Investigating Electrolyte-Reagent-Mineral Interactions in Response to Water Quality Challenges in the Flotation of a PGM Ore

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Plagiarism Declaration

I, **Malibongwe Shadrach Manono**, declare that the work presented in this thesis dissertation is my own, save for that which has been appropriately acknowledged. This thesis dissertation incorporates 6 papers containing work that I performed as part of the scope of this PhD, under the supervision of A/Prof Kirsten Corin and Mrs Jenny Wiese. All work referred to that was done by others is cited or acknowledged appropriately and in accordance with the UCT-Harvard style of referencing so that the originality of the argument I am making in this dissertation is not compromised. Contributions made by co-authors to the jointly authored papers contained in this thesis dissertation are outlined in Chapter 1.

I confirm that I have been granted permission by the University of Cape Town's Doctoral Degrees Board to include the following publications in my PhD thesis, and where co-authorships are involved, my co-authors have agreed that I may include the publications.

Manono, Malibongwe, Corin, Kirsten, & Wiese, Jenny (2018). *Perspectives from literature on the influence of inorganic electrolytes present in plant water on flotation performance*. Physicochemical Problems of Mineral Processing, 54 (4), 1191-1214.

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Abbreviations & Nomenclature

1Plant	Synthetic plant water with a total dissolved solids (TDS) of 1023 mg/L
1SPW	Standard synthetic plant water, the same as 1Plant
3SPW	Synthetic plant water with a TDS of 3069 mg/L
5SPW	Synthetic plant water with a TDS of 5115 mg/L
10SPW	Synthetic plant water with a TDS of 10230 mg/L
Active content	In this thesis, active content refers to the purity of a reagent
Activity	The effective concentration of a particular component in a solution or other system, equal to its concentration multiplied by an *activity coefficient*.
Al^{3+}	Aluminium cation
BMS	Base metal sulphides
C1	First concentrate
C2	Second concentrate
C3	Third concentrate
C4	Fourth concentrate
Ca^{2+}	Calcium cation
$CaCl_2$	Calcium chloride
$Ca(NO_3)_2$	Calcium nitrate
$Ca(NO_3)_2.4H_2O$	Calcium nitrate 4-hydrate
$CaSO_4$	Calcium sulphate
$CaOH^+$	Calcium hydroxo species
$Ca(OH)_2$	Calcium hydroxide
˚C	Degrees centigrade
Cl^-	Chloride anion
cm	Centimetres
CMC	Carboxymethyl cellulose

CMR	Centre for Minerals Research
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate anion
Cs^+	Cesium cation
Cu	Copper
$CuSO_4$	Copper sulphate
DS	Degree of substitution
g/t	Grams per ton
Electrolyte	Ionic species
Foam	A mass of bubbles formed on or in liquid without solid particles
Froth	A mass of bubbles formed on or in liquid with solid particles
g/mol	Grams per mol
Guar	Guar gum
I	Ionic strength measured in $mol.dm^{-3}$
K^+	Potassium cation
La^{3+}	Lanthanum cation
Li^+	Lithium cation
L/min	Litres per minute
$[M^+]$	Molar concentration of species M^+
Mg^{2+}	Magnesium cation
$MgCl_2$	Magnesium chloride
$Mg(OH)_2$	Magnesium hydroxide
$Mg(NO_3)_2$	Magnesium nitrate
$Mg(NO_3)_2.6H_2O$	Magnesium nitrate 6-hydrate
$MgSO_4.7H_2O$	Magnesium sulphate heptahydrate
min	Minute

mm	Millimetres
$mol.dm^{-3}$	Molarity in mol per cubic decimetre
M_r	Relative molecular weight
Na^+	Sodium cation
Na_2CO_3	Sodium carbonate
NaCl	Sodium chloride
$NaNO_3$	Sodium nitrate
Na_2SO_4	Sodium sulphate
NFG	Naturally Floatable Gangue
NH_4^-	Ammonium anion
Ni	Nickel
NO_2^-	Nitrite anion
NO_3^-	Nitrate anion
PGE	Platinum Group Element
PGM	Platinum Group Mineral
Po	Pyrrhotite
P.Z.C.	Point of zero charge
rpm	Revolutions per minute
s	Seconds
SIBX	Sodium isobutyl xanthate
SO_4^{2-}	Sulphate anion
TDS	Total dissolved solids usually measure in mg/L
UCT	University of Cape Town
µm	Micron
XRF	X-Ray Fluorescence

Synopsis

Froth flotation is a physicochemical process that enables the separation of valuable minerals and unwanted gangue minerals contained in an ore. It utilises the differences in surface properties of the minerals to be separated. Among other factors affecting flotation, water is a major factor as it acts as a reagent and transport medium. Therefore, it stands to reason that the quality of the water used in the process matters. 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 operations. This necessitates proactive management strategies and initiatives aimed at understanding the impact that water could have on flotation and other water intensive processes. The development of such initiatives relies on the provision of sound and fundamental scientific evidence examining and decoupling the effects of water quality on the sub-processes of flotation. This would enable the creation of alternative operating conditions at which flotation could still occur without significant effects on production and profitability. Recycling of process water has for many years been the mining industry's solution to reducing reliance on municipal water because mining operations are often located in arid regions. It has become clear that the recirculation of water in flotation circuits results in the accumulation of dissolved solids, electrolytes, unspent reagents and biological matter possibly resulting in poor flotation performance or alternatively high costs associated with water treatment. Given that water is both a reagent and transport medium in flotation, changes in its quality can significantly affect flotation performance through electrolyte-reagent-mineral interactions.

This study has investigated whether there are any dominant or synergistic electrolyte-reagent interactions occurring during flotation which may impact negatively on the flotation performance. Interactions occurring in both the pulp phase and the froth phase were investigated through established bench scale flotation techniques. On the basis of available literature, investigations were carried out to identify inorganic electrolytes which had the biggest impact on froth stability as well as those which had a dominant role on depression, and specifically CMC efficacy on gangue management. A Merensky ore, typical of the South African Bushveld Igneous Complex was selected as previous work within the Centre for Minerals Research was conducted on ores of similar mineralogy. Three-phase bench scale flotation and froth column tests were performed to examine the effect of increasing ionic strength of plant water and CMC dosage on froth stability and gangue recovery. Two-phase batch flotation and froth column tests were performed at various electrolytic conditions to assess the effect of ionic strength, electrolyte type and pH on froth stability using water recovery, foam height and foam collapse time as key performance indicators of froth stability. Settling tests, adsorption

studies, zeta potential measurements as well as inorganic electrolyte speciation determination were considered in order to elucidate the role of water quality on gangue depression. Talc and pyrrhotite were selected as proxies for naturally floatable gangue (NFG) and sulphides respectively in order to simulate the possible behaviour of a Merensky ore.

Increasing the ionic strength resulted in increased solids and water recoveries suggesting an enhancement in froth stability. When the effect of ionic strength on CMC behaviour was investigated under changing pH, results showed that contrary to findings at pH 9 which showed increases in solids recovery with increasing ionic strength, solids recovered decreased with increasing ionic strength at pH 11. This suggested that at higher pH levels above pH 10 there are hydroxy species present which inhibit the floatability of mineral particles either by forming layers on the mineral particles which hinder the action of the collector or through depressant efficacy enhancement. The speciation diagrams indicated that beyond pH 10, species such as $CaOH^+$ increased in concentration especially at the higher ionic strength. Furthermore the zeta potential results for talc and pyrrhotite showed that at pH 11, the potentials were less negative compared to pH 9 for all synthetic plant waters proving that at pH 11 the pulp chemistry would exhibit a more depressive nature onto mineral particles owing to increased concentrations of positively charged hydroxo species at pH 11 compared to pH 9. These hydroxy species such as $CaOH^+$ would adsorb onto the negatively charged mineral particle, reducing the negative surface charge of the mineral particle. Water recoveries increased with increasing ionic strength at both pH 9 and pH 11. These findings were further supported by 2-phase froth column tests in which water recoveries, foam height, and foam collapse time increased with increasing ionic strengths. This increase in froth stability with increasing ionic strength at both pH conditions is attributed to an increase in the $[Ca^{2+}]$, $[Mg^{2+}]$ and $[SO_4^{2-}]$ which reduces bubble coalescence.

Upon the determination of NFG recovery, entrained gangue recovery and total gangue recovery, it became clear that, at increasing ionic strength, there was a decrease in the recovery of NFG and entrained gangue per g of water recovered. The decrease in the recovery of NFG and entrained gangue per unit water was attributed to the coagulative nature of gangue in the presence of highly concentrated electrolytes and CMC. The fact that total NFG recovery did not change with water quality at a fixed CMC dosage but decreased with increasing ionic CMC dosage is indicative of the strong susceptibility of NFG depression to CMC dosage to an extent that at hyper dosages such as 500 g/t, all NFG is depressed completely. However, given the relationship between solids entrained and water recovery, the total recovery of entrained gangue increased with increasing ionic strength due to increased volumes of water which reported to the concentrate at increasing ionic strength.

It was also shown that there was no change in sulphide recovery with increasing ionic strength. This was indicative of preferential adsorption of CMC onto gangue at the conditions tested. Higher solids recoveries or mass pulls were largely due to increased gangue recovery, mainly entrained gangue, which increased with increasing ionic strength. It was thus postulated that at increased ionic strengths, CMC coagulated gangue particles whilst indirectly destabilising the froth and retarding the action of electrolytes on froth stability through the removal of froth stabilising NFG. In order to examine coagulation at increasing ionic strengths, settling tests were performed on a Merensky ore and on pure talc. The results showed reduced settling time with increasing ionic strength and increasing CMC dosage suggesting that in a flotation cell, highly concentrated electrolytes would assist in depression by enhancing the coagulation of gangue and thereby decreasing their floatability. This can be attributed to increased concentrations of Ca^{2+} and $CaOH^{+}$ which adsorb onto gangue; adsorption of which is the mechanism through which the chemisorption of CMC onto gangue occurs.

In considering the effect of ionic strength and CMC dosage on froth stability, three phase froth column test results showed that the froth collapse time and froth height increased with increasing ionic strength due to an increase in the concentration of inorganic electrolytes which inhibit the coalescence of bubbles. In fact, Ca^{2+}, Cl^{-}, Mg^{2+}, Na^{+}, NO_3^{-} and SO_4^{2-}, which are present in the tested synthetic plant waters, are all reported in literature to have the ability to retard bubble coalescence, thus additive interactive effects in the tested systems should have been present. It was further shown that the addition of CMC resulted in a froth destabilization. The coagulation findings suggested that the presence of inorganic electrolytes enhanced the adsorption of CMC onto gangue due to changes on the mineral surface charge imposed by inorganic electrolytes. Microflotation results in the presence of CMC showed a decrease in the recovery of talc with increasing ionic strength whilst the presence of CMC did not affect the flotation behaviour of pyrrhotite. The adsorption results agreed with the microflotation results and the coagulation findings in that there was less residual CMC, meaning that more CMC was adsorbed onto the mineral surface with increasing ionic strength of plant water. In line with these findings, it was shown that the zeta potential of minerals, both talc and pyrrhotite, although investigated separately, increased (i.e. became less negative) with increasing ionic strengths.

Thus, this work showed that increasing the ionic strength of plant water increased the concentration of inorganic electrolytes present in process water which acted on the mineral surface, passivating the mineral surface as seen through the less negative zeta potential in high ionic strengths. This would in turn create an environment conducive for an acid-base interaction between the hydroxyl species coated mineral particles (base) and highly negatively charged CMC ligand (acid), enhancing the preferential adsorption of CMC onto gangue as shown by the increase in the absorbed CMC concentration onto talc. The increased CMC adsorption would consequently assist in the formation of CMC-gangue mineral flocs with an induced coagulative and hydrophilic nature as shown by the shorter settling time in increasing ionic strength.

Further investigations were carried out with single salts of cations and anions common in process water in order to identify whether there were any ions with the greatest froth stabilising action and gangue depression; Although Sulphide recoveries did not change with specific ions, the sulphide grades were affected by ion type owing to changes in gangue recoveries. Sulphide grades were higher with divalent ions compared to monovalent ions. It was also shown that salts containing NO_3^- resulted in the lowest froth stability, as indicated by water recoveries and froth collapse time, compared to those which contained SO_4^{2-} and Cl^- in solution. Ca^{2+} and SO_4^{2-} resulted in the highest froth stability compared to Na^+. This can be attributed to a better inhibition of bubble coalescence in divalent ions compared to monovalent ions. The divalent Ca^{2+} and Mg^{2+} resulted in the lowest gangue recoveries compared to the monovalent Na^+. NO_3^- resulted in the least gangue recoveries compared to SO_4^{2-} and Cl^-. These findings suggested an enhanced hydrophilic nature onto gangue by divalent cations than monovalent cations with an even greater impact in NO_3^- containing solutions-. Similarly, coagulation measurements showed an enhanced coagulation in NO_3^- compared to SO_4^{2-} with greater coagulation achieved in Ca^{2+} compared to Na^+. An increase in the order of $Ca(NO_3)_2 > CaSO_4 > NaNO_3 > Na_2SO_4$ in the zeta potential of talc and pyrrhotite was seen. This supported the enhanced coagulation and depression in Ca^{2+} and NO_3^- containing systems.

Thus, the findings of this work offer an opportunity to better understand water quality effects on flotation and their implications on froth stability and gangue management. Also, it has been shown that specific ion effects on froth stability and gangue management exist. Overall this study has shown that bench scale flotation techniques such as batch flotation, froth column flotation and microflotation can be used to understand the effect that water quality can have on a specific ore or mineral and that such techniques can be complemented with established surface chemistry laboratory techniques such as adsorption, coagulation and zeta potential to understand the interactions occurring in the air-water, air-solids and solids-water interfaces responsible for a particular flotation performance.. Through lower gangue recoveries, improved coagulation, increased adsorption and zeta potential, it can be concluded that the divalent Ca^{2+} is most likely to improve gangue depression and even more so in the presence of CMC compared to monovalent Na^+. Moreover due to its causing a reduction of bubble coalescence, Ca^{2+} could result in improved froth stabilities and less entrainment. The monovalent Na^{+} showed higher gangue recoveries but lower water recoveries due to its weaker froth stabilising action compared to the divalent $Ca^{2+.}$ The higher gangue recoveries could be attributed to entrainment, meaning that given the lower froth stabilising action, Na^{+} richer solutions are most likely to lead to higher entrainment of gangue. Through higher water recoveries and higher froth collapse time results, it has been shown that SO_4^{2-} ions result in better froth stabilities compared to Cl^{-} and NO_3^{-} ions, and would thus need to be monitored carefully for the desired froth stability.

Thus, this work demonstrated the role of inorganic electrolytes on CMC efficacy and gangue depression using adsorption, coagulation and zeta potential results. These results correlated well with this study's batch flotation and microflotation results. Also, these showed evidence to the suggestions and deductions drawn out of the bench scale flotation results on the effects and mechanisms through which inorganic electrolytes affect gangue and froth stability. This study also demonstrated that the divalent Ca^{2+} had the greatest froth stabilising effect and the greatest depressive effect on gangue compared to the monovalent Na^{+}. Moreover, it provided evidence suggesting that solutions containing NO_3^{-} were depressive on gangue and less froth stabilising compared to SO_4^{2-} and Cl^{-}. Findings of this work showed experimental evidence of the nature of CMC-electrolyte interaction in the pulp phase and its implications on the froth phase and gangue depression.

It is believed that findings of this work offer an opportunity for flotation operations to tailor or control their water quality towards a desired flotation outcome. It may be possible that in order to combat changes in water quality, should closed water cycles be implemented, an operation could adjust their reagent suite to obtain a manageable grade and recovery and alleviate the high cost associated with cleaning of on-site water.

Statement of Originality

This study **offers an opportunity to expand** on the work that's currently gone into **understanding the chemistry of reagents** into froth flotation **over and beyond** current knowledge on the tripartite **specific ion-specific reagent-specific mineral** interactions occurring in the pulp phase. This work's approach was such that **interactive effects of electrolytes and reagents** in flotation were considered in a way that would give a more **comprehensive perspective into the effects and mechanisms** of water quality in froth flotation, particularly that of PGM/BMS containing ores. It is acknowledged that work which considers ionic strength has been previously published, however most of the work previously published by others was preliminary and did not adequately cater for very high ionic strengths or prove the nature of the depressant-ionic strength interaction as is seen in this thesis dissertation. Additional to this is the fact that previous studies only consider the recovery of the valuable minerals, negating the effect seen in the froth phase and the gangue management opportunities seen in this work.

Such expansion in knowledge is considered important in answering the question **"What should the chemistry of process water be in order to achieve desired flotation performance?".** Thus, the contributions of this work to the body of knowledge are outlined below.

- The role of inorganic electrolytes on CMC efficacy and gangue depression was demonstrated using adsorption, coagulation and zeta potential results which correlated well with batch flotation and microflotation performance.
- It was demonstrated that the divalent Ca^{2+} had the biggest effect on froth stability and hydrophilicity compared to the monovalent Na^{+}.
- Evidence suggesting that solutions containing NO_3^- were depressive on gangue and less froth stabilising compared to SO_4^{2-} and Cl^-.
- Evidence of the nature of CMC-electrolyte interaction in the pulp phase and its implications on the froth phase and gangue depression.

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CHAPTER 1 INTRODUCTION

1.1 Background

South Africa's Bushveld Igneous Complex (BIC) hosts the world's largest Platinum Group Elements (PGE) deposits. It is the Merensky reef, the Upper Group 2 (UG2) reef and the Platreef ore bodies that are exploited for their PGE and base metal sulphides (BMS) content among other ore bodies within the BIC. Base metal sulphides (BMS) occur along with Platinum Group Metals (PGM). The Merensky reef in particular has been mined for years; although its head grade may be dwindling, one of the mineralogical characteristics of the Merensky ores is that they contain 1% base metal sulphides. This BMS content comprises of 45% pyrrhotite ($Fe_{1-x}S$), 32% pentlandite ($Fe_9Ni_9S_8$) and 16% chalcopyrite ($CuFeS_2$) (Liddel *et al.*, 1986). The typical mineral composition of a Merensky ore given in Table 1.1. As evident from Table 1.1., majority of the minerals in the ore are gangue minerals in the form of silicates. Talc in particular is problematic due to its hydrophobicity which renders it naturally floatable (Smith and Warren, 1989; Wiese *et al.*, 2005). Thus, the beneficiation of this ore requires techniques that are able to target the valuable minerals from these silicates.

Table 1.1: Typical Merensky ore composition (Liddel et al., 1986).

Mineral	**Abundance (%)**
Talc	0.5-2
Feldspar	20-40
Pyroxene	50-70
Sulphide	<1
Other	6-7

The mining industry faces a challenge of developing innovative, economical and environmentally safe methods by which the BMS-PGE content can be extracted and separated from the non-sulphide gangue. Current approaches have sought to complement or improve existing techniques. One such existing technique is froth flotation. This technique exploits the differences in the physico-chemical properties of minerals present in the ore so as to separate valuable minerals from gangue. It is, however, acknowledged that this technique is complex in that it has to be carefully controlled so as to selectively float the value bearing sulphides from the non-sulphide gangue minerals.

Management and control of this process requires an acknowledgement of the fact that the hydrodynamics and chemistry of the environment may have serious implications to the success of the process. As such, the chemistry of the environment is controlled through the addition of chemical reagents to ensure that the necessary selectivity is achieved. These reagents, inter alia, may be in the form of collectors meant to induce the hydrophobicity of sulphides or polymeric depressants chosen carefully to induce the hydrophilicity of non-sulphide gangue such as chlorite, chromite, feldspar, pyroxene, and talc. Reagent suites or regimes had been developed. However constant changes and challenges on ore mineralogy and environmental restrictions on the use of natural and scarce resources demand that further investigative work be conducted. The low availability of fresh water nearby mining locations is one of the major threats to the success of froth flotation since water acts as both a reagent and a transport medium.

Owing to the scarcity of water alternative waters such as treated sewage water and ground water are being explored for their suitability for the process. Other strategies are driven towards the management of the existing process water through recycling, reuse and reduction. However these may also introduce strange substance such as high dissolved solids, high concentrations of inorganic electrolytes, unspent reagents and biological matter which may very well affect the chemistry of flotation. A number of studies have been carried out on the question of inorganic electrolytes (Liu *et al.*, 2014). Studies showed that various aspects of flotation such as activation, entrainment, froth stability, hydrophobicity, the hydrophilicity of gangue, and depression can be impacted by changes in the salinity of process water (Liu *et al.*, 2014). A robust literature review on the influence of water quality on these aspects is given in Chapter 2.

It is on these basis that this study argues that excellence in water management in mineral processing requires an understanding of the effect of water quality at a fundamental level where flotation is monitored against changing ions and ionic strength conditions (Liu *et al.*, 2014). Previous research showed that an increase in the ionic strength of plant water resulted in increases in the amount of solids and water reporting to the concentrate (Corin *et al.*, 2011; Shackleton *et al.*, 2012). **Two major hypotheses** were made as regards **mechanisms at play** without much fundamental evidence:

- Increasing ionic strength results in an **increase in froth stability** owing to the effect of inorganic electrolytes on bubble coalescence inhibition (Craig *et al.*, 1993; Quinn *et al.*, 2007).

- Increasing ionic strength led to an **enhancement in the depression** of naturally floatable gangue owing to an increased electrolyte-CMC adsorptive interaction on (at) the mineral surface (Burdukova *et al.*, 2008; Laskowski *et al.*, 2007).

The impact of water quality, specifically process water ionic strength on Cu-Ni-PGM flotation performance has gained much focus and speculations are made on certain ions such as Ca^{2+} and SO_4^{2-} as being key role players on reagent-mineral interactions affecting flotation upon water recirculation and reuse. However much of the work available in literature **has not decoupled ionic strength and specific ion effects**. Also, there is little evidence to support the claims on froth stability and depression, hence the need to investigate mechanistically how flotation is affected by changing water chemistry. There is still a growing need to identify the role players (in as far as electrolyte type is concerned) within process water in influencing entrainment, frothability, hydrophobicity, and hydrophilicity in the flotation of base metal sulphide mineral containing ores.

Building on the work done by others, research has been conducted in this area to help understand the negative and positive effects of the different process water inorganic electrolytes and elucidate their effects on reagent behaviour and thereby establish whether there are controlling mechanisms with regards to the interactions between electrolytes, reagents and mineral particles.

1.2 Problem Statement

The interaction of inorganic electrolytes with reagents in the flotation of sulphides bearing ores and associated gangue has been studied (Liu *et al.*, 2014). However, there is no comprehensive scientific research on the influence of inorganic electrolytes on PGM bearing ores. It has been shown that specific inorganic electrolytes such as Ca^{2+} and SO_4^{2-} can affect the wettability of gangue minerals (Liu *et al.*, 2014). These could also hinder the adsorption of collectors onto valuable minerals and concurrently enhance or retard froth stability. A review on literature 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 (Liu *et al.*, 2014). 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. It is thus unclear as to whether there are any dominant, synergistic and or antagonistic interactions responsible for the influence of water quality on Cu-Ni-PGM flotation performance.

It thus 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.

1.3 Scope of Work

This work considers an overall hypothesis that there are electrolytic conditions in PROCESS WATER (as regards electrolyte type and concentration) whose influence on electrolyte-reagent interaction in the flotation of a Pt bearing ore is significant owing to their varying effects on frothability and hydrophilicity. And thus, two main objectives are considered which form the scope of this work:

- ✓ Identify the effects which ions in water have on **stability of the froth**.
- ✓ Identify the effects which ions have on the **hydrophilicity of gangue**.

One polysaccharide depressant was selected for this study and used at various dosages, that is, the anionic sodium carboxymethyl cellulose (CMC) since it is widely used in PGM flotation circuits targeting the depression of naturally floatable gangue such as talc. Other reagents such as collectors and frothers were kept constant so as to replicate typical Cu-Ni-PGM concentrator normal standards in terms of their dosages.

The standard UCT synthetic plant water recipe, normally referred to as 1SPW, was used throughout the testwork with ion mass concentrations (ppm) multiplied by 3, 5 and 10 times achieve the so called 3SPW, 5SPW and 10SPW recipes. This was done to simulate a recirculation of process or plant water that results in ions built-up by the same factor of accumulation.

Single salts containing divalent Ca^{2+}, Mg^{2+}, SO_4^{2-} ions and monovalent Cl^-, NO_3^-, Na^+ ions were chosen to study the specific ion effects on froth stability and their effect on the mechanism of CMC adsorption on talc and pyrrhotite. The effect of organic constituents of recycled process water were not considered in this study.

Various techniques such as froth column, adsorption studies, coagulation, zeta potential measurements and microflotation were employed to obtain information as to the nature of the interaction between minerals (Merensky ore, talc and pyrrhotite systems), ions and CMC. Details regarding the Chapters in which these techniques are described are given in Table 3.1.

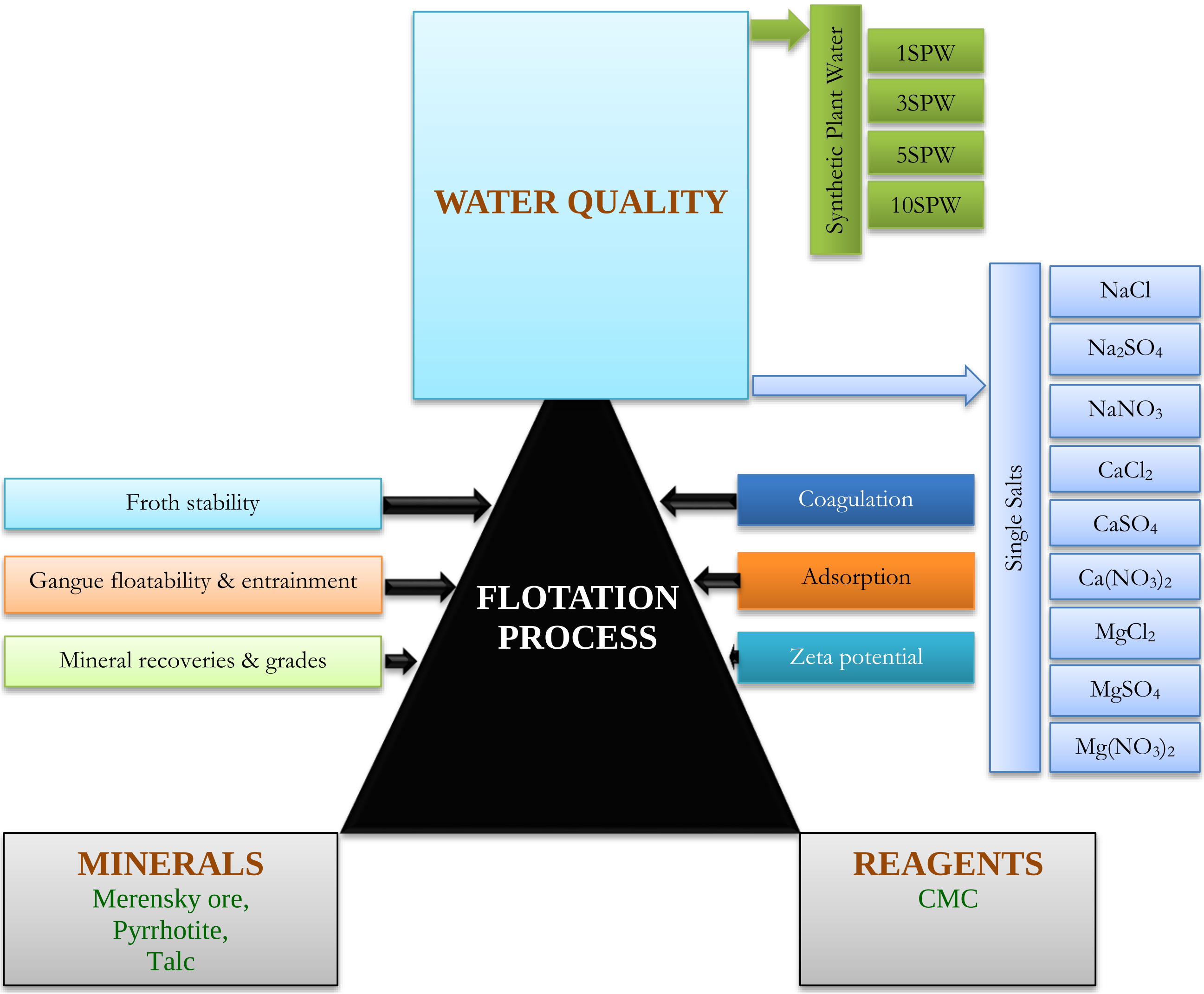

Figure 1.1: A schematic representation of the scope of work.

Figure 1.1 represents a schematic diagram of the Scope of Work. On the basis of the two main objectives, the scope of work considered various synthetic plant waters at increasing ionic strengths, various inorganic salts common in process water, CMC dosages of 0, 100 and 500 g/t using batch flotation, froth column and settling tests and a Merensky ore. Microflotation of talc and pyrrhotite, adsorption studies of CMC onto talc and pyrrhotite, settling tests and zeta potentiometer measurements of talc and pyrrhotite were also investigated in order to deepen the understanding of electrolyte-reagent-mineral interactions in Cu-Ni-PGM ores.

1.4 Thesis Layout & Declaration of Contributions by Others on Subsequent Chapters

This thesis is composed of published and submitted papers. A declaration of contributions by co-authors is given for each paper appearing in this dissertation of thesis.

Chapter 2 Manono, Malibongwe, Corin, Kirsten, and Wiese, Jenny (2018). *Perspectives from literature on the influence of inorganic electrolytes present in plant water on flotation performance*. Physicochemical Problems of Mineral Processing, 54 (4), 1191-1214.

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 Ca^{2+} and 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*

This paper presents a critical review of the current literature on the impact of water quality in sulphide flotation with a major interest on electrolyte-reagent-mineral interactions occurring in the pulp phase and their implications for the froth phase and flotation performance. This chapter concludes by identifying the gap in literature and a proposal is put forward regarding research necessary to fill the gap of which some of this research is attempted in Chapter 4-8.

Mr M.S. Manono conceptualised the work, conducted the investigation in terms of putting together the literature, wrote the complete paper whilst A/Prof K.C. Corin and Mrs J.G. Wiese assisted with conceptualisation, proofread and edited the manuscript.

Chapter 3 details the research questions, hypotheses, aims and objectives. These objectives attempt to address some of the research gaps identified in **Chapter 2**. A summary of all the experimental techniques used in this study is also presented (further experimental details appear in Chapter 4-8).

Chapter 4 Manono, Malibongwe, Corin, Kirsten, and Wiese, Jenny (2018). *Water quality effects on a sulfidic PGM ore: Implications for froth stability and gangue management*. Physicochemical Problems of Mineral Processing, 54(4), 1253-1265.

Abstract

Polysaccharide depressants play a crucial role in the flotation of sulfidic PGM bearing ores as they prevent naturally floatable gangue (NFG) from reporting to the concentrate. This action is regarded as critically important because less dilution of the concentrate means lower costs for downstream processes. However, abnormal water conditions such as high concentrations of ions in the flotation system can modify the selectivity of these depressants. It is well known that the existence of selected electrolytes in water can alter the behaviour of some polysaccharide depressants by enhancing their adsorption onto gangue minerals and thereby prevent naturally floatable gangue from moving into the froth phase. Concurrently these same electrolytes may enhance frothability owing to their stabilising effect on the bubbles within the system. Plant water at various ionic strengths was investigated against sodium carboxymethyl cellulose (CMC) dosages in order to understand electrolyte-depressant interactive effects during the flotation of a Merensky ore in a batch flotation cell, using entrainment, rate of NFG recovery, and total gangue recovery as proxies. The study showed that the NFG recovery per unit mass of water decreased with increasing ionic strength at all CMC dosages, however the total amount of gangue reporting to the concentrate increased with increasing ionic strength at all CMC dosages. Thus, this paper considers the effects of both ionic strength and CMC dosage within flotation. It further investigates whether any interactive effects exist between froth stability and entrainment when considered simultaneously.

Keywords: *Depressant behaviour, Electrolytes, Entrainment, Froth Stability, Water quality*

This paper investigates the influence of ionic strength and CMC dosage on froth stability and NFG depression. It has also shown that under a fixed depressant dosage increases in solids recoveries were largely a result of increased entrained gangue recovery owing to increased froth stability.

Mr M.S. Manono conceptualised the work, conducted the experimental tests, wrote the complete paper whilst A/Prof K.C. Corin and Mrs J.G. Wiese assisted with conceptualisation, advised on the experimental test work, proofread and edited the manuscript.

Chapter 6 Manono, M.S., Matibidi, K., Thubakgale, C.K., Corin, K.C., and Wiese, J.G. (2017). *Water Quality in PGM Ore Flotation: The effect of Ionic Strength and pH*. In: Wolkersdorfer C., Sartz L., Sillanpää M., and Häkkinenm A. (Editors) 13th International Mine Water Association Congress (IMWA2017) - Mine Water & Circular Economy, Lappeenranta University of Technology, Lappeenranta, Finland, vol. 2, pp. 777-784.

Abstract

Water and its chemistry are important variables in froth flotation. The presence of electrolytes in water may form either hydroxo species or precipitates in the flotation pulp when the process pH is altered. This may alter the chemical interactions that enable the process. This study investigates the interactive effect of plant water ionic strength and pH in the flotation of a sulphidic PGM bearing ore. Results suggest that water quality variations may have effects at both the air-water interface as well as the mineral air interface.

***Keywords**: Froth stability, Ionic strength, pH, Water quality, Water recovery*

This paper focuses on ionic strength of water and pH on the flotation of a PGM ore. Cu-Ni recoveries and grades as well as froth stability data are presented. This paper showed that when the pH goes beyond natural pH 9, hydroxo species are present; these hydroxo species result in the depression of solids with increasing ionic strength of plant water.

As Mr K. Matibidi's BTech supervisor, Mr M.S. Manono conceptualised the idea, 3-phase batch flotation experiments were conducted by Mr K. Matibidi under the co-supervision of Mrs C.K. Thubakgale. To complement these tests, Mr M.S. Manono performed the 2-phase experimental test work on the Batch flotation cell as well as the froth column. Mr M.S. Manono wrote this paper, Mrs C.K. Thubakgale, A/Prof K.C. Corin and Mrs J.G. Wiese proofread and edited the manuscript.

Chapter 6 Manono, M.S., Corin, K.C., & Wiese, J.G. (2018). *Process Water Effects on Mineral-Depressant Adsorption in Sulphide Flotation*. In Conference Proceedings of the XXIX International Minerals Processing Congress (IMPC2018), 15-21 September 2018, Moscow, Russia. (Full oral presentation).

Abstract

It has been suggested that hydroxo species, particularly those of calcium, selectively adsorb onto gangue minerals. Such species enhance the depressive action of carboxymethyl cellulose (CMC) onto gangue via an acid-base interaction between the positively charged mineral surface and the negatively charged CMC molecule. Thus, the hydrophilicity of gangue minerals is enhanced, preventing the dilution of the concentrate. However, as there is little evidence to support these claims it is important to investigate. Adsorption data and mineral surface charge analyses will allow a fundamental understanding into how electrolytes and their ionic strengths affect gangue-depressant adsorption. It is strongly anticipated that decoupling these effects will allow process operators to tailor their process water quality needs towards best flotation operating regimes and in the long run effect closed water circuits. Thus, using talc and pyrrhotite as proxies, this work investigates the influence of the ionic strength of process water on the adsorption of CMC onto minerals in sulphide flotation.

Keywords: *Adsorption, carboxymethyl cellulose, coagulation, depressants, ionic strength, water quality*

This paper examines the effect of changes in ionic strength of water on the adsorption of CMC onto talc and pyrrhotite in order to ascertain claims of enhanced CMC efficacy on NFG depression in saline water made in Chapter 4 and Chapter 5. Adsorption studies showed that CMC adsorbed better onto talc under higher ionic strengths whilst settling tests showed an enhancement in the electrocoagulation talc.

Mr M.S. Manono conceptualised the work, wrote the manuscript whilst A/Prof K.C. Corin and Mrs J.G. Wiese assisted with conceptualisation, advised on the experimental test work, proofread and edited the manuscript.

Chapter 7 Manono, M.S., Corin, K.C., and Wiese, J.G. (2016). *The influence of electrolytes present in process water on the flotation behaviour of a Cu-Ni containing ore*. Minerals Engineering, vol. 96-97, pp. 99-107.

Abstract

Calcium and magnesium ions in process water have been reported to have significant influence on froth stability and flotation recovery, however little research has been done to identify influential ions during the flotation of PGE containing ores. Thus, the purpose of this study was to investigate the effect of typical electrolytes present in process water on the flotation of a Merensky ore. The ionic strength was kept constant at 0.0213 $\text{mol}\cdot\text{dm}^{-3}$ for all electrolyte solution. Cation and anion effects were investigated and each electrolyte compared with the standard synthetic plant water. The results showed higher amounts of solids recovered for all sodium electrolytes whereas calcium and magnesium electrolytes resulted in similar solids recovery. NO_3^-ions resulted in significantly higher Cu and Ni grades than Cl^- and SO_4^{2-} ions. The results seem to suggest that the influence of ion type depends on its ability to enhance or retard gangue activation.to investigate the effect of typical electrolytes present in process water on the flotation of a Merensky ore. The ionic strength was kept constant at 0.0213 $\text{mol}\cdot\text{dm}^{-3}$ for all electrolyte solution. Cation and anion effects were investigated and each electrolyte compared with the standard synthetic plant water. The results showed higher amounts of solids recovered for all sodium electrolytes whereas calcium and magnesium electrolytes resulted in similar solids recovery. NO_3^- ions resulted in significantly higher Cu and Ni grades than Cl^- and SO_4^{2-} ions. The results seem to suggest that the influence of ion type depends on its ability to enhance or retard gangue activation.

Keywords: *Gangue depression; Froth stability; Ionic strength Electrolytes; Water recovered*

This paper considers specific ion effects on the floatability of Cu and Ni of a Merensky ore using solids & water recoveries, Cu & Ni recoveries and grades as key performance indicators. It was speculated that an electrolyte's influence could be linked to its influence and interactive effect on froth stability/bubble coalescence inhibition and or gangue minerals depression.

Mr M.S. Manono conceptualised the work, conducted the experimental tests, wrote the complete paper whilst A/Prof K.C. Corin and Mrs J.G. Wiese assisted with conceptualisation, advised on the experimental test work, proofread and edited the manuscript.

Chapter 8 Manono, M.S., Corin, K.C., & Wiese, J.G. *Specific Ion Effects on Froth Stability and Gangue Depression*. Minerals Engineering. (Under review)

Abstract

Mineral concentrators are becoming increasingly aware of the importance of the quality of water they feed into their milling and flotation circuits. It is speculated that different inorganic constituents of process water may yield different flotation results owing to electrolyte-reagent-mineral interactions occurring in the pulp phase which are speculated to be specific to ion type, reagent type and mineral or ore type. This thus requires an understanding of different specific ion effects on both the pulp phase and froth phase phenomena such that process water chemistry can be monitored and controlled in a manner that does not negatively affect flotation performance. Previous research has shown that inorganic electrolytes may impact mineral hydrophobicity and floatability and could in turn affect froth stability, entrainment and thus mineral grades and recoveries. In this study, the floatability of a Merensky ore is tested on a bench scale in various single salt solutions, *viz.*, $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, NaCl, $NaNO_3$ and Na_2SO_4 in order to examine specific ion effects on gangue recovery and froth stability. Froth stability, flocculation and zeta potential tests are conducted in order to ascertain specific ion effects on froth stability and gangue depression. The findings of this work have shown that NO_3^- exhibited strong depression compared to Cl^- and SO_4^{2-}. SO_4^{2-} and Cl^- had better froth stability compared to NO_3^-. It was also shown that the divalent Ca^{2+} and Mg^{2+} showed strong depression and froth stabilisation compared to the monovalent Na^+.

