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## Perspectives from literature on the influence of inorganic electrolytes present in plant water on flotation performance

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**Abstract:** The interaction of inorganic electrolytes with reagents in the flotation of sulphidic PGM bearing ores is not well explored. It has been shown that specific inorganic electrolytes such as  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  can affect the wettability of gangue minerals. These could also hinder the adsorption of collectors onto valuable minerals and concurrently enhance or retard froth stability. This presents a challenge as regards understanding what the overarching or controlling mechanisms of interaction between electrolytes, reagents and minerals are as well as predicting how flotation performance will be affected. This review shows that studies in literature have simplified the question of electrolyte-reagent-mineral interactions and that current approaches have not provided fundamental solutions to the challenge of water quality. It is proposed that the complexity of the flotation system requires an in-depth knowledge of the individual electrolyte-reagent-mineral interactions so as to establish whether there are any dominant or synergistic interactions. Such in-depth knowledge should enable the development of pulp chemistry control measures against water quality variations in flotation.

**Keywords:** Electrolytes, Flotation reagents, Froth stability, Physicochemical interactions, Water quality

### 1. Introduction

There are many variables which affect the flotation process, directly and indirectly. Crozier (1992) has listed up to 25 clearly identifiable parameters which affect froth flotation performance, although this can be more fully described by over 100 variables with water being one of the key variables. Water is an important parameter in froth flotation in that it acts both as a reagent and transport media and its chemistry changes can significantly affect flotation performance by affecting electrolyte-reagent-mineral interactions, consequently affecting gangue mineral hydrophilicity, valuable minerals hydrophobicity, froth stability as well as possible effects on entrainment (Boujounoui et al., 2015; Corin and Wiese, 2014; Farrokhpay and Zanin, 2012; Liu et al., 2013.; Manono et al., 2013; Manono et al., 2012; Moimane et al., 2016a, 2016b; Rao and Finch, 1989; Shackleton et al., 2012; Wang and Peng, 2014). Current environmental restrictions on water usage which are aimed at addressing the global scarcity of water require that mining operations recycle and reuse water within their flotation circuits. This necessitates proactive initiatives aimed at understanding the impact that water could have on a flotation plant and the creation of alternative operating conditions at which flotation could still occur without significant effects on production and profitability. This, of course, relies not only on the understanding of the impact but the provision of sound and fundamental scientific examination and explanations to the effects of water quality in flotation. Such fundamental science would enable the development of management protocols to possibly identify streams within the circuit whose process chemistry does not depend so heavily on water chemistry and in this way, costs and energy would be saved on internal or external process water treatment plants. Recycled water in most cases is used as make-up water, which is usually obtained from the water used in other process environments on the mine site (Ross et al., 1984; Viviers, 1979). According to Barker (1986) ions present in recirculated plant water can be divided into three categories, namely, (i) ions common to the water system such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and

Mg<sup>2+</sup>; (ii) ions added during leaching such as H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>; and (iii) ions obtained during milling such as Fe<sup>2+</sup> and Fe<sup>3+</sup>. Cations like Mg<sup>2+</sup> and Ca<sup>2+</sup> have been investigated (Burdukova, 2007; Ikumapayi et al., 2012). These metal ions are hydrolysed in solution to form intermediate species which may be unstable. The hydroxides of these metal cations are relatively insoluble and precipitate out in alkaline conditions and may have detrimental effects in flotation (Barker, 1986; Laskowski et al., 2007). However, these studies have simplified the question of electrolyte-reagent-mineral particle interactions, in that, these focused more on interactions with individual electrolyte-individual reagent-individual mineral (i.e. electrolyte-collector, electrolyte-depressant on specific sulphides). Also, mostly Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> have been investigated as opposed to the other common inorganic electrolytes in flotation process water. The complexity of the flotation system should be acknowledged, by collating the knowledge developed on individual reagent interaction so as to establish whether there are any dominant or synergistic interactions. It is also vital that research establishes whether there is competition in such electrolyte-reagent interactions. Thus, this paper corroborates available literature on water quality in sulphides flotation. Interactions occurring in both the pulp phase and the froth phase are considered and a proposal is put forward regarding the potential for future studies.

## 2. How water quality and scarcity affect flotation

Water plays a vital role in flotation as its quality may have a direct impact on the efficiency of the process (Levay et al., 2001; Liu et al., 2014; Muzenda, 2010; Rao and Finch, 1989; Shackleton et al., 2012; Slatter et al., 2009). It is of paramount importance that the quality of process water is known and is carefully monitored to prevent any detrimental effects on mineral flotation processes.

The emergence of stringent laws and policies on water usage across heavy manufacturing industries coupled with requirements for the minimisation of mine water discharge and minimal fresh water feed from municipal sources has given rise to process water recirculation in mines which in turn threatens the quality of process water (Peters and Meybeck, 2000). It cannot be disputed that the recirculation of water ensures prevention of environmental pollution from mine water discharge or effluent (Carlson et al., 2002; Johnson, 2003). However, in order for mining operations to meet these demands of zero waste water effluent from their operations and minimal reliance on municipal water, water recycling is often perceived as the best alternative. Slatter et al. (2009) studied the effects of water quality on process operations, particularly, a sulphidic-PGE (Platinum Group Elements) based mineral concentrator. Their findings showed that the recycled water within flotation plants had the advantage of lowering the need to receive new water into the process, lowering the amount of discharge and allowing for the retention of some reagents, thereby lowering reagent consumption and associated costs. Recycling of water also showed detrimental effects on valuable mineral recoveries and grades due to the accumulation of electrolytes and biological substances which may have negatively affected reagent interactions in the pulp phase and thereby caused unfavourable implications on the froth phase. Forssberg and Hallin (1988) suggested that water recycling may have a negative impact on raw material beneficiation and this effect may be seen months after recycling has commenced as was also suggested by Rao and Finch (1989). Other disadvantages associated with the recycling of water are a decrease in reagent efficiency as a result of contaminants, an increase in suspended solids within the recycled water and secondary effects of increased pollutant levels in the recycle waters such as chemical and microbiological oxidants Slatter et al. (2009).

In most Cu-Ni-PGM ore concentrators, recycled water is often sourced from tailings dams and classification ponds, these are often referred to as long cycle-recycle waters, whereas the other sources of recycled waters are thickener overflows, dewatering and filtration units which may be directly connected to the concentrator and are referred to collectively as short cycle-recycle waters (Johnson, 2003; Levay et al., 2001; Roderick et al., 1985). Recycled water, characteristically constitutes of Ca<sup>2+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, sulphides, thiosalts, base metals, collectors, frothers, activators, depressants, colloidal materials such as silicates, clays and iron hydroxides and natural organic materials (Bulut and Yenial, 2016). Metal ions found in the tailings water precipitate when lime is added to the tailing dams (Forssberg and Hallin, 1988). This emphasises the need to investigate and gain fundamental insight into the influence of pH in flotation as it (pH) changes the water/pulp chemistry directly. Due to oxidation processes in the pond, tailings return water usually has a low oxygen content and oxidation potential.

It has also been said that recycled water from tailings dams may have incredibly high conductivities compared to fresh water due to evaporation and therefore concentration of the ions, however, the higher conductivities may decrease due to dilution during high rainfall and snow melt seasons (Muzenda et al., 2011).

One of the problems associated with the use of recycle water is process chemical residues which may accumulate in the tailings dams. Ore dissolution and reagent addition causes various elements or compounds to accumulate in solution and this may alter the chemistry of the system (Rey et al., 1966). Recycled waters in general have an increased level of total dissolved solids (TDS) which results in an increase in the specific gravity (SG) of the water which affects the slurries and thus the pulp chemistry (Rao and Finch, 1989). If the SG of the plant is kept constant whilst that of water is increasing it will lower solids percentage throughput within the plant; and with increased electrolyte concentration due to particle to particle segregation, the slurry viscosity may increase affecting mineral floatability as well as classification and pumping (Rao and Finch, 1989). The separation of minerals by flotation depends on the differences in the surface properties of the minerals and these surface properties are affected by solution characteristics such as passivation of mineral surfaces which may occur due to ion precipitation (Arnold and Aplan, 1986; Muzenda, 2010). This phenomenon may have negative effects on the flotation process owing to detrimental changes in the surface chemistry of the mineral. A study conducted by Lutandula and Mwana (2014) on a copper-cobalt ore showed that chemical and biological constituents of recycled water, mainly those deriving from the degradation of reagents, alter the chemistry of the system resulting in significant decreases in the grades and recoveries of Cu and Co in the concentrate. It was also found that an increase in slurry dissolved oxygen occurred due to increases in the dissolved carbon dioxide produced through the hydrolysis of bicarbonate ions as indicated by Equation 1-3.



