionic strength concentration and pH using a three factor, two level full factorial design. pH and the interaction between pH and IS were identified to be the most significant parameters influencing recovery of the mineral. It was concluded that precipitation at high pH (11.6) was the major contributor to low recoveries of the mineral under the conditions of those experiments. All factors were found to contribute to the Eh of the solution but no conclusions could be drawn between Eh and recovery of galena under the range of conditions tested. It was further concluded that the influence of Eh is bounded by mechanisms such as precipitation which occurs at high pH.

Batch flotation tests were conducted on a Pb bearing ore also using a full factorial design in which concentration of hydrogen peroxide, pH and ionic strength were investigated as factors in two levels. The analysis of the design indicated that the concentration of hydrogen peroxide and pH were the significant factors influencing recovery of Pb within the ore and hydrogen peroxide concentration notably being the strongest influence on Eh. Pb recoveries were noted to be higher in the absence of hydrogen peroxide indicating mineral recovery under reducing conditions of the order of -350 mV to -400 mV. Recovery of the mineral was attributed to under-potential deposition or reduction of galena with xanthate below the oxidation potential of dixanthogen. At the condition of hydrogen peroxide addition Eh values were measured to be positive with the lowest potential being at 2.75 mV which is near the dixanthogen oxidation potential of 5.8 mV at the conditions investigated. These oxidising conditions yielded low recovery of Pb (>20 % change) albeit slightly improved grades. Improvement in grade was attributed to further oxidation of magnetite through oxidation reactions with hydrogen peroxide.

## 5.0 References


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