Keywords: *Froth Stability, Gangue, Inorganic Electrolytes, Specific ions, Sulphides, Talc, Water*

This paper considers the specific ions present within the plant water mixture and their effects on the selected Cu-Ni-PGM ore flotation performance. Flocculation, zeta potential and froth stability data are also presented as a follow up to the gangue activating or depression specific ion effect question which rises out of the work presented in Chapter 7.

Mr M.S. Manono conceptualised the work, wrote the manuscript whilst A/Prof K.C. Corin and Mrs J.G. Wiese assisted with conceptualisation, advised on the experimental test work, proofread and edited the manuscript.

Chapter 9 concludes this thesis dissertation by presenting a concluding discussion which analyses and consolidates all the key findings from **Chapter 4-8**. **Chapter 9** is significant in that it threads together the thesis argument in a cohesive manner. Recommendations for future work are also presented.

This work arose from a much larger project in collaboration with industry and academic partners, the aim of which was to develop a water management protocol for flotation given the increase in the occurrence of recirculated process water which leads to increased inorganic and organic substances in such closed water circuits. It became clear from the onset that fundamental work needed to be done to provide findings, through established bench scale techniques, that will inform the protocol development part of the said project. It was decided that there was a need to investigate the inorganic electrolytes in process water on critical aspects of flotation. *This is the first robust and comprehensive study on inorganic electrolytes in water on their effect on froth stability and carboxymethyl cellulose efficacy on gangue of a platinum group minerals (PGM) bearing ore.* Findings of this work will benefit both the academic and industry partners as regards tools that can be used in determining process water effects on sulfidic PGM ores. It was therefore deemed necessary to publish articles in peer-reviewed journals and present findings of this work in peer-reviewed international conferences as the study progressed. Reviewers provided vital feedback that was helpful on the progress of this study.

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CHAPTER 2 PERSPECTIVES FROM LITERATURE ON THE INFLUENCE OF INORGANIC ELECTROLYTES PRESENT IN PLANT WATER ON FLOTATION PERFORMANCE

2.1 Justification

Water as a scarce natural resource; its scarcity and its ever increasing demand both domestically and industrially poses a challenge to mining especially in cases where mines are placed in arid areas. It is no doubt that one of the greatest tests that the mining industry faces is how well mine managers will manage their water and ensure that the mining business is sustainable. The mining industry's response to this challenge has been a consideration of other alternative sources of water such as treated sewage water, ground water and recycling and reusing water within its operations. In the context of sustainability, major focuses of water recycling in the mineral processing industry have been to: **firstly** reduce the demand of fresh water because the production and transportation of fresh water is usually expensive and can to a certain extent affect the operating costs of mineral processing plants; and **secondly** reduce the volume of effluent. Effluents from the process operations are potentially detrimental to the environment as they can contain both suspended solids as well as many toxic chemicals in solution and there may be financial costs associated with the discharge or even possibilities of mine closure due to non-compliance and lack of responsiveness on water usage and environmental management. Therefore such considerations, clearly point to the need to understand onsite water treatment, recycling, reduction and reuse in the minerals processing industry, particularly in a process such as froth flotation which has a strong reliance on water and whose pulp chemistry could be negatively altered if fundamental studies are not carried out to understand the implications of accumulated inorganic electrolytes on the pulp chemistry and flotation as a whole. Thus, a literature survey into electrolyte-reagent-mineral interactions was commissioned in response to water quality challenges in the flotation of sulphidic ores.

2.2 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 Ca^{2+} and 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.

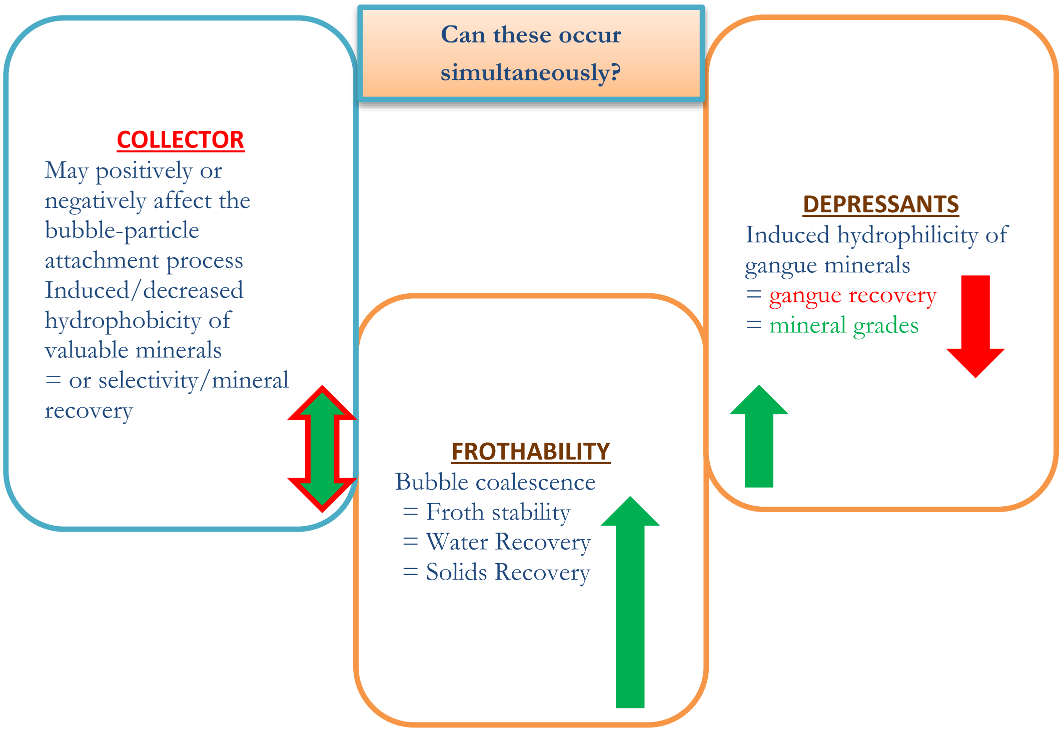
KEYWORDS

Electrolytes, Flotation reagents, Froth stability, Physicochemical interactions, Water quality

2.3 Highlights

- Water quality variations could have beneficial and detrimental implications on flotation.
- Water quality may alter the sub-processes of flotation.
- Ions may enhance froth stability whilst retarding gangue floatability at the same time.
- An in-depth knowledge of the individual electrolyte-reagent-mineral interactions is required.
- There is a need to establish whether there are any dominant or synergistic interactions.

2.4 Graphical Abstract



2.5 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.*, 2014.; 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 CO_3^{2-}, HCO_3^-, Cl^-, Ca^{2+} and Mg^{2+}; (ii) ions added during leaching such as H^+ and SO_4^{2-}; and (iii) ions obtained during milling such as Fe^{2+} and Fe^{3+}. Cations like Mg^{2+} and Ca^{2+} 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^{2+} and SO_4^{2-} 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.

2.6 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^{2+}, Cl^-, Mg^{2+}, Na^+, SO_4^{2-}, K^+, 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 2.1-2.3.

$$NaHCO_{3(s)} = Na^{+}_{(aq)} + HCO_{3}^{-}{}_{(aq)} \quad (2.1)$$

$$HCO_{3}^{-}{}_{(aq)} + H_2O = H_2CO_{3(aq)} + OH^{-} \quad (2.2)$$

$$3H_2O + CO_{2(aq)} = 2H_3O^{+} + CO_3^{2-} \quad (2.3)$$

From Equation 2.2, 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 SO_4^{2-} ions had a positive effect on recoveries, but the level of influence varied from one mineral to another. High concentrations of Cu^{2+} in solution increased the recovery of chalcopyrite, sphalerite, galena and pyrrhotite; however Cu^{2+} ions depressed sphalerite at low concentrations. Zn^{2+} ions at low concentrations depressed the recovery of all the mineral phases, but high concentrations of Zn^{2+} improved the recoveries of chalcopyrite, sphalerite, and pyrrhotite. Mg^{2+} was shown to depress galena, chalcopyrite, and sphalerite at high concentrations whereas 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.

2.7 The Effect of Electrolytes on Flotation Reagents: The Pulp Phase Phenomena

2.7.1 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.

2.7.2 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 Ca^{2+} and 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 KNO_3, $Ca(NO_3)_2$ and $Mg(NO_3)_2$. Increasing the ionic strength of the solution increased the adsorption efficacy of CMC onto talc, however, this effect was stronger for the divalent cations, Ca^{2+} and Mg^{2+}, compared to the monovalent cation 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, 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 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 Ca^{2+} and K^+ electrolytes. Parolis *et al.* (2008) also left out any discussion on the role of the NO_3^- ions. Burdukova *et al.* (2008) investigated the effect of Ca^{2+} on the adsorption of CMC onto the basal planes of New York talc where the influence of a solution containing $Ca(NO_3)_2$ was compared to one containing KNO_3 as well as with de-ionised water. This study found that the presence of Ca^{2+} enhanced the adsorption density of the CMC. This was attributed to the increased concentration of $CaOH^+$ 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 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 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 K^+ or Ca^{2+} cations are equal and therefore cancel out such that the focus becomes that of the monovalent K^+ vs. the divalent Ca^{2+} cations.

2.7.3 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 2.4-2.5.

$$Pb^{2+}_{(aq)} + 2EX^{-}_{(aq)} = Pb(EX)_{2(aq)} \qquad (2.4)$$

$$Pb(EX)_{2(aq)} = Pb(EX)_{2(surf)} \qquad (2.5)$$

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 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 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 (X_2) or metal xanthate (MX_2), with a rebalancing of charge through the cathodic reduction of dissolved oxygen as shown in Equation 2.6-2.8.

$$2X^- = X_2 + 2e^- \tag{2.6}$$

$$MS + 2X^- = MX_2 + S + 2e^- \tag{2.7}$$

$$0.5O_2 + H_2O + 2e^- = 2OH^- \tag{2.8}$$

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.

2.7.4 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^- 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. Figure 2.1 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 Figure 2.1 (Fuerstenau *et al.*, 1985).

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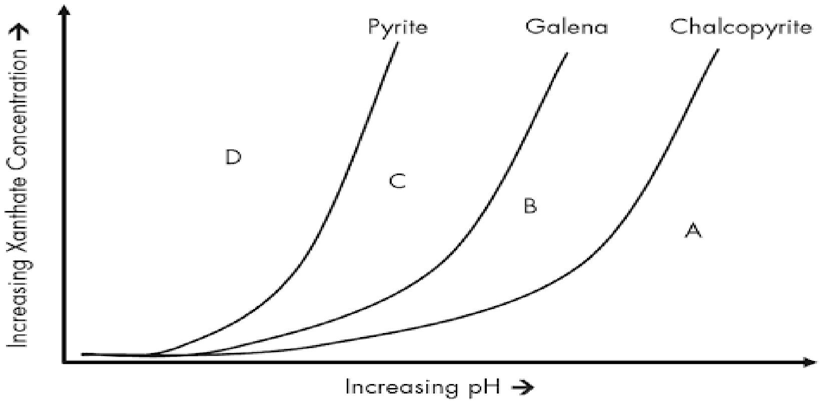


Figure 2.1: pH response curves for sulfhydryl collector adsorption on different sulphide minerals (Fuerstenau et al., 1985). The boundaries, A, B, C and D, are an indication of where and when the specific mineral will be hydrophobic enough for its floatability (Kawatra and Darling, 2011).

Figure 2.1 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 Figure 2.2. 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).

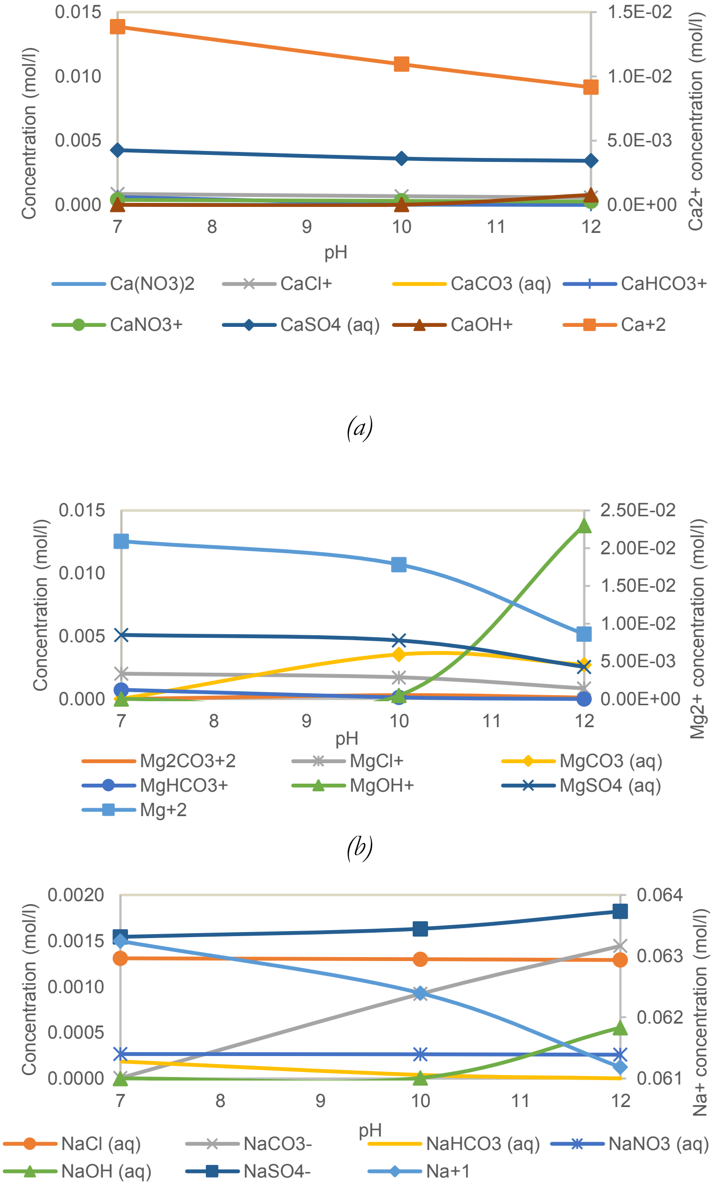
Metal ions hydrolyse in alkaline pH solutions and precipitate hydrophilic metal hydroxides, sulphates or carbonates if their concentrations are above their respective solubility limits (Laskowski *et al.*, 2007). The formation of metal hydroxides is influenced by aqueous pH (Font *et al.*, 1999). Reyes-

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 Cu^{2+} but at pH 7 the amount of $CuOH^+$ present became significant, while at pH 9 the majority of the copper was present as $Cu(OH)_2$ with a small quantity of $CuOH^+$ based on the equilibria presented in Equation 2.9-2.10.

$$Cu^{2+} + OH^- = CuOH^+ \tag{2.9}$$

$$CuOH^+ + OH^- = Cu(OH)_{2(S)} \tag{2.10}$$

In the presence of xanthate, at alkaline pH, Cu^{2+} firstly forms $Cu(OH)_2$ which then subsequently reacts with xanthate ions to form CuX_2. Activation is, however, generally thought to be dependent on the formation of 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 $Fe(OH)_3$ and a metal deficient sulphide, $Fe_{(1-x)}S_{1.13}$ (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).



(a)

(b)

(c)

Figure 2.2: (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.

Figure 2.2 shows that at high pH values, the concentration of Ca^{2+}, Mg^{2+} and Na^{+} 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).

2.8 The Role of Electrolytes on Bubble Coalescence and Froth Stability: Implications into the Froth Phase Phenomena

2.7.1 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 2.11 (Kurniawan *et al.*, 2011).

$$DFS = V_f/Q \tag{2.11}$$

Where DFS is the dynamic froth stability, Vf 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 2.1). 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^{-3}) 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).

2.7.2 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_3, KI, K_2SO_4, $CuSO_4$, K_3PO_4 and $Co(NO_3)_2$ 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, $AlCl_3$, $MgSO_4$, Na_2SO_4, $CaCl_2$, $MgCl_2$, NaCl, LiCl, and NaBr on bubble coalescence and the interfacial gas transfer in aqueous solution and the results are shown in Table 2.1. 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 2.1: Bubble coalescence transition concentration in different electrolytes (Lessard and Zieminski, 1971).

Salt	***Transition concentration, mol.dm^{-3} (50 % coalescence)***
$MgSO_4$	0.032
$AlCl_3$	0.035
$MgCl_2$	0.055
$CaCl_2$	0.055
Na_2SO_4	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 $LaCl_3$, $MgCl_2$ and $MgSO_4$ were able to give good flotation responses whereas electrolytes such as NaCl, LiCl, KCl, CsCl and NH_4Cl 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, KCl, NaCl, Na_2SO_4, $CaCl_2$, and $MgSO_4$, 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 mol.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.

2.9 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). Figure 2.3 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).

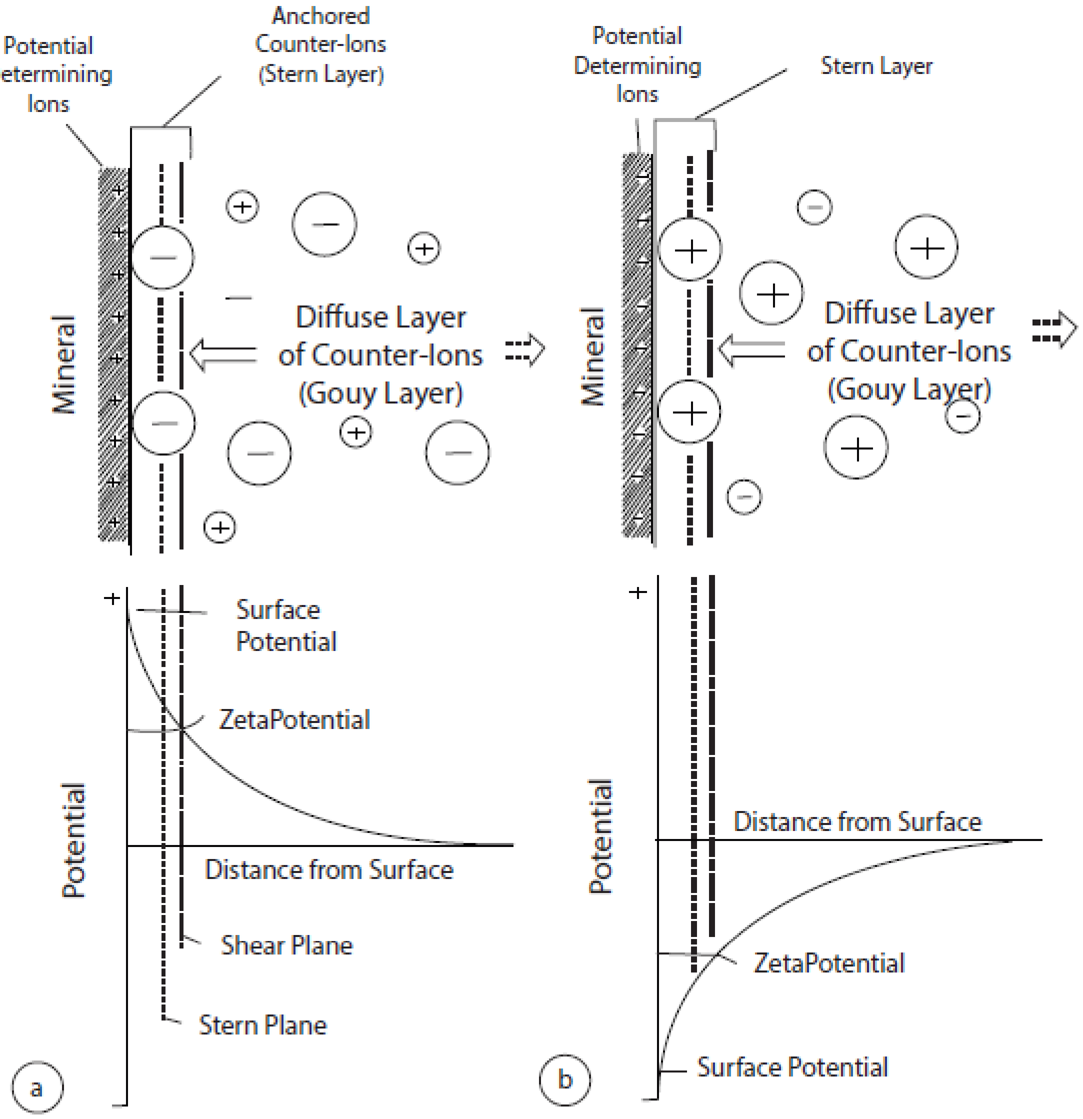


Figure 2.3: The electrical double layer at the mineral surface in an aqueous solution with (a) Positively charged potential determining ions (b) Negatively charged potential determining ions (Bulatovic, 2007, Fuerstenau, 1982).

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 Figure 2.4 were reported by Kelly and Spottiswood (1982).

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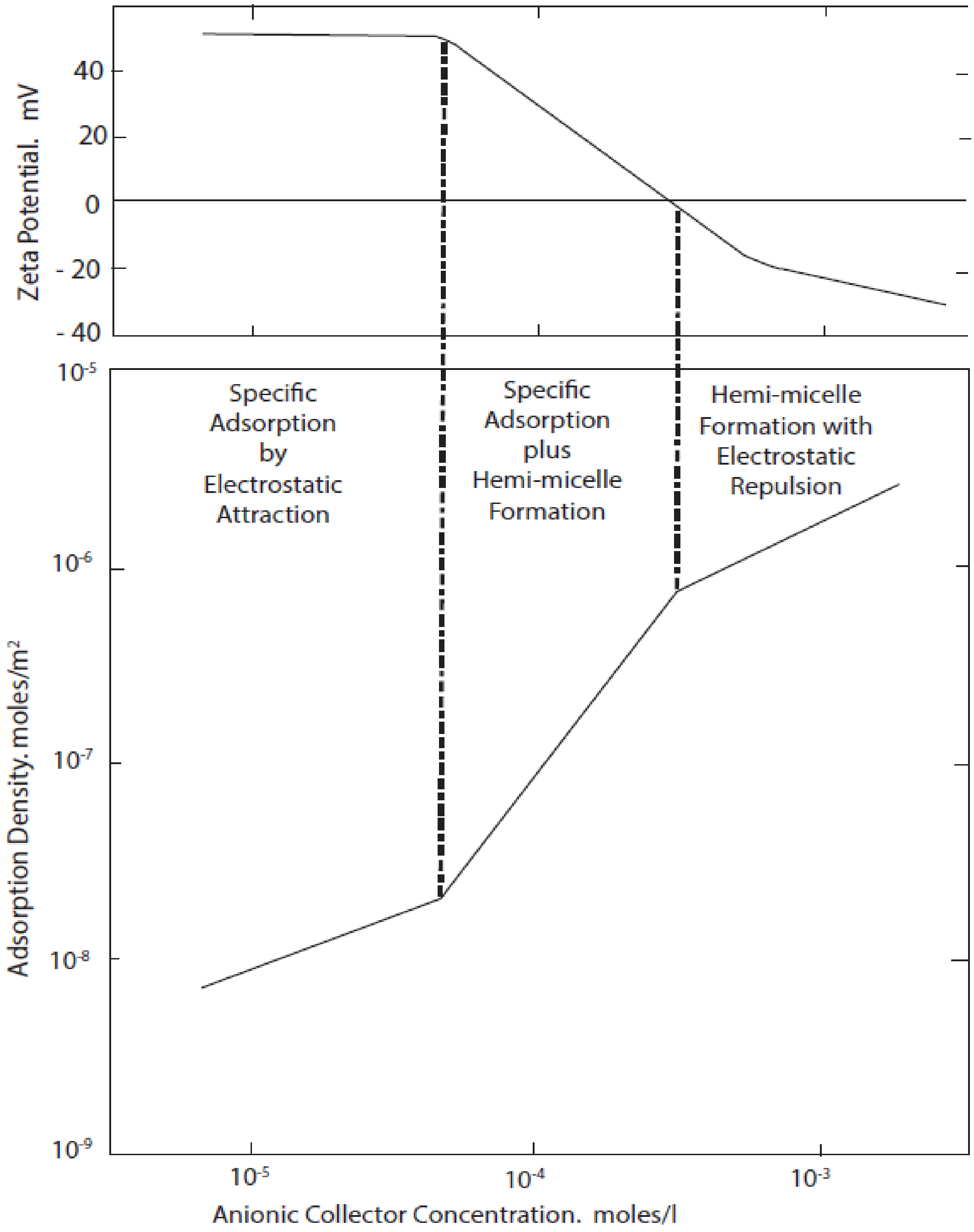

Figure 2.4: Adsorption isotherm and corresponding zeta potential.

Figure 2.4 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 Figure 2.5.

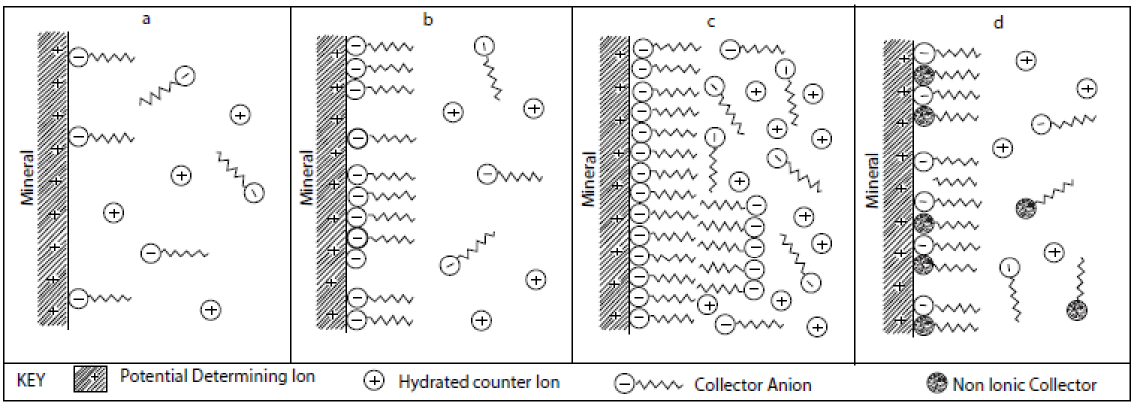

Figure 2.5: A schematic representation of the mineral solution interface in the presence of an anionic collector (a) Single adsorption at low concentration (b) Hemi-micelle (c) Multilayer adsorption (d) Co-adsorption of the neutral molecules (Gaudin, 1932).

It is illustrated in Figure 2.4 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. Figure 2.5 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).

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 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 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 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 absorb 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 Ca^{2+} and 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.

2.10 A Summary and Critic of Literature Perspectives

The Tables 2.2-2.4 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 2.2: 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)	• Ca^{2+} and thiosulphate ions: – Activated the flotation of sulphides with xanthate – Improved the selectivity of nickel separation. – Increased xanthate adsorption onto sulphide minerals. • $MgCl_2$ and $CaCl_2$: – Reduced the floatability of molybdenite and chalcopyrite at $pH > 9$. – Depressing effect was proportional to their concentrations. – Reduced both the hydrophobicity and surface charge of $CuFeS_2$ and MoS_2.
Ikumapayi and Rao (2015)	• Ca^{2+} and SO_4^{2-} ions resulted in: – Marginally lower recoveries of $CuFeS_2$ and PbS using PAX. – ZnS floatability increase in SIBX. – The presence of surface oxidized sulfoxy species and surface calcium carbonates and/or calcium sulphate on $CuFeS_2$ and PbS at flotation pH 10.5 as revealed by FTIR and XPS studies. – Surface species influencing xanthate adsorption. – Surface-oxidized sulfoxy and carbonate species on ZnS surface at pH 11.5. – Higher $CuFeS_2$, PbS, and ZnS recoveries from two different complex sulphide ores.
Shackleton *et al.* (2012)	• In the absence of reagents: – Addition of cation and anion to deionised water reduced moncheite, pentlandite and pyroxene recovery. • Upon xanthate addition: – The recovery of moncheite and pentlandite increased. – 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. – 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. – Xanthate seemed to counteract both the effects of ionic strength and cation and anion concentrations in process water. • It was concluded that there seems to be a synergistic effect between ionic strength and ion concentration in process water. • The ions in the process water seemed to play a more significant role compared to ionic strength in mineral surface alteration and floatability.

Table 2.3: 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)	• Ca^{2+} and Mg^{2+} ions increased the adsorption of depressants onto talc. • Adsorption increased with an increase in the ionic strength. • Ca^{2+} ions reacted with the carboxylic acid groups of CMC. • Ca^{2+} ions adsorbed onto talc in the form of $CaOH^+$ ions. • $CaOH^+$ ions on the surface increased the number of the available metallic sites, thus promoting CMC adsorption. • An acid-base mechanism of interaction with metal hydroxo species on the mineral surface.

Table 2.4: 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)	• High flotation recoveries in the presence of electrolytes. • Bubble size decreased and gas hold-up increased with an increase in [NaCl]. • At a 0.4 M NaCl, the gas dispersion properties were comparable to those of 10 ppm MIBC. • $AlCl_3$ had the highest effect on froth stability followed by $CaCl_2$ and NaCl. • Froth stability increased with increasing ion valence. • Surface tension reduction (on solutions containing MIBC and DF250) was greater in NaCl/KCl compared to distilled water. • Finer bubbles in the presence of electrolytes than with frothers were generated. • Recovery by true flotation and entrainment increased. • Frothability increased sharply with increasing pH. • Increase in electrical repulsive forces at the bubble surface. • Reduction in the electrostatic interactions between particle and bubble. • The thinning of the liquid film between bubbles was retarded. • Bubble coalesce decreased with increasing concentration. • Slow inter-bubble film drainage occurred.

2.10.1 *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 Ca^{2+}, Mg^{2+}, sulphate and bicarbonate ions on sulphide minerals has been investigated (Barker, 1986; Ikumapayi *et al.*, 2012; Rao *et al.*, 2016). Ca^{2+} adsorption on pyrite, galena and other sulphide minerals is reported to increase with increasing pH and Ca^{2+} concentration thereby hindering the collector from adsorbing onto surface of the mineral (Gaudin and Charles, 1953; Rao e*t al.*, 2016). It has been shown that an increase in the concentration of divalent cations, Ca^{2+} and 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.*, 2015; 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, 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 $mol.dm^{-3}$ 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 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 Ca^{2+} adsorbs readily by electrostatic attraction. The presence of 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 Ca^{2+} and 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 $CaOH^+$ and magnesium as the $Mg(OH)_2$ 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 $M\text{-}OH^+$ 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 $M\text{-}OH^+$ 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 2.5.

Table 2.5: 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 Ca^{2+}, Mg^{2+} and 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.

2.10.2 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 2.6.

Table 2.6: 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.*

2.10.3 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. Ca^{2+}) would enhance the anionic thiol collector adsorption and thus impart the desired hydrophobicity on the value bearing sulphide minerals. Concurrently, 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.

2.11 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.

2.12 Acknowledgements

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CHAPTER 3 RESEARCH APPROACH

3.1 Aims & Key Questions

In line with the identified gap in literature, this study considers the effects of ionic strength, electrolyte type and their ionic strength on the froth phase, using froth stability as a key indicator, as well as effects on the pulp phase with a keen focus on the efficacy of CMC on gangue depression. This is aimed at gaining a better understanding on the simultaneous enhancement of froth stability and hydrophilicity and the mechanism through which this occurs. Thus, for the purpose of this study the specific objectives of this work are structured in the form of key questions and consider the froth phase and the pulp phase in order to identify dominant or controlling electrolytic process water conditions which impact on froth stability and hydrophilicity using a Merensky ore and selected minerals.

The effects of water quality on the froth phase consider the following key questions:

- ✓ Which ions have the biggest impact on froth stability?
- ✓ How does the ionic strength of plant water affect froth stability?

The effects of water quality on the pulp phase consider the following key questions:

- ✓ How does the ionic strength and ion type of plant water affect CMC adsorption onto selected minerals (talc and pyrrhotite) common to a Merensky ore?
- ✓ How does the ionic strength and ion type of plant water affect the surface charge of selected minerals (talc and pyrrhotite) common to a Merensky ore?

Considering the key questions put forward, the main research question is: **what role does the presence of electrolytes in high concentration (as a result of water recycling) play on flotation reagent behaviour as a result of possible alterations in electrolyte-CMC-solids interactions in the flotation of a PGM containing ore?**

3.2 Hypotheses

There are electrolytic conditions in process water (as regards electrolyte type and ionic strength) whose influence on electrolyte-reagent interaction in the flotation of a PGM bearing ore is more pronounced owing to modifications on frothability, mineral collection, and gangue activation or deactivation. **Thus, the specific research or key hypotheses in line with the Main Hypothesis and Key Questions are:**

Froth phase phenomena hypotheses:

- ✓ *Increased concentrations of divalent cations in process water will increase froth stability owing to their stronger ability to reduce bubble coalescence compared to monovalent cations.*
- ✓ *An increase in the ionic strength of process water increases the stability of the froth because the electrolytes in process water retard bubble coalescence.*

Pulp phase phenomena hypothesis:

- ✓ *An increase in the ionic strength of plant water will increase CMC adsorption onto selected minerals (talc and pyrrhotite) common to a Merensky ore due to the reduction of the negative surface charge as a result of increased concentrations of cations and hydroxo species adsorbed onto the mineral surface which enable an interaction between CMC and the passivated mineral surface*

3.3 Summary of Experimental Techniques

Table 3.1 gives a summary of the key questions that this thesis dissertation is addressing, the conditions being varied and fixed, the experimental techniques used to address the corresponding key question as well as performance indicators or measures that this dissertation is reporting on as a means to answering the key questions. Details on the experimental techniques are given in the subsequent results chapters as indicated in the column entitled "Experimental technique" in Table 3.1.

Table 3.1: Research Approach to Investigate Research Questions.

Phase	Key Question	Conditions	Indicator /Measure	Experimental technique
Froth	1. Which ions have the biggest impact on froth stability?	Fixed IS – varying ions	3-phase Water recovery Froth Height Froth collapse time	Batch Flotation (Chapter 7 & 8) Froth Column (Chapter 8)
	2. How does the ionic strength of plant water affect froth stability?	Fixed ion/recipe – varying IS	2-phase Water Recovery 3-phase Water recovery Froth Height Froth collapse time	Batch Flotation (Chapter 4 & 5) Froth Column (Chapter 4 & 5)
Pulp	1. How does the ionic strength and ion type of plant water affect depressant adsorption onto selected minerals (talc and pyrrhotite) common to a Merensky ore?	Fixed IS – varying reagents Fixed reagents – varying IS	NFG recovery Talc & Pyrrhotite recoveries Adsorbed concentration Settling time	Batch Flotation (Chapter 4& 8) Microflotation (Chapter 6 &8) Du Bois Method (Chapter 6) Flocculation (Chapter 4, 6, & 8)
	2. How does the ionic strength and ion type of plant water affect the surface charge of selected minerals (talc and pyrrhotite) common to a Merensky ore?	Fixed IS – varying ions Fixed ion/recipe – varying IS Fixed IS – varying chemistry	Zeta Potential	Zetasizer (Chapter 6 & 8)

CHAPTER 4 WATER QUALITY EFFECTS ON A SULFIDIC PGM ORE: IMPLICATIONS FOR FROTH STABILITY AND GANGUE MANAGEMENT

4.1 Rationale, Key Questions & Hypotheses

The development of water management protocols in flotation relies on the provision of sound and fundamental scientific evidence examining and decoupling the effects of water quality on the sub-processes of flotation. Work done by Corin *et al.* (2011) and Corin and Wiese (2014) showed that, inter alia, froth stability increases with increasing ionic strength as in the case of increased frother dosages and that increased ionic strength recovered far more water and therefore entrained gangue compared to increases in frother dosage. This study considers the interactive effects of both ionic strength and depressant dosage on froth stability and entrainment with key questions and hypotheses outlined in Section 4.1.1 and 4.1.2 respectively in order to understand the potential influence of recycling into the pulp chemistry and implications on the froth phase as would be measured by mineral floatability and froth stability indicators.

4.1.1 Key Questions

- How do changes in the ionic strength of plant water affect froth stability?
- How do changes in the ionic strength of plant water affect the efficacy of CMC on gangue depression?

4.1.2 Hypotheses

- *An increase in the ionic strength of process water increases the stability of the froth because the electrolytes in process water retard bubble coalescence.*
- *An increase in the ionic strength of plant water will decrease the floatability of gangue owing to increased concentrations of cations and hydroxo species adsorbed onto the mineral surface which enable an interaction between CMC and the passivated mineral surface.*

4.2 Abstract

Polysaccharide depressants play a crucial role in the flotation of sulfidic PGM bearing ores as they prevent naturally floatable gangue (NFG) from reporting to the concentrate. This action is regarded as critically important because less dilution of the concentrate means lower costs for downstream processes. However, abnormal water conditions such as high concentrations of ions in the flotation system can modify the selectivity of these depressants. It is well known that the existence of selected electrolytes in water can alter the behaviour of some polysaccharide depressants by enhancing their adsorption onto gangue minerals and thereby prevent naturally floatable gangue from moving into the froth phase. Concurrently these same electrolytes may enhance frothability owing to their stabilising effect on the bubbles within the system. Plant water at various ionic strengths was investigated against sodium carboxymethyl cellulose (CMC) dosages in order to understand electrolyte-depressant interactive effects during the flotation of a Merensky ore in a batch flotation cell, using entrainment, rate of NFG recovery, and total gangue recovery as proxies. The study showed that the NFG recovery per unit mass of water decreased with increasing ionic strength at all CMC dosages, however the total amount of gangue reporting to the concentrate increased with increasing ionic strength at all CMC dosages. Thus, this paper considers the effects of both ionic strength and CMC dosage within flotation. It further investigates whether any interactive effects exist between froth stability and entrainment when considered simultaneously.