From Equation 2, the formation of carbonate ions can take place in the pulp leading to the precipitation of copper and cobalt ion liberated in solution by oxide minerals through dissolution in water (Lutandula and Mwana, 2014). A recent study by Boujounoui et al., (2015) on the influence of water quality on the flotation performance of complex sulphide ores suggested that  $\text{SO}_4^{2-}$  ions had a positive effect on recoveries, but the level of influence varied from one mineral to another. High concentrations of  $\text{Cu}^{2+}$  in solution increased the recovery of chalcopyrite, sphalerite, galena and pyrrhotite; however  $\text{Cu}^{2+}$  ions depressed sphalerite at low concentrations.  $\text{Zn}^{2+}$  ions at low concentrations depressed the recovery of all the mineral phases, but high concentrations of  $\text{Zn}^{2+}$  improved the recoveries of chalcopyrite, sphalerite, and pyrrhotite.  $\text{Mg}^{2+}$  was shown to depress galena, chalcopyrite, and sphalerite at high concentrations whereas  $\text{Ca}^{2+}$  depressed sphalerite at high concentrations. The authors then concluded that "These factors, with their ranges of influence, will be the subject of further investigations to determine the nature of the interactions between them and their effects on recoveries. An optimization study will be carried out to determine the parameters that have the greatest influence on recoveries." In line with Boujounoui et al. (2015), it is the premise of this paper that there is an ever growing need to understand the influence of water quality, electrolyte levels in particular (on mineral flotation) at a fundamental level so as to ensure that the quality of water and reagent chemistry is controlled in such a way that mineral flotation performance is optimised as should indeed be the focus of future studies and for the sustainability of the flotation process. Thus, the subsequent sections consider electrolyte-reagent interactions on mineral surfaces in flotation in order to understand key influences on the pulp and froth phase so as to draw implications on flotation performance as well as probing into areas which have not yet been addressed in literature.

### 3. The effect of electrolytes on flotation reagents: the pulp phase phenomena

#### 3.1. Introduction

Various reagents are used in flotation to manipulate the chemical environment and improve selectivity within the flotation system ensuring high performances in terms of grades and recoveries and if possible

at the lowest cost. According to Wiese et al. (2007) and Yin et al. (2016) the reagent suite needs to be selected carefully for maximum platinum group minerals (PGMs) and base metal sulphides (BMS) recovery. Reagents are added to perform specific roles that manipulate the pulp chemistry and enhance the differences in mineral surface hydrophobicity to create suitable froth phase behaviour. Bradshaw et al. (2004) have shown that it is necessary to assess the reagent's behaviour holistically and evaluate its effects both in the pulp and froth phases as material is recovered by true flotation and by entrainment. Thus, this necessitates a thorough review on the interactions of electrolytes present in plant water with the most common industrial flotation reagents used in PGM ore concentrators. Reagents used in froth flotation of minerals can be broadly classified into three types, namely; collectors, frothers and regulators (depressants, activators and pH modifiers). A brief literature review is given to the effect of ions and pH on polysaccharide depressants, and thiol collectors as it is relevant to studies on the effect of water quality in the flotation of PGM and BMS ores.

### 3.2. The effect of electrolytes present in process water on polysaccharide depressant behaviour

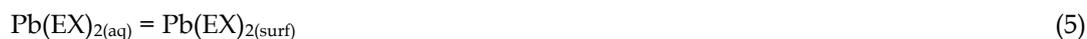
It is known that polymer adsorption on talc and the subsequent depression of naturally floatable gangue (NFG) minerals is influenced by many variables. These include polymer type and concentration, molecular weight, degree of substitution, pH, and ionic strength (Khraisheh et al., 2005; Parolis et al., 2008; Shortridge et al., 1999; Yin et al., 2016). Many studies have been carried out to determine how the presence of ions in plant water will affect the depression of NFG (Corin and Wiese, 2014; Khraisheh et al., 2005). These studies have shown that in the presence of cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , the depression activity of carboxymethyl cellulose (CMC) on talc is enhanced indicating that the ionic strength of the solution plays a crucial role in CMC adsorption onto talc. However, a detrimental effect of these ions is that they may inadvertently activate the unwanted gangue or depress the targeted mineral. It is therefore of vital importance to understand the behaviour of depressants targeting NFG in the presence of high ionic strength plant water so as to predict the optimum plant performance.

Shortridge et al. (1999) investigated the influence of electrolytes on the effectiveness of polysaccharides in the flotation of talc; a study which had a very keen interest on how anion type and ionic strength affected the depressing efficacy of CMC and modified guar gum using microflotation. This study specifically investigated single salt solutions of  $\text{KNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$ . Increasing the ionic strength of the solution increased the adsorption efficacy of CMC onto talc, however, this effect was stronger for the divalent cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , compared to the monovalent cation  $\text{K}^+$ . It was postulated that the cations adsorbed onto the talc surface and thereby decreased its hydrophobicity. Also, it was found that the presence of these cations in solution reduced the zeta potential of talc thus reducing the electrostatic repulsion between the talc surface and CMC molecules. This consequently increased the adsorption of CMC molecules onto talc. It is worth noting that the interactive effect of the anions, namely,  $\text{NO}_3^-$  in solution was not mentioned in the discussion. Another study by Parolis et al. (2008) came to the same conclusions and added that intrinsic viscosity studies showed that the interaction of CMC with  $\text{Ca}^{2+}$  ions was more complex than a simple electrostatic masking of the negatively charged carboxyl groups. The precipitation of metal hydroxyl species on the talc surface was shown not to play a significant role in the binding of CMC to talc in  $\text{Ca}^{2+}$  and  $\text{K}^+$  electrolytes. Parolis et al. (2008) also left out any discussion on the role of the  $\text{NO}_3^-$  ions. Burdukova et al. (2008) investigated the effect of  $\text{Ca}^{2+}$  on the adsorption of CMC onto the basal planes of New York talc where the influence of a solution containing  $\text{Ca}(\text{NO}_3)_2$  was compared to one containing  $\text{KNO}_3$  as well as with de-ionised water. This study found that the presence of  $\text{Ca}^{2+}$  enhanced the adsorption density of the CMC. This was attributed to the increased concentration of  $\text{CaOH}^+$  ions on the mineral surface, which facilitated polymer adsorption through acid-base interactions. It was further stated that there was an increase in the coiling of CMC molecules which is a result of their reaction with  $\text{Ca}^{2+}$  ions. It is worth mentioning that none of the findings gave any view on possible interactive effects that would have occurred due to the presence of  $\text{NO}_3^-$ . This begs the question; were these anions just spectator ions? Such lack of reference to the presence of these anions in solution assumes that their interactive effects with either  $\text{K}^+$  or  $\text{Ca}^{2+}$  cations are equal and therefore cancel out such that the focus becomes that of the monovalent  $\text{K}^+$  vs. the divalent  $\text{Ca}^{2+}$  cations.

### 3.3. The effect of electrolytes present in process water on thiol collector behaviour

Hancer et al. (2001) proposed that if a collector adsorbs at the salt interface, it will displace interfacial water or penetrate through the structure of water. If the structure of water is strongly hydrogen bonded due to the presence of structure making anions and cations, it becomes difficult for collector molecules to reach the surface and be adsorbed. However, if those ions have a tendency to destroy the structure of water and create a condition for the adsorption of collector molecules, the flotation of soluble salt minerals becomes feasible.

Xanthates adsorb onto the mineral surface through charge transfer between the collector and the mineral surface whereas dithiocarbamate (DTC) adsorbs via the formation of metal-thiolate on the mineral surface (Ngobeni and Hangone, 2013). McFadzean and O'Connor (2014) found that the reaction of SEX with galena occurred via two sequential reactions and proposed the reactions shown in Equation 4-5.



The initial enthalpy of reaction of -65 kJ/mol decreased steadily until the formation of about three pseudomonolayers, whereafter it remained constant at about -10 kJ/mol. Rojas et al. (1998) studied the effect of salt concentration on the adsorption of low charge density electrolytes and interaction between electrolyte coated surfaces. It was postulated that the distinct effect of ionic strength on the adsorbed amount is explained by the balance of four factors that accompany the screening of electrostatic forces by addition of salts: (i) decrease of surface-polyelectrolyte attraction, (ii) increase of competition between the polyelectrolyte and the monovalent cations for adsorption at surface sites, (iii) decrease in free energy cost in creating a charged interface, and (iv) decrease in intra and interchange in repulsion. It was suggested that this behaviour causes an increase in the adsorption (screening-enhanced adsorption). It was also stated that the first two factors decreased the adsorption on mineral sites.

Sulphide ions have been found to decompose xanthate collectors in the presence of oxygen (Shen et al., 2001). Grano et al. (1997) showed that under solution conditions which favour rapid xanthate decomposition by sulphide, xanthate adsorption onto galena is significantly reduced and galena flotation is strongly depressed. The presence of a small amount of strongly hydrophilic lignosulphonate is sufficient to render the molybdenite surface hydrophilic; this hinders the attachment and spreading of any oil collector over the molybdenite surface (Ansari and Pawlik, 2007). Excess hydrogen sulphide, sulphate and sulphite ions may act as depressants in flotation because of their competition with xanthate ions for adsorption sites (Drzymala, 2007; Gush, 2005). However, Bulatovic (2007) has shown that thiosulphate ions are strong reducing agents which react with dissolved ions from the mineral surface and easily form more stable complexes than those with metal xanthates. Shackleton et al. (2012) found that the selectivity between moncheite and pyroxene as well as between pentlandite and pyroxene was significantly reduced in the presence of sodium chloride, especially when a xanthate collector was used.

It has also been reported that the divalent  $\text{Ca}^{2+}$  cations activate the adsorption of the collector ions when the galvanic effect of mill iron is effective (Forssberg and Hallin, 1989). Kirjavainen and Heiskanen (2005) also found that thiosulphates decreased the adsorption of hydrophilic compounds such as metal hydroxides. Allison and O'Connor (2011) conducted a study on the flotation behaviour of pyrrhotite and found that although depressants generally reduce the recovery of pyrrhotite, if a collector, xanthate in particular, is added after  $\text{Cu}^{2+}$  ions the mineral surface may be activated for recovery.

The effects of pulp potential on sulphide mineral flotation are also related to the type of collector used. Depending on the mechanism by which a particular collector adsorbs onto the sulphide mineral surface, the extent of the influence of pulp potential on mineral floatability will vary (Bruckard et al., 2011). An electrochemical theory and interpretation of flotation by Fuerstenau et al. (2007) suggests that sulphide flotation with thiol type collectors results from anodic (oxidation) reaction between the mineral particle and collector, that is, there is a formation of dixanthagen ( $\text{X}_2$ ) or metal xanthate ( $\text{MX}_2$ ), with a rebalancing of charge through the cathodic reduction of dissolved oxygen as shown in Equation 6-8





The pulp potential controls the extent of these reactions, and so influence the efficiency of the flotation process. These reactions also modify the pulp potential, but only to a limited extent. This theory is of interest as it is possible that the electrolytes present in process water affect the conductivity of the solution which may affect the pulp potential.

### 3.4. The effect of solution pH on the flotation process

Recirculated water comes from various process streams on the plant such as thickener overflows and filtrate. These streams have different proportions of dissolved solids and therefore the pH of the process water may vary (Levay et al., 2001).

In solution, the extent of ionisation, charge on the mineral surface and hydrolysis of surfactants are determined by the pH of the slurry (Deng et al., 2004; Sun et al., 2015). In general, the surface of the mineral develops a positive charge in acidic conditions and a negative charge in basic conditions (Kawatra and Darling, 2011; Qin et al., 2017). Ultimately the pH of the slurry affects the selectivity of flotation. This is as a result of solution pH and its constituents being able to either aid or hinder the adsorption of surfactants at the ionised mineral-solution interface (Deng et al., 2004). Hence, the selectivity of flotation is dependent on a delicate balance between pH and the concentration of reagents (Wills and Napier-Munn, 2006). Generally, flotation is carried out in an alkaline slurry as most collectors (including xanthates) are stable in alkaline conditions (Wills and Napier-Munn, 2006).

Adsorption of sulfhydryl collectors such as xanthates onto mineral surfaces is a function of the pH of the slurry because these collector ions compete with OH<sup>-</sup> ions to adsorb onto the mineral surface (Kawatra and Darling, 2011). The pH at which xanthate ions adsorb onto the mineral surface depends on both the concentration of collector in the solution and on the sulphide mineral present (Kawatra and Darling, 2011). It is therefore possible to progressively separate specific minerals using a sulfhydryl collector and manipulating the pH. At any concentration of xanthate (sulfhydryl collector) there is a pH below which the given mineral will float and above which it will not float, this pH is the critical pH. Fig. 1 shows the pH response of the adsorption of sulfhydryl collectors on different mineral surfaces. Note that both xanthate and dithiophosphate collectors yield curves of the nature shown in Fig. 1 (Fuerstenau et al., 1985).

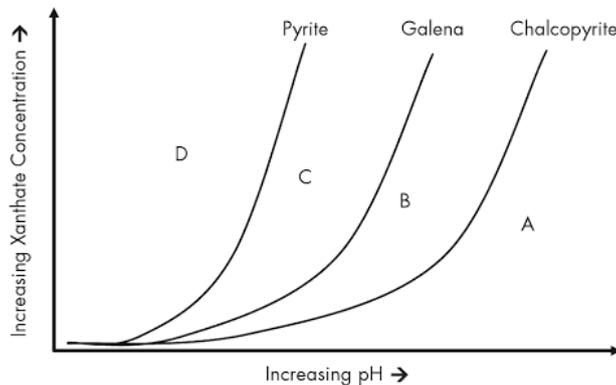


Fig. 1. pH response curves for sulfhydryl collector adsorption on different sulphide minerals (Fuerstenau et al., 1985). The boundaries, A, B, C and D, are an indication of where and when the specific mineral will be hydrophobic enough for its floatability (Kawatra and Darling, 2011)

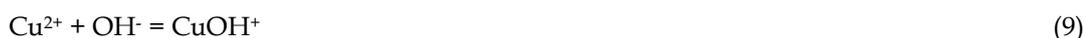
Fig. 1 shows that at a pH and xanthate concentration in region A, xanthate does not adsorb on any mineral and none of the minerals float. If the pH and xanthate concentration is in region B then xanthate only adsorbs on chalcopyrite and only this mineral floats. Once the pH is lowered and both the pH and collector concentration is in region D all the minerals float. Thus it is possible to progressively separate specific minerals by lowering the pH.

It can therefore be seen that with an increase in pH, the recoveries of galena and pyrite decrease. This is attributed to the formation of hydroxide species at high pH values and the precipitation of these

species on the mineral surface as can be seen from the water speciation diagrams shown in Fig. 2. These hydroxide complexes and precipitates coat the mineral surface, either rendering the mineral hydrophilic or hindering its reaction with the collector.

It is evident that the alkalinity of the flotation pulp plays an important role in the flotation of BMS-PGM ores. In order to control pH, some acids are added to the pulp phase, where low pH can be maintained by the addition of sulphuric acid. These chemicals are often used in significant amounts in most flotation processes (Wiese et al., 2005a). Lime or soda ash is often added to the slurry prior to flotation to precipitate heavy metal ions from solution (Muzenda et al., 2011). The alkalinity of the solution acts as the deactivator as these metal ions can activate minerals like pyrite and sphalerite which will report to the concentrate if the alkalinity of the flotation process is too low. Muzenda et al. (2011) reported lower PGM grades and recoveries at the higher pH of 11 and this is because of the reduction in the collection capacity of xanthates as they become more stable at higher pH values and thus less likely to attach to minerals. This phenomenon could also be explained by the depressing nature of oxyhydroxyl species which form at higher pH values, thereby imparting and inducing the hydrophilicity of mineral particles. Muzenda (2010) investigated water quality effects on UG2 ore flotation and showed that higher recoveries for both PGM and chromite were obtainable at a pH of 9 supporting the theory that higher PGM recoveries are coupled with higher chromite recoveries and thus a pH of 9 was suggested as standard practice in sulphidic PGM ore flotation (Wiese et al., 2005b). Wesseldijk et al. (1999) found that chromite could be activated by copper and readily floated with xanthate in a microflotation cell at a pH of 9. At lower pH and in a stronger oxidative environment, chalcocite oxidation produces copper (II) and soluble sulphur species (Chander and Fuerstenau, 1983) which may affect the subsequent adsorption of polymeric dispersant onto chalcocite particles (He et al., 2011).

Metal ions hydrolyse in alkaline pH solutions and precipitate hydrophilic metal hydroxides, sulphates or carbonates if their concentrations are above their respective solubility limits (Laskowski et al., 2007). The formation of metal hydroxides is influenced by aqueous pH (Font et al., 1999). Reyes-Bozo et al. (2014) found that molybdenite flotation decreased from 65% in acidic pH conditions to 50% in alkaline pH conditions. They also found that the flotation response of pyrite at pH 10 with biosolids and Aero 6697 promoter floated up to 40%, this proved that at alkaline pH, biosolids had a higher affinity for Fe – containing species. Martinovic (2004) investigated surface properties of typical gangue minerals found in platinum bearing ores and showed that at acidic pH values (pH 4), copper was present in the form of free  $\text{Cu}^{2+}$  but at pH 7 the amount of  $\text{CuOH}^+$  present became significant, while at pH 9 the majority of the copper was present as  $\text{Cu}(\text{OH})_2$  with a small quantity of  $\text{CuOH}^+$  based on the equilibria presented in Equation 9-10.



In the presence of xanthate, at alkaline pH,  $\text{Cu}^{2+}$  firstly forms  $\text{Cu}(\text{OH})_2$  which then subsequently reacts with xanthate ions to form  $\text{CuX}_2$ . Activation is, however, generally thought to be dependent on the formation of  $\text{Cu}^+$  species. Ramos et al. (2013) found that for chalcopyritic ores, Cu recovery was slightly lower in sea water than in fresh water under similar conditions over the pH range of 7 to 12. They also found that Mo recovery in sea water was strongly depressed at pH higher than 9.5, the conditions under which magnesium hydroxide starts precipitating in sea water. For most sulphide ores, the extent and rate of reaction decreases with an increase in pH due to the increasing formation of oxidation products at the surfaces which hinder mineral-collector interactions (Miller et al., 2005). At pH 9 the oxidation reaction typically results in the formation of  $\text{Fe}(\text{OH})_3$  and a metal deficient sulphide,  $\text{Fe}_{(1-x)}\text{S}_{1.13}$  (Buckley et al., 1985). The masking of the sulphide mineral surface by the formation of hydrophilic metal hydroxide species begins at lower pH values for iron sulphides than for sulphides of copper or nickel. The slow flotation kinetics of pyrrhotite at higher pH values may therefore be due to an inherently lower surface hydrophobicity relative to that of the other sulphides even if significant reaction with collector does occur (Ball and Rickard, 1976).