KEYWORDS

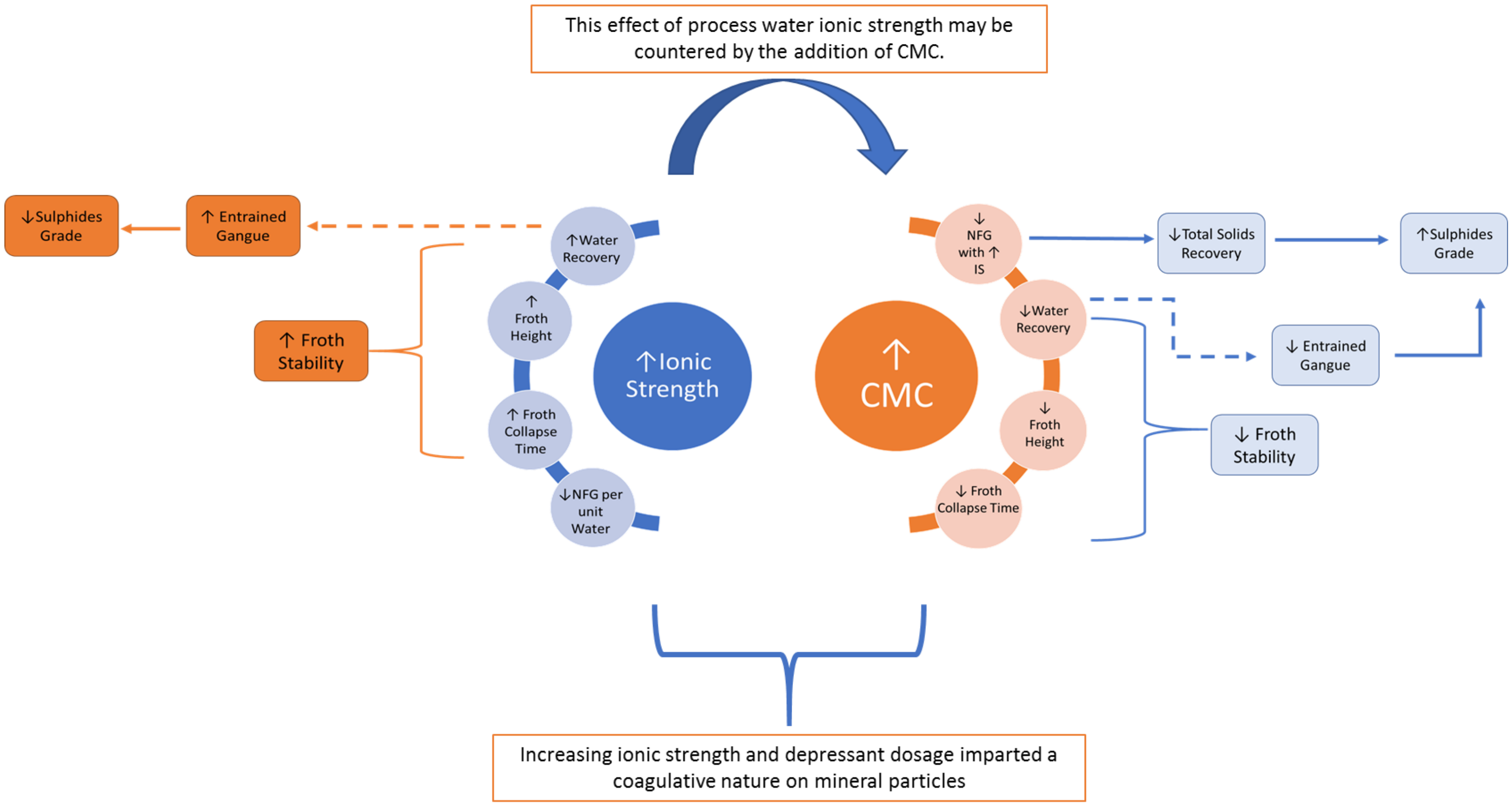
Depressant behaviour, Electrolytes, Entrainment, Froth Stability, Water quality

4.3 Highlights

- Froth collapse time, froth height and water recoveries indicated an increase in froth stability in increasing ionic strengths.
- Increases in solids recovery with increasing ionic strength were largely caused by increases in entrained gangue.
- The froth stabilising action of electrolytes was less effective at higher CMC dosages
- NFG recovery did not change with ionic strength but dropped significantly in the presence of CMC
- Increasing ionic strength and depressant dosage imparted a coagulative nature on mineral particles

4.4 Graphical Abstract

Counter-Active Relationship between Ionic Strength and CMC Dosage on Froth Stability


This effect of process water ionic strength may be countered by the addition of CMC.

Increasing ionic strength and depressant dosage imparted a coagulative nature on mineral particles

4.5 Introduction

It is well known that in flotation, particles can either reach the froth by being attached to the bubbles (true flotation) or by entrainment in the physical movement of the water passing from the pulp zone to the froth zone (Liddell *et al.*, 1986). While true flotation is selective and is responsible for the collection of the hydrophobic valuables, entrainment is unselective and results in unwanted gangue reporting to the flotation concentrate (Smith and Warren, 1989; Yianatos *et al.*, 1988). It is for this reason that flotation plant operating procedures have to be directed towards maximising the recovery by true flotation whilst minimising contributions to the concentrate by entrainment. The contribution of the entrained material to overall flotation increases linearly with an increase in water recovery (Warren, 1985). This suggests that there is an interactive effect between froth stability and entrainment as previous studies have shown that water recovery can be used as an indication of froth stability (Corin and Wiese, 2014; Corin *et al.*, 2011; Manono *et al.*, 2013, 2012). It is also known that naturally floatable or hydrophobic gangue such as talc predominantly enters the concentrate by true flotation; therefore polysaccharide depressants are used to increase the selectivity of the flotation process by adsorbing onto the surface of the hydrophobic gangue particles (Bradshaw *et al.*, 2005; Dhliwayo, 2005; Shortridge *et al.*, 2003; Wiese, 2009); thus the recovery of gangue is reduced through rendering naturally floatable gangue (NFG) non-floatable (Robertson, 2003). It is known that polymer adsorption on talc and the subsequent depression of NFG is influenced by many variables. These include polymer type and concentration, molecular weight, degree of substitution, pH, and ionic strength (Parolis *et al.*, 2008; Shortridge *et al.*, 2003, 1999). Shortridge *et al.* (2003) and Burdukova (2007) have shown that the depression of gangue minerals such as talc is improved in the presence of divalent cations such as Mg^{2+} and Ca^{2+}, and that the ionic strength of the solution plays a crucial role in CMC adsorption onto talc. Therefore taking cognisance of the enhancement of polysaccharides NFG depression by divalent cations and the fact that most flotation circuits use recycled water containing high amounts of dissolved ions. These factors might contribute to the complexity of the flotation process by negatively or positively affecting the efficiency of the flotation process through complex or less understood reagent interactions (Slatter *et al.*, 2009). With the rise in the use of extremely saline water in flotation (George, 1996; Haig-Smillie, 1972; Ikumapayi *et al.*, 2012; Laskowski *et al.*, 2003; Nesset *et al.*, 2007; Paulson and Pugh, 1996, Peng and Seaman, 2011; Pugh *et al.*, 1997; Quinn *et al.* 2007), many studies have been carried out to determine how the presence of ions and increases in the ionic strength of plant water can affect the depression of NFG in sulphide flotation (Becker *et al.*, 2009; Corin *et al.*, 2011; Manono *et al.*, 2012; Muzenda, 2010; Shortridge *et al.*, 2003; Wiese, 2009). Barker (1986) showed that an increase in the concentration of the divalent cations, Ca^{2+} and Mg^{2+}, resulted in an increase in the recovery of pyrite, and a dramatic decrease in gangue recovery. It was further theorised that in an alkaline medium Ca^{2+} reacts with products of sulfur oxidation and atmospheric carbon dioxide to form calcium sulphate and calcium carbonate films, these films usually increase the hydration of pyrite and thus increase the depression of pyrite by hindering the collector from adsorbing onto the surface of pyrite (Glembotskii *et al.*, 1972; Klaasen and Mokrousov, 1963). Concurrently froth stability was increased with the addition of these divalent cations. An increase in the concentration of cations such as Na^+, Ca^{2+} and Mg^{2+} resulted in an increase in pyrite recovery, a slight decrease in gangue recovery, and an improved froth stability. Previous research on talc and pyrite established that Ca^{2+} ions added as lime used for pH adjustment are reported to contribute to the depression of mineral particles (Barker, 1986; Burdukova, 2007; Iwasaki *et al.*, 1980; Laskowski *et al.*, 2007). Above pH 7, the surface of minerals such as pyrite and talc is negatively charged, and calcium adsorbs readily by electrostatic attraction. The presence of Ca^{2+} ions hinders the collector to mineral reaction on the pyrite surface. Also it has been established that in the presence of cations such as Ca^{2+} and Mg^{2+}, the depression activity of carboxymethyl celluloses on talc is enhanced, however a detrimental effect of these ions is that they may activate the unwanted gangue, or depress the targeted mineral (Zhang *et al.*, 1997). A recent study which considered the effect of various single salt solutions on the flotation of a similar ore to that of the present study suggested that NO_3^- had a depressing effect in flotation as it resulted in superior Cu and Ni grades compared to Cl^- and SO_4^{2-} (Manono *et al.*, 2016). A study by Corin *et al.* (2011) on the effect of the ionic strength of plant water on a Merensky type ore showed that an increase in the ionic strength of plant water from 0.0241 to 0.0723 mol.dm-3 did not significantly affect the recovery of the sulphide minerals, however it was noticeable that the concentrate grades were decreased significantly as solids and water recoveries were noted to have increased. The higher solids and water recoveries which were observed at higher ionic strength were due to an increase in the total gangue reporting to the concentrate. Also, Corin and Wiese (2014), in a comparative study of ionic strength and frother dosage, showed that increasing the ionic strength of plant water resulted in far more total entrained gangue compared to increases in frother dosage. However, the entrained gangue per unit water decreased with increasing ionic strength of process water; as a result, increasing the ionic strength had a relatively negative influence on Cu and Ni grades compared to increased frother dosages, suggesting the importance of the influence of ionic strength in process water on the stability of the froth and entrainment. From these findings it is speculated that the increase in ionic strength affected the selectivity of the system in that depressant behaviour and froth stability were altered; and these, among others, are the basis of the current work. It is important to note that not much evidence was given to ascertain the claims of increased froth stability in increasing ionic strength.

Kracht *et al.* (2016) showed that entrainment depends on the surfactant type; these findings are in agreement with McFadzean *et al.* (2016) who also showed that entrainment and true flotation had a strong reliance on the frother (or surfactant type). It is of cardinal importance to understand the role of the ionic strength of process water on the stability of the froth and entrainment given that electrolytes at increased ionic strength have been shown to exhibit a frother-like behaviour in flotation.

Altogether, the literature presented here provides a baseline to understanding the role of ions and their concentration as well as depressant dosage on both the depression of gangue minerals and froth stability in the flotation of sulfidic mineral ores. However, there is little research that considers the interactive effects of both ionic strength and depressant dosage in relation to froth stability and entrainment. Thus, this paper attempts to consider the effects of both ionic strength and depressant dosage in flotation. It further looks to investigate whether any interactive effects exist between these two factors when considered simultaneously.

4.6 Materials & Methods

4.6.1 Benchscale Flotation

A PGM bearing ore sample was obtained from the Merensky reef of the Bushveld Igneous Complex (BIC) of South Africa. Mineralogical analyses were performed on the sample using QEMSCAN and the mineralogy data shown in Table 4.1 was obtained. The received bulk sample was crushed, blended, riffled and split using a rotary splitter into 1 kg samples. The prepared 1 kg ore samples were milled in synthetic plant water (at the required ionic strength) at 66% solids using a laboratory scale Eriez stainless steel rod to achieve a grind of 60% passing 75 μm. The mill had a diameter of 200 mm, charged with 20 stainless steel rods of varying diameter in the following ratio: 6 x 25 mm, 8 x 20 mm and 6 x 16 mm. The desired grind size was achieved after approximately 14 minutes of milling. Standard synthetic plant water (Wiese *et al.*, 2005) was used as the base water quality with a total dissolved solids (TDS) of 1023 mg/L and an ionic strength (IS) of 0.0242 mol.dm^{-3}. This standard synthetic plant water (1SPW) used to resemble typical South African Cu-Ni-PGM concentrator water quality (Wiese *et al.*, 2005). In preparing 3SPW, 5SPW and 10SPW, the amount of ions in the synthetic plant water was increased to 3069 mg/L, 5115 mg/L, and 10230 mg/L TDS respectively as shown in Table 4.2.

As per Wiese *et al.* (2005), the milled slurry was transferred to a 3 L Barker batch flotation cell. The volume of the cell was made up to generate 35% solids (pulp density) using synthetic plant water (at the required ionic strength). The cell was fitted with a variable speed drive and the pulp level was controlled manually. The impeller speed was set to 1200 rpm. An air flow rate of 7 L/min was maintained for all flotation experiments and a constant froth height of 2 cm was sustained throughout by the addition of synthetic plant water at the required ionic strength. Concentrates were collected at 2, 6, 12 and 20 min respectively by scraping the froth into a collecting pan every 15 s. A feed sample was taken before and a tails sample after each flotation test. Water usage was monitored throughout. Feeds, concentrates and tails were filtered, dried and weighed before analysis. All batch flotation tests were conducted in duplicate and reproducibility was found to be within 5% mass and water recovery standard error. The collector and frother dosages were kept constant throughout the study at 150 g/t sodium isobutyl xanthate (SIBX) and 40 g/t polyglycol frother (DOW 200) respectively. The polymeric depressant used was Depramin 267, a sodium carboxymethyl cellulose (CMC) with a molecular weight of 325 000 g/mol, purity of 72% and degree of substitution of 0.68. Tests were conducted in the absence of CMC (0 g/t CMC) and in the presence of the CMC at dosages of 100 and 500 g/t., corrected for active content as is industry practice. The experimental procedure was such that the collector solution was added to the mill, as Wiese *et al.* (2005) showed this to have a significant effect on flotation performance. The collector, SIBX, was supplied by Senmin. Depramin 267 was supplied by AkzoNobel Functional Chemicals. The frother, DOW 200, was supplied by Betachem. All the chemical salts used to make up the synthetic plant water solutions were supplied by Merck. In performing the required mass balance, total Cu and Ni assays of all samples were carried out using a Bruker S4 Explorer XRF Spectrometer. Total S assays were conducted using a LECO DR423 sulfur analyser. Upon acquiring the total Cu, Ni and S assays of all samples (from feed, concentrate and tails) and making use of the compositions given in Table 4.1, the necessary flowsheet and mass balancing were carried out. The findings of Wiese (2009) which reported a total depression of naturally floatable gangue upon the addition of CMC beyond 300 g/t were considered in the mass balance. Thus at the selected CMC dosage of 500 g/t, all gangue that reports to the concentrate would do so through entrainment rather than true flotation. The method developed by Wiese (2009) allows for the computing of the degree of entrainment. This in turn enables the computing of entrained gangue and NFG recoveries at each CMC dosage. It is worth mentioning that for the given ore, the degree of entrainment decreased with increasing ionic strength as reported in Manono *et al.* (2012) and that values reported therein enabled the determination of the NFG recovery results shown in Figure 4.5.

Table 4.1: Modal Composition: Sulphide and Gangue Minerals Present in the Ore as Determined by QEMSCAN.

Mineral	**Weight %**
Pentlandite	0.31
Chalcopyrite	0.25
Pyrrhotite	0.44
Pyrite	0.08
Other sulphides	0.02
TOTAL sulphides	1.09
Plagioclase	43.38
Orthopyroxene	32.60
Olivine	0.59
Clinopyroxene	7.48
Talc	3.51
Serpentine	0.80
Chlorite	0.83
Phlogopite	0.46
Quartz	0.67
Calcite	0.18
Oxides	8.10
Other	0.32
TOTAL	100.00

Table 4.2: Synthetic Plant Water Types and their Ion Compositions.

Water type	**Ca^{2+} (ppm)**	**Mg^{2+} (ppm)**	**Na^{+} (ppm)**	**Cl^{-} (ppm)**	**SO_4^{2-} (ppm)**	**NO_3^{-} (ppm)**	**CO_3^{2-} (ppm)**	**TDS (mg/L)**	**IS [M]**
1SPW	80	70	153	287	240	176	17	1023	0.0242
3SPW	240	210	459	861	720	528	51	3069	0.0727
5SPW	400	350	765	1435	1200	880	85	5115	0.1212
10SPW	800	700	1530	2870	2400	1760	850	10230	0.2426

4.6.2 Froth Column Tests

In order to investigate whether there are any interactive effects and the nature thereof between the ionic strength of plant water and CMC depressant dosage on froth stability; froth collapse time and froth height measurements were obtained from a 3-phase froth column cell. The froth column was made of Perspex with a diameter of 10 cm and a height of 1 m. The air flow rate of the column was maintained at 7 L/min. A pore-2 frit was used to regulate the bubble size produced by the air entering the column. 1 kg ore samples were milled in the presence of synthetic plant water and 150 g/t SIBX. The milled slurry was transferred into a bucket where CMC was added such that the dosage was 0, 100 or 500 g/t and allowed to condition for 3 minutes, thereafter DOW 200 frother was added at 40 g/t and allowed to condition for 1 minute. The slurry was then pumped into the column until a height of 200 mm was reached; thereafter, simultaneously, the pump was stopped and the inlet valve to the column was closed to prevent slurry backflow. The agitator inside the column was switched on once the slurry reached the level of the impeller. Air was sparged into the column and a rotameter was used to maintain the air flow rate as mentioned. Once the froth stopped rising; reaching equilibrium, the froth height was measured, and immediately after, the air flow was stopped and the froth collapse time was recorded. A schematic diagram of the column is shown in McFadzean *et al.* (2016).

4.6.3 Coagulation Tests

1 kg ore samples of the selected Merensky ore were milled in the presence of water at the required ionic strength to achieve a grind of 60 % passing 75 µm. The slurry was transferred into a 3 L Barker batch flotation cell and synthetic plant water was added in order to make up 35 % solids by volume. Thereafter, CMC was added at a dosage of 0 g/t, 100 g/t or 500g/t and was allowed to condition for 3 minutes whilst agitating the pulp at an impeller speed of 1200 rpm. The impeller was then stopped and the time it took for the particles to settle to a near clear supernatant above the settled solids was recorded. The level of the interface between the supernatant and the settled particles for 1SPW 0g/t CMC condition was marked and kept constant for all the runs so that there was consistency in the results as well as allowing for a comparison in settling time with different water types and depressant dosage. This meant that the 1SPW 0 g/t CMC condition was used as the baseline for all other conditions.

4.7 Results

4.7.1 The Effect of Ionic Strength of Plant Water and Depressant Dosage on Sulphides Floatability & Froth Stability

The total amount of solids recovered, water recovered, total sulfides (S) recovery, total sulfides (S) grade, and NFG recovery results are presented for all water qualities investigated in the absence and presence of CMC.

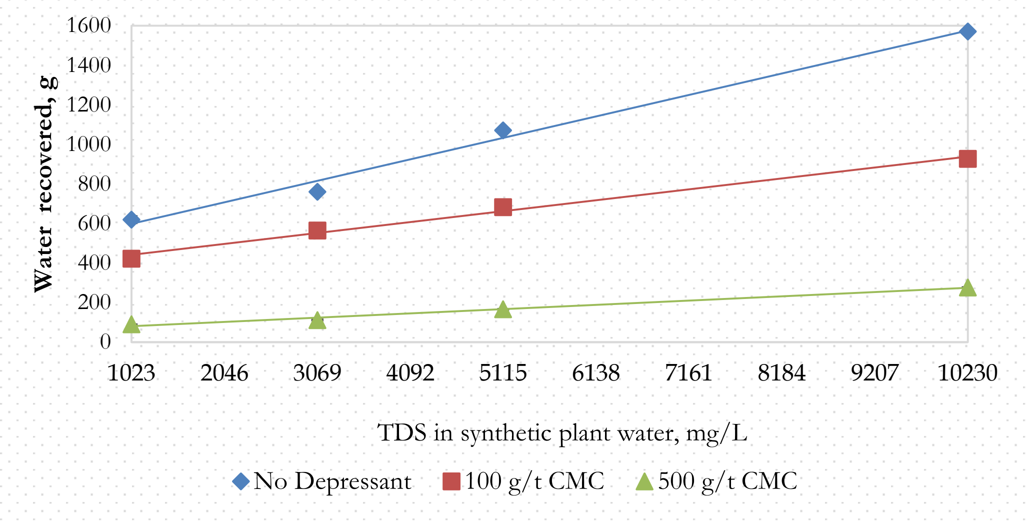


Figure 4.1: The amount of water reporting to the concentrate as a function of total dissolved solids in plant water from the 3-phase batch flotation tests.

Figure 4.1 shows the total amounts of water recovered at all CMC dosages. These results indicate that the recovery of water decreased with increasing CMC dosage at all ionic strengths of plant water but an increase in the ionic strength of plant water increased the amount of water recovered.

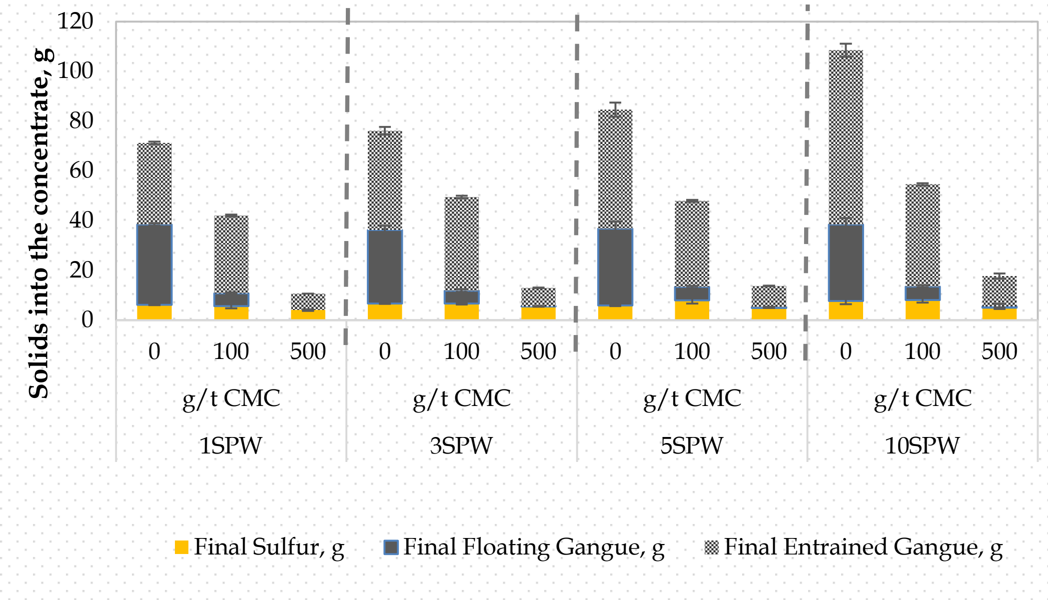


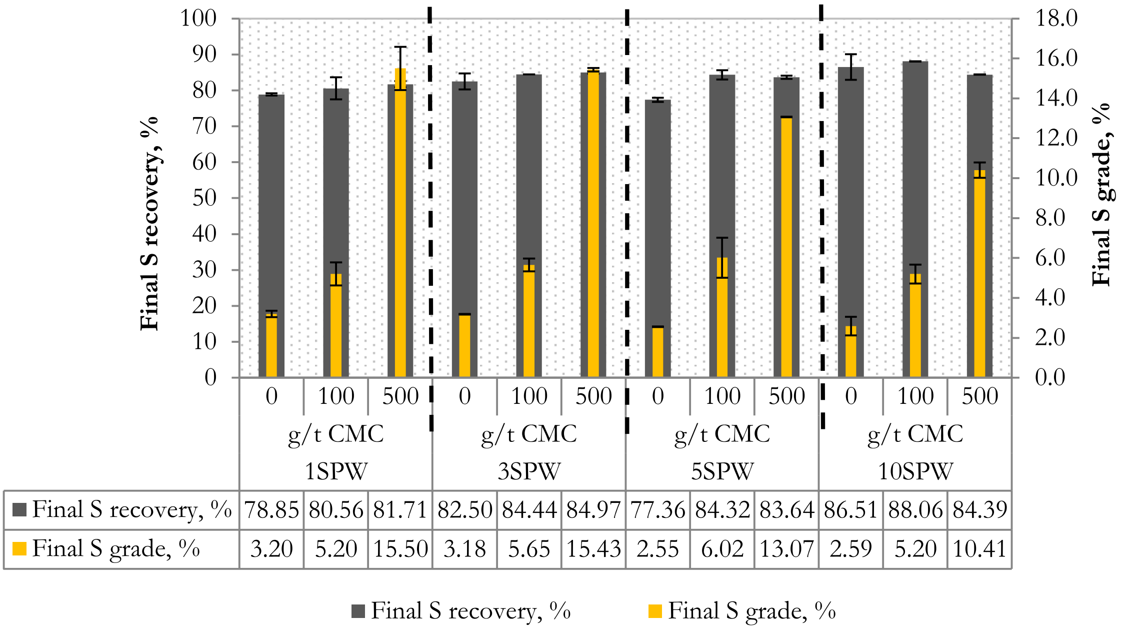
Figure 4.2: The amount of solids reporting to the concentrate for all conditions tested.

Figure 4.2 shows the total amount of solids reporting to the concentrates for all tested conditions. This is split into three fractions, namely, floating gangue (NFG), entrained gangue and sulfides (sulfur). The results depicted in Figure 4.2 illustrate that at all depressant conditions, the total amount of solids recovered increased with an increase in the ionic strength of plant water as previously reported in Manono *et al.* (2012).

Changes in water quality, in the absence of CMC (i.e. at 0 g/t CMC), seemed not to have affected the amount of floating gangue, instead the total amount of entrained gangue increased with increasing ionic strength whilst a trend of a slight increase in the amount of sulfides was reported.

At a depressant dosage of 100 g/t, a decrease in the amount of NFG and entrained gangue is observed compared to 0 g/t for each corresponding ionic strength, however, the trend of a constant amount of NFG in increasing ionic strengths was sustained and that the fraction of entrained gangue increased with increasing ionic strength although this was still significantly lower than its comparative values in the absence of CMC. Generally, the total amount of sulfides reporting to the concentrate increased with increasing ionic strength at 100 g/t, reporting values that are comparatively higher than the 0 g/t for 5SPW and 10SPW.

At the higher dosage of 500 g/t, CMC proved its strong depressing ability in that the total amount of solids decreased greatly at all ionic strengths, this is mostly due to the much greater decrease in the entrained gangue owing to the depression of NFG which destabilises the froth and this is discussed later. Also, at 500 g/t CMC, there remained a general trend of an increase in total entrained gangue and sulfides with increasing ionic. Little or no NFG reported to the concentrates at all ionic strengths.



	1SPW			3SPW			5SPW			10SPW		
g/t CMC	0	100	500	0	100	500	0	100	500	0	100	500
■ Final S recovery, %	78.85	80.56	81.71	82.50	84.44	84.97	77.36	84.32	83.64	86.51	88.06	84.39
■ Final S grade, %	3.20	5.20	15.50	3.18	5.65	15.43	2.55	6.02	13.07	2.59	5.20	10.41

Figure 4.3: Final total sulphide recoveries and grades for all synthetic plant water types and depressant dosages.

Figure 4.3 shows the cumulative final total sulphide recovery and grade for all tested conditions. It can be said that the recovery of sulfides (S) increased with increasing ionic strength and that increases in depressant dosages were not detrimental to the recovery of sulfides (S). Also, it is interesting to note that the highest total sulphide recoveries were obtained with 10SPW for all depressant dosages. However, the grades decreased with increasing ionic strength of plant water at all depressant dosages. Moreover, an increase in the concentrate grade was observed upon increases in CMC dosage. The trend of a decrease in the concentrate grade with increasing ionic strength was more pronounced at 500 g/t CMC compared to 0 and 100 g/t CMC, particularly when comparing 5SPW and 10SPW to baseline water quality (1SPW).

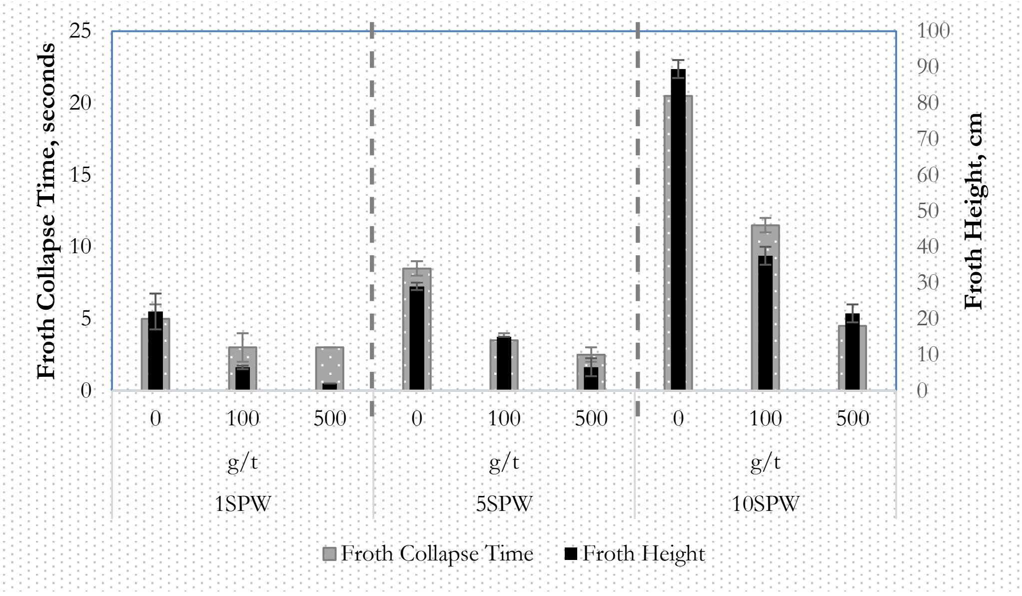


Figure 4.4: Three-phase froth collapse time as a function of water type and CMC depressant dosages.

Figure 4.4 shows the time (on the primary y-axis) that it took for the froth to collapse to its initial height. The maximum froth height results are also shown on the secondary y-axis. These results show that the froth collapse time increased in increasing ionic strengths of plant water. However, an increase in CMC dosages resulted in a decrease in the froth collapse time. These findings clearly show an increase in froth stability with increasing ionic strength whilst the addition of CMC destabilised the froth.

4.7.2 Interactive Effect of Ionic Strength of Plant Water and Depressant Dosage on the Floatability of Gangue

Corin *et al.* (2011) investigated the effect of ionic strength (up to the ionic strength of 3SPW) on a similar ore using guar and showed that the floatability of NFG per unit mass of water decreased with increasing ionic strength. They ascribed their findings to a coagulative impartation on NFG by guar in increased ionic strength. Therefore it was deemed important for this study to consider the floatability of NFG per unit mass of water at higher ionic strengths (i.e. 5SPW and 10SPW) and to ascertain whether similar findings would be obtained with CMC. Furthermore, settling tests were performed to further ascertain the claims of a coagulative impartation onto NFG in increased ionic strengths in the presence of polysaccharides. The results of the floatability of NFG and coagulation of the Merensky ore are presented in Figure 4.5 and Figure 4.6 respectively.

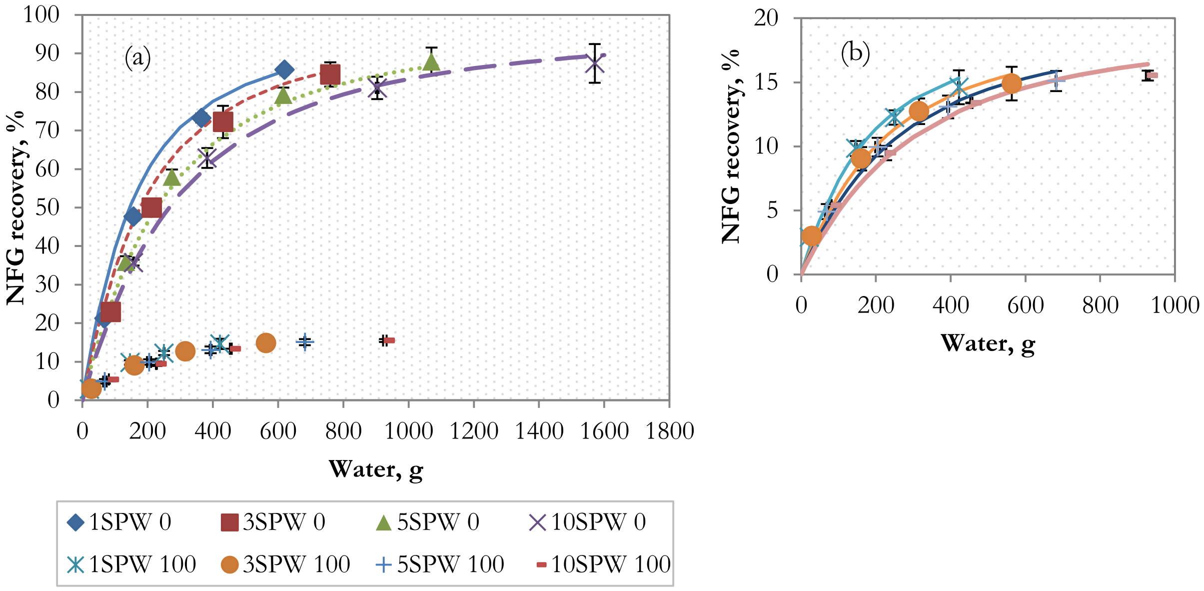


Figure 4.5: NFG recovery as a function of the amount of water recovered for all ionic strengths of plant water at (a) 0 g/t and 100 g/t CMC (b) 100 g/t showing a zoomed in version of the data shown in (a).

The data presented in Figure 4.5 was fitted into a first order model. It is evident that the floatability of NFG per g of water decreased with increasing ionic strength at both 0 g/t and 100 g/t CMC. Moreover, it is also interesting to note that total NFG recovery decreased significantly with increasing CMC dosage such that no floating gangue reported to the concentrate at 500 g/t CMC as seen Figure 4.2.

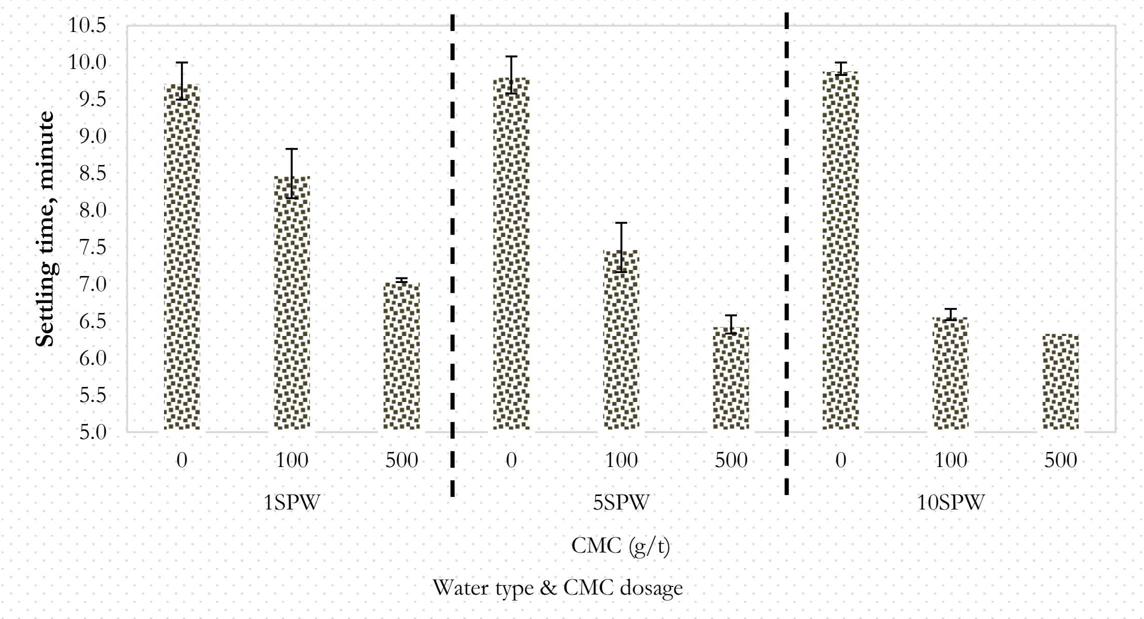


Figure 4.6: Settling time as a function of water type and CMC depressant dosages.

Figure 4.6 shows the settling time of the Merensky ore solids for each water type in the presence and absence of CMC. Figure 4.6 shows a clear trend of a decrease in the settling time of solids with increasing CMC dosage for each water type. In the presence of CMC, the settling time decreased with increasing ionic strength of plant water. However, in the absence of CMC the trend was somewhat different in that increases in ionic strength did not affect the settling time of solids.

4.8 Discussion

4.8.1 Effect of Ionic Strength and Depressant Dosage on Frothability

This study has shown that as the ionic strength increased, the amount of solids and water recovered and the froth collapse time increased at all depressant dosages. This was indicative of an enhancement in froth stability by the increases in the ionic strength of plant water. This effect is attributed to the presence of inorganic electrolytes such as Ca^{2+} which inhibit bubble coalescence as reported by Craig (2004) and Quinn *et al.* (2007). It is important to note that with the investigated synthetic plant waters, the concentration of Ca^{2+} increases from 80 to 800 mg/L as shown in Table 4.2. Work within the CMR by Manono *et al.* (2013) showed that the bubble size decreased with increasing ionic strength whilst foam collapse time increased with an increase in ionic strengths in 2-phase systems.

This present study has also shown that increasing the ionic strength resulted in an increase in total entrained gangue, and thereby increased the amount of solids recovered as a result of increased water recoveries. It has been postulated that water and solids recovery are a good indication of froth stability (Wiese *et al.*, 2010). Therefore, the increase in the ionic strength of plant water stabilised the froth and thereby increased the amount of entrained gangue reporting to the concentrate. This ionic strength froth stabilising effect is attributed to the fact that the presence of inorganic electrolytes in process water reduce the surface hydration of the naturally hydrophobic minerals which provides attractive forces between the air bubbles and the particles (Klassen and Mokrousov, 1963). This reduction is known to primarily occur at high ionic strengths, where specific adsorption of cations may change the surface charge of the particles and cause strong attraction between the particles (Dishon *et al.*, 2009). However, this theory is limited in that it does not account for the minerals that are not naturally hydrophobic. The phenomenon of an increase in froth stability with increasing ionic strength could also be explained by the fact that inorganic electrolytes at high ionic strength tend to reduce the zeta potential of bubbles and particles. This leads to a compression of the electrical double layer. Consequently, the repulsive forces are reduced, thereby leaving the hydrophobic force as the only dominant force in the flotation system. This in turn results in increased solids and water recoveries and a more stable froth (Paulson and Pugh, 1996).

It was also illustrated that an increase in CMC dosage resulted in a decrease in solids recovery, water recovery and froth collapse time at all ionic strengths evaluated. However, the decrease varied with ionic strength, showing that the degree to which CMC t destabilised the froth was affected by the ionic strength of the process water used. The increase in CMC dosage not only resulted in a decrease in floatable gangue recovery, but also indirectly destabilised the froth because of the removal of froth stabilising floatable gangue such as talc as shown in Figure 4.5 which clearly shows that the floatability of NFG per unit water decreased with increasing ionic strength whilst a comparison between the total NFG recovery at 0 g/t and 100 g/t provides evidence of a strong decrease in NFG recovery with increasing CMC dosage as can be seen in Figure 4.2 and Figure 4.5 (Bradshaw *et al.*, 2004; Shortridge *et al.*, 2003; Steenberg and Harris, 1984). The significant decrease in water recovery at a CMC dosage of 500 g/t in comparison to a dosage of 100 g/t is evidence of the impact of CMC dosage on froth stability, and it shows that at 100 g/t dosage, the froth stabilising gangue was present in reasonable amounts as can be seen in Figure 4.2. The froth collapse time results presented in Figure 4.4 are in agreement with these findings in that the froth collapse time decreased with increasing CMC dosage. This behaviour was observed for all ionic strength conditions. It is thus postulated that an increase in the ionic strength increased the amount of gangue (both floating gangue and entrained gangue) present in the froth phase and therefore stabilised the froth. This is attributed to the reduction in the repulsive force between the bubble and the mineral particles at increased ionic strength (Ozdemir *et al.*, 2009). This postulation suggests that cations such as Ca^{2+} and Mg^{2+} present in the thin liquid film around the surface of the bubble enable the bubble-particle attachment of the negatively charged mineral particle such as chalcopyrite and or talc through an electrostatic attractive interaction. This causes a stabilisation of the froth.