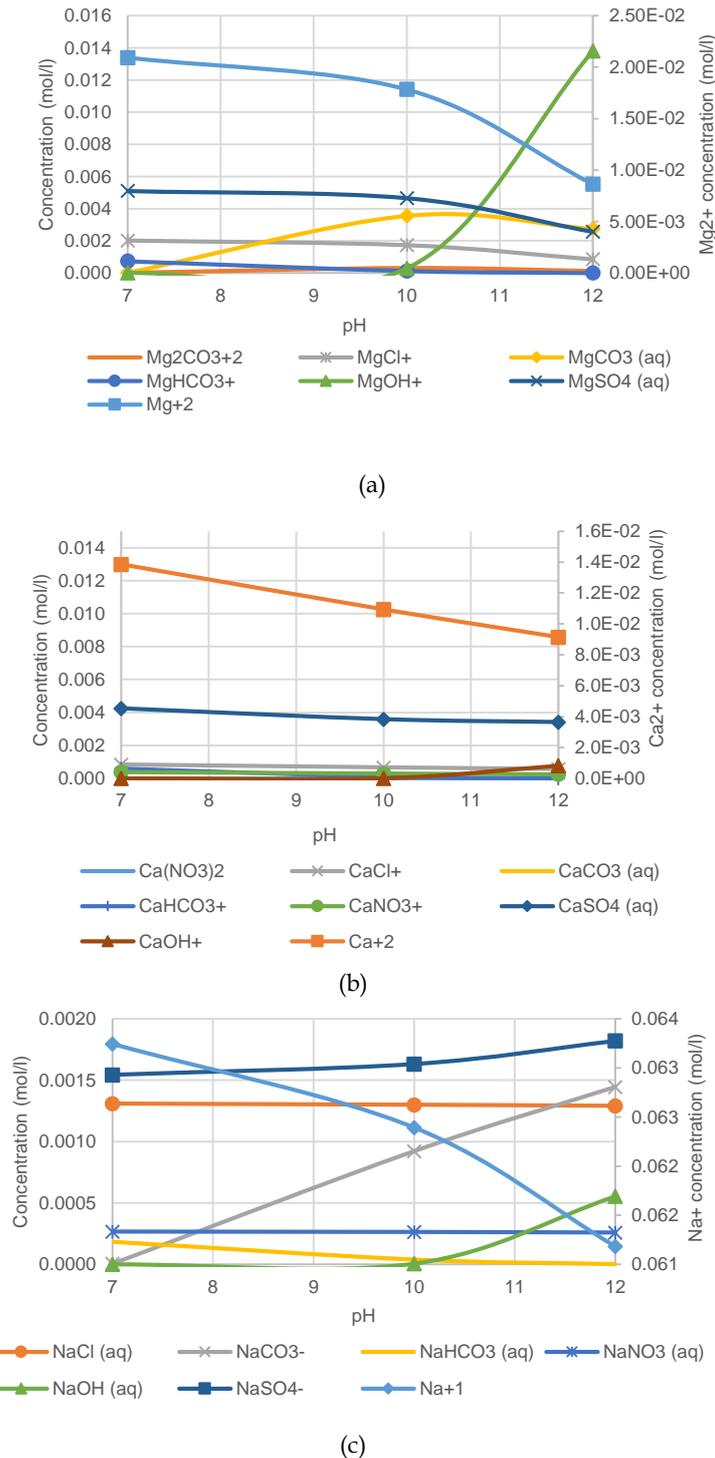


Fig. 2. (a), (b) and (c) are speciation diagrams of calcium, magnesium and sodium in plant water of 0.1860 M ionic strength (equivalent to a TDS of 10230 mg/L). These were generated using Visual Minteq 3.1

Fig. 2 shows that at high pH values, the concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> decreases and the concentration of their respective hydroxides increases. The precipitation of these hydroxides as previously stated coats the mineral surface and results in the mineral being rendered hydrophilic or the reaction of the collector on the mineral surface being hindered.

The reduction in mineral surface hydrophobicity due to the precipitation of hydrophilic metal hydroxides could compromise the efficiency of the particle-bubble attachment process (Koh et al., 2009; Schwarz and Grano, 2005). Its consequences are associated with lower amounts of mineral particles

entering the froth, which might compromise the efficiency of the formation of stable particle-bubble aggregates (Ata, 2012; Lima et al., 2016).

#### 4. The role of electrolytes on bubble coalescence and froth stability: implications into the froth phase phenomena

##### 4.1. The effect of electrolytes on froth stability

Froth structure and froth stability are known to play a very important role in determining the mineral grade and recovery achievable in the flotation process (Wang et al., 2014). Froth stability is mainly dependent on the frother (type and concentration) as well as the amount and nature of the suspended particles, in particular, particle size and hydrophobicity (Schwarz and Grano, 2005; Zheng et al., 2006). Frothing agents are employed in flotation to facilitate air dispersion into fine bubbles and stabilise froth (Ramos et al., 2013). Due to the sensitivity of the flotation process to water quality, an accumulation of both organic and inorganic ions in the process water may also affect froth stability (Bıçak et al., 2012). A stable froth zone allows for the efficient transportation of the materials for downstream processing, while entrainment of gangue is directly proportional to the amount of water recovered from the froth phase (Zheng et al., 2006). Wiese and Harris (2012) found that an increase in the frother dosage increased the stability of the froth resulting in enhanced recovery of valuable minerals. Lekki and Laskowki (1975) observed that only in the presence of hydrophobic particles would a salt solution form a stable froth. They also noted that inorganic electrolytes fall into the category of surface inactive agents while frothers are surface active. At high electrolyte concentration, bubbles become more stable and do not coalesce even in the absence of a frother (Bıçak et al., 2012).

Dynamic froth stability can be determined by using the Bikerman method as shown in Equation 11 (Kurniawan et al., 2011).

$$DFS = \frac{V_f}{Q} \quad (11)$$

where DFS is the dynamic froth stability,  $V_f$  is the foam volume and  $Q$  is the gas volumetric flow rate. Aktas et al. (2008) reported that dynamic froth stability is strongly dependent on the particle size, showing that finer particles increased froth stability. Kurniawan et al. (2011) investigated froth stability in coal flotation using  $MgCl_2$ ,  $NaCl$  and  $NaClO_3$  solutions in the absence and presence of Dowfroth 250. Their findings showed that in the presence of Dowfroth 250,  $MgCl_2$  resulted in the most stable froth, while  $NaClO_3$  resulted in the lowest froth stability as well as the lowest mineral recovery.

Kurniawan et al. (2011) also found that for both  $NaCl$  and  $MgCl_2$ , coal recovery, dynamic froth stability and froth bubble size changed considerably with the addition of these salts below their concentration transition point (see Table 1). Castro et al. (2013) reported that water with an increased concentration of electrolytes exhibited an increased frothing ability. A study of the effects of water chemistry on froth stability and surface chemistry of a Cu-Zn sulphide ore by Bıçak et al. (2012) suggested that the rate of coalescence of air bubbles decreased either due to the frother molecules absorbed at the air-water interface, or the presence of a stable layer on the surface of the bubbles. This is in agreement with Yousef et al. (2003) who stated that plant studies using seawater and process water with high salt content resulted in voluminous and stable froths due to the frothing properties of dissolved ions. Bıçak et al. (2012) concluded that dissolved metal ions and sulfoxy ions mainly in the form of  $SO_4^{2-}$  and  $S_2O_3^{2-}$  had an influence on both froth stability and surface chemistry. Elsewhere, the froth stability increases with increasing ion concentration in water were attributed to increased stability of the water layer between air bubbles (Corin and Wiese, 2014; Manono et al., 2012). Tao et al. (2000) and (Schwarz and Grano, 2005) linked water recovery with froth stability in flotation and found that a more stable froth was accompanied by an increase in water recovery. Corin and Wiese (2014) and Corin et al. (2011) investigated the effect of ionic strength of plant water on valuable and gangue recovery in platinum bearing ore from the Merensky reef, and observed that the increase in ionic strength of their systems resulted in increased water and solids recoveries suggesting an increase in froth stability; this speculation was further supported by a 2-phase study conducted by Manono et al. (2013) on froth or foam properties which showed that an increase in ionic strength led to an increase in water or foam recoveries, increase in gas hold-up, increase in foam height, and a decrease in foam collapse rate. In

addition to this, Corin and Wiese (2014) compared effects of increases in ionic strength with increases in frother dosage on froth stability and concluded that "it may be possible to interchangeably use frother dosage and solution ionic strength to tailor the solids and water recoveries needed from an operation" as a result of the increased water and solids recoveries at increased ionic strengths which were comparable to results obtained with increases in frother dosage.

Bournival et al. (2012) studied NaCl and MIBC as bubble coalescence inhibitors in relation to froth flotation and found that NaCl at higher concentrations was as effective as MIBC in preventing bubble coalescence in a dynamic environment. They also showed that a very concentrated solution of NaCl (in the order of 0.1-0.5 mol.dm<sup>-3</sup>) must be used in order to achieve a desired froth stability and these findings were in agreement with studies carried out on mineral flotation in solutions of highly concentrated inorganic electrolytes (Pugh et al., 1997; Quinn et al., 2007; Rao et al., 2016).

#### 4.2. Effect of electrolytes on bubble coalescence

Bubble coalescence is a particularly complex phenomenon especially when it takes place in saline or seawater, since both the surface active compound (frother) and surface-inactive compound (inorganic salt/electrolytes) are able to inhibit bubble coalescence and thereby reduce bubble size (Castro et al., 2013). The coalescence of bubbles can be completely prevented at frother concentrations exceeding a certain concentration known as the critical coalescence concentration (CCC) (Grau et al., 2005; Laskowski and Castro, 2015; Laskowski et al., 2003). Inorganic electrolytes also inhibit bubble coalescence and increase gas holdup in flotation (Quinn et al., 2007). Marrucci and Nicodemo (1967) measured the average bubble size in a bubble column in the presence of a number of different electrolytes, viz., KCl, KOH, KNO<sub>3</sub>, KI, K<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub> and Co(NO<sub>3</sub>)<sub>2</sub> at various superficial gas velocities and concluded that the electrolytes increased the electrical repulsion forces at the bubble surface, inhibiting coalescence between bubbles. Lessard and Zieminski (1971) investigated the effects of inorganic electrolytes, AlCl<sub>3</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, NaCl, LiCl, and NaBr on bubble coalescence and the interfacial gas transfer in aqueous solution and the results are shown in Table 1. The coalescence experiments consisted of contacting a number of pairs of bubbles and evaluating the coalescence percentage as a function of solute concentration. Their findings showed the existence of a sharp transition concentration which enabled a comparison of the effectiveness of the salts; the concentration resulting in 50% bubble coalescence inhibition was defined as the transition concentration at which coalescence was sharply reduced. These concentrations correlated well with ionic entropy of solution and the self-diffusion ability of water in solution.

Table 1. Bubble coalescence transition concentration in different electrolytes  
(Lessard and Zieminski, 1971)

Salt	Transition concentration, mol/dm <sup>3</sup> (50 % coalescence)
MgSO <sub>4</sub>	0.032
AlCl <sub>3</sub>	0.035
MgCl <sub>2</sub>	0.055
CaCl <sub>2</sub>	0.055
Na <sub>2</sub> SO <sub>4</sub>	0.061
LiCl	0.160
NaCl	0.175
NaBr	0.220
KCl	0.230

Castro et al. (2013) investigated the effect of frothers on bubble coalescence and foaming in electrolyte solutions as well as seawater and showed that MIBC and DF250 exhibited different surface activities and thereby yielded different degrees of bubble coalescence. This was owing to possible differences in the surface active species in the two industrial frothers as well as interactions with the electrolytes in solution. It was also observed that finer bubbles were generated in the electrolyte solutions than in the presence of frothers alone. The specific effects of electrolytes on bubble coalescence

were thought to be related to their effects on the water structure and hence the hydrophobic interactions (Wang and Peng, 2014). A study of the effects of electrolytes on bubble coalescence in non-aqueous solvents and aqueous electrolyte solutions was conducted by Henry et al. (2007) and Henry and Craig (2010). They proposed the mechanism for coalescence inhibition in which some electrolyte combinations modify the hydrodynamic boundary condition at the air-water interface suggesting that bubble coalescence inhibition was driven by non-equilibrium concentration gradients of solutes at the interface.

Craig et al. (1993) suggested that the reduction in the hydrophobic attraction between the bubbles in solution by electrolytes may explain the inhibition of coalescence. Pugh et al. (1997) postulated that the electrolytes which produce stable bubbles in solution (and dissolve less gas) appear to achieve higher flotation response, whereas the electrolytes which have no effect in inhibiting coalescence of the bubbles yield low flotation recovery. They also found that the electrolytes with smaller strongly charged and hydrated cations (divalent and trivalent) such as  $\text{LaCl}_3$ ,  $\text{MgCl}_2$  and  $\text{MgSO}_4$  were able to give good flotation responses whereas electrolytes such as  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{KCl}$ ,  $\text{CsCl}$  and  $\text{NH}_4\text{Cl}$  were able to give an intermediate flotation performance owing to an increasing surface tension-electrolyte concentration gradient which resulted in flotation recovery increases. Quinn et al. (2007) studied the critical coalescence concentration of inorganic salts and found that the critical coalescence concentration was achievable for a series of coalescence inhibiting inorganic salts, namely,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ , and  $\text{MgSO}_4$ , and two commercial frothers, viz., MIBC and DF 250. Their findings showed that the decrease in bubble size correlated with ionic strength giving a critical coalescence ionic strength of ca.  $0.33 \text{ mol}\cdot\text{dm}^{-3}$  for most electrolytes. They later concluded that their findings helped explain why the Raglan nickel concentrator could operate without frother addition.

Interactions between frother and saline water have been proposed and it is said that with increasing frother concentration, the surface tension of the solution decreases but the ability of a frother to decrease the surface tension of the solution increases in electrolyte solutions (Castro et al., 2013; Craig et al., 1993). It was suggested that the coalescence in pure water might also be caused by strong hydrophobic attraction forces which opposed the hydrodynamic repulsion existing between the colliding bubbles. However there has been no explanation as regards mechanisms by which the stronger surface tension reduction occurred in frother-saline water systems.

## **5. Inorganic electrolytes on the mineral-water interface & the electrical double layer: perspectives on mechanisms of interaction**

The nature and properties of the mineral-water interface are a critical importance in flotation. There are mainly two factors affecting these properties, viz., the interaction of water molecules with the mineral surface, and the electrical double layer at the mineral-water interface. Thus, oriented water layers on the mineral surface can significantly affect the wettability of the mineral surface; the nature of adsorption at the interface could also be impacted (Chander and Fuerstenau, 1985, 1983; Fuerstenau et al., 1988a). When the mineral surface is brought into contact with a polar medium like water, several ions from the mineral surface are transferred into solution through dissolution (Klassen and Mokrousov, 1963). Consequently, the surface of the mineral becomes electrically charged. Ions of the opposite charge to the exposed mineral surface, counter ions, in water are attracted to the exposed mineral surface, whereas ions of the same charge as the exposed mineral surface, co-ions, are repelled from the exposed mineral surface. As a result of this, an electrical double layer is produced which by definition is a separation of electrical charge at the mineral-water interface, that is, the positive and negative charge, with the whole system being electrically neutral (Fuerstenau, 1982). Fig. 3 is a schematic representation of a mineral surface and the electrical double layer. This schematic also represents what is known as the Stern model of the electrical double layer (Fuerstenau, 1982).

Ions that are chemisorbed on the mineral surface establish, determine and control the mineral surface charge and are termed potential determining ions. These may be ions which are from the exposed mineral surface, hydrogen or hydroxyl ions, collector ions that form insoluble salts with ions in the mineral surface, or ions that form complex ions with the ions on the mineral surface and or ions present in the process water/aqueous solution (Bulatovic, 2007; Fuerstenau and Mishra, 1980; Klassen and Mokrousov, 1963). The surface charge on a mineral is determined by the adsorption density of the potential determining ions on the mineral surface. The adsorption of ions from solution at the mineral-

water interface is dependent on the chemical composition and the structure of the mineral surface and the electrical double layer at the interface. The adsorption can be due to chemical reactions between the adsorption species and the ions comprising the mineral surface, that is, chemisorption, or it can be physical adsorption of counter ions in the double layer (Fuerstenau, 1982).

In a study of the adsorption of sodium dodecyl sulfonate on alumina, the adsorption isotherm and the corresponding zeta potential data shown in Fig. 4 were reported by Kelly and Spottiswood (1982).

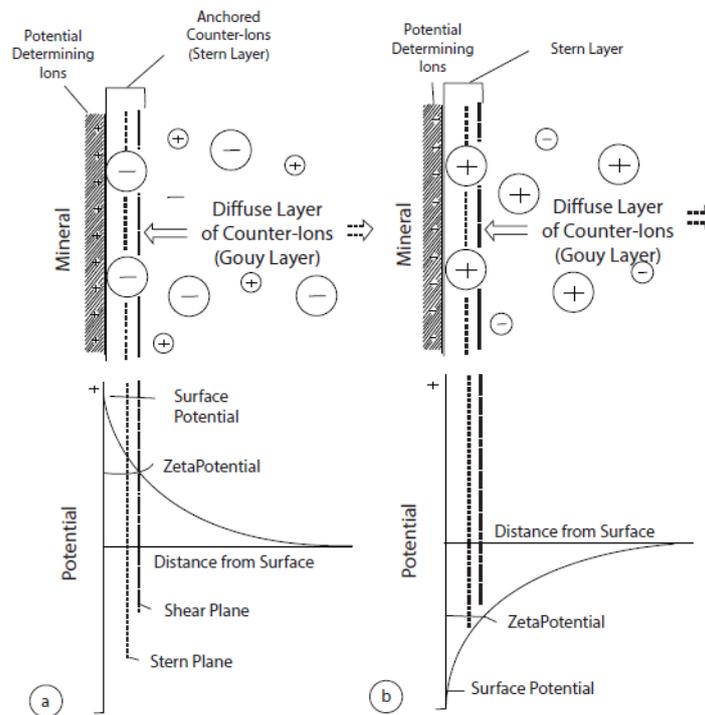


Fig. 3. The electrical double layer at the mineral surface in an aqueous solution with (a) Positively charged potential determining ions (b) Negatively charged potential determining ions (Bulatovic, 2007, Fuerstenau, 1982)

Fig. 4 shows that the adsorption isotherm had three distinct regions where the concentration of the collector was low, anions adsorbed by electrostatic attraction at the positively charged alumina surface. When the concentration of the anions was increased, the adsorption density became sufficiently high for any interaction between the hydrocarbon ligand to occur. This resulted in hemi-micelle formation (Kelly and Spottiswood, 1982). When the collector ions reach a concentration of about the same level as the critical micelle concentration of the bulk solution at the mineral-water interface, the adsorbed collector ions associate into patches on the mineral surface in much the same way as micelles form in the bulk solution. A schematic of this phenomenon is shown in Fig. 5.