The findings of this study have shown evidently that ions in process water promote froth stability and thereby promoting the attachment of mineral particles, and hence the increase in solids and water recovery. However, the promotion of CMC's depressive ability on NFG in increased ionic strengths had an indirect effect on froth stability. These findings are in agreement with Laskowski *et al.* (2007) who showed that the presence of Mg^{2+} and Ca^{2+} in flotation enhanced the ability of CMC in depressing naturally floatable gangue. It was postulated that there occurred an enhancement of the acid-base interaction between the hydrolysable divalent cations on the surface of talc and the highly negatively charged CMC ligand such that through heterocoagulation talc particles were prevented from floating. Also, Wiese (2009) who investigated the behaviour of polysaccharides on two different Merensky ores, speculated that the presence of Mg^{2+}, Ca^{2+}, and SO_4^{2-} imparted a coagulative nature on the adsorbed talc-depressant species and thereby induced their hydrophilicity and indirectly destabilised the froth. These findings are in agreement with Manono et al. (2018) who showed that the adsorption of CMC onto talc increased with increasing ionic strength of plant water as a result of the passivation of talc particles in increasing ionic strengths.

The solids settling results presented in Figure 4.6 provide evidence to the coagulation postulation made by Corin *et al.* (2011) in that in the presence of CMC, the settling time for the selected Merensky ore decreased with increasing ionic strength and CMC dosage and this further explains the decrease in the floatability of NFG recovery per unit water shown in Figure 4.5. Therefore, this shows that the influence of ionic strength on floatability depends largely on the effect that electrolytes have on reagent-mineral interactions occurring in the pulp phase as well as their resulting implications on the froth phase. This therefore shows that both the direct and indirect effects on froth stability are critically important.

4.8.2 *Effect of Ionic Strength of Plant Water and Depressant Dosage on Gangue Recovery*

In line with studies by Corin *et al.* (2011) and more recently by Sheni *et al.* (2017), although these papers investigated much lower ionic strengths (up to that of 5SPW) with Corin *et al.* (2011) mainly focusing on modified guar gum instead of CMC, total entrained gangue seems to have had a strong dependence on the ionic strength of plant water owing to the effect that ionic strength had on water recoveries (and therefore froth stability) as already discussed. These findings are supported by the decrease in the recovery of NFG per unit mass of water and the clear decrease in settling time with increasing ionic strength and CMC dosage. This indicates that as the ionic strength increased, the coagulative nature of the solids increased, particularly the NFG particles, slowing their upward mobility at higher ionic strength and consequently decreasing their flotation and entrainment per unit mass of water. It has been shown that entrainment is strongly related to water recovery (Engelbrecht and Woodburn, 1975; Warren, 1985), and it has been postulated that a decrease in water recovery also decreases the entrainment of particles (Dhliwayo, 2005). However, the findings of this work showed increases in total entrained gangue with increasing ionic strength owing to an increase in water recovery as shown in Figure 4.1 and Figure 4.2.

Solids and water recovery findings have shown that the presence of CMC could mitigate the impact of ions on froth stability as shown by a significant drop in the amount of solids and water reporting to the concentrate. It was found that the amount of solids reporting to the concentrate dropped drastically at 100 g/t and 500 g/t. The depression of solids at 500 g/t depressant dosage was dramatically higher than at 0 g/t and 100 g/t owing to CMC's indirect effects on froth stability and entrainment. These findings are complemented by the total sulfides recoveries and grades which showed clear changes in total sulfides grades in the presence of a depressant in that the increases in grades were more pronounced compared to when to when CMC was not added to the flotation cell. This is attributed to the decrease in the entrained gangue with increasing CMC dosage. Increases in ionic strength gave rise to decreases in the sulfide grades owing to the increases in the entrained gangue with increasing ionic strength. However, changes in ionic strength had a very minimal effect on total sulfides recovery. This behaviour was also observed in the settling time results shown in Figure 4.6 in that in the absence of CMC, the settling time had little or no dependence on the ionic strength of plant water but much dependence was observed in the presence of CMC. This further shows the strong depressive effect of CMC on naturally floatable gangue in the presence of electrolytes such as Ca^{2+} and Mg^{2+}. A summary of the effects of ionic strength and CMC dosage on gangue and froth stability is shown in Figure 4.7.

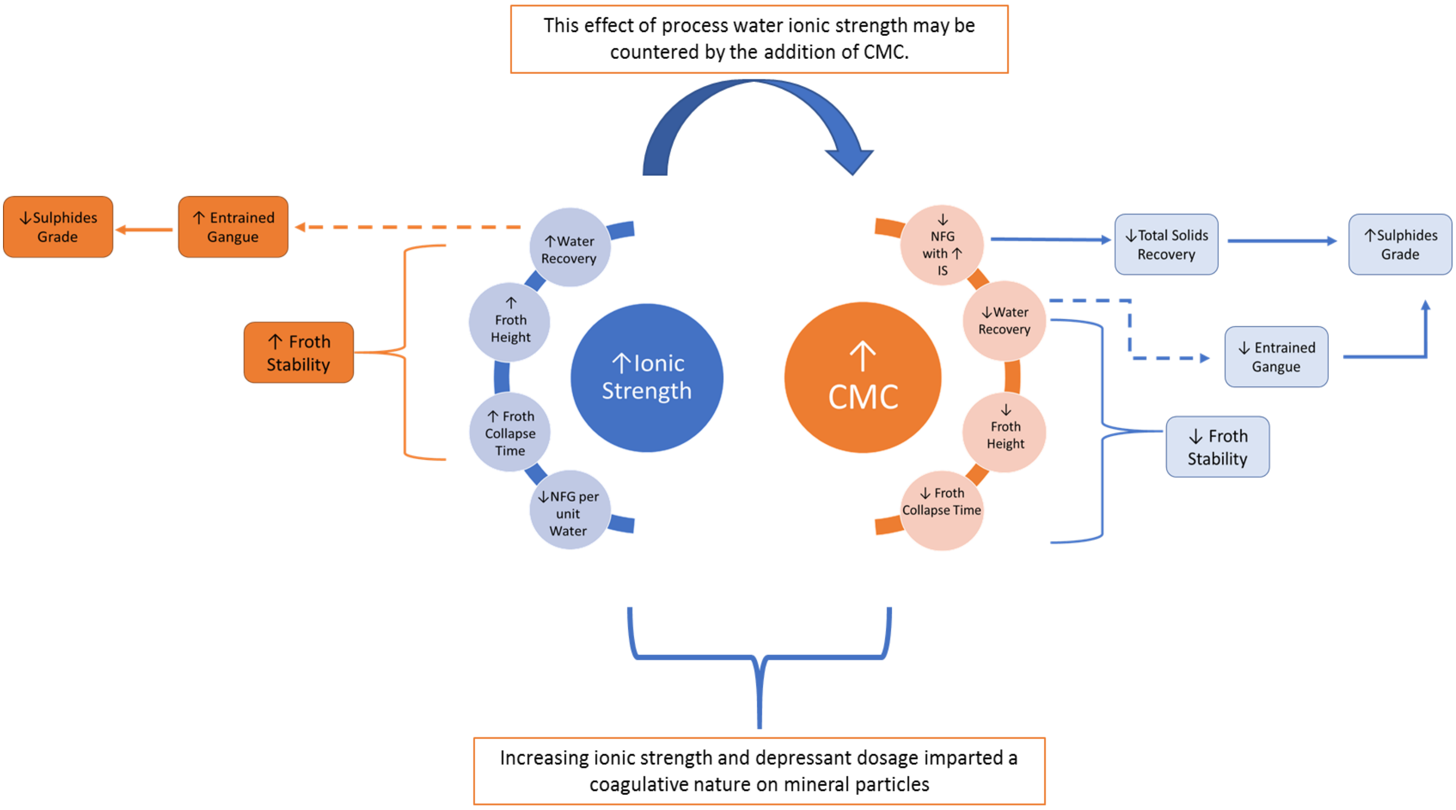


Figure 4.7: A schematic summary of the counter-active relationship between increases in ionic strength and CMC dosage on the stability of the froth.

4.9 Conclusions

An increase in ionic strength resulted in:

- An increase in water recovery, indicating an enhancement in froth stability,
- An increase in the froth collapse time, indicating an enhancement in froth stability,
- A decrease in NFG recovery per unit water due to increases in ionic strength which possibly imparted a coagulative nature on the solids thereby negatively affecting their floatability,
- An increase in total entrained gangue owing to an increase in water recovery, and

- A decrease in total sulphide grades due to the increase in total entrained gangue which diluted the concentrate.

An increase in CMC dosage resulted in:

- Decreases in water recoveries, froth collapse time, froth height; froth stability decreased owing to the depression of froth stabilising NFG,
- A decrease in the recovery of NFG owing to the depressive action of CMC in the presence of electrolytes,
- A decrease in solids recovery and an increase in total sulphide grades owing to an enhanced depression of NFG and a decrease in total entrained gangue due to CMC's indirect effect on froth stability, and
- An increase in the coagulation of solid particles.

The findings of this work have shown that there is a counter-active relationship between ionic strength and CMC dosage on froth stability. Increases in process water ionic strength result in increased froth stability which in turn results in decreases in sulfide grades. This effect of process water ionic strength is countered by the addition of CMC.

4.10 Acknowledgements

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CHAPTER 5 WATER QUALITY IN PGM ORE FLOTATION: THE EFFECT OF IONIC STRENGTH AND PH

5.1 Rationale, Key Questions and Hypotheses

Considering increases in ionic strength, an analysis of the speciation diagrams for the investigated inorganic electrolytic solutions shows the variety of species which could be present under varying pulp chemistry conditions as seen in Chapter 2, Figure 2.2. Thus pH may also have an impact and the formation of various hydroxo species beyond standard flotation conditions (pH 9) was investigated.

5.1.1 Key Questions

- How does an increase in ionic strength and pH affect froth stability?
- How does an increase in ionic strength and pH affect the floatability of the selected ore?

5.1.2 Hypotheses

- *Increasing the ionic strength and pH will increase froth stability owing to a decrease in bubble coalescence caused by the increased concentrations of inorganic electrolytes.*
- *An increase in ionic strength and pH causes a decrease in solids recoveries whilst concurrently increasing Cu-Ni grades owing to the depressive of gangue in the presence of hydroxo species at pH 11.*

5.2 Abstract

Water and its chemistry are important variables in froth flotation. The presence of electrolytes in water may form either hydroxo species or precipitates in the flotation pulp when the process pH is altered. This may alter the chemical interactions that enable the process. This study investigates the interactive effect of plant water ionic strength and pH in the flotation of a sulphidic PGM bearing ore. Results suggest that water quality variations may have effects at both the air-water interface as well as the mineral air interface.

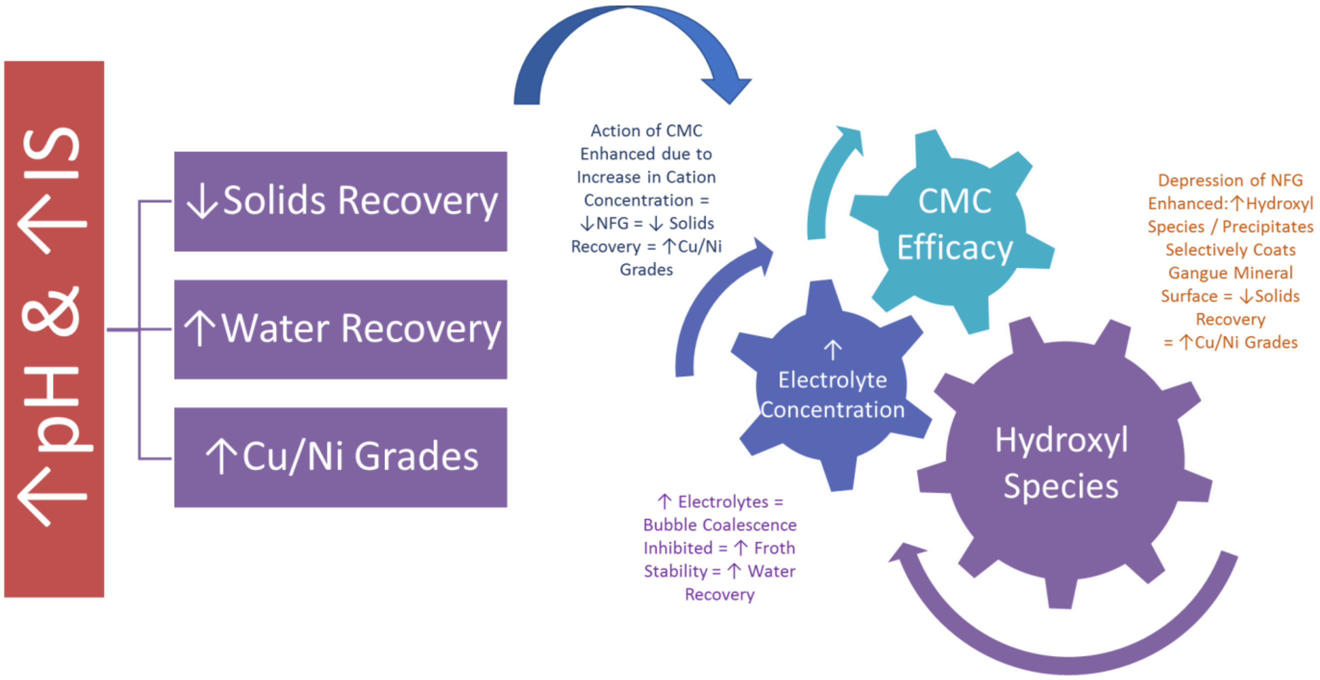
KEYWORDS:

Froth stability, Ionic strength, pH, Water quality, Water recovery

5.3 Highlights

- The increase in both pH and ionic strength favours high water recoveries which indicates froth stabilisation as a result of bubble coalescence inhibition by electrolytes.
- An increase in both pH and ionic strength resulted in a decrease in solids recovery despite an increase in water recovery.
- Mineral recoveries and grades showed a higher sensitivity to ionic strength at pH 11 compared to pH 9. This finding is attributed to the enhancement of the depression of naturally floatable gangue minerals at pH 11 due to the presence of hydroxo species.
- At pH 11, increasing the ionic strength increases froth stability whilst concurrently inducing the hydrophilicity of mineral particles.

5.4 Graphical Abstract



5.5 Introduction

The quest for a cleaner and safer environment with clean surface and ground water has led to increased recycling of process water within the minerals processing industry. Since the chemistry of process water is entirely different from fresh water and changes as water is recycled, there is a concern about the possible effects of its constituents (ion type, ionic strength etc.) on the efficiency of the flotation process (Rao and Finch, 1989). Studies have shown that recycled process water in mineral processing has a high salinity, contains heavy metal ions, flotation reagents, organics and other pollutants (Slatter *et al.*, 2009). Therefore, process water treatment and reuse has much academic and industrial relevance (Chen *et al.*, 2008).

In response to the scarcity of fresh water, and the tight environmental legislation on water usage, PGM bearing ore flotation circuits make use of recycled process water. However, the chemistry of recycled process water may alter the performance of the flotation system. It is therefore required to understand the effects of these elements on the flotation process. Electrolytes in recycled process water can hinder the collector from adsorbing onto the mineral surface (Wang *et al.*, 2014; Hancer *et al.*, 2001). It has been reported that ions such as Ca^{2+}, $S_2O_3^{2-}$ and SO_4^{2-} may activate pentlandite and pyrrhotite mineral surfaces at normal process pH 9 while $S_2O_3^{2-}$ and Ca^{2+} compete with xanthate for adsorption on pentlandite surfaces (Hodgson and Agar, 1989). Shackleton *et al.* (2003) stated that Ca^{2+} ions can chemisorb onto the pentlandite surface, replacing metal ions at the surface and possibly reducing particle surface hydrophobicity. Metal ions hydrolyse in alkaline pH and may deposit as hydrophilic metal hydroxides, sulphates or carbonates on the mineral surfaces (Fuerstenau *et al.*, 1999). The reduction in mineral surface hydrophobicity could compromise the efficiency of the particle – bubble attachment sub-process and consequently the performance of the flotation system (Koh *et al.*, 2009, Schwarz and Grano, 2005). Ionic strength and the type of cations in solution can have an influence on the extent of activation. The presence of divalent cations in solution like Mg^{2+} or Fe^{2+} can compete with metal ions like Cu^{2+} on the mineral surface (Lascelles *et al.*, 2001). Studies by Parolis *et al.* (2008) and Shortridge *et al.* (2003) showed that the depression of naturally floatable gangue and the efficacy of carboxymethyl cellulose (CMC) were very much dependent upon the type and ionic strength of the electrolytes present in solution. They showed that when divalent cations (Ca^{2+} and Mg^{2+}) were present, depression was greater than when monovalent cations were present (K^{+}); and that increasing the ionic strength of the electrolytic conditions resulted in even greater depression of the naturally floatable gangue.

The presence of electrolytes can improve particle-bubble attachment efficiency through compressing the electric double layer and thus reducing the electrostatic repulsion between particles and bubbles (Kurniawan *et al.*, 2011). Electrolytes are favourable to the formation of smaller more stable bubbles due to the influence of electrolytes on gas dispersion properties (bubble size, gas hold-up etc.). Smaller bubbles increase the particle-bubble collision probability (Pugh *et al.*, 1997; Bićak *et al.*, 2012) and thereby improve particle-bubble attachment efficiency (Hewitt *et al.*, 1994). An increase in electrolyte concentration increases the density of ions in the bulk solution resulting in counter-ion diffusion into the Stern layer, which increases attraction forces and decreases repulsion forces (Wang *et al.*, 2014). The impact of ionic strength on bubble size is attributed to the fact that inorganic ions in water seem to slow inter-bubble drainage and thereby inhibit bubble coalescence and promote stability in the froth phase (Barker, 1986; Craig *et al.*, 1993).

However, whether there is an interactive effect of ionic strength of plant water and pH is not well understood. In literature these two parameters have been studied individually. The pH has been investigated mostly on single salt electrolytes in order to simplify the complex water chemistry. This approach does not truly represent the complex water chemistry in flotation circuits and would not allow plant operators to predict the impact of ionic strength and pH when more than one hydroxo species, inorganic complex or precipitate is present in the system. Therefore, the purpose of this study is to investigate the interactive effect of ionic strength and pH on the floatability of a PGM containing ore with a keen focus on the depression of gangue as well as froth stability.

5.6 Materials & Methods

1 kg ore samples were milled at 66% solids in synthetic plant water for 15 minutes in order to obtain a grind of 60% passing 75µm. The milled slurry was transferred into a 3 L Barker flotation cell. The volume of the cell was made up to generate 35% solids using synthetic plant water (at the required ionic strength). The cell was fitted with a variable speed drive and the pulp level was controlled manually. The impeller speed was set at 1200 rpm. An air flow rate of 7 L/min was maintained for all flotation experiments and a constant froth height of 2 cm was sustained throughout. Reagents were dosed and allowed to condition as shown in Table 5.1. Concentrates were collected at 2, 6, 12 and 20 minutes respectively by scraping the froth into a collection pan every 15 seconds. A feed sample was taken before each flotation test and a tails sample after each flotation test. Water usage and pH were monitored throughout the tests. Feeds, concentrates and tails were filtered, dried and weighed before analysis. The flotation test work was carried out at pH 9 and pH 11. The addition of reagents and

sequence thereof is shown in Table 5.1. Synthetic plant water (Table 5.2) of various ionic strengths (IS) and total dissolved solids (TDS) was used throughout the test work. All the reagents were supplied by Senmin. Copper and nickel assays were conducted at UP (University of Pretoria) using X-Ray Fluorescence (XRF) and Leco was used for determination of sulphur. For the 2-phase batch flotation test work only the water type and pH were varied. Prepared plant water solutions were transferred directly to a 3 L Barker flotation cell. The operating conditions of the cell were maintained as in the 3-phase test work with the frother, DOW 200, dosed at 40 ppm. The collection of (foam) concentrates was done at 2, 6, 12 and 20 minutes respectively by scrapping the foam into a collecting pan every 15 seconds. Two phase froth column tests were conducted for all the water types as presented in Table 5.2 at pH 9 and pH 11with a frother dosage of 5 ppm DOW 200. A full experimental set up and operation of the University of Cape Town (UCT) Centre for Minerals Research (CMR) froth column which was used to obtain the foam height and collapse time presented in this study is given in Manono *et al.* (2013). All tests were conducted in duplicate in order to ensure reproducibility and reliability of the tests data. Standard error bars are shown in each graph presented and the standard error was well below 5 % for each data presented.

Table 5.1: Reagents addition and sequence.

Reagent	Type	Dosages (g/t)	Conditioning time (min)
Collector	SIBX	150	15
Depressant	Sendep 30E	0, 100, 500	3
Frother	DOW200	40	1

Table 5.2: Concentration of ions present in synthetic plant water (SPW).

Water type	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	Cl^{-} (ppm)	SO_4^{2-} (ppm)	NO_3^{-} (ppm)	CO_3^{2-} (ppm)	TDS (mg/L)	IS [M]
1SPW	80	70	153	287	240	176	17	1023	0.0242
5SPW	400	350	765	1435	1200	880	85	5115	0.1212
10SPW	800	700	1530	2870	2400	1760	850	10230	0.2426

5.7 Results & Discussion

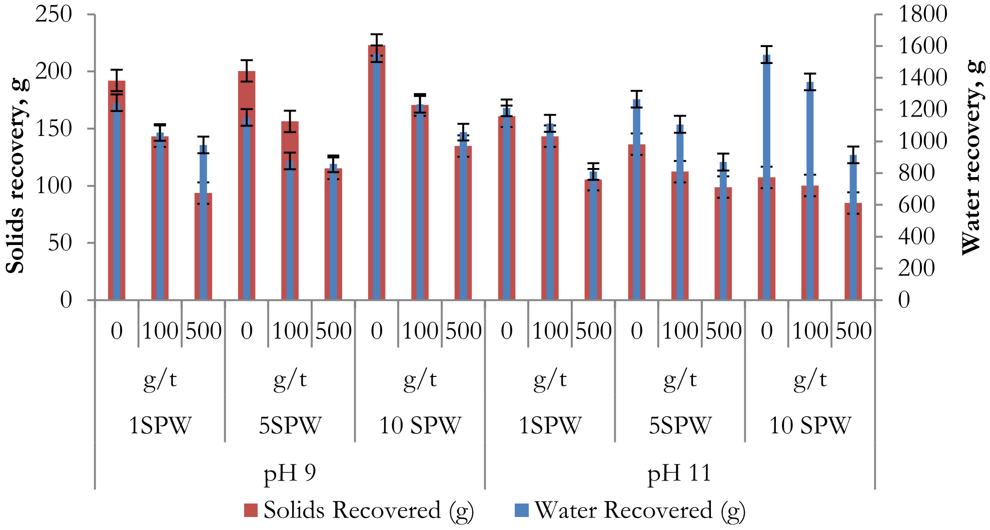


Figure 5.1: Final solids and water recovery for all tested conditions.

From Figure 5.1, it is evident that at pH 9, both the solids and water recoveries decreased with an increase in depressant dosage for all ionic strength conditions. Further to this, it can be seen that with increasing ionic strength (at pH 9), the recovery of solids and water was higher compared to lower ionic strengths. Interestingly, at pH 11 an opposite trend was observed regarding the effect of ionic strength on solids recovery. Here, the solids recovery decreased as the ionic strength of plant water increased. The water recovery however increased at increasing ionic strengths as is the case at pH 9.

The increase in water recovery with increasing ionic strength of process water is speculated to have been caused by an enhancement in froth stability due to the presence of high amounts of ions (Corin *et al.*, 2011; Ejtemaei *et al.*, 2016; Wiese *et al.*, 2007) except for the decrease seen between 3SPW and 5SPW which could be linked to different species acting on the mineral species. The increase in water recovery at a pH 11 is attributed to the excessive presence of hydroxyl ions which may have caused an increase in the stability of the froth. It is believed that increasing the ionic strength of plant water and pH inhibits bubble coalescence retarding inter – bubble drainage (Craig *et al.*, 1993; Manono *et al.*, 2013; Wiese, 2009; Yousef *et al.*, 2003).

The decrease in solids recovery at pH 11 with increasing ionic strength is believed to have been as a result of the presence of ions, hydroxo species and precipitates that can influence the mineral surface by changing the hydrophobicity of the mineral and hindering the collector from adsorbing onto the mineral surfaces (Biçak *et al.*, 2012; Bickerman, 1953). This in agreement with Ikumapayi *et al.* (2012) who showed that the adsorption of calcium and sulphate ions led to the reduction of the negative surface charge and the xanthate adsorption to the mineral surface resulting in less solids recovery. These findings are also in agreement with Tadie *et al.* (2016) who investigated the application of potential control to the flotation of galena under varying pH who showed that at pH 11.8, the recovery of galena dropped significantly compared to pH 9.2, indicating the depressing effect of hydroxyl ions at higher pH.

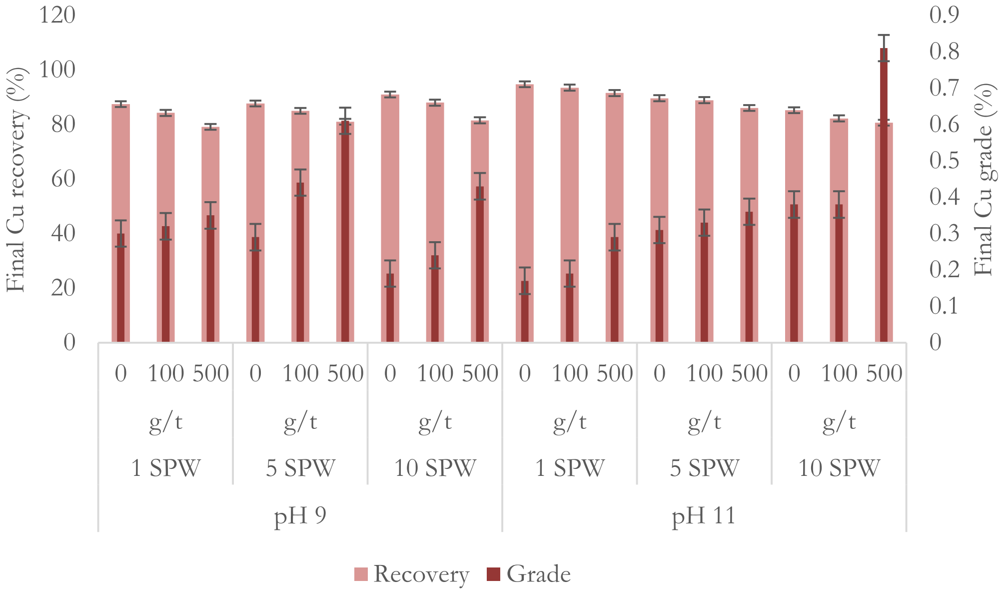


Figure 5.2: Final Cu recovery and grade of all tested conditions.

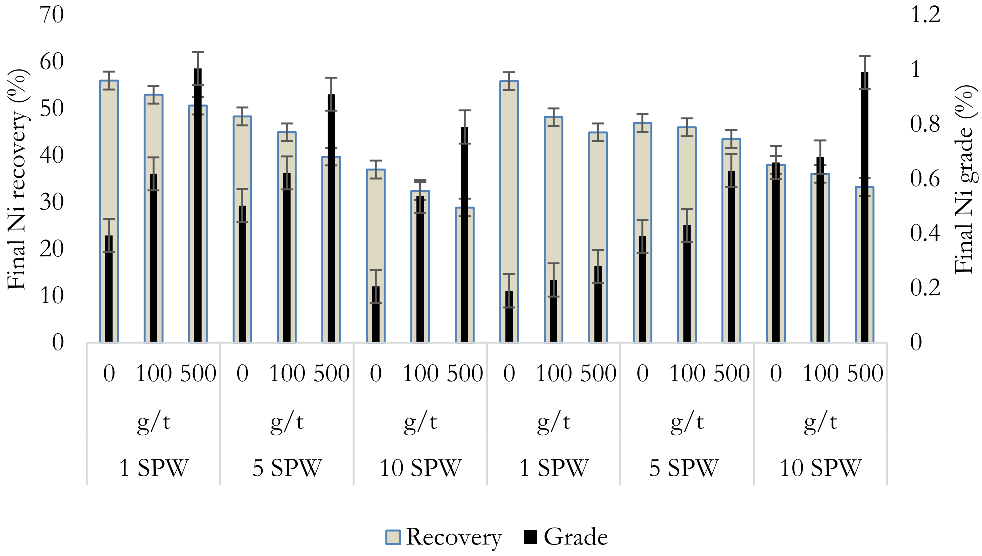


Figure 5.3: Final Ni recovery and grade for all tested conditions.

Figure 5.2 and Figure 5.3 depicts the final Cu and Ni recovery and grade respectively. At pH 9, it is shown that an increase in depressant dosage resulted in a decrease in mineral recovery, as expected. However, an increase in ionic strength resulted in a slight increase in mineral recovery, which agrees with the increased solids recoveries. Cu and Ni grades increased with an increase in depressant dosage, as expected, however there was a decrease in mineral grades with increasing ionic strength. Mineral recoveries are lower when the pH is increased from 9 to 11. It is also worth noting that at pH 11 mineral grades tend to increase with increasing ionic strength. It must be noted that the 91% recovery of Ni for 1SPW at 0 g/t could be due to an experimental error from the elemental assays.

The increase in mineral recoveries with increasing ionic strength is evidence of the froth stabilizing effect of increased ionic strength which is also evident in the solids recovery shown in Figure 5.1 at pH 9 (Craig *et al.*, 1993). A decrease in the Cu and Ni grade at pH 9 with increasing ionic strength could be an indication that the increase in froth stability resulted in more gangue being recovered to the concentrate as previously reported by Corin *et al.* (2011), Corin and Wiese (2014) and Manono *et al.* (2012). The trend of an increase in the Cu and Ni recoveries and grades with increasing ionic strength at pH 11 could be attributed to a possibly enhanced depressant (CMC) selectivity or the hydroxyl species and precipitates which may have selectively deposited onto gangue minerals, inducing their hydrophilicity, enhancing their coagulative nature with the result of poor adsorption of the collector. These findings are in agreement with Parolis *et al.* (2008) who showed that the presence of divalent ions such as Ca^{2+} improved the depressive nature of CMC.

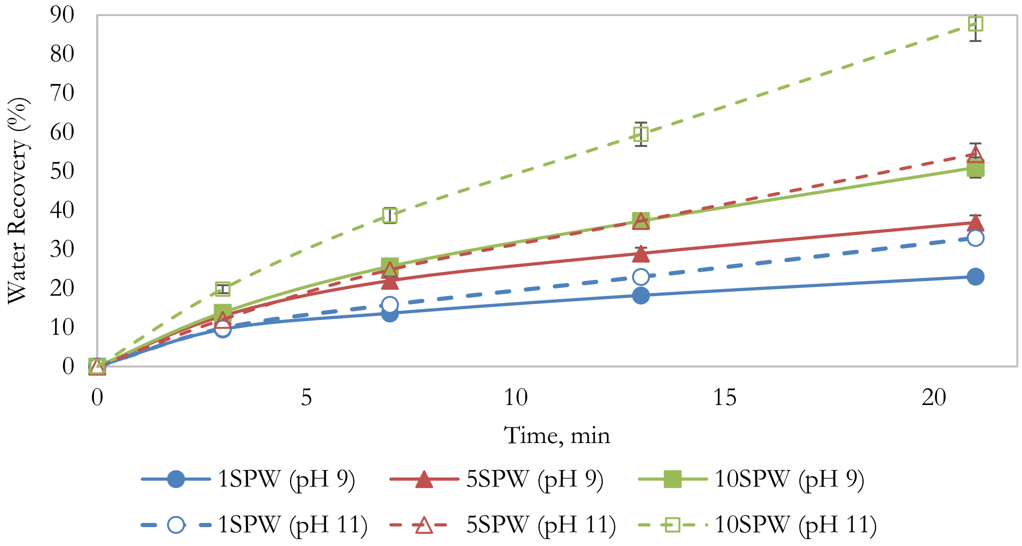
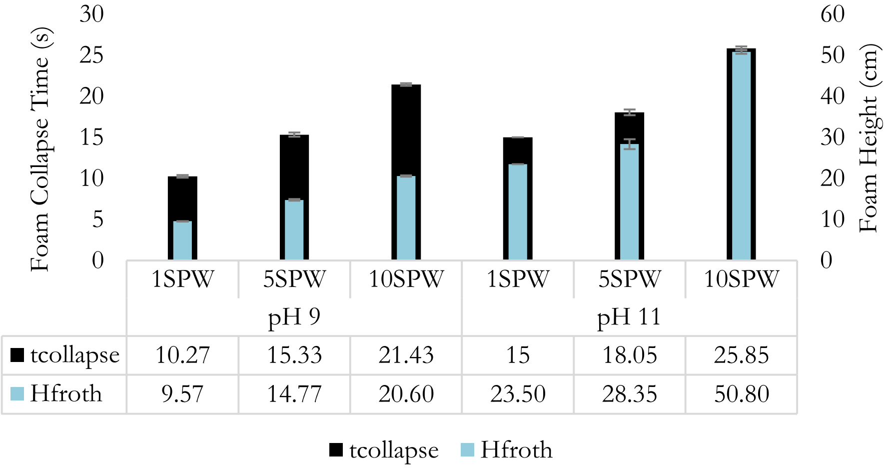


Figure 5.4: The effects of ionic strength and pH on water recovery as a function of time.

Figure 5.4 illustrates the effect of ionic strength and pH on water recovery as a function of time. It is shown that the rate of water recovery increased with increasing ionic strength as well as with increasing pH.



	1SPW	5SPW	10SPW	1SPW	5SPW	10SPW
		pH 9			pH 11	
■ tcollapse	10.27	15.33	21.43	15	18.05	25.85
■ Hfroth	9.57	14.77	20.60	23.50	28.35	50.80

Figure 5.5: Effect of ionic strength and pH on foam height and foam collapse time.

Figure 5.5 illustrates the effects of ionic strength and pH on foam height and foam collapse time. Both foam height and foam collapse time increased with increasing ionic strength and pH. The higher pH resulted in higher foam height and longer foam collapse time compared to the lower pH.

A frother dosage of 5 ppm was chosen in the 2-phase experiments so as to elucidate frothing effects of ionic strength and pH as this dosage is below the selected frother's critical coalescence concentration. The results shown in Figure 5.4 and Figure 5.5 are indicative of an enhancement in froth stability with increased ionic strength and increased pH and are in agreement with the batch flotation performance given in Figure 5.1. It is postulated that this froth stabilising effect of ionic strength and pH is a result of a decrease in bubble size owing to an inhibition of bubble coalescence which is (mechanistically) attributed to a decrease in inter-bubble drainage rate and the stability of the inter-bubble film (Craig *et al.*, 1993).

5.8 Conclusions

It is clear that the increase in both pH and ionic strength favour high water recoveries which indicates froth stabilisation. It was also shown that an increase in both pH and ionic strength resulted in a decrease in solids recovery despite an increase in water recovery. This finding was attributed to the enhancement of the depression of naturally floatable gangue minerals, which is a result of hydroxyl species and precipitates which may have selectively coated the gangue mineral surfaces as the ionic strength increased at pH 11.

5.9 Acknowledgements

The authors would like to thank Senmin, the University of Cape Town and Vaal University of Technology for their respective contributions towards this work. This work is supported in part by the National Research Foundation (NRF) of South Africa (Grant numbers 99262 and 103641). Any opinions, findings, conclusions or recommendations expressed in any publication generated by NRF supported research is that of the authors and the NRF accepts no liability whatsoever in this regard. Financial and technical contributions from the South African Minerals to Metals Research Institute (SAMMRI) and its members are also acknowledged.

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CHAPTER 6 PROCESS WATER EFFECTS ON MINERAL-DEPRESSANT ADSORPTION IN SULPHIDE FLOTATION

6.1 Rationale, Key Questions & Hypotheses

Research on sulphide and PGM containing ores suggests that the ionic nature of the process water used as transport medium in flotation is key to the depression of floatable gangue as shown in Chapter 4 and Chapter 5. The literature review presented in Chapter 2 suggests that hydroxo species, particularly those of calcium, selectively adsorb onto gangue minerals. It appears that these hydroxo species enhance the depressive action of carboxymethyl cellulose (CMC) onto gangue via an acid-base interaction between the positively charged mineral surface and the negatively charged CMC molecule. Thus, the hydrophilicity of gangue minerals is enhanced preventing the dilution of the concentrate. However, as there is little evidence to support these claims it is important to investigate. Adsorption data and mineral surface charge analyses will allow a fundamental understanding into how electrolytes and their ionic strengths affect gangue-depressant adsorption. It is strongly anticipated that decoupling these effects will allow process operators to tailor their process water quality needs towards best flotation operating regimes and in the long run effect closed water circuits. Thus, using talc and pyrrhotite, this work investigates the influence of the ionic strength of process water on the adsorption of depressants onto talc and pyrrhotite.

Also, coagulation and flocculation are two well established and important phenomena in water treatment circuits. Chemicals and polymers are added in water clarifiers to induce the coagulative-flocculative nature of solid particles by forming larger aggregates of the solid particles and thereby increasing their settling rate. Polymers such as polysaccharides are added into froth flotation circuits to render gangue or non-valuable minerals hydrophilic and consequently gangue is prevented from reporting to the concentrate. Recent flotation research on PGM ores speculates that changes in the ionic strength of inorganic electrolytes may affect the coagulative-flocculative nature of solid particles in flotation pulps. This could well have considerable implications on the hydrophilicity of gangue minerals owing to interactions between process water inorganic electrolytes, the polymers and solid particles. Thus, this study also considers the effect of the ionic strength of process water on the settling rate of talc particles using carboxymethyl cellulose which has implications for talc depression under conditions of water recycling and re-use in flotation.

6.1.1 Key Questions

- How does the ionic strength of plant water affect the floatability of talc and pyrrhotite?

- How does the ionic strength of plant water affect CMC adsorption onto talc and pyrrhotite?
- How does the ionic strength of process water affect the coagulation of talc?