It is illustrated in Fig. 4 that the zeta potential changes from positive to negative upon an increase in the concentration of the collector anions. The electrostatic interaction opposes the specific adsorption effects, so the slope of the adsorption isotherm decreases. However, adsorption continues to increase despite the decrease in the adsorption isotherm. For adsorption beyond a complete monolayer, multilayer adsorption can occur. This is, however, clearly undesirable when a hydrophobic mineral surface is required. Hemi-micelles, and also micelles are limited to a maximum number of surfactant ions because of the electrostatic repulsion between the charged "heads" of the ions. Fig. 5 demonstrates the lowering of the critical micelle concentration at the mineral surface. Changes in zeta potential are a result of the effects of the adsorption of ions onto the mineral surface, whether by electrostatic attraction, chemisorption or chemical reaction. The relationship between the electrophoretic velocity and zeta potential depends on the magnitude of the product  $K_a$ , which is, relative magnitudes of the particle radius and a double layer thickness. The zeta potential value can be reduced either by a change of the potential determining ion concentration or by an increase in the ionic strength of the solution (Gaudin, 1932; Gaudin and Charles, 1953)

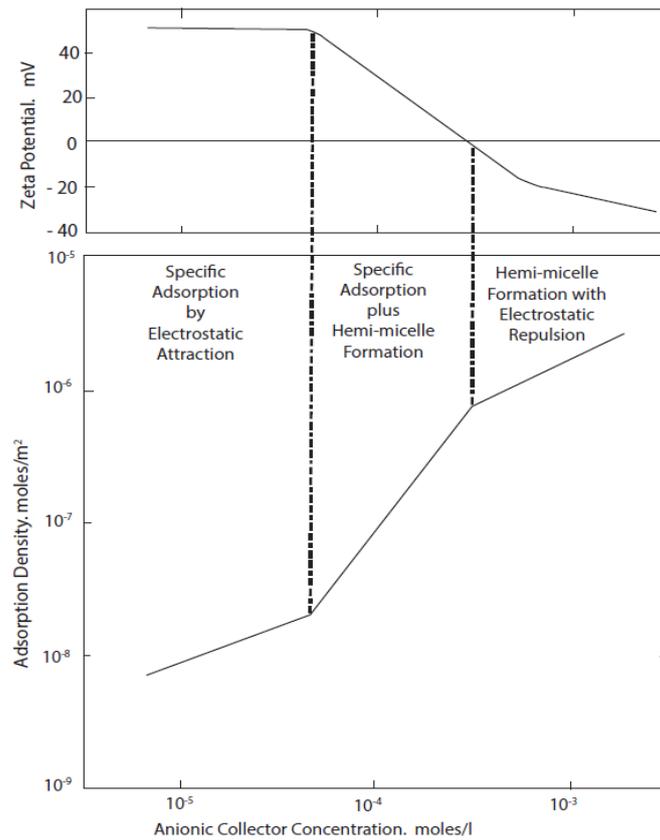


Fig. 4. Adsorption isotherm and corresponding zeta potential

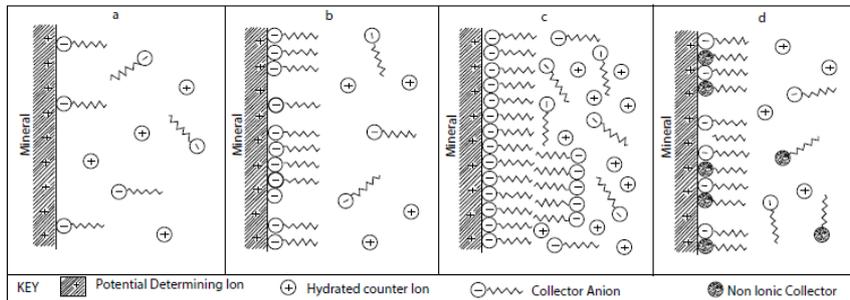


Fig. 5. A schematic representation of the mineral solution interface in the presence of an anionic collector (a) Single adsorption at low concentration (b) Hemi-micelle (c) Multilayer adsorption (d) Co-adsorption of the neutral molecules (Gaudin, 1932)

There is a qualitative parallel between flocculation and small zeta potential (attraction) and dispersion and large zeta potential (repulsion). The attachment of the mineral to the bubble consists of the following steps: the approach of the bubble to the mineral surface, the formation of the thin water film between the bubble and the mineral surface, the rupture of this film due to thinning, the retreat of the water molecules and the establishment of a contact angle (Fuerstenau and Mishra, 1980). Shengo et al. (2014) showed that thiosulphate ions also alter mineral surface properties and possibly contribute to dissolution. Dishon et al. (2009) showed that at high electrolyte concentrations, the adsorption of cations may change the surface charge of the particles and cause strong attraction between the particles. However, Klassen and Mokrousov (1963) suggested that the adsorption of salt ions disrupts the hydration layers surrounding mineral particles. Frost et al. (2002) found that the surface alteration of malachite was supported by decreases in the absorbance level within the whole spectral region as well by the appearance of new infrared bands which could be assigned to the vibration characteristics of S-O bonds of the sulphates. Investigations on the role of  $Ca^{2+}$  ions in modulating the surface properties of

molybdenite and in controlling the interaction between molybdenite and the most predominant gangue mineral, namely quartz, in copper porphyries showed that the floatability of fine molybdenite particles decreased significantly when  $\text{Ca}^{2+}$  ions and silica coexisted in the flotation pulp (Li et al., 2015). According to Raghavan and Hsu (1984) this phenomenon could be attributed to the adsorption of  $\text{Ca}^{2+}$  ions on molybdenite and quartz, reducing the magnitude of the negative surface charge and therefore causing heterocoagulation of molybdenite and quartz. While Ikumapayi et al. (2012) found that the adsorption of  $\text{Ca}^{2+}$  and other metal ions that exist in process water resulted in a reduction in the negative surface charge and the xanthate adsorption onto galena which proved detrimental to galena flotation. Studies conducted by Espinosa-Gomez et al. (1987) and Rao and Finch (1989) showed that the negative surface charge on pyrochlore was reduced by the adsorption of cationic species which hindered the adsorption of cationic amine collectors on pyrochlore surfaces.

The coverage of the colloidal iron oxide (hematite) slimes originating from steel grinding media, iron sulphide minerals and non-sulphide gangue on sulphide mineral surface can reduce the mineral surface hydrophobicity and therefore significantly depress the flotation of sulphide minerals (Bandini et al., 2001). Humic acid, abundant in some natural waters, has been shown to readily adsorb on molybdenite surfaces and result in decreased hydrophobicity and floatability of molybdenite (Lai et al., 1984). Corin et al. (2011) studied the effect of water quality on the entrainment of naturally floatable gangue (talc) in the flotation of platinum group elements, using a modified guar gum as a depressant, and found that an increase in the ionic strength resulted in a decrease in the amount of talc entrained per unit water. The proposed mechanism for this phenomenon was that the coagulative nature of talc particles increases with increasing ionic strength because  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions were adsorbed onto the talc particle surfaces resulting in a lower surface charge and electrostatic repulsion which also resulted in the reduction of entrained mineral particles. The presence of bacteria in process water could also pose potential risks for flotation performance as bacteria such as gamma-proteobacteria have been reported to reduce the floatability of apatite due to their interactions with calcium containing minerals resulting in strong flocculation (Evdokimova et al., 2012; Levay et al., 2001). Kusuma et al. (2014) investigated the interaction mechanism between pentlandite and gangue minerals by zeta potential and surface force measurement and found that AFM measurements show attractive interaction between the silicon nitride tip and magnesite surface on approach, mainly due to the dominant van der Waals attraction over the weak electrical double layer repulsion.

Table 2. A summary of key findings, speculations and perspectives from literature on the influence of ions on froth stability

Author(s)	Froth stability
Bıçak et al. (2012), Castro et al. (2013), Christenson and Yaminsky (1995), Craig et al. (1993), Corin et al. (2011), Farrokhpay and Zanin (2011), Marrucci and Nicodemo (1967), Marrucci (1969), Lessard and Zieminski (1971), Pugh et al. (1997), Ramos et al. (2013) and Quinn et al (2007)	<ul style="list-style-type: none"> <li>• High flotation recoveries in the presence of electrolytes.</li> <li>• Bubble size decreased and gas hold-up increased with an increase in <math>[\text{NaCl}]</math>.</li> <li>• At a 0.4 M NaCl, the gas dispersion properties were comparable to those of 10 ppm MIBC.</li> <li>• <math>\text{AlCl}_3</math> had the highest effect on froth stability followed by <math>\text{CaCl}_2</math> and NaCl.</li> <li>• Froth stability increased with increasing ion valence.</li> <li>• Surface tension reduction (on solutions containing MIBC and DF250) was greater in NaCl/KCl compared to distilled water.</li> <li>• Finer bubbles in the presence of electrolytes than with frothers were generated.</li> <li>• Recovery by true flotation and entrainment increased.</li> <li>• Frothability increased sharply with increasing pH.</li> <li>• Increase in electrical repulsive forces at the bubble surface.</li> <li>• Reduction in the electrostatic interactions between particle and bubble.</li> <li>• The thinning of the liquid film between bubbles was retarded.</li> <li>• Bubble coalesce decreased with increasing concentration.</li> <li>• Slow inter-bubble film drainage occurred.</li> </ul>

## 6. A summary and critic of literature perspectives

Tables 2-4 represent a summary of key findings from literature as regards the position of previous authors on the interaction of inorganic electrolytes on collectors, depressants and frothing behaviour.

Table 3. A summary of key findings, speculations and perspectives from literature on ion-depressant interactions and their effects on hydrophilicity/depression

Author(s)	Electrolyte-depressant
Burdukova et al. (2008); Cuba-Chiem et al. (2008); Khraisheh et al. (2005); Morris et al. (2002); Parolis et al. (2007, 2008); and Shortridge et al. (2000)	<ul style="list-style-type: none"> <li>• <math>\text{Ca}^{2+}</math> and <math>\text{Mg}^{2+}</math> ions increased the adsorption of depressants onto talc.</li> <li>• Adsorption increased with an increase in the ionic strength.</li> <li>• <math>\text{Ca}^{2+}</math> ions reacted with the carboxylic acid groups of CMC.</li> <li>• <math>\text{Ca}^{2+}</math> ions adsorbed onto talc in the form of <math>\text{CaOH}^+</math> ions.</li> <li>• <math>\text{CaOH}^+</math> ions on the surface increased the number of the available metallic sites, thus promoting CMC adsorption.</li> <li>• An acid-base mechanism of interaction with metal hydroxo species on the mineral surface.</li> </ul>

Table 4. A summary of key findings, speculations and perspectives from literature on ion-collector interactions and their effects on hydrophobicity

Author(s)	Electrolyte-collector (Hydrophobicity)
Chen et al. (2009); Fuerstenau et al. (1988); Kirjavainen et al. (2002ab); Kirjavainen and Heiskanen (2007) and Hirajima et al. (2016)	<ul style="list-style-type: none"> <li>• <math>\text{Ca}^{2+}</math> and thiosulphate ions: <ul style="list-style-type: none"> <li>– Activated the flotation of sulphides with xanthate</li> <li>– Improved the selectivity of nickel separation.</li> <li>– Increased xanthate adsorption onto sulphide minerals.</li> </ul> </li> <li>• <math>\text{MgCl}_2</math> and <math>\text{CaCl}_2</math>: <ul style="list-style-type: none"> <li>– Reduced the floatability of molybdenite and chalcopyrite at <math>\text{pH} &gt; 9</math>.</li> <li>– Depressing effect was proportional to their concentrations.</li> <li>– Reduced both the hydrophobicity and surface charge of <math>\text{CuFeS}_2</math> and <math>\text{MoS}_2</math>.</li> </ul> </li> </ul>
Ikumapayi and Rao (2015)	<ul style="list-style-type: none"> <li>• <math>\text{Ca}^{2+}</math> and <math>\text{SO}_4^{2-}</math> ions resulted in: <ul style="list-style-type: none"> <li>– Marginally lower recoveries of <math>\text{CuFeS}_2</math> and <math>\text{PbS}</math> using PAX.</li> <li>– <math>\text{ZnS}</math> floatability increase in SIBX.</li> <li>– The presence of surface oxidized sulfoxy species and surface calcium carbonates and/or calcium sulphate on <math>\text{CuFeS}_2</math> and <math>\text{PbS}</math> at flotation <math>\text{pH} 10.5</math> as revealed by FTIR and XPS studies.</li> <li>– Surface species influencing xanthate adsorption.</li> <li>– Surface-oxidized sulfoxy and carbonate species on <math>\text{ZnS}</math> surface at <math>\text{pH} 11.5</math>.</li> <li>– Higher <math>\text{CuFeS}_2</math>, <math>\text{PbS}</math>, and <math>\text{ZnS}</math> recoveries from two different complex sulphide ores.</li> </ul> </li> </ul>
Shackleton et al. (2012)	<ul style="list-style-type: none"> <li>• In the absence of reagents: <ul style="list-style-type: none"> <li>– Addition of cation and anion to deionised water reduced moncheite, pentlandite and pyroxene recovery.</li> </ul> </li> <li>• Upon xanthate addition: <ul style="list-style-type: none"> <li>– The recovery of moncheite and pentlandite increased.</li> <li>– Pyroxene recovery also increased in the presence of xanthate, particularly at the higher ionic strength of process water. This was attributed to the inadvertent activation of the pyroxene mineral surface especially in the presence of moncheite and pentlandite dissolution products, viz. Pd, Bi, Te, Fe and Ni.</li> <li>– Selectivity between moncheite and pyroxene as well as between pentlandite and pyroxene was significantly reduced in the presence of sodium chloride than in de-ionised water.</li> <li>– Xanthate seemed to counteract both the effects of ionic strength and cation and anion concentrations in process water.</li> </ul> </li> <li>• It was concluded that there seems to be a synergistic effect between ionic strength and ion concentration in process water.</li> <li>• The ions in the process water seemed to play a more significant role compared to ionic strength in mineral surface alteration and floatability.</li> </ul>

### 6.1. The influence of electrolytes present in process water in the pulp phase

It is well known that processes occurring in the pulp phase can be divided into two parts, firstly, the reactions between the collector and mineral to render the mineral hydrophobic; and then secondly the attachment of the mineral particles to air bubbles rising through the pulp into the froth phase (Goodall, 1992).

The formation of the hydrophobic surface is dependent on the surface properties of the mineral. Both the electrical double layer at the mineral-water interface and the interaction of water molecules with the surface affects the surface properties (Fuerstenau, 1982). Contact of the mineral surface with water molecules releases ions into solution and causes the surface to become electrically charged, that is, the pulp solution affects the electrical double layer. Ions carrying an opposite charge to that of the exposed mineral surface are attracted to the mineral surface whereas those of like charge are repelled from the mineral surface which affects bubble-particle attachment (Fuerstenau and Mishra, 1980).

The detrimental effect of ions has been associated with either depression of the target mineral or activation of the unwanted gangue (Zhang et al., 1997). In general, the interactive effect of ions on sulphide minerals is not well documented in literature but the specific effect of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , sulphate and bicarbonate ions on sulphide minerals has been investigated (Barker, 1986; Ikumapayi et al., 2012; Rao et al., 2016).  $\text{Ca}^{2+}$  adsorption on pyrite, galena and other sulphide minerals is reported to increase with increasing pH and  $\text{Ca}^{2+}$  concentration thereby hindering the collector from adsorbing onto surface of the mineral (Gaudin and Charles, 1953; Rao et al., 2016). It has been shown that an increase in the concentration of divalent cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , results in an increase in the recovery of valuable minerals, and a dramatic decrease in gangue recovery during the flotation of sulphidic ores (Boujounoui et al., 2015a; Corin and Wiese, 2014; Slatter et al., 2009; Shackleton et al., 2012; Wang and Peng, 2014). These studies have also shown that froth stability increases with the addition of divalent cations. An increase in the concentration of the monovalent cation,  $\text{Na}^+$ , resulted in an increase in pyrite recovery and a slight decrease in gangue recovery along with improved froth stability. Recent studies by Corin et al. (2011) and Corin and Wiese (2014) on the effect of the ionic strength of plant water on the flotation performance of a Merensky type ore showed that an increase in the ionic strength of plant water from 0.0241 to 0.0723 mol.dm<sup>-3</sup> led to increased recoveries of the chalcopyrite and pentlandite as well as discernible decreases in the concentrate grade as froth stability was noted to have increased and thus the higher solids and water recoveries at higher ionic strength resulted in more NFG reporting to the concentrate although the rate of NFG flotation decreased with increasing ionic strength of plant water. These studies also showed that the detrimental effect of increasing ionic strength on concentrate grades could be countered by the addition of a suitable depressant whose performance would be enhanced by the presence of electrolytes in plant water. One of the mechanisms proposed for the enhancement in depressant efficacy by certain electrolytes is that in an alkaline medium  $\text{Ca}^{2+}$  reacts with products of sulphur oxidation and atmospheric carbon dioxide to form calcium sulphate and calcium carbonate films, these films usually increase the hydration of NFG and thus increase the depression of NFG (Glembotskii et al., 1972; Klassen and Mokrousov, 1963). It has also been shown that calcium ions added as lime used for pH adjustment contribute to the depression of gangue minerals (Barker, 1986; Burdukova, 2007). Above pH 7, the surface of NFG such as talc and pyrite is negatively charged, and  $\text{Ca}^{2+}$  adsorbs readily by electrostatic attraction. The presence of  $\text{Ca}^{2+}$  ions hinders the collector-mineral reaction on the pyrite surface.

Multivalent cations have profoundly influenced the flotation of silicates and their effects are well reported. Salts of divalent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were found to coagulate silica more readily (Burdukova et al., 2008; Deng et al., 2014; Laskowski et al., 2007; Parolis et al., 2008). On quartz, calcium is thought to be adsorbing as  $\text{CaOH}^+$  and magnesium as the  $\text{Mg}(\text{OH})_2$  precipitate. These ions are thought to be responsible for the flocculation of quartz suspensions and the depression in the cationic flotation of silica in an alkaline pulp solution (Iwasaki et al., 1980). Calcium has been reported to activate quartz in anionic flotation (Lloyd, 1981).

The mechanism for the adsorption of these cations is said to be due to hydrogen ions and the presence of  $\text{M-OH}^+$  complexes (M being the metal ion). This results in a decrease in the negative charge of the quartz surface (Laskowski and Castro, 2014; Laskowski et al., 2007). Activation by  $\text{M-OH}^+$  ions in flotation is due to the dehydration of the surface allowing the air-mineral interface to hold little or no water. Metal ions are, however, adsorbed as hydrated ions. A layer of water molecules then separates the bubble from the mineral surface thus depressing the quartz (Laskowski et al., 2007).