6.1.2 Hypotheses

- *An increase in the ionic strength of process water increases the recovery of minerals owing to an enhancement in bubble-particle attachment.*
- *An increase in the ionic strength of plant water increases the adsorption of CMC onto the mineral surface due to the interaction of depressants with electrolytes on the mineral surface.*
- *An increase in the ionic strength of process water will increase the coagulative nature of talc owing to an enhancement in the adsorption of CMC onto talc.*

6.2 Abstract

It has been suggested that hydroxo species, particularly those of calcium, selectively adsorb onto gangue minerals. Such species enhance the depressive action of carboxymethyl cellulose (CMC) onto gangue via an acid-base interaction between the positively charged mineral surface and the negatively charged CMC molecule. Thus, the hydrophilicity of gangue minerals is enhanced, preventing the dilution of the concentrate. However, as there is little evidence to support these claims it is important to investigate. Adsorption data and mineral surface charge analyses will allow a fundamental understanding into how electrolytes and their ionic strengths affect gangue-depressant adsorption. It is strongly anticipated that decoupling these effects will allow process operators to tailor their process water quality needs towards best flotation operating regimes and in the long run effect closed water circuits. Thus, using talc and pyrrhotite as proxies, this work investigates the influence of the ionic strength of process water on the adsorption of CMC onto minerals in sulphide flotation.

KEYWORDS

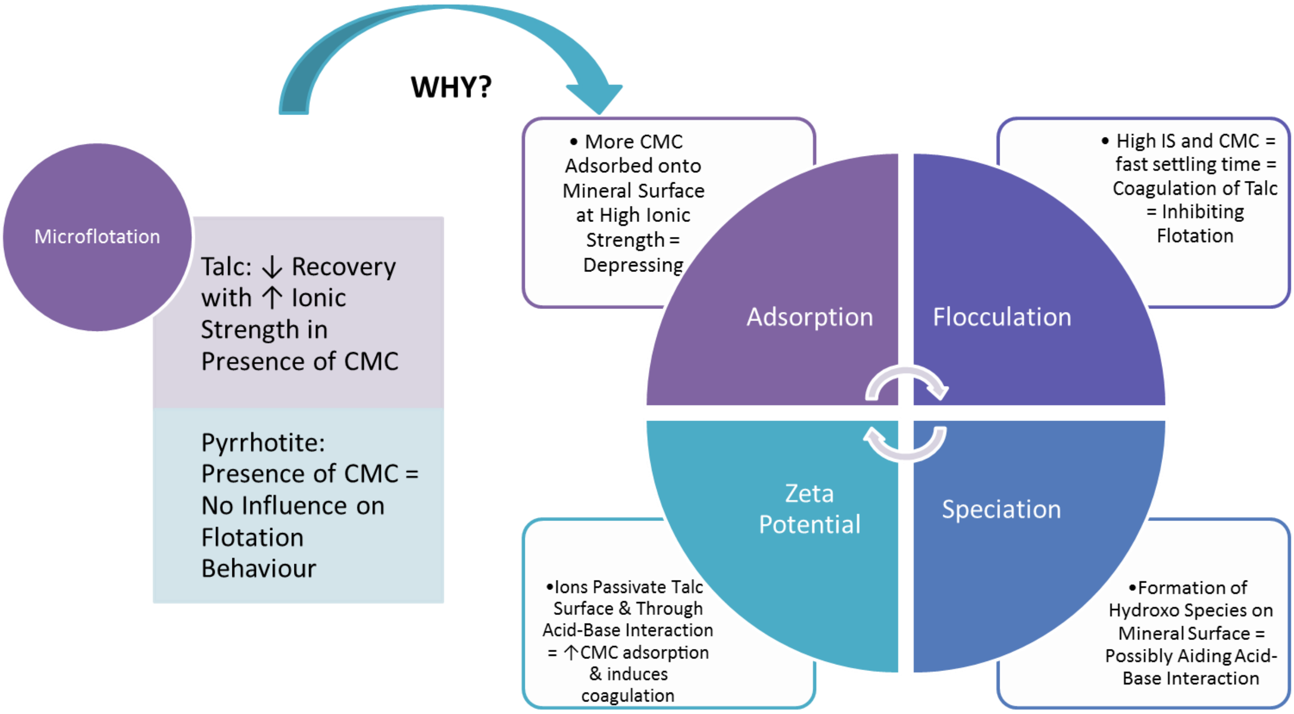
Adsorption, Carboxymethyl cellulose, Coagulation, Depressants, Ionic strength, Water quality

6.3 Highlights

- The rate of recovery of pyrrhotite and talc increased with increasing ionic strength in the absence of CMC.

- Increases in ionic strength decreased the rate of recovery of talc in the presence of CMC.
- CMC adsorption onto talc and pyrrhotite increased with increasing ionic strength.
- The coagulation of talc increased with increasing ionic strength and CMC dosage.

6.4 Graphical Abstract



6.5 Introduction

The phenomenon of gangue depression in mineral flotation is of critical importance as regards the attainment of a required concentrate grade. This thus suggests that the depressant of choice has to have a highly selective affinity for the targeted gangue minerals. This would ensure the necessary prevention of gangue from reporting to the concentrate without inadvertently depressing the value bearing mineral. The chemistry of the environment regulates the manner in which gangue depression occurs. In sulphide flotation, polysaccharides are used as depressants of choice to depress naturally floatable gangue which may in the case of Merensky ores exist as talc. The two widely used polysaccharides in the South African context are carboxymethyl cellulose (CMC) and modified guar gum. It is suggested that polysaccharides depress gangue by rendering the surface of gangue hydrophilic or by preventing the formation of hydrophobic layers on gangue mineral surface, forming large gangue aggregates and thereby increasing their heterocoagulative nature (Shortridge *et al.*, 1999).

The mechanism through which these polysaccharides adsorb at the mineral surface seemed unclear, in fact, a number of mechanisms had been proposed by the end of the 20th Century and these were said to be "rarely founded on detailed experimental evidence" (Pugh, 1989). These mechanisms, as detailed by recent papers, included hydrogen bonding, electrostatic interactions, hydrophobic interactions and or acid-base interactions (Jenkins and Ralston, 1998; Parolis *et al.*, 2008).

Morris *et al.* (2002) investigated CMC adsorption at the talc–water interface as a function of the ionic strength and pH of a KCl solution. Their findings showed that at low ionic strengths and more alkaline pH, the adsorption density of CMC was low whereas at high ionic strength and high pH, the adsorption density was high. They concluded that the depression of talc had a strong dependence on the solution ionic strength and pH and that it was a reduction in the electrostatic repulsive force between the negatively charged carboxyl group and the negatively charged talc that enabled an increase in the adsorption density at high ionic strength and low pH. Pawlik *et al.* (2003) showed that CMC in brine (50 % KCl/NaCl) adsorbed very strongly and in large quantities onto minerals such as illite and dolomite compared to CMC in distilled water. At increased ionic strength it was also reported that the CMC macromolecules coiled in solution, reduced the intrinsic viscosity and thereby increasing coagulation. Burdukova *et al.* (2008) showed a greater adsorption of CMC into talc in the presence of a 0.01 M $Ca(NO_3)_2$ solution compared with a 0.01 M KNO_3 at pH 9. Furthermore, these authors also suggested that the presence of Ca^{2+} induced the coiling of CMC's macromolecules. These findings complemented the work of Parolis *et al.* (2008) who also showed that Ca^{2+} and Mg^{2+} ions increased the adsorption of CMC depressants onto talc compared to K^+ ions at ionic strengths of 10^{-3} M and that the adsorption was even higher at increased ionic strength. Additionally, Feng *et al.* (2013) showed that the pH of solution is an important parameter in the adsorption of CMC onto mineral surfaces in that Ca^{2+} and Cu^{2+} were far more at pH values above 9 in depressing gangue.

On the other hand, it has been reported that a great amount of heavy metal ions such as Cu^{2+}, Zn^{2+} and Pb^{2+} adsorb onto the highly anionic pyrrhotite (Allison and O'Connor, 2011). This adsorption is said to occur via an attractive force between the divalent cations and the negatively charged surface of pyrrhotite. The negatively charged collector ligand then adsorbs onto the passivated pyrrhotite thereby inducing its hydrophobicity. However, Hodgson and Agar (1989) reported that Ca^{2+}, $S_2O_3^{2-}$ and SO_4^{2-} were found to be active on the pyrrhotite surface at the normal process pH, it was found that that Ca^{2+} competed with xanthate for adsorption on the surface of pyrrhotite rendering pyrrhotite less hydrophobic such that xanthate dosage had to be increased to impart the necessary hydrophobicity. This begs the question as to whether any competition exists between the anionic collector and the anionic depressant as regards their adsorption onto the pyrrhotite surface with active inorganic electrolytes. Moreover, previous work conducted at the Centre for Minerals Research on a Merensky ore showed that the use of saline water resulted in a decrease in the rate of naturally floatable gangue and a decrease in the degree of entrainment per unit water in the presence of CMC (Corin and Wiese, 2014). These observations were attributed to a greater adsorption of CMC onto talc in increased ionic strength as well as a resultant froth destabilisation.

In the flotation of sulphidic ores such as the Merensky type, the targeted base metal sulphides (BMS) (chalcopyrite, pentlandite, pyrrhotite etc.) make up about 1% of the ore, the rest being gangue (floatable and non-floatable). Forty five percent of this BMS content is mostly in the form of pyrrhotite. Floating gangue is mostly in the form of talc and exists in the ore raw feed at mass percentages of ca. 1-4%. There exist pyrrhotite-pentlandite and pyrrhotite-PGMs composites which make the floatability of pyrrhotite a topic of interest in Cu-Ni-PGM concentrators (Becker *et al.*, 2009). Given water quality variation in Cu-Ni-PGM concentrators, it is thus necessary to examine the adsorption of pyrrhotite under varying ionic strengths of plant water Also the existence of talc, although in small quantities, in Merensky ores is problematic due to its natural hydrophobicity which causes it to dilute the concentrates if preventative measures are not put in place such as the addition of selective and suitable depressants such as CMC. Thus, the adsorption of CMC onto talc is of critical importance and this study considers the efficacy of CMC as a talc depressant in saline plant water.

6.6 Materials & Methods

6.6.1 Materials

Pure minerals of key interest in this investigation were talc and pyrrhotite (with a 4C superstructure). 1 kg of each mineral type was supplied by Ward's Natural Science Establishment NY. These were crushed manually using a hammer to 100 % passing 1000 μm sieve. The crushed samples were pulverised and the fraction of +38-106 μm was used for all the test work. Given that pyrrhotite readily oxidises in air, samples thereof were purged with N_2 and stored in a refrigerator.

6.6.2 Depressant Preparation

The polysaccharide used was the CMC, Depramin 267, with a molecular weight of 325 000 $g.mol^{-1}$, a density of 1.43 $g.mL^{-1}$, a degree of substitution of 0.62, and purity of 72%. Distilled water was used to prepare 1% solutions of CMC. In order to ensure complete hydration of the CMC in solution, the 1% CMC solution was stirred for 2 hrs.

6.6.3 Synthetic Plant Water Preparation

Synthetic plant water (SPW) recipes were prepared based on a standard plant water developed at the Centre for Minerals Research (CMR) at the University of Cape Town (UCT) to mimic actual process water (Wiese *et al*., 2005a). These synthetic plant water types were prepared as shown in Table 6.1 by the addition of known masses of single salts to distilled water such that the total dissolved solids of 1SPW was 1023 mg/L (with an ionic strength of 0.0213 mol.dm^{-3}). Multiplying the TDS by 5 and 10 would yield 5SPW and 10SPW.

Table 6.1: Synthetic plant water types and their ion compositions.

Water type	**Ca^{2+} (ppm)**	**Mg^{2+} (ppm)**	**Na^{+} (ppm)**	**Cl^{-} (ppm)**	**SO_4^{2-} (ppm)**	**NO_3^{-} (ppm)**	**CO_3^{2-} (ppm)**	**TDS (mg/l)**	**IS [M]**
1SPW	80	70	153	287	240	176	17	1023	0.0242
5SPW	400	350	765	1435	1200	880	85	5115	01212
10SPW	800	700	1530	2870	2400	1760	850	10230	0.2426

6.6.4 Microflotation

Figure 6.1 shows a schematic diagram of the microflotation cell developed by Bradshaw *et al.* (1998) at the CMR. When air is introduced at the base of the cell through a microsyringe, the air and particles can make contact, the loaded bubbles (bubble-particle aggregates) rise to the top of the cell, deflect off the cone at the top of the cell and report to the launder where the concentrates are collected.

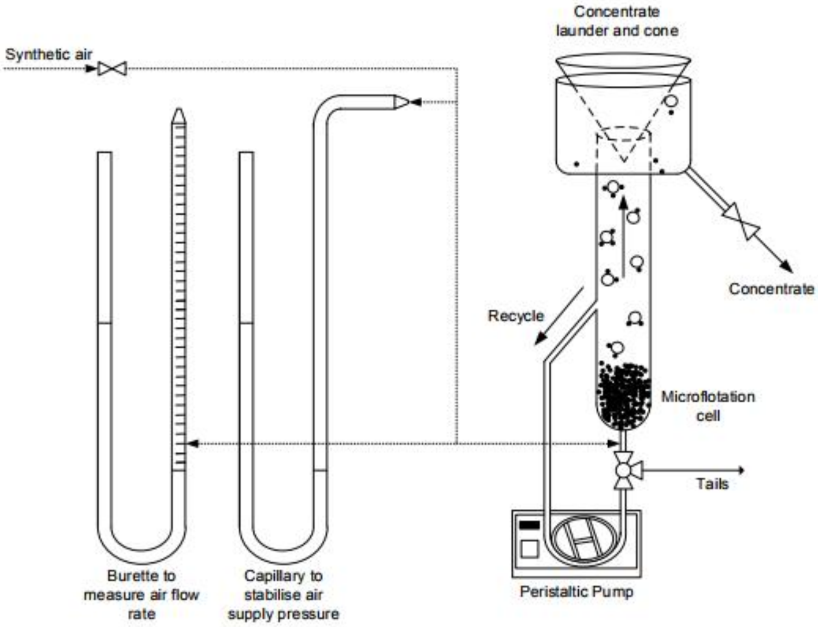


Figure 6.1: A schematic representation of the UCT CMR microflotation cell (Nyabeze and McFadzean, 2016).

Microflotation tests were performed using 3 g of pyrrhotite or talc at a size fraction of +38-106 µm. 50 mL of the particular water quality was added to the mineral sample; the mixture was then ultra-sonicated for 5 minutes to allow for good dispersion of the mineral mixture. The suspension was then transferred to the microflotation cell and the pulp was circulated by a peristaltic pump set at 90 rpm. 90 µL (300 g/t) of 1% CMC solution was then added to the cell and conditioned for 1 minute. The cell was then topped up with the particular water quality to the 250 mL mark. Through a microsyringe, air was introduced at the base of the cell at a flow rate of 7 mL/min. Concentrates were then collected at 2, 6, 12 and 20 minutes of flotation and a tailings sample was taken after the last concentrate was collected. The concentrates and tailings were filtered, dried and weighed. The procedure was repeated for the various water qualities and all runs were done in duplicate to minimise experimental error.

6.6.5 Adsorption Studies

In order to investigate the extent to which CMC adsorbs onto isolated systems of talc and pyrrhotite under varying ionic strengths of process water. 90 mL of the particular synthetic plant water was measured into a conical flask and 270 µL of the 1% CMC stock solution was added to it. This was followed by the addition of 9 g of either talc or pyrrhotite and thereafter the contents of the conical flask was conditioned in an Ecobath for 3 minutes (Mhlanga *et al.*, 2012). This meant that the initial concentration of CMC in the conical flask was 30 mg.L^{-1} (equivalent to 300 g/t). Immediately after conditioning, the solution (supernatant) from the conical flask was filtered using a 0.22 µm Millipore syringe filter. The determination of CMC concentration in the filtrate was made possible through the use of the du Bois calorimetric method (du Bois *et al.*, 1956). The amount of CMC adsorbed onto the mineral surface was calculated by deducting the concentration in the supernatant from the initial 30 mg/L. The experiments were conducted in triplicate for each synthetic plant water.

6.6.6 Flocculation Tests

It has been speculated in literature that the presence of inorganic electrolytes in CMC containing flotation systems impart a heterocoagulative nature on floatable gangue (Burdukova *et al.*, 2008; Laskowski *et al.*, 2007; Manono *et al.*, 2012). This speculation is largely supported by the observation of large talc-CMC coils/aggregates, and decreases in the rate of talc recovery per unit water with increasing ionic strength of plant water (Manono *et al.*, 2012; Parolis *et al.*, 2008). Thus, classical flocculation-coagulation tests in the form of settling tests were performed. Talc in the absence and presence of CMC under varying ionic strengths was tested. Each test was duplicated to minimise error. 9 g of talc was added to 90 mL of particular synthetic plant water in a 100 mL beaker to make a slurry containing 10% solids. The prepared slurry was allowed to mix for a period of 1 minute using a magnetic stirrer and thereafter the pH of the slurry was adjusted to 9 using NaOH or HCl. Immediately after adjusting the pH, the suspension was mixed at 300 rpm for 3 minutes both in the absence and presence of CMC. A 90 µL solution of CMC was added to the 100 mL beaker for tests containing CMC. The conditioning time of 3 minutes was chosen as this is typical of the standard UCT batch and microflotation procedure. After mixing, the slurry was carefully transferred to a 100 mL graduated cylinder. A stop watch was used to measure the time that it would take for talc solid particles to settle. The contents of the measuring cylinder were carefully monitored until a clear supernatant liquid was observed against a clear background after which timing was stopped and the settling time recorded. A baseline picture was taken, printed and displayed next to the test rig to serve as a reference point for all settling tests.

6.6.7 Zeta Potential Tests

Firstly, synthetic plant water solutions of the water type under investigation were added into six test beakers, the pH solution was adjusted using dilute stock solutions of HCl and NaOH such that there existed a test beaker with a pH of 2, 4, 6, 8 and 10. Secondly, 0.0625 g of a prepared mineral (talc or pyrrhotite) sample with a particle size of -25 µm were added onto each of the six test beakers. Thirdly, the suspension containing test beaker was placed on a magnetic stirrer for 15 minutes. The pH of the suspension was again measured and corrected as necessary. And finally, 1 mL of suspension was transferred into a Malvern Dip Cell and inserted into a Malvern Zetasizer for zeta potential measurements. All zeta potential measurements were performed in triplicate to ensure reproducibility and reliability of the test results. It is important to note that for each pH condition, the third step was performed just before zeta potential measuring so as to avoid any unnecessary time dependent reactions with the ions that would blind the comparability of the results from one pH to another.

6.7 Results & Discussion

6.7.1 The Microflotation Response of Pyrrhotite and Talc to Process Water Ionic Strength

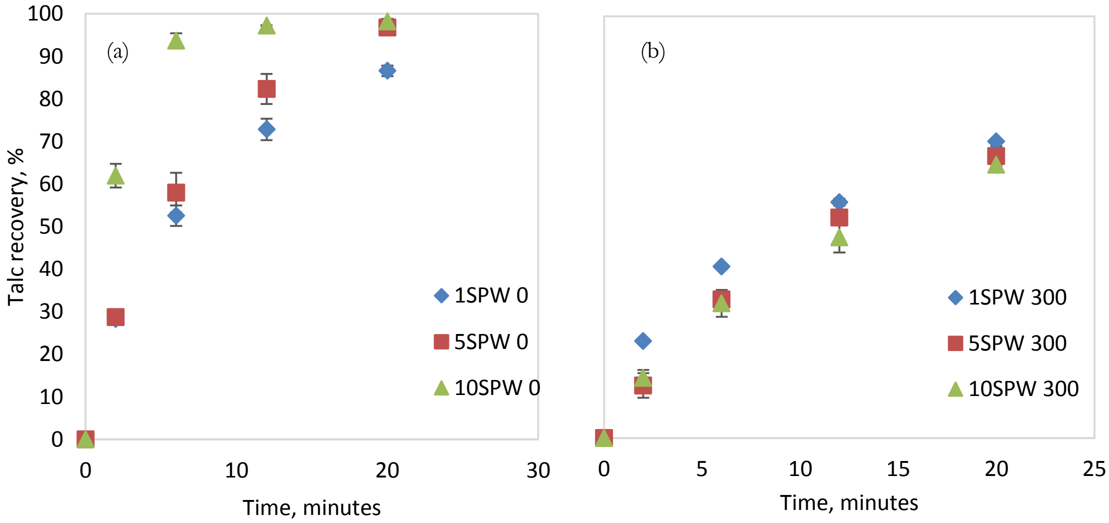


Figure 6.2: Talc recoveries as a function of time under increasing ionic strength conditions and (a) in the absence of CMC, (b) in the presence of CMC at 300 g/t.

Figure 6.2 shows the flotation recoveries for talc under varying ionic strength conditions. The results presented in (a) were in the absence of CMC whereas those in (b) were in the presence of 300 *g/t* CMC. Figure 6.2(a) shows that the recovery of talc and its flotation rate increased with increasing ionic strength. However, an opposite trend was observed when CMC was added at 300 *g/t*, a slight decrease in talc recoveries with increasing ionic strength. Furthermore, comparing Figure 6.2 (a) to (b) it is clear that the addition of CMC decreased the recovery of talc. The trend of a decrease in the recovery of talc with increasing ionic strength in the absence of CMC could be linked to an enhanced bubble-particle attachment which increased bubble loading. It has been reported that inorganic electrolytes compress the electrical double layer, this is potentially a result of cations surrounding the thin liquid film around the bubble, ensuring a decrease in any repulsive forces that there may be in the system, enhancing electrostatic interactions between the negatively charged talc and the cations (such as Ca^{2+} and Mg^{2+}) on the surface of the bubble film thereby increasing bubble particle collions (Farrokhpay and Zanin, 2012). Also electrolytes are reported to cause bubble size reductions similar to that of frothers. These increases in ionic strength must have led to an increase in the total bubble surface area to which bubble-particle attachment occured and thus in this way led to increases in recovery. Thus it is proposed that in the absence of depressant, firstly, the bubble size decrease effect is evident and secondly an increase in the electrostatic interactions between the cations on the surface of the bubble and the negatively charged talc surface can be seen. These are supported by Manono *et al.* (2013) who investigated bubble size, froth height, froth follapse time and water recovery as indicators of froth stability varying ionic strength of synthetic plant and reported a decreases in bubble size, increases in froth height, froth collapse time and water recoveries with increasing ionic strength.

The presence of CMC resulted in a further decrease in the recovery of talc under all ionic strengths as shown in Figure 6.2 (a) and (b), it was noted that there was an even further decrease in the recoveries with increasing ionic strength as shown in Figure 6.2 (b). This observation is in line with Corin and Wiese (2014) who showed a clear decrease in the rate of NFG (talc) recovery with increasing ionic strength proposing that increases in ionic strength increased the adsorption of CMC onto talc and thereby imparted a coagulative nature onto talc particles .

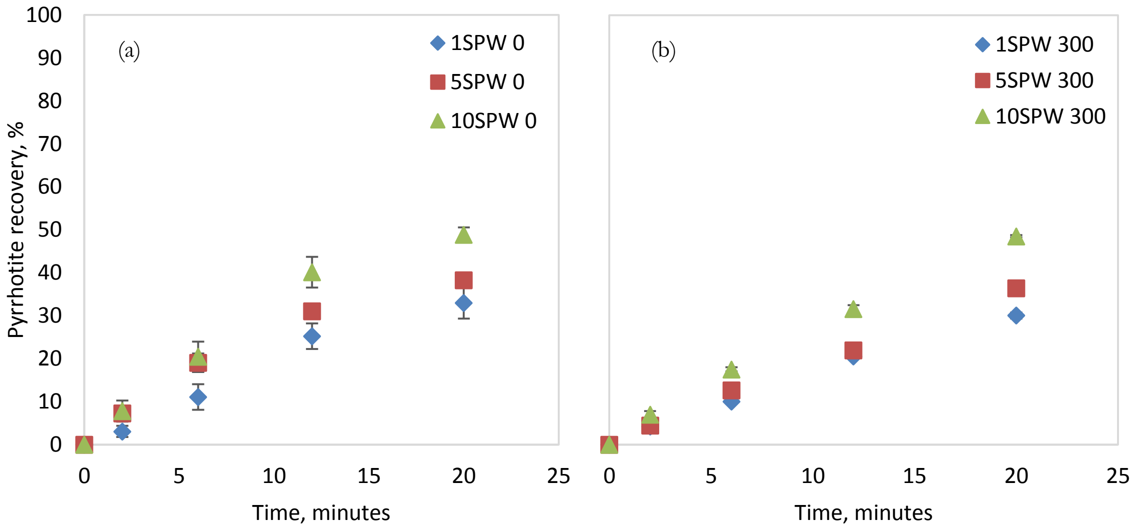


Figure 6.3: Pyrrhotite recoveries as a function of time under increasing ionic strength conditions and (a) in the absence of CMC, (b) in the presence of CMC at 300 g/t.

Figure 6.3 shows the microflotation data for pyrrhotite: (a) presents the observations in the absence of CMC and (b) presents the observations in the presence of CMC at 300 *g/t*. Figure 6.3 shows an increase in the pyrrhotite recovery with increasing ionic strength however there is no evidence of a depressant effect when considering both (a) and (b). In sulphidic ore flotation, the target is not to depress the sulphides but ensure that the pulp chemistry allows for selective depression of naturally floatable gangue.

6.7.2 Investigation of the Adsorption of CMC onto Pyrrhotite and Talc under Increased Ionic Strength of SPW

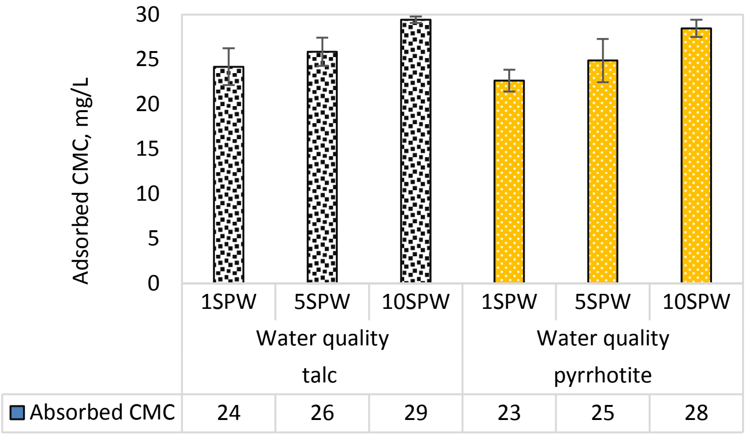


Figure 6.4: Total concentration of CMC absorbed onto the mineral surface as a function of the ionic strength of SPW.

Figure 6.4 shows the concentration of CMC that was adsorbed onto the mineral surface for both talc and pyrrhotite, calculated by difference from that remaining in the supernatant. For both the talc and pyrrhotite, there was an increase in the adsorption of CMC with increasing ionic strength. This trend is in agreement with the microflotation findings, particularly for talc where a decrease in recoveries in the presence of CMC with increasing ionic strength was attributed to an enhancement in the adsorption of CMC onto talc. Inorganic single salts containing Ca^{2+}, Mg^{2+} and Na^{+} have been reported to increase depressant adsorption, particularly in the presence of divalent cations (Burdukova *et al.*, 2008; Laskowski *et al.*, 2007; Parolis *et al.*, 2008; Shortridge *et al.*, 1999).

6.7.3 *Effect of Ionic Strength on the Settling Time of Talc Particles*

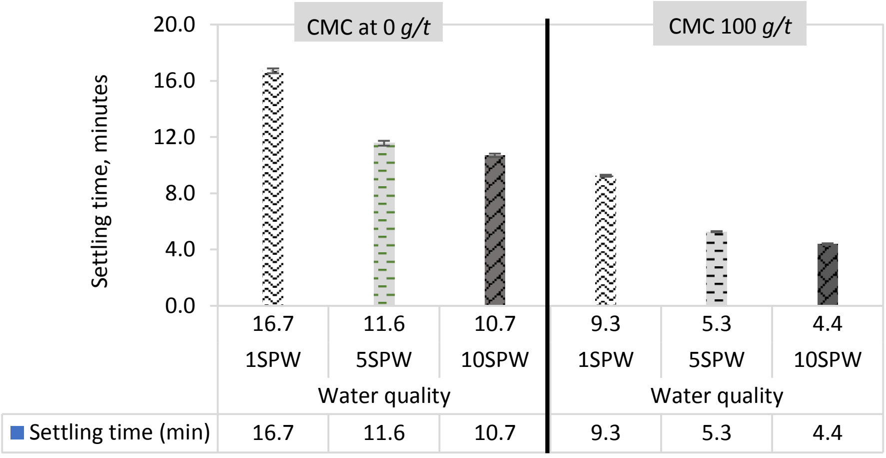


Figure 6.5: Solids settling time as a function of the ionic strength of SPW.

The settling time of talc particles in the presence and absence of CMC at varying ionic strength of SPW is shown in Figure 6.5. Talc particles settled faster as the ionic strength of plant water increased. However, the settling of talc particles was even quicker in the presence of CMC, indicating that increases in ionic strength alone without the addition of CMC enhanced the coagulation of talc particles.

6.7.4 *Effect of Ionic strength on the Zeta Potential of Talc and Pyrrhotite Particles*

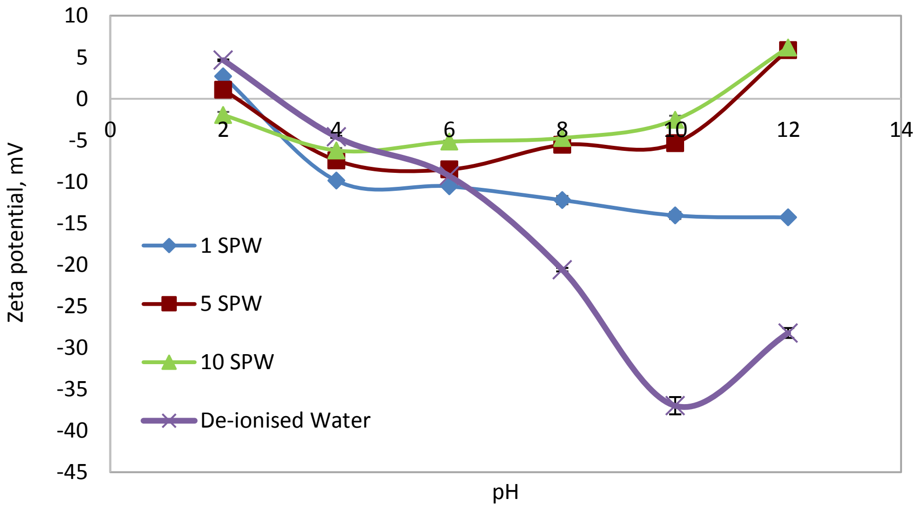


Figure 6.6: The zeta potential of talc as a function of pH under increasing ionic strength of plant water.

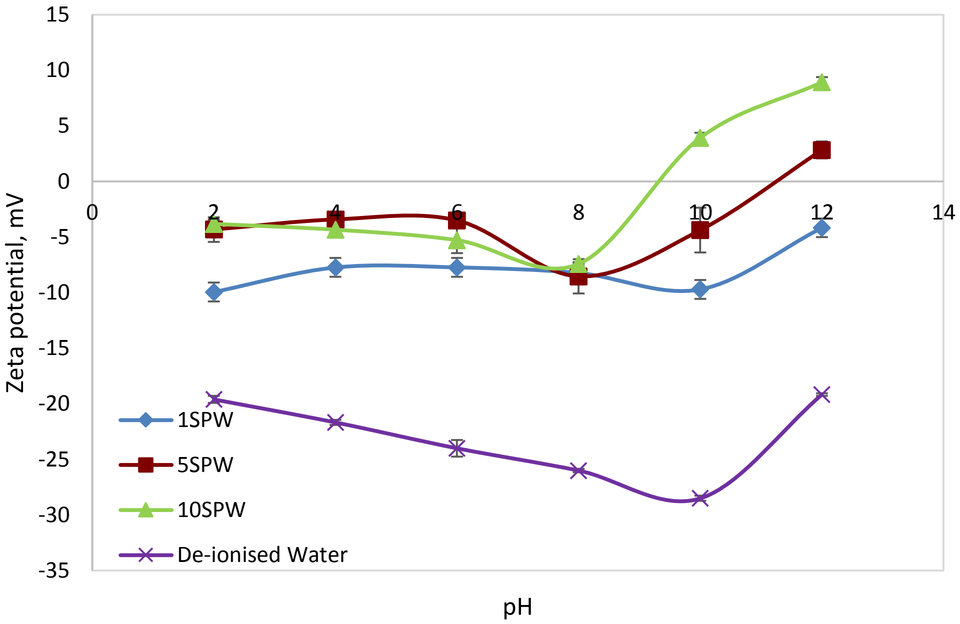


Figure 6.7: The zeta potential of pyrrhotite as a function of pH under increasing ionic strength of plant water.

Figure 6.6 and Figure 6.7 show the zeta potential over pH 2-12 under varying ionic strength of synthetic plant water for talc and pyrrhotite respectively. These data are all in the absence of CMC. It is clear that for both minerals the zeta potential became less negative across the studied pH range with increasing ionic strength of plant water. At pH 8, the zeta potential of talc in 5SPW is the same as that of talc in 10SPW. This perculair behaviour is also seen with pyrrhotite. At about pH 11 and above, the zeta potential became of talc completely positive.

The sudden increase in the zeta potential with increasing pH and ionic strength is attributed to the presence of hydroxo species on the surface of the mineral as previously proposed in Laskowski *et al.* (2007). These results further support the theory of an induced acid-base interaction between the passivated mineral surface and the highly negatively charged CMC as a mechanism through which CMC adsorption onto minerals such as talc occur in flotation pulps.

6.7.5 Effect of Ionic strength and pH on the Inorganic Electrolyte Speciation

Figure 6.8 to Figure 6.13 are speciation diagrams of anions in H^+, calcium, magnesium and sodium ions in plant water of 0.0242 mol·dm^{-3} (1SPW), 0.1212 mol·dm^{-3} (5SPW) and 0.2426 mol·dm^{-3} (10SPW) ionic strengths. These were generated using Visual MinteQ software (3.1, Jon Petter Gustafsson, KTH, Stockholm, Sweden). Figure 6.8 and Figure 6.9 illustrate the speciation of 1SPW from pH 2 to pH 12, these are split into anion and specific cation speciation diagrams for the purpose of a better illustration of the speciation changes occurring in 1SPW as pH varies. The logic is applied over those speciation diagrams for 5SPW in Figure 6.10 and Figure 6.11, and for 10SPW in Figure 6.12 and Figure 6.13.

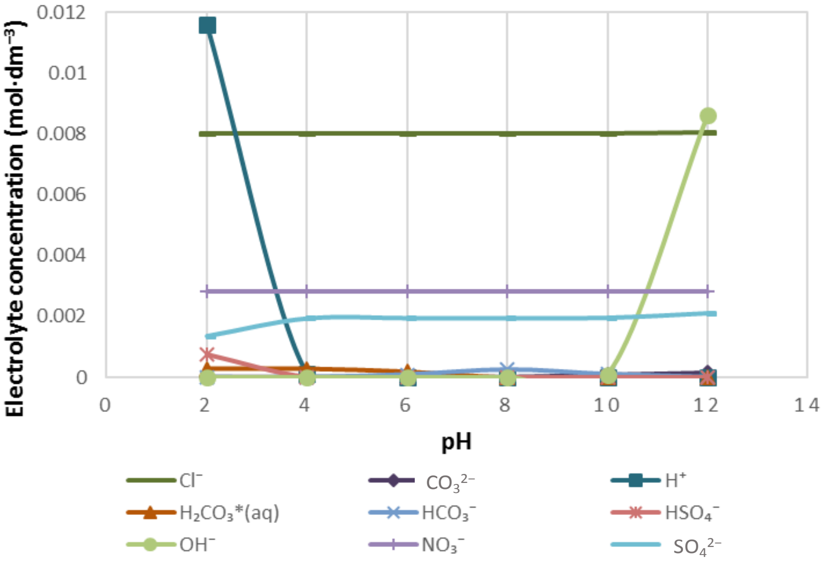
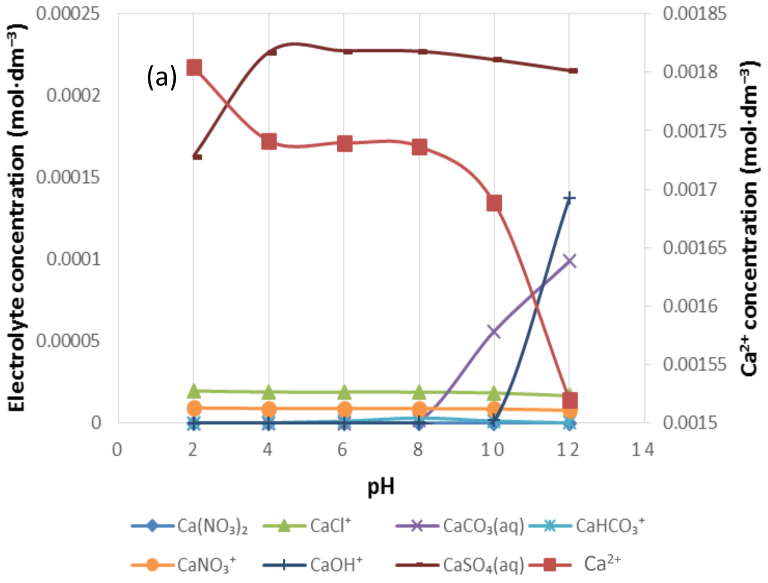
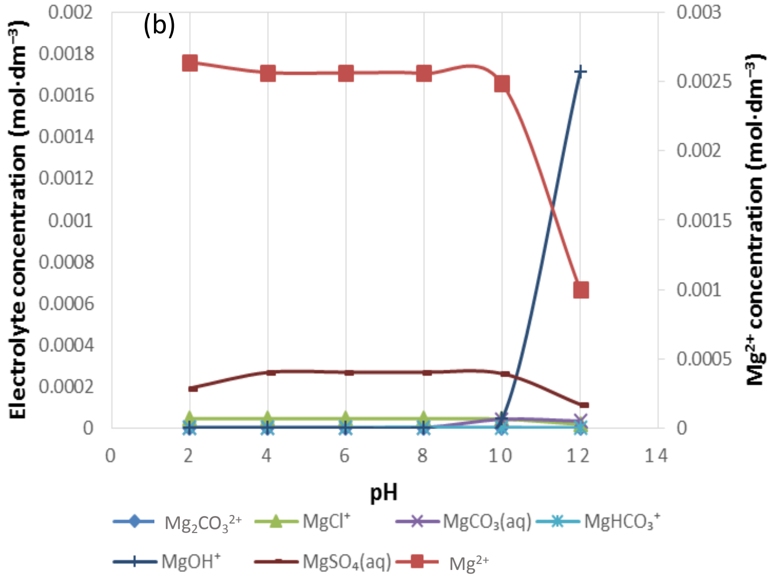


Figure 6.8: The distribution of Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-} to H^+ in 1SPW.

Figure 6.8 demonstrates the distribution of Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-} to H^+ in 1SPW for a pH range of 2–12. It can be seen that the concentration of Cl^- and NO_3^- remained fairly constant across the given pH range and were not distributed to any H^+ ions. However, CO_3^{2-} and SO_4^{2-} were distributed to H^+ ions such that H_2CO_3(aq), HCO_3^- and HSO_4^- formed. It is also interesting to note that H_2CO_3 and HSO_4^- are seen at pH 2–4, whereas HCO_3^- appears at pH 6–9. Worth mentioning is the fact that at pH > 10, [OH^-] rises whereas with [H^+] increases ions as the pH of 1SPW drops below pH 4.


(a)
Electrolyte concentration (mol·dm^{-3})
0.00025
0.0002
0.00015
0.0001
0.00005
0
Ca^{2+} concentration (mol·dm^{-3})
0.00185
0.0018
0.00175
0.0017
0.00165
0.0016
0.00155
0.0015
0
2
4
6
8
10
12
14
pH
Ca(NO$_3$)$_2$
CaCl$^+$
CaCO$_3$(aq)
CaHCO$_3^+$
CaNO$_3^+$
CaOH$^+$
CaSO$_4$(aq)
Ca^{2+}


(b)
Electrolyte concentration (mol·dm^{-3})
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Mg^{2+} concentration (mol·dm^{-3})
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
2
4
6
8
10
12
14
pH
Mg$_2$CO$_3^{2+}$
MgCl$^+$
MgCO$_3$(aq)
MgHCO$_3^+$
MgOH$^+$
MgSO$_4$(aq)
Mg^{2+}

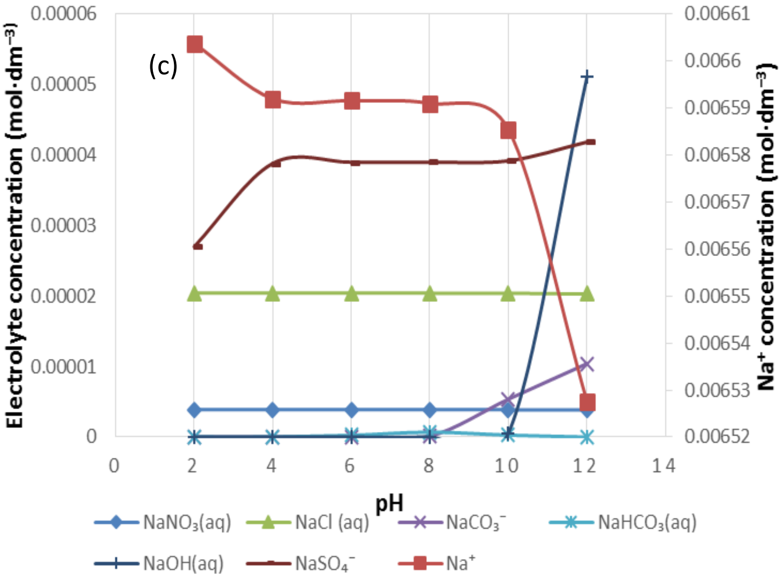


Figure 6.9: The speciation of (a) Ca^{2+}, (b) Mg^{2+} and (c) Na^{+} in 1SPW.

Figure 6.9 shows the distribution of Ca^{2+}, Mg^{2+} and Na^{+} in 1SPW for a pH range of 2–12. It can be seen that the divalent cations are present in solution at higher concentrations than the monovalent Na^{+} (i.e., $[Mg^{2+}] > [Ca^{2+}] > [Na^{+}]$). The concentration of $CaSO_4$(aq), $MgSO_4$(aq) and $NaSO_4^-$(aq) in each individual cation species distribution seems to be higher than all other inorganic complex species as seen in Figure 6.9a, 6.9b and 6.9c respectively. These are followed by an evident presence of $CaCl^{+}$, $MgCl^{+}$ and NaCl. An increase in the concentration of $CaCO_3$(aq), $MgCO_3$(aq) and $NaCO_3^-$ beyond pH 8 can also be observed.

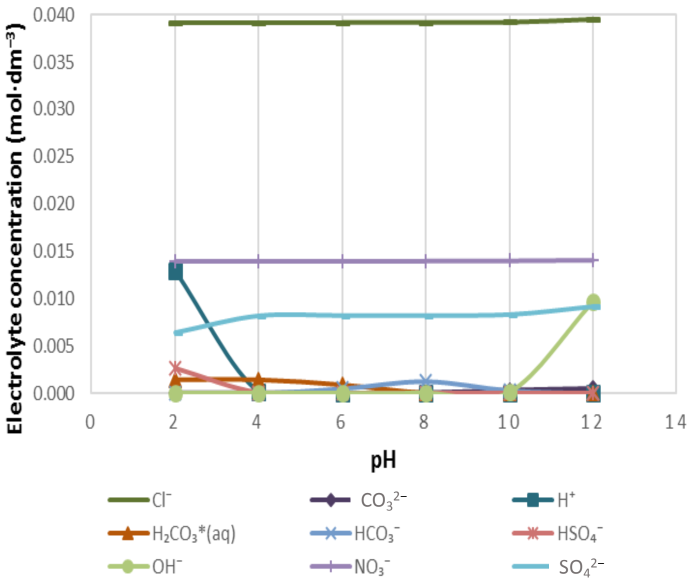
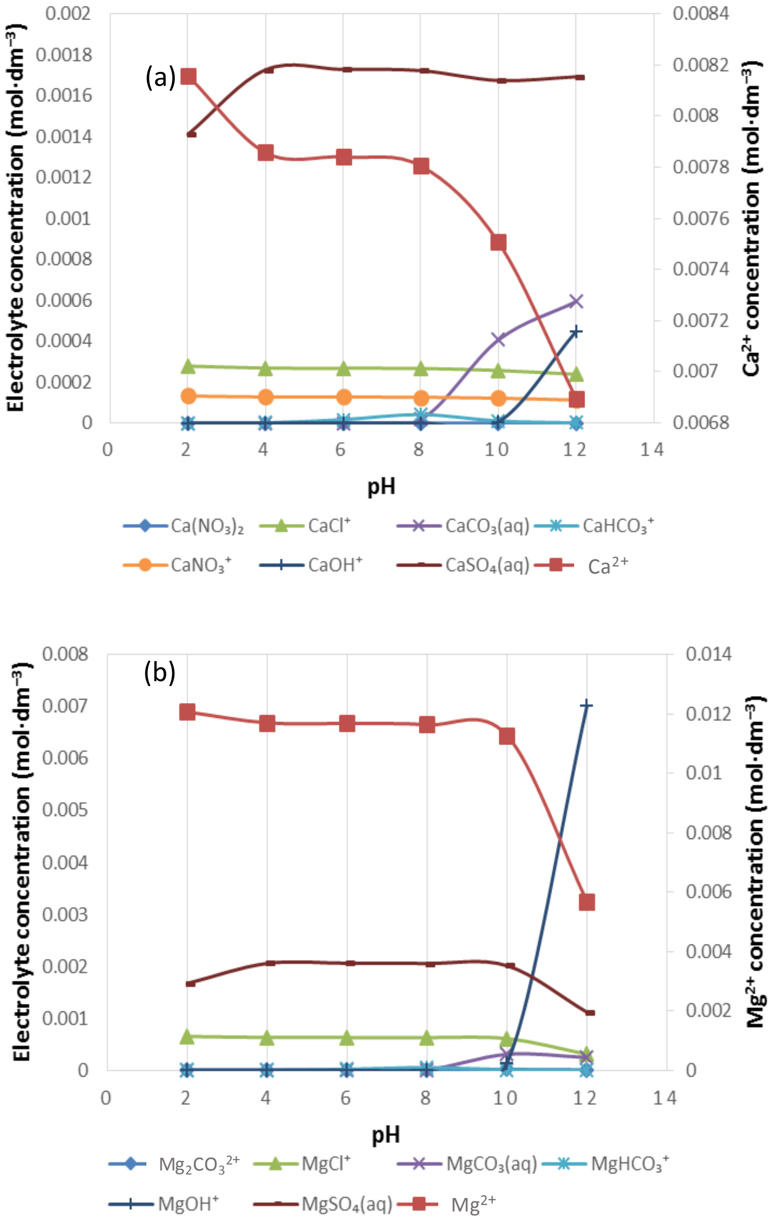


Figure 6.10: The speciation of cation-free anions in 5SPW.

Figure 6.10 illustrates the distribution of Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-} to H^+ in 5SPW for a pH range of 2–12. It can be seen that Cl^- and NO_3^- were not distributed to any H^+ ions in solution. However, CO_3^{2-} and SO_4^{2-} were distributed to H^+ ions and formed species such as H_2CO_3(aq), HCO_3^- and HSO_4^- as [H^+] decreased evidently with an increase in pH between pH 2–4. Between pH 2–8, there was an apparent presence of H_2CO_3(aq), though decreasing with an increase in pH until pH 8. HSO_4^- as the pH increases beyond pH 2. There was an evident increase in the [HCO_3^-] from pH 4 to pH 8 and thereafter the concentration of HCO_3^- decreased. Also, beyond pH 10, there was a significant increase in [OH^-].


(a)
Electrolyte concentration (mol·dm⁻³)
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Ca²⁺ concentration (mol·dm⁻³)
0.0084
0.0082
0.008
0.0078
0.0076
0.0074
0.0072
0.007
0.0068
0
2
4
6
8
10
12
14
pH
Ca(NO₃)₂
CaCl⁺
CaCO₃(aq)
CaHCO₃⁺
CaNO₃⁺
CaOH⁺
CaSO₄(aq)
Ca²⁺
(b)
Electrolyte concentration (mol·dm⁻³)
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Mg²⁺ concentration (mol·dm⁻³)
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
2
4
6
8
10
12
14
pH
Mg₂CO₃²⁺
MgCl⁺
MgCO₃(aq)
MgHCO₃⁺
MgOH⁺
MgSO₄(aq)
Mg²⁺

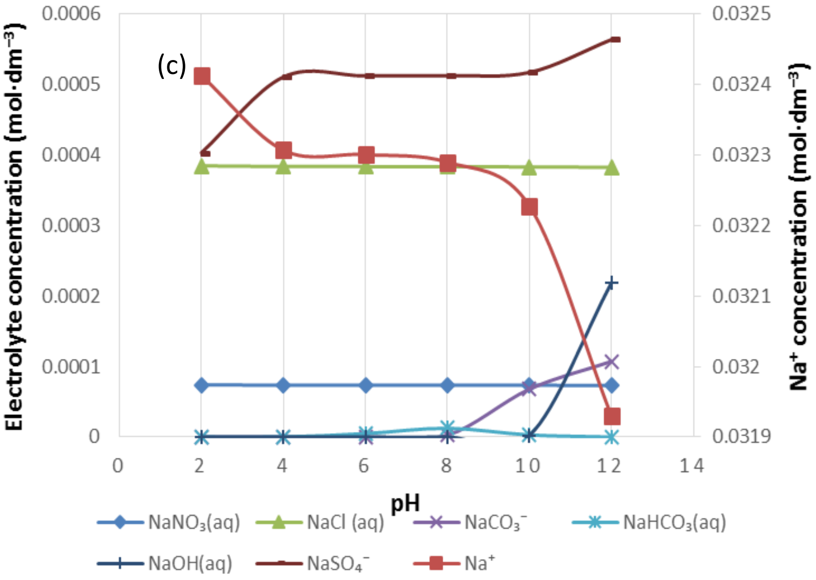


Figure 6.11: The speciation of (a) Ca^{2+}, (b) Mg^{2+} and (c) Na^{+} in 5SPW.

Figure 6.11 shows the distribution of Ca^{2+}, Mg^{2+} and Na^{+} in 5SPW for a pH range of 2–12. As the pH increases from pH 2, $[Mg^{2+}]$, $[Ca^{2+}]$ and $[Na^{+}]$ decrease and thus other species form. In Figure 10a it can be seen that the concentrations of $CaCl^{+}$ and $CaNO_3^{+}$ remained the same despite increases in pH. At pH > 2, the presence of $CaSO_4(aq)$ supersedes any other Ca^{2+} bearing species in solution. At pH > 2 there is an increase in $[CaHCO_3^{+}]$ and decreases again at pH > 10. At pH > 8, there is an increase in $[CaCO_3(aq)]$ whilst $[CaOH^{+}]$ rises at pH > 10. In Figure 6.11b a strong presence of $MgCl^{+}$ and $MgSO_4(aq)$ is seen, though not higher than Mg^{2+}. $MgSO_4(aq)$ decreases at pH > 10. Evident increase in the concentration of $MgCO_3(aq)$ is seen at pH > 8. Furthermore, a significant increase in $[MgOH^{+}]$ occurs at pH > 10. Figure 6.11c shows the speciation of Na^{+} in 5SPW; there is an increase in the concentration of $NaSO_4^{-}(aq)$ beyond any other Na^{+} species above pH 3. An increase in the concentration of $NaHCO_3(aq)$ is seen at pH > 6 which then drops at pH > 8. $[NaCO_3^{-}]$ increases as pH increases from pH 8 whilst $[NaOH(aq)]$ increases as the pH of 5SPW increases from pH 10.

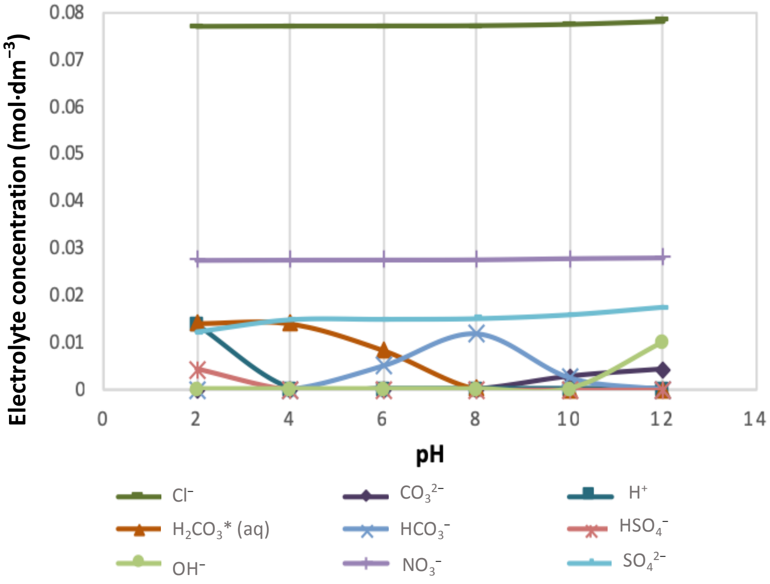
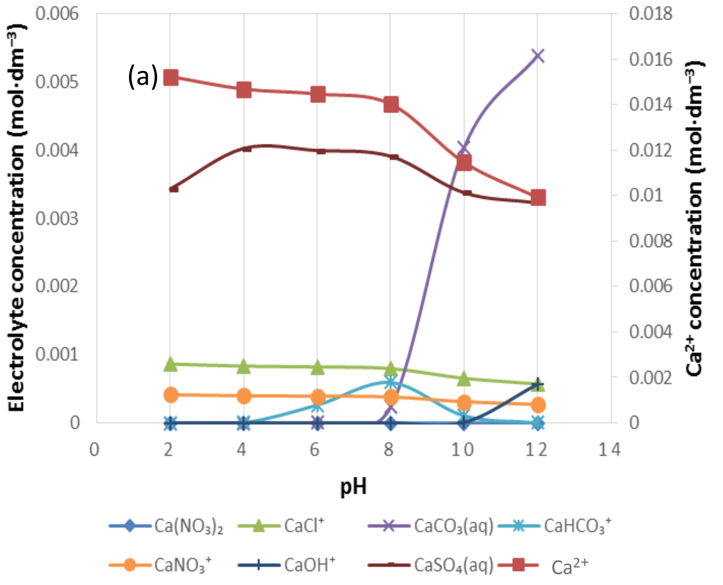
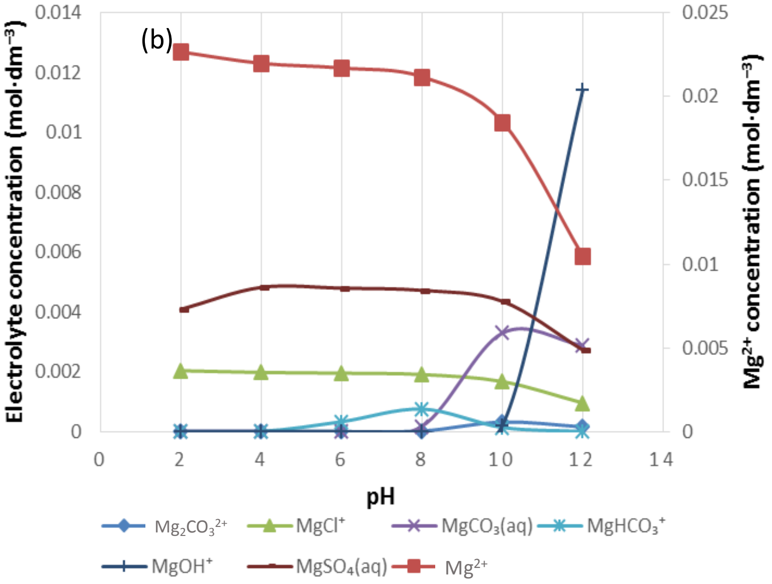


Figure 6.12: The speciation of cation-free anions in 10SPW.

Figure 6.12 depicts the distribution of Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-} to H^+ in 10SPW for a pH range of 2–12. It can be seen that all the anions that were added from the 10SPW single salts recipe were distributed to H^+ ions in solution except Cl^- and NO_3^-. Between pH 2–4 a decrease in the concentrations of HSO_4^- to an apparent minimum is seen as the concentration of H^+ ions decreases with an increase in pH whereas the concentrations H_2CO_3(aq) becomes an apparent minimum at about pH 8. A rise in the concentration of HCO_3^- is seen from pH 4 until it reaches a maximum at pH 8 and drops again to a negligible value after pH 10. There is an apparent rise in the concentrations of CO_3^{2-} and OH^- as the pH of 10SPW increases beyond pH 10.


(a)
Electrolyte concentration (mol·dm⁻³)
0.006
0.005
0.004
0.003
0.002
0.001
0
Ca²⁺ concentration (mol·dm⁻³)
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
2
4
6
8
10
12
14
pH
Ca(NO₃)₂
CaCl⁺
CaCO₃(aq)
CaHCO₃⁺
CaNO₃⁺
CaOH⁺
CaSO₄(aq)
Ca²⁺


(b)
Electrolyte concentration (mol·dm⁻³)
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Mg²⁺ concentration (mol·dm⁻³)
0.025
0.02
0.015
0.01
0.005
0
0
2
4
6
8
10
12
14
pH
Mg₂CO₃²⁺
MgCl⁺
MgCO₃(aq)
MgHCO₃⁺
MgOH⁺
MgSO₄(aq)
Mg²⁺

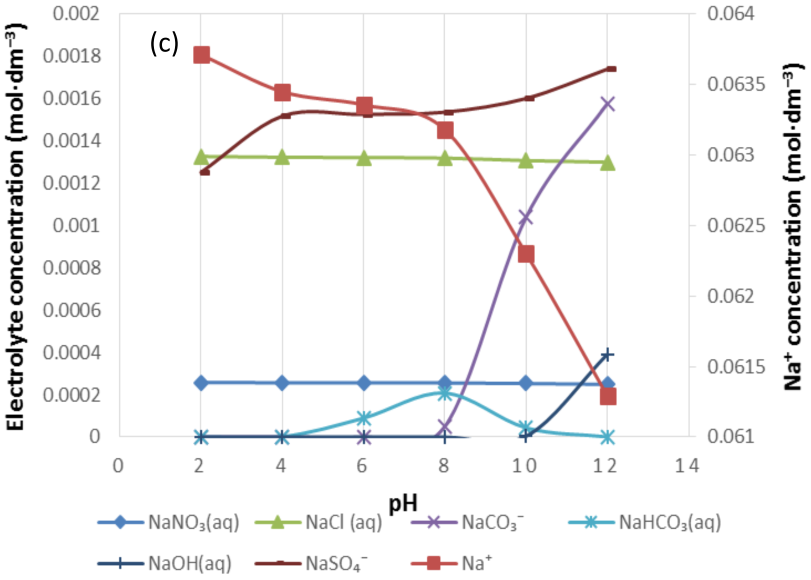


Figure 6.13: The speciation of (a) Ca^{2+}, (b) Mg^{2+} and (c) Na^{+} in 10SPW.

Figure 6.13 shows the distribution of Ca^{2+}, Mg^{2+} and Na^{+} in 10SPW for a pH range of 2–12. As the pH increases from pH 2, [Mg^{2+}], [Ca^{2+}] and [Na^{+}] decrease and thus other species form. It can be seen that in Figure 6.13a,b there is a strong presence of $CaSO_4$(aq) and $MgSO_4$(aq) in solution. A similar observation can be made from Figure 6.13c with regard to $NaSO_4^-$, although this anionic species shows to have the highest concentration at pH 7 in Na distribution. Also, at pH > 7 $CaCO_3$(aq), $MgCO_3$(aq) and $NaCO_3^-$ showed an apparent increase in concentration whereas $CaHCO_3^+$, $MgHCO_3^+$ and $NaHCO_3$(aq) were seemingly significant at 4 < pH < 12.

Figure 6.8 to Figure 6.13 illustrate that at higher pH values of the pulp compared to pH 9 where the flotation of Cu-Ni-PGM sulfides often occurs, the concentration of Ca^{2+}, Mg^{2+} and Na^{+} decreases whilst the concentration of their respective hydroxides, carbonates and sulfoxy species increases. This trend is particularly stronger in the divalent Ca^{2+} and Mg^{2+} speciation compared to the monovalent Na^{+}. Furthermore, it can be seen that the increase in ionic strength from 0.0242 to 0.2426 mol.dm^{-3} increases the concentration of the hydroxo species. Therefore it stands to reason that the effect of these hydroxo species in 10SPW would have a stronger effect on the interactions occurring in the pulp phase of flotation. The species present at the various pH values and ionic strength correlate well with the zeta potential results in that the mineral surface is more passivated at pH 9 and above showing the passivated nature of the hydroxo species and their increased concentrations on the mineral surface charge. Thus the zeta potential trend of the minerals is ascribed to these hydroxo species which may render the mineral particles hydrophilic and coagulative as seen in the floatability and coagulation of talc.

6.8 Conclusions

The microflotation results, for a system containing CMC, indicated a decrease in the recovery of talc with increasing ionic strength whilst the presence of CMC did not affect the flotation behaviour of pyrrhotite. The adsorption results agreed with these findings in that more CMC was adsorbed onto the mineral surface as the ionic strength of SPW increased. Also, the settling time decreased with increasing ionic strength with an even further decrease upon the addition of CMC resulting in the fastest settling time in the most saline water (10SPW).

It is proposed, from the findings of this investigation, that increases in ionic strength of process water enhance the adsorption of CMC onto naturally floatable gangue, imparting a coagulative nature onto the gangue mineral particles and thereby inhibiting their flotation.

The zeta potential observations clearly showed that electrolytes present in process water, as seen in the speciation diagrams, act on the mineral surface, passivating the mineral surface, and through the proposed acid-base interaction between the mineral surface and CMC; CMC adsorbs preferentially onto the mineral surface, forming large mineral-CMC flocs with an enhanced coagulative and hydrophilic nature and thereby resulting in their depression in flotation.

6.9 Acknowledgements

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6.10 References

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CHAPTER 7 THE INFLUENCE OF ELECTROLYTES PRESENT IN PROCESS WATER ON THE FLOTATION BEHAVIOUR OF A CU-NI-PGE ORE

7.1 Rationale, Key Questions & Hypotheses

Previous research suggests that water quality effects on flotation performance may be linked to specific inorganic electrolytes or ions in solution affecting the pulp chemistry of flotation, some of these inorganic electrolytes are said to be effective in retarding bubble coalescence and thus enhancing froth stability while others may inhibit the collector from adsorbing at the mineral surface (Corin *et al.*, 2011; Muzenda, 2010; Slatter *et al.*, 2009). Some inorganic electrolytes such as those of $CaSO_4$ and $CaCO_3$ may form slime coatings in solution and may thus be depressive in nature. Based on perspective from literature and findings of Chapter 2-6, it was deemed necessary to carry out an investigation into the influence of inorganic electrolytes in the form of single salts on the floatability of a Cu-Ni-PGE bearing Merensky ore. Single salts were carefully selected in an attempt to determine possible controlling ions in process water. Thus, the key questions and hypotheses addressed in this chapter are outlined below.

7.1.1 Key Questions

- How does the floatability of the selected ore change in varying single salt solutions?

7.1.2 Hypotheses

- *Single salt solutions containing the divalent Ca^{2+} and Mg^{2+} will result in higher water, total solids, Cu and Ni recoveries at the expense of the Cu and Ni grades compared to solutions containing the monovalent Na^{+} owing to greater froth stabilising action of the divalent cations*

- *SO_4^{2-} and NO_3^{-} will result in lower solids recoveries and improved grades owing to their gangue deactivation/depression owing to their formation of slime coating around the surface of the mineral.*

7.2 Abstract

Calcium and magnesium ions in process water have been reported to have significant influence on froth stability and flotation recovery, however little research has been done to identify influential ions during the flotation of PGE containing ores. Thus, the purpose of this study was to investigate the effect of typical electrolytes present in process water on the flotation of a Merensky ore. The ionic strength was kept constant at 0.0213 mol·dm^{-3} for all electrolyte solution. Cation and anion effects were investigated and each electrolyte compared with the standard synthetic plant water. The results showed higher amounts of solids recovered for all sodium electrolytes whereas calcium and magnesium electrolytes resulted in similar solids recovery. NO_3^- ions resulted in significantly higher Cu and Ni grades than Cl^- and SO_4^{2-} ions. The results seem to suggest that the influence of ion type depends on its ability to enhance or retard gangue activation.

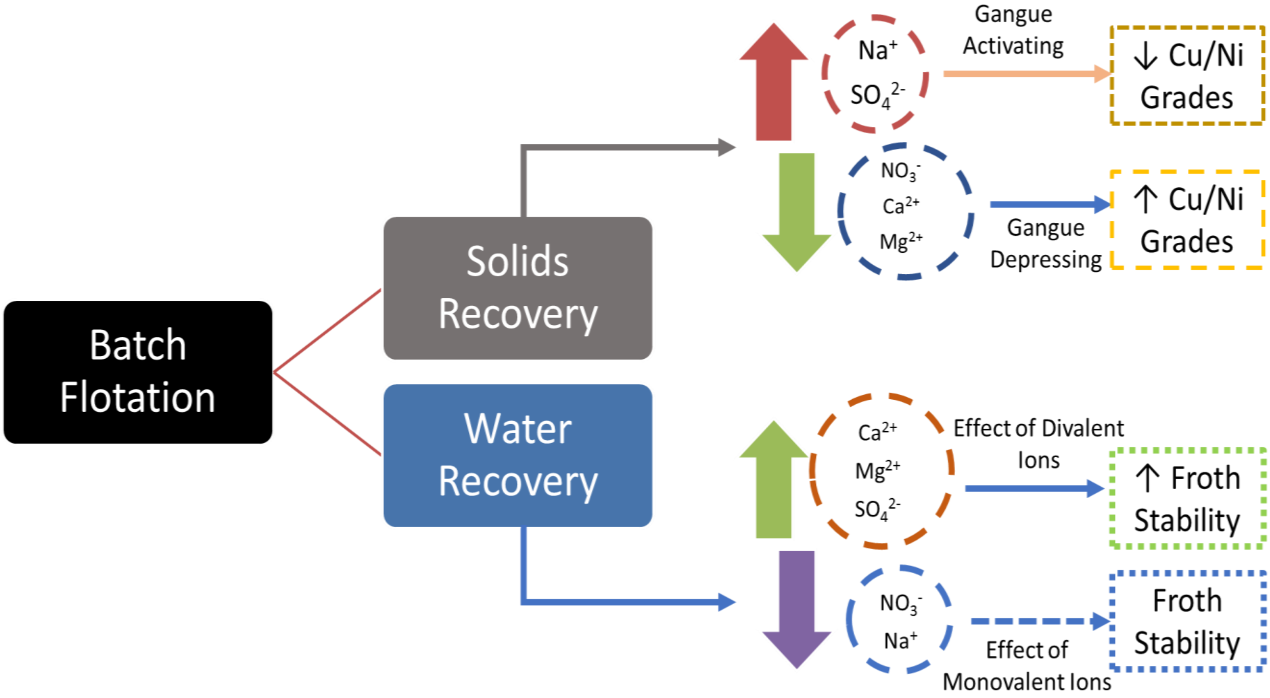
KEYWORDS

Gangue depression; Froth stability; Ionic strength Electrolytes; Water recovered

7.3 Highlights

- Cl^- and SO_4^{2-} led to higher solids recovery than NO_3^-.
- Ca^{2+} and Mg^{2+} resulted in higher water recoveries than Na^+.
- NO_3^- resulted in lower Cu and Ni recoveries than Cl^- and SO_4^{2-}.
- NO_3^- resulted in higher Cu and Ni grades than Cl^- and SO_4^{2-}.
- Na^+ gave lower Cu and Ni grades than Ca^{2+} and Mg^{2+}.

7.4 Graphical Abstract



7.5 Introduction

Globally, the availability of fresh water is steadily decreasing, and it is speculated that the trend will inevitably continue as the world's population rises and emerging economies continue to increase water consumption levels which negatively affect climate change. The global mining business community is increasingly recognising the 'war on water' which has economic, social and environmental implications. However effective response to this challenge needs guidance, tools, standards and schemes to enable change to more sustainable practices. Mining organisations will inevitably be required and regulated to devise strategic water management frameworks as a means to effectively rise to this water challenge facing the global community (Liu *et al.*, 2013). Over the last decade, many new initiatives and concepts such as the recycle, reduce and reuse initiative, have evolved to address this crisis, business leaders in the minerals industry together with civil society and government are working untiringly to ensure success in this struggle. The use of recycled water, during the flotation of Platinum Group Elements (PGEs), is known for its impact on the quality of the process water (Liu *et al.*, 2013; Ikumapayi *et al.*, 2012; Slatter *et al.*, 2009; Levay *et al.*, 2001; Liu and Finch, 1993). Fundamental studies and plant operations have shown that the quality of process water, in particular the increase in ionic strength, has significant effects on the recovery of valuable minerals and gangue due to modifications in the surface chemistry and reagent behaviour (Manono *et al.*, 2012, 2013; Ikumapayi *et al.*, 2012; Corin *et al.*, 2011; Muzenda, 2010; Wiese *et al.*, 2005, Zhang *et al.*, 1997, Iwasaki *et al.*, 1980; Viviers, 1979). Excellence in water management requires an understanding of the effect of water quality at a fundamental level, where the flotation process is monitored against changing ions and ionic strength conditions and other process and plant variables (Liu *et al.*, 2013). An extensive literature review on how the ionic strength of plant water affects the flotation behaviour of a metal sulphides based ore is reported by Manono *et al.* (2013, 2012) and Corin *et al.* (2011). Fundamental research has shown that increasing the ionic strength of plant water resulted in an increase in the amount of solids and water reporting to concentrate (Corin and Wiese, 2014; Manono *et al.*, 2012; Corin *et al.*, 2011). However, these studies focused more on the impact of ionic strength without decoupling ionic strength from ion type. Therefore, research is needed to establish whether there is any synergistic effect between the ionic strength, ion type and concentration in process water. In other words, there is still a growing need to identify the role players (in as far as electrolyte type is concerned) within process water in influencing frothability and flotation behaviour of base metal sulphides containing mineral ores as Liu *et al.* (2013) mentioned, that the pathways by which a particular water constituent affects flotation performance may be different for each mineral and reagent combination.

It is thus of ample regard to conduct research in this area to help understand the negative and positive effects of the different process water electrolyte constituents.

Therefore, an investigation into the effect of ion type on the floatability of a Merensky ore was commissioned in order to determine the controlling ions in synthetic plant water, thus the ions selected are those that are present in synthetic plant water, viz., Ca^{2+}, Cl^{-}, Mg^{2+}, NO_3^{-}, Na^{+}, and SO_4^{2-}. For the purpose of this study, it was deemed sufficient to test these ions at the ionic strength of standard synthetic plant water (1SPW) which resembles standard plant water.

7.6 Materials & Methods

A sample typical of the Merensky reef was obtained. The bulk sample was crushed, blended, riffled and split using a rotary splitter into 1 kg samples. Table 7.1 shows the mineralogy of the ore. The 1 kg ore samples were milled, at 66% solids in synthetic plant water (1SPW) and single salt solutions, using a laboratory scale stainless steel rod mill to achieve a grind of 60% passing 75 µm. Standard UCT plant water (Wiese *et al.*, 2005) was used as the base water quality (1SPW) and the ion/electrolyte type was varied as shown in Table 7.2. The standard UCT plant water is a recipe whereby distilled water is modified by the addition of inorganic salts to ensure that the water contained similar amounts of ions typically found in Merensky ore flotation plants.

Table 7.1: Modal composition: sulphide and gangue minerals present in the ore as determined by QEMSCAN.

Mineral	**(%)**
Pentlandite	0.31
Chalcopyrite	0.25
Pyrrhotite	0.44
Pyrite	0.08
Other sulphides	0.02
TOTAL sulphides	1.09
Plagioclase	43.38
Orthopyroxene	32.60
Olivine	0.59
Clinopyroxene	7.48
Talc	3.51
Serpentine	0.80
Chlorite	0.83
Phlogopite	0.46
Quartz	0.67
Calcite	0.18
Oxides	8.10
Other	0.32
TOTAL	100.00

Table 7.2: Ions present in standard synthetic plant water and the electrolyte solutions.

Water type	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	Cl^{-} (ppm)	SO_4^{2-} (ppm)	NO_3^{-} (ppm)	CO_3^{2-} (ppm)	TDS (ppm)	Ionic Strength [M]
1SPW	80	70	153	287	240	176	17	1023	0.0213
NaCl	-	-	490	755	-	-	-	1245	0.0213
Na_2SO_4	-	-	326	-	682	-	-	1009	0.0213
$NaNO_3$	-	-	490	-	-	1321	-	1810	0.0213
$CaCl_2$	285	-	-	503	-	-	-	788	0.0213
$CaSO_4$	213	-	-	-	512	-	-	725	0.0213
$Ca(NO_3)_2$	285	-	-	-	-	880	-	1165	0.0213
$MgCl_2$	-	173	-	503	-	-	-	676	0.0213
$MgSO_4$	-	129	-	-	512	-	-	641	0.0213
$Mg(NO_3)_2$	-	173		-	-	880	-	1053	0.0213

The milled slurry was transferred to a 3 L Barker flotation cell. The volume of the cell was made up to generate 35% solids using the required electrolyte solution. The cell was fitted with a variable speed drive and the pulp level was controlled manually. The impeller speed was set to 1200 rpm. An air flow rate of 7 L/min was maintained for all flotation experiments and a constant froth height of 2 cm was sustained throughout. The cell height was controlled and kept at 2 cm by the addition of the electrolyte solution being tested. Concentrates were collected at 2, 6, 12 and 20 min respectively by scraping the froth into a collecting pan every 15 s. A feed sample was taken before and a tails sample after each flotation test. Feeds, concentrates and tails were filtered, dried and weighed before analysis. All batch flotation tests were conducted in duplicate and reproducibility was found to be within 5% mass recovery standard error. 150 g/t sodium isobutyl xanthate (SIBX) collector and 40 g/t DOW 200 frother were used for all experiments. The collector solution was added to the mill, as Wiese *et al.* (2005) showed this to have a significant effect on flotation performance.

The collector, SIBX, was supplied by Senmin. The frother, DOW 200, was supplied by Betachem. All the chemical salts used to make up synthetic plant water and electrolyte solutions were supplied by Merck.

Copper and total nickel analysis of all samples was conducted using a Bruker S4 Explorer XRF Spectrometer. Sulphur analysis was carried out using a LECO DR423 sulphur analyser. Assuming the stoichiometries for chalcopyrite and pentlandite to be $CuFeS_2$ and $(FeNi)_9S_8$ respectively, the recovery of iron sulphides (including pyrrhotite) can be estimated from the copper, nickel, sulphur values for each concentrate. The recoveries of copper and total nickel can be used to estimate the recoveries of chalcopyrite and pentlandite respectively.

7.7 Results

7.7.1 *Observations*

The results obtained for the final amount of solids and water recovered are shown in Figures 5.1 and 5.2 such that Figure 5.1 gives a clear view of the cation effect and Figure 5.2 the anion effect. In Figure 5.1 the behaviour of the selected ions is also compared to that of 1SPW on the selected Merensky ore.

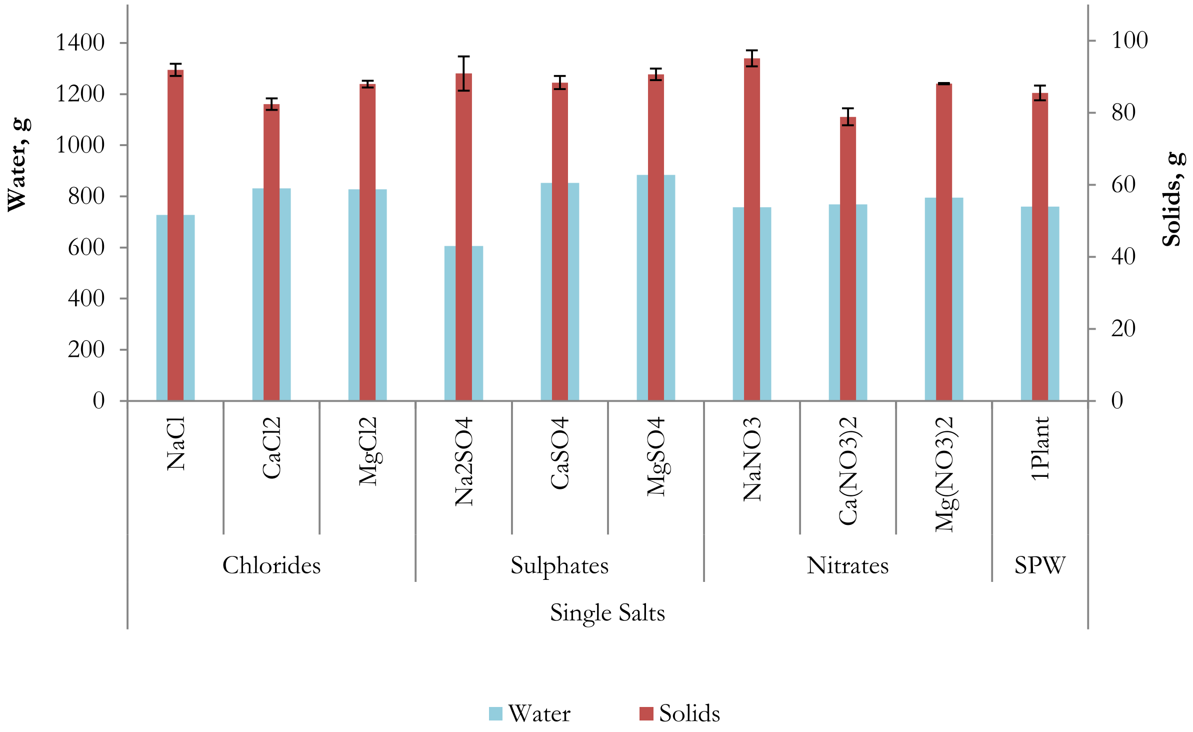


Figure 7.1: Final solids and water recovery for all single salt solutions - the cation effect, in comparison to 1SPW.