Multivalent cations have the ability to hydrolyse in aqueous solutions, depending on their chemical structure and the pH and can have the following effects (Fuerstenau et al., 1988b):

- ✓ a reduction of the zeta potential of the negatively charged oxide surfaces,

✓ an enhancement of the flotation of the negatively charged oxide minerals with anionic collectors,

✓ and improved adsorption on the positively charged oxide surfaces.

Studies on floatability, coagulation, adsorption and electrokinetics have shown that the adsorption of cations increases sharply near the pH at which the metal hydrolyses. Many researchers in this field have proposed different theories explaining the effect of ions and these are summarised in Table 5.

Table 5. Key notes on the effect of ions on adsorption and depression

Authors	Proposed mechanism
Morgan and Stumm (1964)	The effect of multivalent cations was explained in terms of surface complex formation at the mineral surface enhancing the hydrophilicity of the mineral particle.
Laskowski et al. (2007)	Identified the metal hydroxo complexes as the responsible species for inadvertent enhancement in depression which puts special emphasis on the importance of the pH at which flotation is being performed.
Laskowski et al. (2007) and Mchardy (1973)	Suggested that metal hydroxides form at the solid-liquid interface under the conditions where the hydroxide is still soluble in the bulk solution and thereby induce hydrophilicity and depression.

The differences in the postulated theories have been attributed to the narrowness of the pH range over which hydrolysis of the metal cations and precipitation of metal hydroxides occur (Fuerstenau et al., 1988b). It is suggested that for polar solids, the interfacial pH is different from that of the solution (Laskowski et al., 2007). Non-polar solids such as talc have the advantage that their surface charge is low and as a result the hydrogen ion activity at the mineral-water interface must not be appreciably different from the bulk (Burdukova, 2007). The effects of cations on non-polar solids have not received much attention (Fuerstenau et al., 1988b).

Putting the influence of electrolytes and their interactions with reagents in the pulp phase into perspective; it is evident that there is a lack of depth in knowledge on the effect of inorganic electrolytes on collectors and depressant adsorption. However, the little that has been done has put more emphasis on individual or specific ion effects, and thereby developed some understanding and suggestions on specific ion effects on hydrophobicity and hydrophilicity. Also many of these specific ion effects on thiol collector and depressant adsorption have been studied on pure minerals and therefore do not provide a clear picture as to what happens when a real ore is used. This therefore means that there is still a major gap in literature to understand the dominant or controlling inorganic electrolytes in process water influencing collector adsorption, hydrophobicity, depressant adsorption and hydrophilicity. Regarding the influence of electrolytes on polysaccharides; most published work has focused on the effect of specific ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  on polysaccharides depressants with findings that suggested that these ions had a notable effect in inducing the ability of these polysaccharides to attach onto gangue. Such limited published work went as far as showing that the valency or the charge on the ion mattered in as far as depression enhancement is concerned. There are suggestions that divalent cations perform better than monovalent cations in inducing the efficacy of polysaccharides. However, there is growing need for a holistic view on how individual ions in process water affect depressant behaviour as well as the determination of the inorganic electrolytes whose influence is dominant or controlling in the flotation system. Such a fundamental holistic view would also allow for the establishment of whether there are any competing physicochemical interactions in the pulp phase.

## 6.2. The influence of electrolytes present in process water on the froth phase

The froth phase is an important part of the flotation system. The froth phase must be of sufficient volume and stability in order to act as a good medium of separation of valuables from gangue. If the froth is too stable, the separation of gangue does not occur effectively, and if the froth is not stable enough, the recovery of valuable minerals is not achieved. In general, factors that reduce the rate of drainage of the

froth films will increase the stability of the froth (Bıçak et al., 2012). Factors affecting the stability of the froth phase are summarised in Table 6.

Table 6. Factors affecting or determining the stability of the froth phase

Factor or Indicator	Key notes	Authors
Surface tension of the solution	The lower the surface tension the more stable the froth.	Weissenborn and Pugh (1996)
Viscosity of the solution	The more viscous the medium, the slower the drainage of the liquid from between the bubbles and hence the slower the rate of coalescence.	Sett et al. (2015)
Bubble size	The smaller the bubbles forming the froth, the greater the stability of the froth formed.	Finch et al. (2008)
Fine hydrophilic particles	The presence of fine hydrophilic solids can stabilise the froth.	Sarhan et al. (2017, 2016) and Sattar et al. (2013)
Naturally floatable gangue	Gangue minerals reporting to the concentrate such as talc can be froth stabilising.	Wiese and Harris (2012)

Barker (1986) showed that an increase in the ionic strength of solutions containing divalent ions such as  $Mg^{2+}$  and  $Ca^{2+}$  increased the kinematic viscosity. This type of increase causes an increase in the film thickness which causes slower drainage and thus a more stable froth (Corin and Wiese, 2014; Sarhan et al., 2016). It has also been reported that an increase in the ionic strength of metal hydroxides increased the froth stability (Bikerman, 1953). The presence of ions in solution has also been reported to cause an increase in the surface tension and this leads to decreases in the bubble size and increases in froth stability (Barker, 1986).

An extensive amount of work has been published on the influence of certain electrolytes on froth stability both direct individual ion effects as well as indirect individual ion effects on froth stability by reason of specific ion-depressant interaction on froth stabilising gangue such as talc. However, there is little knowledge regarding controlling or dominant interactions (resulting from ion-reagent specific and combined effects) affecting froth stability. It is therefore imperative to establish a fundamental understanding into dominant electrolytes in process water affecting froth stability directly as a result of the action of electrolytes on bubble coalescence. Furthermore, indirect effects arising from the action of electrolytes on polysaccharides which destabilise the froth need to be established.

### 6.3. The existing gap in literature on electrolyte-reagent interactions at the mineral surface in flotation

Previous work indicates that the accumulation of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $S_2O_3^{2-}$  may impact the hydrophilicity of gangue minerals, the hydrophobicity of the targeted value bearing minerals as well as the froth stability of the system, in turn, entrainment could also be impacted. However, previous studies have not dealt sufficiently with the question of whether there are any interactive effects in the system as well as any possibilities of dominant, controlling and or synergistic effects brought about by the presence of electrolytes in process water in as far as electrolyte-reagent interactions at the mineral surface are concerned. It is also important to note that much of the literature presented on electrolytes in flotation has either presented very little research on, or left out if not assumed spectatorship of ions such as  $Cl^-$  and  $NO_3^-$  which are also commonly found in process water. With  $Na^+$  having been shown to be less impacting on CMC and thiol collector adsorption, little research has been reported on its effect in this regard when combined with the anions which are speculated to have strong interactive effects such as  $SO_4^{2-}$ ,  $S_2O_3^{2-}$  and  $NO_3^-$ . This gap in literature suggests that combination effects are not important despite previous publications by Craig et al. (1993) and Henry et al. (2007) which showed that ion combinations impact bubble coalescence which is an important froth stability determining factor.

Furthermore, there are studies in which specific ions such as  $Ca^{2+}$  have shown improvements on the performance of polysaccharides as talc depressants. It was speculated that such inorganic electrolytes

induced the hydrophilicity of talc and thereby enabling stronger depressant adsorption. However, there is little evidence to support these speculations. It is also suggested that the same electrolyte (i.e.  $\text{Ca}^{2+}$ ) would enhance the anionic thiol collector adsorption and thus impart the desired hydrophobicity on the value bearing sulphide minerals. Concurrently,  $\text{Ca}^{2+}$  would increase the stability of the froth such that flotation would require minimal frother dosage to achieve the desired froth stability. These phenomena or ion specific effects beg the question "Is there competition or synergism in the interactions between the water borne inorganic electrolytes, collector anions and the depressant anions occurring at the mineral surface?". Also, these phenomena suggest that there is a need for fundamental studies to decouple electrolyte-reagent-mineral interactions so as to establish whether there are dominant interactions. Such fundamental knowledge would enable the prediction of the overall flotation performance from an understanding of the water chemistry and its associated interactions with reagents and minerals. The effects on flotation performance would thus stem from a thorough understanding of electrolyte-reagent-mineral interactions on mineral recoveries and grades, hydrophobicity, hydrophilicity, froth stability as well as entrainment.

## 7. Conclusions

It has been shown that there is a need to investigate at a fundamental level, the mechanisms of interaction between inorganic electrolytes present in process water and flotation reagents at the mineral surface and thereby predict the resulting effect of these interactions on flotation performance. Also, dominant or controlling interactions under different water quality should be identified or determined in response to the question of water quality on flotation. Thus, it is proposed that the objectives of future studies in this area of research should seek to:

- Identify the controlling inorganic electrolyte-reagent-mineral interactions on froth stability.
- Identify the controlling inorganic electrolytes on mineral-collector adsorption in as far as collector behaviour is concerned.
- Identify the dominant electrolytes on depressant behaviour and on the depression of gangue.
- Identify the role that these electrolyte-reagent interactions have on entrainment.

It is anticipated that outcomes of such fundamental investigative work will help predict and decouple the dominant inorganic electrolyte-reagent-mineral interactions and thus propose reasonable process water conditions based on these dominant interactions for optimum control of flotation plant operations as regards the challenge of water quality, reagent usage and mineral recovery.

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