Figure 7.1 shows the final amount of solids and water recovered for all tested single salt conditions. The results depicted in this figure illustrate the cation effect, and these are compared to those of 1SPW. Regarding the amount of solids recovered, the following are the findings from Figure 7.1: In the Cl^- group, Ca^{2+} resulted in significantly lower amount of solids recovered whilst

Na^+ resulted in a higher amount of solids reporting to concentrate; the SO_4^{2-} group did not show any cation effect on the amount of solids recovered; the NO_3^- group had lower amounts recovered when in solution with Ca^{2+} and higher amounts recovered when combined with Na^+. The results regarding the amount of water recovered were as follows: In the Cl^- group, Ca^{2+} and Mg^{2+}resulted in a significantly higher amount water recovered than the Na^+ containing solution; the SO_4^{2-} group showed a significantly higher amount of water recovered in the presence of Ca^{2+} and Mg^{2+} than when the Na^+ cation was present in water; the NO_3^- group did not show any significant cation effect on the amount of water reporting to concentrate.

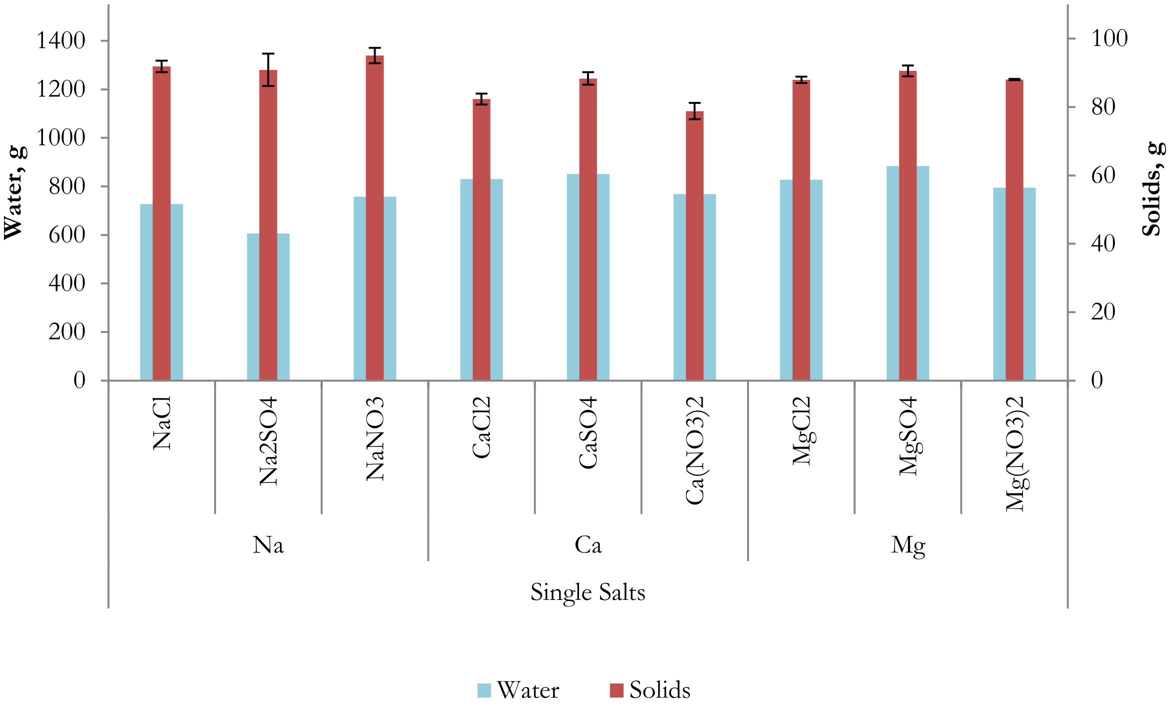


Figure 7.2: Final solids and water recovery for all single salt solutions – the anion effect.

Figure 7.2 shows the anion effect for the same results shown in Figure 7.1. The results showed the following: with Na^+ solutions, no anion effect on the amount of solids recovered; and with Ca^{2+} solutions, a significantly higher amount of solids reporting to concentrate was observed in the presence of SO_4^{2-}; and with Ca^{2+} solutions, there was no anion effect observed on the amount of solids recovered. The study for the anion effect on the amount of water recovered showed the following: Cl^- and NO_3^-resulted in a significantly higher amount of water reporting to concentrate than SO_4^{2-}in the Na^+ group; the Ca^{2+} group showed higher amounts of water recovered with

SO_4^{2-} and a significantly lower amount of water recovered in the presence of NO_3^-, Mg^{2+} containing solutions resulted in a significantly higher amount of water recovered with SO_4^{2-} than with Cl^- and NO_3^-.

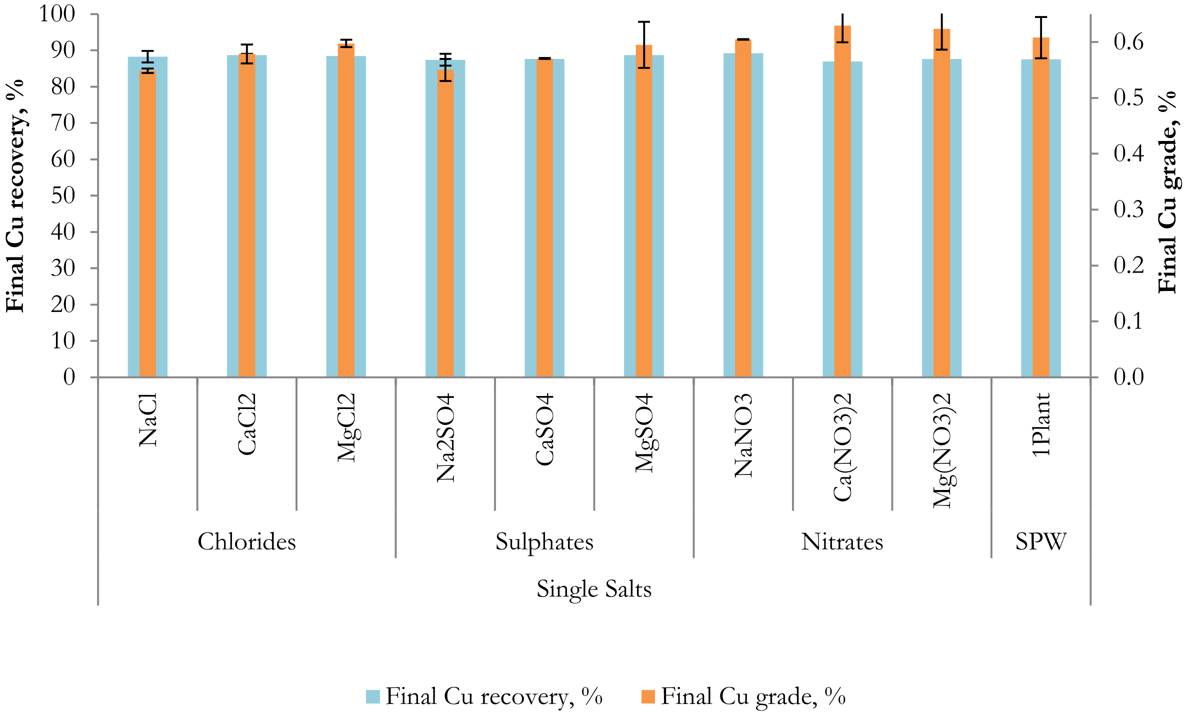


Figure 7.3: Final copper recovery and grade for all single salt solutions – the cation effect, and compared to 1SPW.

Figure 7.3 illustrates the findings obtained for the final Cu recovery and grade for all single salt conditions tested; the cation effect is also shown, i.e. the change in the final Cu recovery and grade with cation type (monovalent or divalent). These results are plotted together with those of 1SPW as a means to detect any ions that deviate from the results obtained when 1SPW was used. The results show the following: with Cl^- solutions, no cation effect on the % Cu recovery; with SO_4^{2-} solutions, no cation effect on the % Cu recovery; and with NO_3^- solutions, a significantly higher % Cu recovery obtained with Na^+ and a significantly lower % Cu recovery obtained with Ca^{2+}. As regards the cation effect on the % Cu grade these results were obtained: Na^+ resulted in a significantly lower % Cu grade with Cl^- solutions; no cation effect with SO_4^{2-} solutions; and no cation effect with NO_3^- solutions.

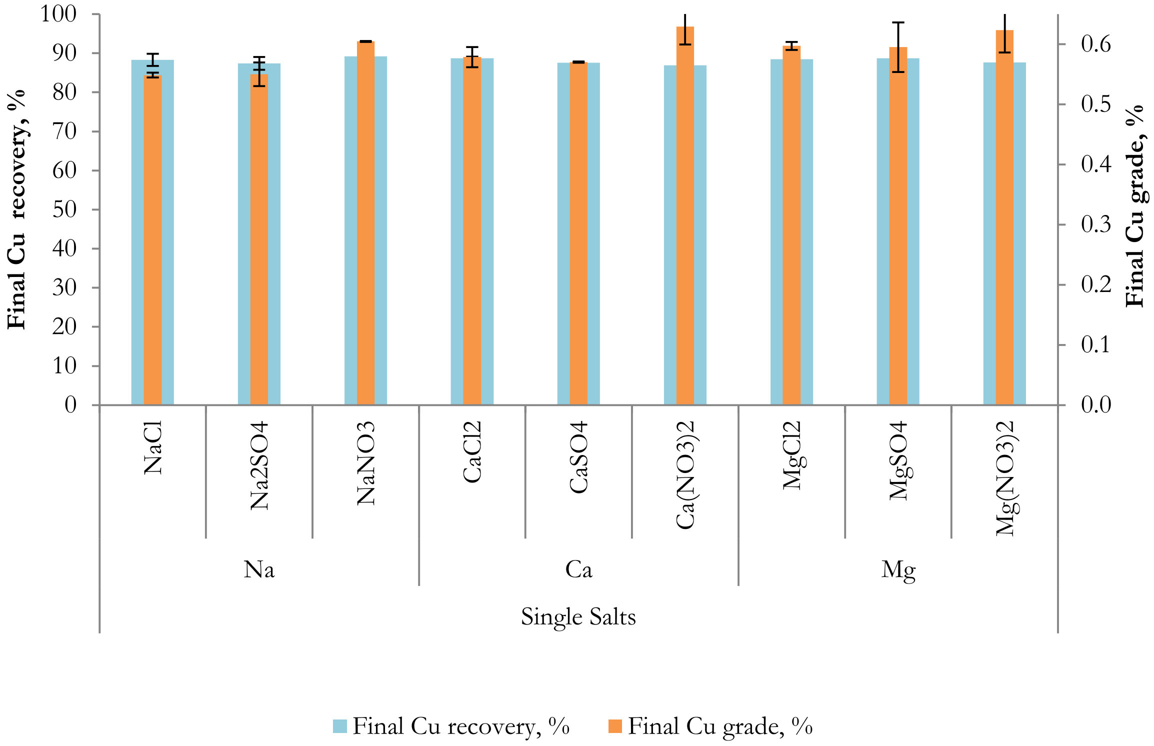


Figure 7.4: Final copper recovery and grade for all single salt solutions – the anion effect.

Figure 7.4 illustrates the results obtained for the final Cu recovery and grade showing the anion effect. It is shown that the final copper recovered remained unaffected by changes in the anion type; the final Cu recovery remained in the region of 90% for all tested conditions. The type of the anion used is however shown to have an impact on the final Cu grade obtained. The results showed the following: with Na^+ solutions, no anion effect on the % Cu recovery; with Ca^{2+} solutions, an anion effect on the % Cu recovery was observed as Cl^- resulted in a significantly higher % Cu recovery; and with Mg^{2+} solutions, a significantly lower % Cu recovery obtained with NO_3^-. As regards the anion effect on the % Cu grade these results were obtained: NO_3^-resulted in a significantly higher % Cu grade with Na^+ solutions.

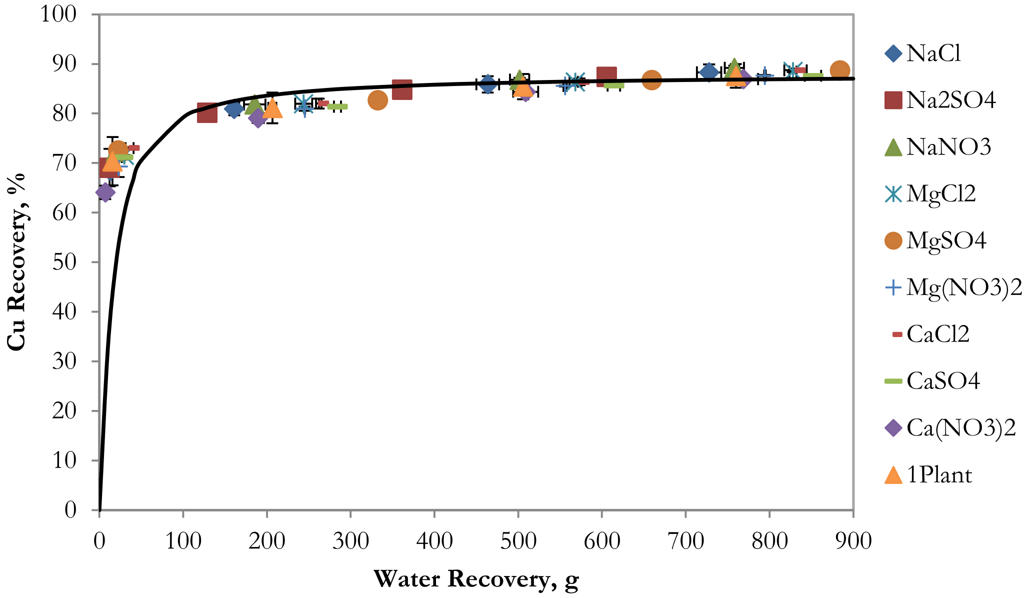


Figure 7.5: Copper recovery versus water recovered for all single salt solutions with 1st order Klimpel model indicated by the solids line.

The recovery of Cu followed a similar trend (1st order Klimpel model) for all tested single salts, and this result was the same as that which was obtained when synthetic plant water was tested at the same ionic strength of 0.0213 mol·dm^{-3}. These ionic solutions yielded the same final Cu recovery as with 1SPW. The maximum Cu recovery attained was about 90% as illustrated in Figures 7.3–7.5. Thus, the use of different single salts at an ionic strength of 0.0213 mol·dm^{-3} was not detrimental to the recovery of Cu since the trends obtained were similar to that obtained with synthetic plant water at the same ionic strength, and that the rate of flotation of Cu remained unchanged. Thus, this did not show any evidence of specific ion effects on copper and or chalcopyrite rate of flotation.

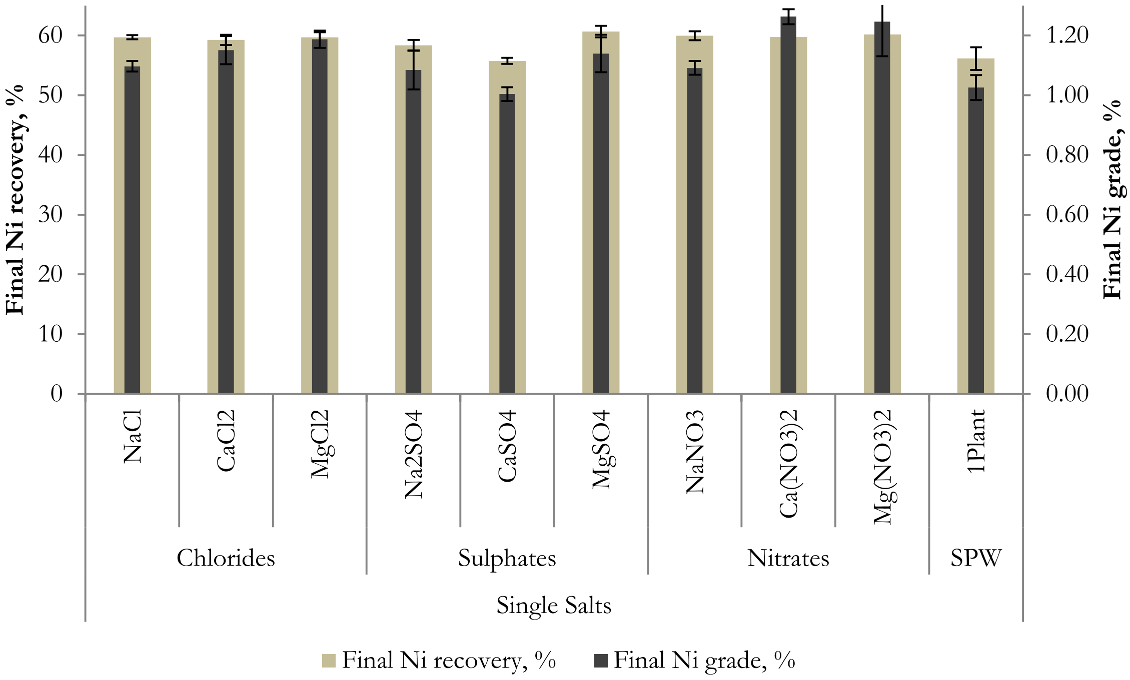


Figure 7.6: Final nickel recovery and grade for all single salt solutions – the cation effect, and compared to 1SPW.

The results for the final Ni recovery and grade are shown in Figure 7.6. A grand mean (% Ni recovery) of 58.93% was obtained with only $CaSO_4$ and 1SPW deviating from this value with % Ni recovery of 55.5% and 56.1% respectively. These results indicate similar Ni recoveries were obtained from the Merensky ore regardless of the salt type; and these results were comparable to those obtained when synthetic plant water was used, maximum Ni recoveries obtained were around 60%. According to this figure it is evident that changing the cation type did not lead to a significant difference in the final Ni grade. An average final Ni grade of 1.1% was achieved in the concentrate. Regarding the % Ni recovery the following occurred: no consistent cation effect was observed across all the anion groups. The results regarding the % Ni grade were as follows: no consistent cation effect was observed across all the anion groups as there were no statistically significant differences.

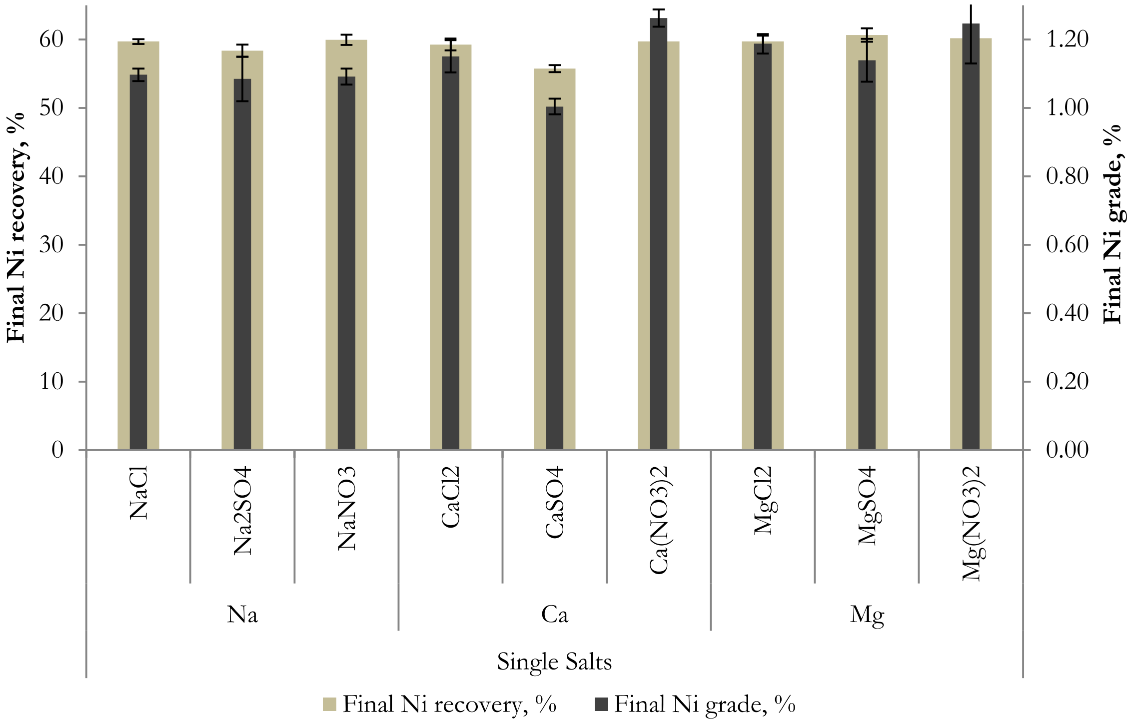


Figure 7.7: Final nickel recovery and grade for all single salt solutions – the anion effect.

Figure 7.7 shows the results for the final Ni recovery and grade for all single salts; the anion effect is illustrated also in Figure 7.7. It can be seen that there were some deviations in Ni grade between the chlorides, sulphates, and nitrates. Regarding the %Ni recovery the following are the findings from Figure 7.7: Mg^{2+} and Na^{+} containing salts did no show an anion effect regarding the %Ni recovery; however, with the Ca^{2+} containing solutions, a significant decrease in the %Ni recovery is obtained in the presence of SO_4^{2-}. The results regarding the %Ni grade were as follows: Mg^{2+} and Na^{+} containing salts did no show an anion effect on the %Ni recovery; however, with the Ca^{2+} containing solutions, a significant decrease in the %Ni grade was obtained in the presence of SO_4^{2-} and significantly higher %Ni grade was obtained with NO_3^{-}as the anion in solution.

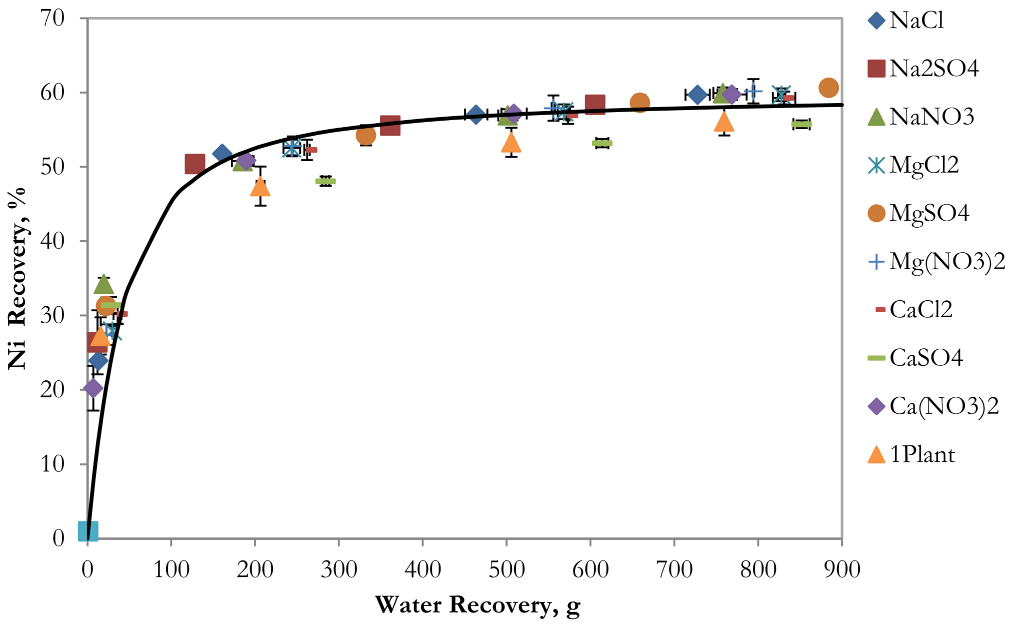


Figure 7.8: Nickel recovery versus water recovered for all single salt solutions with 1st order Klimpel model indicated by the solids lines.

Figure 7.8 shows Ni recoveries vs. water recovered for all tested single salts, and these results were compared to those obtained when using 1SPW. These results showed that the change in single salt type resulted in insignificant deviation in the Ni recovery trend obtained with each salt with regards to the rate of flotation and final Ni recovery except for $CaSO_4$ and 1SPW which resulted in slower flotation rates compared to all the other tested ionic solutions.

7.7.2 Statistical analyses

In order to validate or invalidate the findings of this study, a statistical analysis was carried out on Minitab. This statistical analysis, called ANOM (Analysis Of Means), tested the means or averages of the studied outputs, viz., recoveries and grades for all the conditions examined at the 95% confidence interval. In other words, the averages of each output were tested against the varying flotation conditions of this study. ANOM calculated the total or overall grand mean of the output of interest, and compared the single output condition against the total grand mean; this would then plot the total grand mean, the outputs from all the conditions being examined as well as the 95% confidence interval against the varying conditions as shown in Figure 7.9. If the output mean for a specific condition fell below the lower bound of the confidence interval, it was classified as being significantly lower finding than the grand mean, whereas if the output fell outside of the grand mean and its confidence interval, that outcome would be said to be significantly higher than the grand mean; however if the data point fell within the confidence interval, that is said to be comparable with the grand mean (i.e. there is no significant difference between that specific finding and the total grand mean). Seven ANOM graphs were produced for each output tested since there were 3 anions, 3 cations to examine as well as comparison of the performance of all the salts against 1SPW. An example of the statistical analysis is given for the % Cu recovery findings as shown by Figures 7.9–7.15.

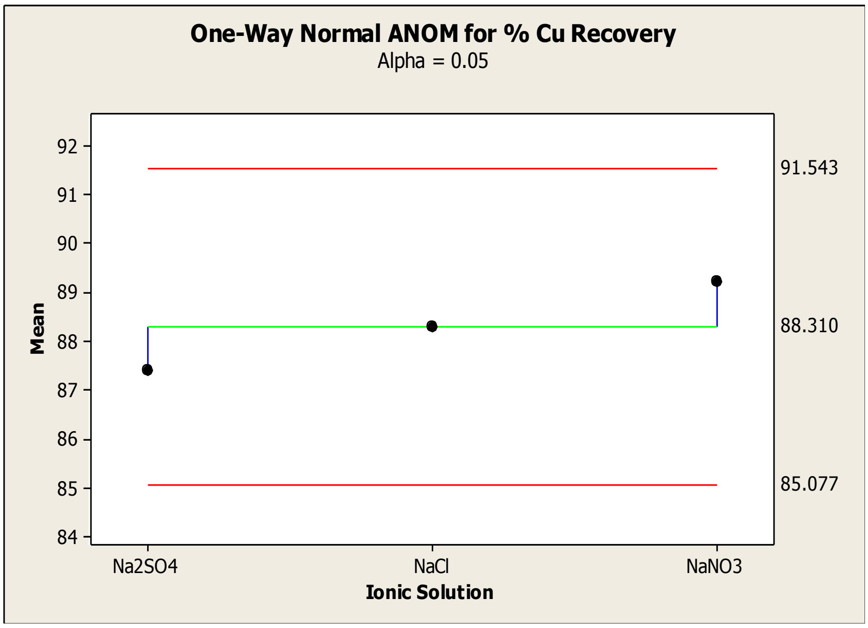


Figure 7.9: Analysis of Means for the % Cu recovery for the determination of the anion effect with Na^+ *solutions.*

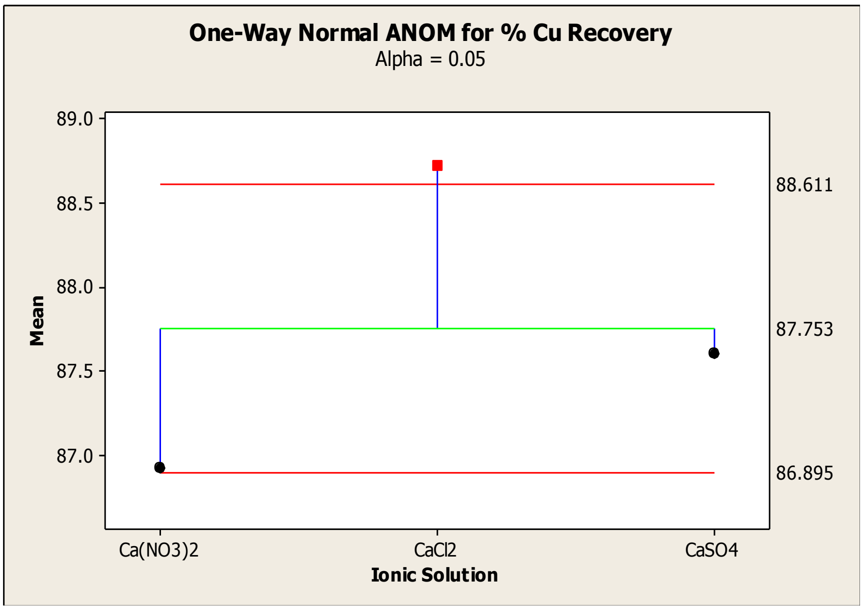


Figure 7.10: Analysis of Means for the % Cu recovery for the determination of the anion effect with Ca^{2+} *solutions.*

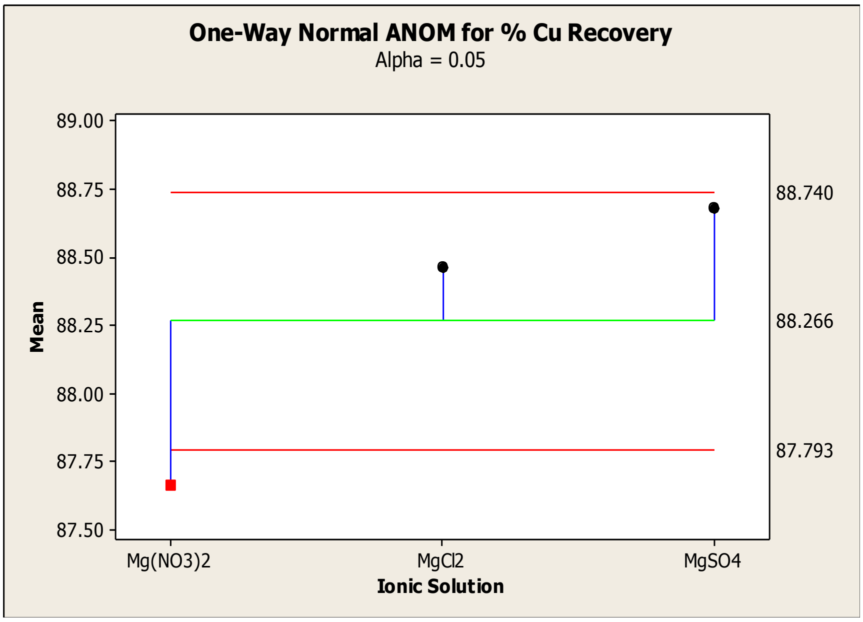


Figure 7.11: Analysis of Means for the % Cu recovery for the determination of the anion effect with Mg^{2+} *solutions.*

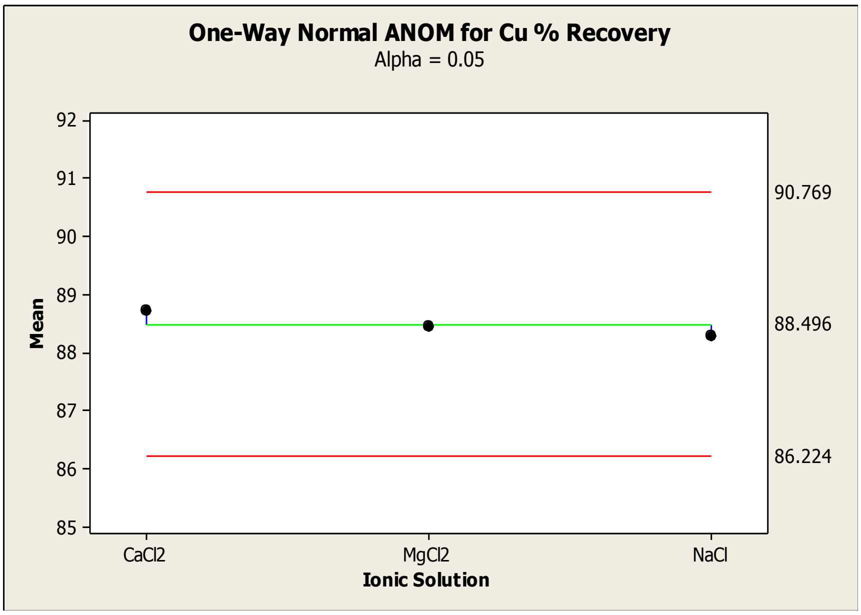


Figure 7.12: Analysis of Means for the % Cu recovery for the determination of the cation effect with Cl^{-} solutions.

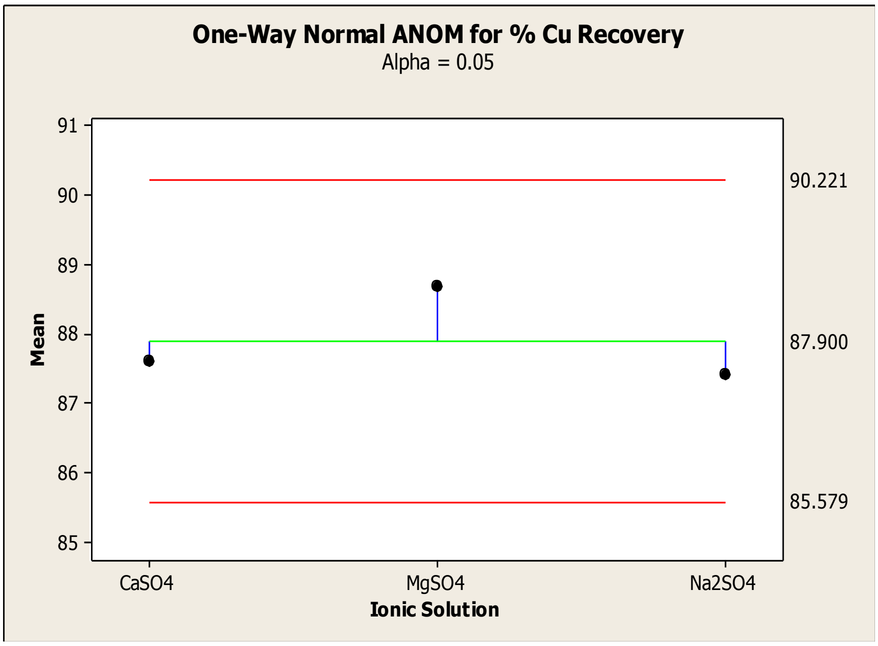


Figure 7.13: Analysis of Means for the % Cu recovery for the determination of the cation effect with SO_4^{2-} solutions.

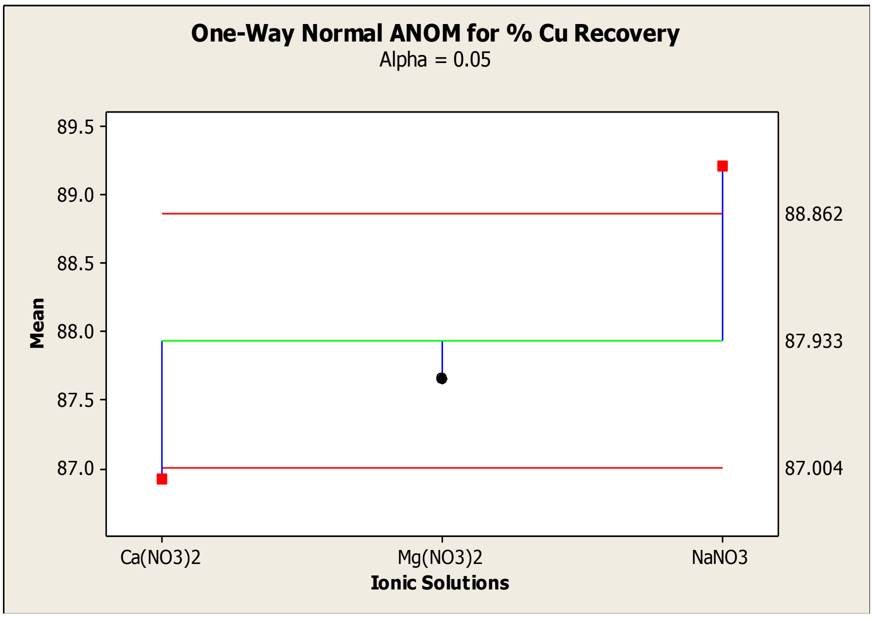


Figure 7.14: Analysis of Means for the % Cu recovery for the determination of the cation effect with NO_3^- solutions.

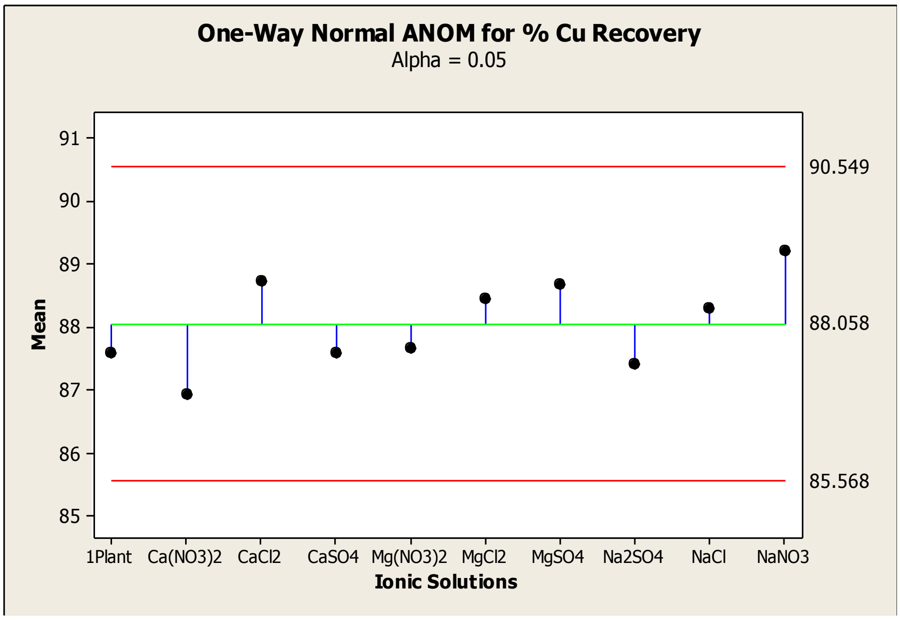


Figure 7.15: Analysis of Means for the % Cu recovery for the determination of the effect of single salts.

7.7.3 Summary

Table 7.3: Studying the anion and or cation effect on the flotation behaviour of a Cu-Ni-PGE ore from the Merensky reef.

Electrolyte	Flotation Condition	Mass (g)	Water (g)	Cu recovery (%)	Cu grade (%)	Ni recovery (%)	Ni grade (%)
Na^+	$NaCl$	–	↑	–	–	–	–
	$NaNO_3$	–	↑	–	↑	–	–
	Na_2SO_4	–	↓	–	–	–	–
Ca^{2+}	$CaCl_2$	–	–	↑	–	–	–
	$Ca(NO_3)_2$	–	↓	–	–	–	↑
	$CaSO_4$	↑	↑	–	–	↓	↓
Mg^{2+}	$MgCl_2$	–	↓	–	–	–	–
	$Mg(NO_3)_2$	–	↓	↓	–	–	–
	$MgSO_4$	–	↑	–	–	–	–
Cl^-	$NaCl$	↑	↓	–	↓	–	–
	$CaCl_2$	↓	↑	–	–	–	–
	$MgCl_2$	–	↑	–	–	–	–
SO_4^{2-}	Na_2SO_4	–	↓	–	–	–	–
	$CaSO_4$	–	↑	–	–	↓	–
	$MgSO_4$	–	↑	–	–	↑	–
NO_3^-	$NaNO_3$	↑	–	↑	–	–	–
	$Ca(NO_3)_2$	↓	–	↓	–	–	–
	$Mg(NO_3)_2$	–	–	–	–	–	–

Table 7.3 illustrates the anion and cation effect. A cationic electrolyte is tested against three anions, namely, Cl^-, NO_3^-, and SO_4^{2-}; anionic electrolytes are tested against three cations, namely, Na^+, Ca^{2+}, and Mg^{2+}. This would allow determine the anion effect (whilst keeping the cation constant) as well as the cation effect (keeping the anion the same). When statistical analyses were performed on the flotation data and or results presented in Figures 7.1–7.8, the results shown in Table 7.3 were obtained. For each electrolyte tested, the average of the category or three means was calculated, and each of the three means was tested against the total grand mean. There were three possible outputs from this statistical analysis, namely, "no significant difference", "significantly higher", and "significantly lower" as shown by the symbols, (–), (↑), and (↓) respectively.

Table 7.4: Effect of single salts on the flotation behaviour of a Cu-Ni-PGE ore from the Merensky reef.

Flotation Condition	Mass (g)	Water (g)	Cu rec (%)	Cu grade (%)	Ni rec (%)	Ni grade (%)
NaCl	↑	↓	–	–	–	–
$NaNO_3$	–	–	–	–	–	–
Na_2SO_4	–	↓	–	–	–	–
$CaCl_2$	↓	↑	–	–	–	–
$Ca(NO_3)_2$	↓	–	–	–	–	↑
$CaSO_4$	–	↑	–	–	↓	↓
$MgCl_2$	–	↑	–	–	–	–
$Mg(NO_3)_2$	–	–	–	–	–	–
$MgSO_4$	–	↑	–	–	–	–

Table 7.4 illustrates the single salts effect. All the tested salt solutions are compared with synthetic plant water (1SPW). The symbols, used in tabling, the effect of these single salts on the flotation behaviour of the Cu-Ni-PGE containing ore, have the same statistical meaning as that already explained above, however in this case the total grand mean for each of the output parameters (i.e. mass pull, water recovered, %Cu recovery, %Cu grade, etc.) is obtained by using 1SPW findings in other words each electrolyte output is compared against 1SPW performance.

7.8 Discussion

7.8.1 Effect of Ion type on the Amount of Solids and Water Recovered

The results have shown that higher amounts of solids report to the concentrate in the presence of Na^+ containing salts, these amounts of solids recovered exceeded those obtained with Ca^{2+} and Mg^{2+} containing salts. It was demonstrated that Mg^{2+} and Ca^{2+} containing salts led to similar amounts of solids recovered, and that all single salts showed similar amounts of water recovered. It was shown that the change in the anion type had no significant effect on the amount of solids and water recovered, but it needs to be stated that the NO_3^- resulted in slightly lower amounts of solids recovered in each cation type. However, a cation effect was observed as Na^+ being a monovalent cation led to increased amounts of solids recovered compared to the divalent Ca^{2+} and Mg^{2+} ions. Single salt solutions containing Ca^{2+} and Mg^{2+} cations resulted in higher water recoveries than Na^+ containing indicating that there could have been a cation effect on frothability (and thereby froth stability) owing to the divalent nature of calcium and magnesium rather than the monovalent sodium cation. This finding is line with documented literature that divalent cations such as Ca^{2+} and Mg^{2+} result in improved frothability compared with monovalent Na^+ cations (Craig, 2004; Craig *et al.*, 1993; Kurnianwan *et al.*, 2011; Ozdemir *et al.*, 2009; Quinn *et al.*, 2007). The increased amount of solids reporting to concentrate in the presence of the monovalent cation, Na^+, compared to the case of the divalent cations is counter intuitive as the expectation was that monovalent cations would result in lower amounts of solids recovered as it was proposed that floatability is improved with higher valency of the electrolytes, this result could be attributed to an ore type (Craig *et al.*, 1993).

The results have evidently shown an anion effect on the amount of solids recovered in that Cl^- and SO_4^{2-} resulted in higher amounts of solids reporting to concentrate, these anions in particular have been shown to inhibit bubble coalescence and thus increase froth stability equally compared to a pure frother such as MIBC, and this phenomenon has also been linked to activation due to galvanic interactions that occur after grinding in a steel mill (Kirjavainen *et al.*, 2002; Quinn *et al.*, 2007). These results agree with literature findings that flotation under hypersaline water conditions yields ultra-stable froths and improved mineral recoveries in Cu-Ni containing ores. The slightly lower amounts of solids recovered with NO_3^- compared to Cl^- and SO_4^{2-} was expected, as it has been shown previously that nitrates tend to retard froth stability in froth flotation due to their ability to retard or deactivate gangue minerals such as talc during the flotation of Cu-Ni containing ores (Slatter *et al.*, 2009).

7.8.2 Effect of Ion type on Cu & Ni Recovery and Grade

Cu recoveries were significantly lower in NO_3^- containing solutions, this suggests that some copper was depressed together with gangue minerals owing to NO_3^- depressing ability. The final Cu recovery achieved was about 90%, whilst that of Ni reached a maximum of about 60%. If the amount of solids recovered findings in Figure 7.1 are compared to Cu and Ni recoveries in Figures 7.3 and Figure 7.6, it can be postulated that the higher amount of solids reporting to concentrate with Na^+ ions was due to gangue activation, and the slightly lower amount of solids recovered with NO_3^- was due to gangue deactivation or prevention from reporting into the concentrates seeing that Cu-Ni recoveries remained fairly unchanged even though the amount of solids recovered increased.

A cation effect was observed on Cu and Ni grades in that Na^+ gave significantly lower Cu and Ni grades as shown in Figure 7.3 and Figure 7.6 respectively, this finding is in agreement with the speculation that the presence of Na^+ gave a slight activation to gangue, hence the dilution of the concentrates. Insignificant differences in the grades when using SO_4^{2-} and Cl^- are noted, however an anion effect became evident as the NO_3^-resulted in significantly higher Cu and Ni grades of 0.65%

and 1.3% respectively owing to the decrease reported in the amount of solids recovered which is speculated to be an inactivation or retarding of gangue particles. Whereas the rest of the anions gave similar Cu and Ni grades of about 0.58% and 1.1% respectively, and these findings were very similar to those obtained when using 1SPW.

The activation of gangue minerals as influenced by ion type is not a completely new phenomenon, Mailula (2004) showed that activation is enhanced in the presence of KNO_3, and the presence of $Ca(NO_3)_2$ showed a decrease on the activation of pyroxene, this work showed exactly the same phenomenon in that gangue activation became more prevalent in the presence of the monovalent Na^+ than in Ca^{2+} and Mg^{2+} solutions. The mechanism involved is not clear but there is evidence that Ca^{2+} ions interfere with the adsorption of a polysaccharide depressant species onto the mineral and hence less xanthate is adsorbed and this will reduce the recovery of gangue minerals such as talc. The difference in metal ions used (i.e. Na^+ and Ca^{2+}) has shown that monovalent and divalent metal ions have different properties and these alter the flotation behaviour. Morris (1997), Parolis *et al.* (2008), and Shortridge *et al.* (2003) also showed that the presence of Ca^{2+} and Mg^{2+} ions in solution reduced the natural flotation of talc. It is thus suggested that the presence of divalent ions have a greater degree of adsorption onto the mineral surface and hence lower recoveries of gangue particles. According to King (1982), the speciation of $Ca(NO_3)_2$, $CaCl_2$, and $CaSO_4$ indicated that at pH 9, the predominant form of the calcium ions in solution was Ca^{2+} with less than 1% of these species being in the form of $CaOH^+$. It leads to the conclusion that it was unlikely that these hydrated monovalent ions played any significant role in adsorption at the talc surface at the pH value used. Two possible mechanisms are that calcium species present at this pH adsorb onto the mineral surface and hence reduce the degree of adsorption or there may be a reaction in solution (Fuerstenau *et al.*, 1988, 1970). No reaction between xanthate and the calcium species is expected thus there would be no expectation of increased hydrophobicity of the mineral surface.

7.9 Conclusions

Na^+ gave slightly higher amounts of solids recovered compared to the divalent cations, and thus showing that a cation effect existed in the system. This behaviour was counterintuitive because based on literature findings monovalent cation solutions tend to yield lower amounts of solids recovered compared to divalent cation solutions. These findings showed that the presence of Na^+ led to gangue activation. The amounts of water recovered obtained for Ca^{2+} and Mg^{2+} were higher compared to Na^+, and this is attributed to the fact that these two divalent cations should exhibit a stronger influence on froth stability compared to Na^+. It was also found that NO_3^- ions resulted in slightly lower solids recovered compared to Cl^- and SO_4^{2-}, this suggesting an anion effect which was attributed to either the depressing ability of nitrates or to gangue deactivation when using NO_3^-.

NO_3^- showed an apparent influence on Cu recoveries compared to all the other ions. It is worthwhile mentioning that Ni recoveries obtained with all single salt solutions did not differ from that which was achieved when using 1SPW water.

The concentrate grades were slightly lower for Na^+ compared to Ca^{2+} and Mg^{2+} owing to the enhanced gangue activation in the presence of Na^+ ions in solution. However, there was a more notable increase on the concentrate grades in the presence of NO_3^- ions compared to the Cl^- and SO_4^{2-} ions due to the deactivation of gangue in NO_3^- solutions. Thus, the concentrates grades depended on whether the ion enhances or retards gangue activation.

It can therefore be concluded that an electrolyte's influence on the flotation performance as regards, the amount of solids and water recovered, valuable mineral recovery and grade, strongly depends on the electrolyte's influence and interactive effect on froth stability/bubble coalescence inhibition and or gangue minerals depression.

Future experiments need to be conducted to separate between the action of electrolytes on depression, deactivation, and on bubble coalescence inhibition.

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CHAPTER 8 SPECIFIC ION EFFECTS ON FROTH STABILITY AND GANGUE MANAGEMENT

8.1 Rationale, Key Questions & Hypotheses

The work presented in Chapter 7 considered specific ions present in process water and their effects on the flotation of a Cu-Ni-PGM ore. Much of the conclusions made from that work gave rise to speculation of there being gangue depression and/or froth stability implications without much fundamental evidence to back it up. Thus, the purpose of this Chapter 8 is to ascertain whether there were specific ion effects on gangue depression and froth stability. Coagulation, zeta potential and froth stability results are also presented as a follow up to the gangue activation or depression by specific ions which arose from the work presented in Chapter 7.

8.1.1 Key Questions

- What are the ions with the biggest froth stabilising action?
- What are the ions with the most coagulation on mineral particles?
- How does the zeta potential of mineral particles change with various inorganic electrolytes?

8.1.2 Hypotheses

- *Ca^{2+} and SO_4^{2-} results in the most froth stabilising action compared to Na^{+}, NO_3^{-} and Cl^{-} owing to their divalent which renders them as better bubble coalescence inhibitors.*
- *Ca^{2+} imparts the highest depression of gangue and therefore coagulation owing to an enhanced mineral passivation in the presence of divalent cations forming stronger hydroxo species such as $CaOH^{+}$ over monovalent cations (Na^{+}), rendering gangue mineral particles hydrophilic.*
- *Ca^{2+} results in the less negative zeta potential of minerals owing to an enhanced mineral passivation in the presence of divalent cations forming stronger hydroxo species such as $CaOH^{+}$ over monovalent cations (Na^{+}).*

8.2 Abstract

Mineral concentrators are becoming increasingly aware of the importance of the quality of water they feed into their milling and flotation circuits. It is speculated that different inorganic constituents of process water may yield different flotation results owing to electrolyte-reagent-mineral interactions occurring in the pulp phase which are speculated to be specific to ion type, reagent type and mineral or ore type. This thus requires an understanding of different specific ion effects on both the pulp phase and froth phase phenomena such that process water chemistry can be monitored and controlled in a manner that does not negatively affect flotation performance. Previous research has shown that inorganic electrolytes may impact mineral hydrophobicity and floatability and could in turn affect froth stability, entrainment and thus mineral grades and recoveries. In this study, the floatability of a Merensky ore is tested on a bench scale in various single salt solutions, *viz.*, $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, NaCl, $NaNO_3$ and Na_2SO_4 in order to examine specific ion effects on gangue recovery and froth stability. Froth stability, flocculation and zeta potential tests are conducted in order to ascertain specific ion effects on froth stability and gangue depression. The findings of this work have shown that NO_3^- exhibited strong depression compared to Cl^- and SO_4^{2-}. SO_4^{2-} and Cl^- had better froth stability compared to NO_3^-. It was also shown that the divalent Ca^{2+} and Mg^{2+} showed strong depression and froth stabilisation compared to the monovalent Na^+.

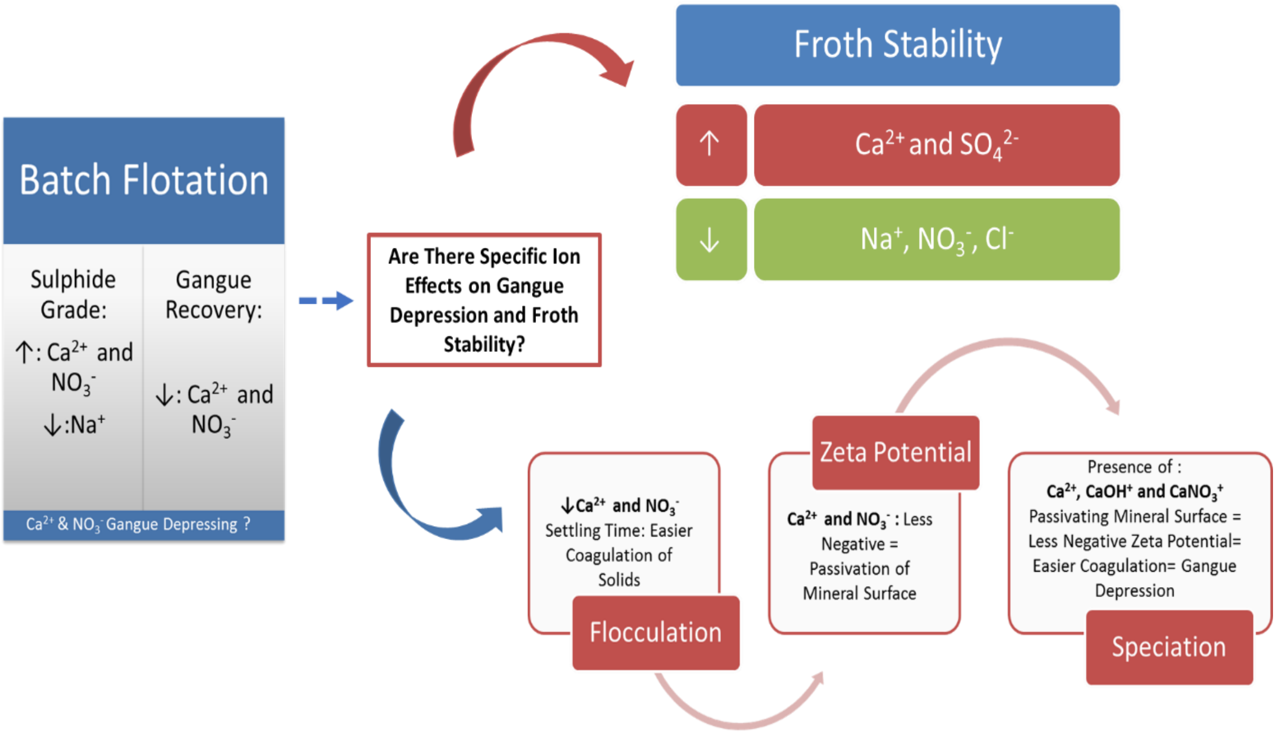
KEYWORDS

Froth Stability, Gangue, Inorganic Electrolytes, Specific ions, Sulphides, Talc, Water

8.3 Highlights

- SO_4^{2-} and Ca^{2+} proved to have a greater froth stabilising action compared to Cl^-, NO_3^- and Na^+.
- Both NO_3^- and Ca^{2+} increased the depression of gangue as shown by the lower gangue recoveries.
- Ca^{2+} and NO_3^- resulted in a less negative zeta potential compared to Na^+ and SO_4^{2-}.
- Coagulation was enhanced in Ca^{2+} and NO_3^- containing solutions.

8.4 Graphical Abstract



8.5 Introduction

It is known that the pulp chemistry in sulphide flotation has an important role on froth stability and ultimately on mineral recoveries and grades owing to interactions taking place at the air-water, air-solids, and water-solids interfaces. These interactions affect critical aspects of flotation such as the resulting (i) hydrophobicity or hydrophilicity of the mineral particle, (ii) bubble coalescence and its impact on froth stability, and (ii) entrainment. It is also important to mention that these aspects of flotation are interrelated (e.g. effects on hydrophobicity may have implications on froth stability). Any change effected by these on the pulp chemistry could change flotation performance. Recently, it is being acknowledged that water should be considered as a reagent in flotation and as such its quality becomes an important factor to consider as it may alter the pulp chemistry and thereby affecting of flotation. Rao and Finch (1989) demonstrated that recycled water may negatively affect mineral recoveries and grades owing to an accumulation of inorganic and organic substances which alter the pulp chemistry and thereby affecting flotation. A study conducted by Muzenda (2010) showed that recycled process water containing Cu^{2+}, Pb^{2+} and Fe^{2+} had adverse effects on the flotation of a Cu-Ni-PGM ore from the UG2 reef of the Bushveld Igneous Complex of South Africa in that there occurred an inadvertent activation of non-sulphide gangue which decreased the concentrate grades. Liu *et al.* (2013) suggested that some electrolytes could inhibit the adsorption of xanthates on sphalerite due to a competition for adsorption onto the mineral surface between xanthates and inorganic electrolytes present in process water. Castro *et al.* (2013) showed that the flotation of molybdenite in the presence of Mg^{2+} concentrated pulp resulted in molybdenite depression due to the presence of magnesium hydroxyl complexes and colloidal magnesium hydroxide coatings onto molybdenite particles rendering them hydrophilic. Laskowski *et al.* (2007) also showed that the presence of high Ca^{2+}concentration in process water improved the adsorption of CMC onto talc through an acid-base interaction. Presented work on electrolyte-reagent-mineral interactions on mineral hydrophobicity seems detached from the consequences and implications that such interactions have on the froth phase despite some evidence on inorganic electrolyte effects on gas dispersion properties. It is known, from recent studies, that certain electrolytes present in process water exhibit frother-like gas dispersion properties in that they inhibit bubble coalescence. Biçak *et al.* (2012) suggested that the sensitivity of flotation to water quality is such that an accumulation of both organic and inorganic ions in the process water may also affect the froth stability. Corin and Wiese (2014) also reported that the quality of the process water impacted froth stability in that they showed that increases in frother dosage and ionic strength of plant water could be used interchangeably. Quinn *et al.* (2007) documented that concentrators processing sulphides in Western Australia and in some parts of Chile did not add frothers in their flotation circuits due to the high salinity (40 000 to 60 000 mg/L) of their process water. A study conducted by Barker (1986) showed that divalent cations such as Ca^{2+} and Mg^{2+} in solution resulted in an increase in the kinematic viscosity compared to the monovalent Na^{+} and K^{+}, concurrently froth stability increased. Barker (1986) proposed, as a mechanism, that the increase in the kinematic viscosity caused an increase in the liquid film thickness of the bubble, causing a slower drainage and thus a more stable froth. Biçak *et al.* (2012) showed that at high electrolyte concentrations, bubbles became more stable and did not coalesce even in the absence of a frother. Kurniawan *et al.* (2011) investigated froth properties in coal flotation using $MgCl_2$, NaCl and $NaClO_3$ solutions in the absence and presence of Dowfroth 250. It was found that in the presence of Dowfroth 250, $MgCl_2$ led to generation of smaller bubbles, most stable froth and higher recoveries compared to NaCl, while $NaClO_3$ resulted in the lowest froth stability, a similar trend was observed on the recoveries. Castro *et al.* (2013) reported that water with an increased concentration of electrolytes showed an important degree of frothing ability. The study by Biçak *et al.* (2012) showed that the rate of coalescence of air bubbles decreased either due to the frother molecules absorbed on the air-water interface, or by the presence of a stable liquid film layer on the surface of the bubbles. This was in agreement with Yousef *et al.* (2003) who stated that flotation plants which use seawater and process water with high salinity are likely to experience voluminous and stable froth due to the frothing properties of dissolved ions. Biçak *et al.* (2012) concluded that dissolved metal ions and sulphide ions mainly in the form of SO_4^{2-} and $S_2O_3^{2-}$ have serious influences on both froth stability and surface chemistry. It was then hypothesised that increased froth stability in concentrated electrolytes were caused by an increased stability of the water layer between air bubbles (Biçak *et al.*, 2012). Corin *et al.* (2011) reported higher solids and water recoveries in increasing ionic strengths of artificial plant water and suggested that these were caused by increased froth stability. This supported the findings of Schwarz and Grano (2005) and Tao *et al.* (2000) who linked water recovery with froth stability in flotation as more stable froths were accompanied by an increase in water recovery. Bournival *et al.* (2012) investigated NaCl and MIBC as bubble coalescence inhibitors in relation to froth stability. It was found that NaCl at higher concentrations was as effective as MIBC in preventing bubble coalescence in a dynamic environment. Castro *et al.* (2013) stated that the coalescence of bubbles in flotation is a particularly complex phenomenon especially when it takes place in saline or seawater, since both a surface active compound (frother) and a surface inactive compound (inorganic salt) are able to stabilise bubbles against coalescence and therefore reduce bubble size giving rise to stable froths. These findings were also in support of Grau *et al.* (2005) and Laskowski *et al.* (2003) who showed that bubble coalescence could be completely prevented at frother concentrations exceeding a certain concentration known as critical coalescence concentration (CCC). Inorganic electrolytes also inhibited bubble coalescence (Laskowski *et al.*, 2003). Interactions between frothers and inorganic electrolytes have been proposed by Castro *et al.* (2013) who showed that increasing frother concentration resulted in a decrease in the solution surface tension but the ability of a frother to decrease surface tension of a solution was increased in the presence of a coalescence inhibiting inorganic electrolyte. On the basis of the presented literature, a number of mechanisms has been proposed to better understand the action of inorganic electrolytes in flotation. These range from the action of inorganic ions in (i) disrupting the hydration layers surrounding the particles and enhancing bubble-particle attachment, (ii) reducing the electrostatic interactions, and (iii) increasing the charge on the surface of the bubbles to prevent primary bubble coalescence. However, as previously mentioned, there is little evidence for work that considers the action of electrolytes on bubble coalescence and froth stability in relation to the action of ions on interactions occurring in the pulp phase affecting mineral hydrophobicity which should bring about implications onto the froth phase phenomenon. Thus fundamental work is required to consider gangue depression and froth stability in Cu-Ni-PGM sulphidic ores since previous work showed that in these ores much of the effects have great implications on gangue management rather than on the recovery of sulphides owing to the small sulphides content in the ores.

The literature presented suggests that analyses and understanding of the influence of each specific process water constituent on flotation has both technical and financial potential benefits in that costs could be saved on waste water treatment if research proves that some flotation circuits could still perform at their best in recycled process water containing constituents which would previously have been removed. This allows for an implementation of closed water circuits in flotation processes and a contribution to the sustainability of the process. There would be minimal process water discharge to the environment, minimal make-up water requirement, a reduction in process water treatment before reuse, saving on treatment costs, and a reduction in fresh reagent dosing. Thus, the aim of this study is to ascertain whether there are ions in flotation with dominant effects on gangue depression and froth stability.

8.6 Materials & Methods

8.6.1 Water

In this investigative work, synthetic plant water (hereafter referred to as 1SPW or 1Plant) and various single salt solutions of the ionic strength and compositions shown in Table 8.1 were prepared. These aqueous synthetic plant water and single salt solutions were made up of distilled water and inorganic salts to ensure that the concentration of the water contained the required total dissolved solids (TDS) and ionic strength.

Table 8.1: Chemical compositions of synthetic plant water and the various single salt solutions tested in this study.

Water type	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	Cl^{-} (ppm)	SO_4^{2-} (ppm)	NO_3^{-} (ppm)	CO_3^{2-} (ppm)	TDS (ppm)	Ionic Strength [M]
1SPW	80	70	153	287	240	176	17	1023	0.0213
NaCl	-	-	490	755	-	-	-	1245	0.0213
Na_2SO_4	-	-	326	-	682	-	-	1009	0.0213
$NaNO_3$	-	-	490	-	-	1321	-	1810	0.0213
$CaCl_2$	285	-	-	503	-	-	-	788	0.0213
$CaSO_4$	213	-	-	-	512	-	-	725	0.0213
$Ca(NO_3)_2$	285	-	-	-	-	880	-	1165	0.0213
$MgCl_2$	-	173	-	503	-	-	-	676	0.0213
$MgSO_4$	-	129	-	-	512	-	-	641	0.0213
$Mg(NO_3)_2$	-	173		-	-	880	-	1053	0.0213

8.6.2 Inorganic electrolyte speciation calculation

In order to investigate specific ion effects on interactions occurring in the pulp phase of flotation, inorganic electrolyte speciation calculations were carried out using Visual MINTEQ (version 3.1). Visual MINTEQ is an open source chemical equilibrium modelling software for the prediction or calculation of ion speciation in water based on thermodynamic equilibrium data (Wang *et al.*, 2016).

8.6.3 Ore preparation and milling for batch flotation

A Cu-Ni-PGM containing ore from the Merensky reef which is within the Bushveld Igneous Complex of South Africa was used throughout the bench scale flotation tests. The bulk sample was crushed, riffled and split into samples weighing 1 kg using a rotary splitter. The 1 kg ore samples were milled in a tumbling mill in the presence of the particular water type under study with SIBX dosed at 150 g/t in order to achieve a grind size of 60% passing 75 µm to make a slurry of 66% solids in the mill. It is important to note that this grind is typical of industrial concentrator rougher circuits concentrating Merensky ores. The grinding media used in the mill were 20 rods of stainless steel with varying diameters; 6 x 25 mm, 8 x 20mm, 6 x 16 mm. The milled slurry was transferred into a 3 L UCT Barker batch flotation cell immediately. The mineral composition of this ore is shown in Table 8.2. It can be seen that the dominant sulphide matter contained in this is pyrrhotite, pentlandite and chalcopyrite and thus forming about 1% of the overall ore feed grade with the rest being gangue minerals.

Table 8.2: Modal Composition: Sulphide and Gangue Minerals Present in the Ore as Determined by QEMSCAN.

Mineral	(%)
Pentlandite	0.31
Chalcopyrite	0.25
Pyrrhotite	0.44
Pyrite	0.08
Other sulphides	0.02
TOTAL sulphides	1.09
Plagioclase	43.38
Orthopyroxene	32.60
Olivine	0.59
Clinopyroxene	7.48
Talc	3.51
Serpentine	0.80
Chlorite	0.83
Phlogopite	0.46
Quartz	0.67
Calcite	0.18
Oxides	8.10
Other	0.32
TOTAL	100.00

8.6.4 Batch flotation procedure

In order to investigate the effect of the various process water inorganic electrolytes on flotation performance, the standard UCT bench scale 3 L Batch flotation procedure was employed. The milled slurry was transferred to the cell and the water quality under investigation was added to the cell in order to ensure a pulp density of 35%; thereafter an impeller was switched on and set to an agitation speed of 1200 rpm. A syringe was used to draw out a feed sample which would later be filtered, dried and weight for S assays. A polyglycol frother in the form of DOW 200 was added to the cell at a dosage of 40 g/t and allowed to condition for 1 minute after which an air supply valve to the cell was opened in order to ensure a constant volumetric air flowrate of 7 L/min. A froth build-up occurred until a constant froth height of 2 cm. It is worth mentioning that the concentrates were collected in 15 seconds intervals. Once all four concentrates were collected and that batch flotation was stopped, a tails sample was also drawn out. The concentrate 'launders' or collection pans were weighed in order to account for the amount of water reporting to the concentrate and thereafter the samples were filtered, dried, weighed and analysed for S in the UCT Chemical Engineering Analytical services laboratory using an in-house Leco. It was deemed sufficient to perform all tests in duplicate for reproducibility and the error bars are shown in the batch flotation results.

8.6.5 Two-phase froth column procedure

Specific ion effects on froth stability were investigated using a two-phase foam column test rig. These tests were considered important since previous work published in Manono *et al.* (2016) suggested that some inorganic electrolytes were more froth stabilising than others although these suggestions emanated only from water recoveries data without much fundamental evidence. The test rig is discussed in detail in Manono *et al.* (2013). Two-phase froth column tests were conducted for various single salts in distilled water at pH 9 both in the absence and in the presence of a frother (DOW 200). Tests conducted in the presence of a frother were dosed DOW 200 to ensure a dosage of 5ppm. pH was adjusted using a stock solution of NaOH to achieve the desired pH before the solution was added into the column where the initial air-water interface height was measured. Air was pumped into the froth column at a flowrate of 2 L/min. This allowed for the development of the foam phase until an equilibrium froth height was reached. This equilibrium condition was reached after approximately 3 minutes for selected single salt solutions ($CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, NaCl, $NaNO_3$ and Na_2SO_4). The equilibrium condition is defined as the state at which bubble collapse rate at the top of the foam is equal to the air flow rate through the sparger which is situated at the bottom of the column. Once equilibrium was reached, air was stopped, immediately thereafter the foam collapse time was measured (i.e. the time taken for the foam to collapse to the initial air-water interface). All experiments were performed in duplicate.

8.6.6 Settling Tests

In order to investigate whether the presence of inorganic electrolytes in process water imparted any coagulative-flocculative nature on the mineral particles as proposed by Wiese (2009) and Corin *et al.* (2011), standard settling tests were performed using settling time as the key performance indicator. These settling tests were performed for single salt solutions of $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, NaCl, $NaNO_3$ and Na_2SO_4 at a total ionic strength of 0.0213 $mol.dm^{-3}$ with each test performed in duplicate. 9 grams of a Merensky ore were added to 90 mL of the water under investigation in a 100 mL glass beaker to make a 10% solids mixture. The contents of the glass beaker were mixed and conditioned adequately for 1 minute using a magnetic stirrer. The pH of the suspension was adjusted to pH 9 using stock/dilute solutions of NaOH or HCl. The suspension was allowed to mix at 500 rpm for 4 minutes in order to disperse the mixture immediately after pH adjustment. The slurry was then carefully transferred to a 100 mL graduated cylinder. The stop watch was set in order to determine the settling time. The graduated cylinder was carefully monitored until a clear supernatant liquid was observed against a clear background. A picture was taken, printed and stuck next to the working bench to serve as a basis for the clear supernatant liquid for the remaining tests.

8.6.7 Zeta Potential Measurement

A Malvern Zetasizer 4 was used to investigate the effect of single salts on the zeta potential of talc and pyrrhotite at varying pH values. Mineral samples were obtained from Ward's Science. Each of the minerals (talc and pyrrhotite) were crushed using a hammer and pulverized thereafter. These were then sieved and screened to 100% passing 25 µm. Immediately after sieving, the pyrrhotite was purged with nitrogen and refrigerated to prevent oxidation. Single salt solutions of $Ca(NO_3)_2$, $CaSO_4$, $NaNO_3$ and Na_2SO_4 were used as dispersants on the Malvern Zetasizer 4 machine. For each salt, 6 aliquots of 25 mL were measured and were adjusted to pH values of 2, 4, 6, 8, 10 and 12 using NaOH and HCl. These were allowed to condition for 20 minutes. Thereafter, 0.0625g of mineral was added to the 25 mL conditioned dispersant, stirred and left to stand for 1 minute. 2 mL of the supernatant solution was then pipetted into the capillary tube and placed into the Malvern Zetasizer 4. A calibration time of 2 minutes was allowed and each reading was taken 3 times. This procedure was repeated for all the different dispersants for both talc and pyrrhotite minerals.

8.6.8 Statistical Analyses

Statistical analyses were carried out on the batch flotation results so as to ascertain whether the selected inorganic electrolytes affected the flotation performance of the Cu-Ni-PGM ore differently. These analyses were carried out using Minitab 18.1 ANOM (analysis of means). This method uses the output means (e.g. %S grades) for all conditions (flotation condition – salts in this case) and calculated an overall mean so called grand mean This is to say that, the ANOM tool determines the total or overall grand mean of the output of interest. It then compares the single output condition against the total grand mean; this would then plot the total grand mean, the outputs from all the conditions being examined as well as the 95% confidence interval against the varying condition. This would be such that if an output mean for a specific condition falls below the lower bound of the confidence interval, it would be said that specific condition resulted in an output mean significantly lower than the grand mean, whereas if the output fell outside the upper bound of the 95% confidence interval, that said condition is said to have resulted in an output that is significantly higher than the grand mean. However, if the a specific condition led to an output that fell within the confidence interval, that output is said to be comparable with the grand mean (i.e. there is no discernable difference between that specific finding and the total grand mean). The statistical analyses and observations are well described in each of the ANOM results/graphs presented in this paper

8.7 Results

8.7.1 Effect of Single Salts on Total Sulphides, Gangue and Water Recoveries and Total Sulphides Grades

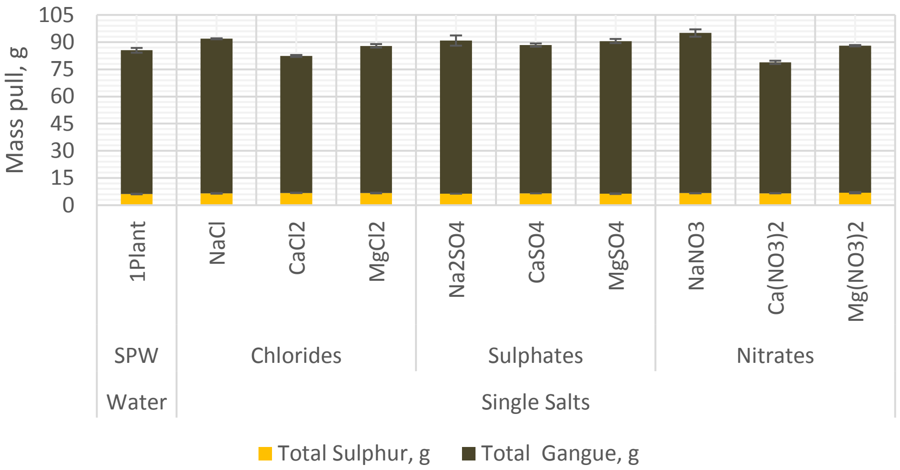


Figure 8.1: The amount of solids reporting to the concentrate for all conditions tested.

Figure 8.1 shows the total mass pull (i.e. the total amount of solids reporting to the concentrate) for all the inorganic electrolytic solutions in which the wet milling and flotation of the selected Merensky ore was conducted. The mass pull is presented as two fractions, namely, the sulphides and gangue. It is shown that the amount of sulphides reporting to the concentrate did not change with single salt type and the recovered mass of sulphides was the same as that recovered in the presence of synthetic plant water; these results are further supported by the ANOM performed on these data in Figure 8.2 and Figure 8.3; where it is shown that there is no significant difference between the means of the mass of sulphides obtained with different single salts and plant water. However the amount of gangue reporting to the concentrate showed a dependence on the ions present in the single salt solution. $Ca(NO_3)_2$ and $CaCl_2$ resulted in a significant decrease in total gangue recovery compared to other single salts whilst $NaNO_3$ resulted in a significant increase in gangue reporting to the concentrate as shown in Figure 8.3.

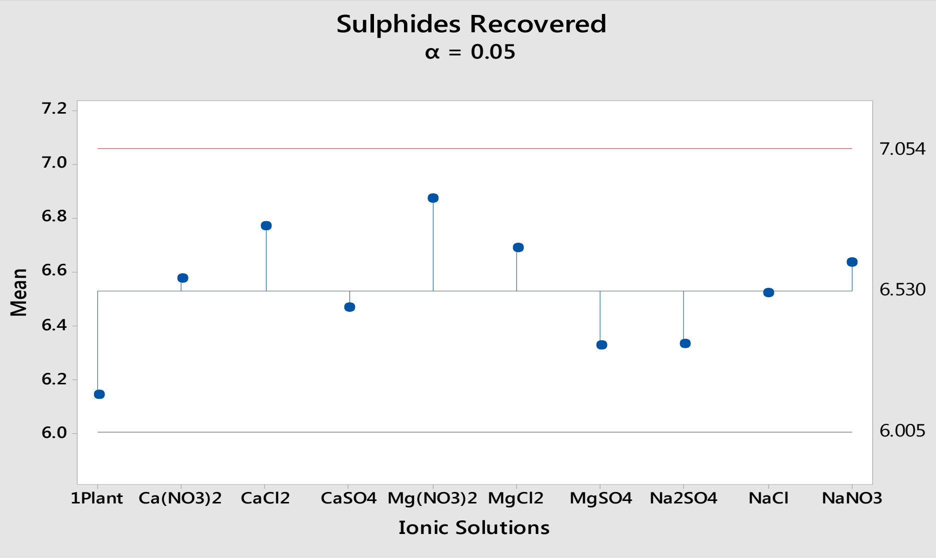


Figure 8.2: ANOM of the amount of sulphides in grams reporting to the concentrate for all single salts and synthetic plant water.

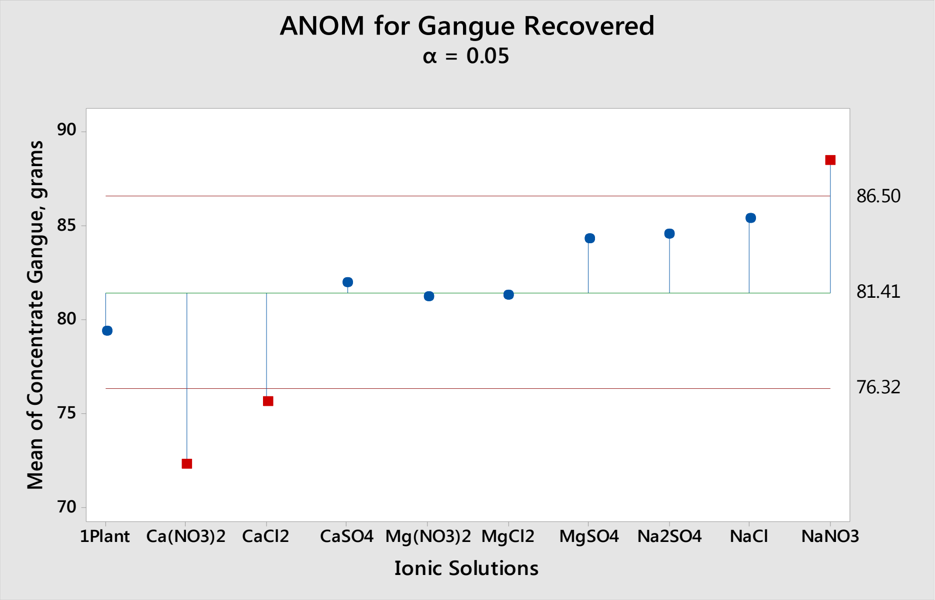


Figure 8.3: ANOM of the amount of gangue in grams reporting to the concentrate for all single salts and synthetic plant water.

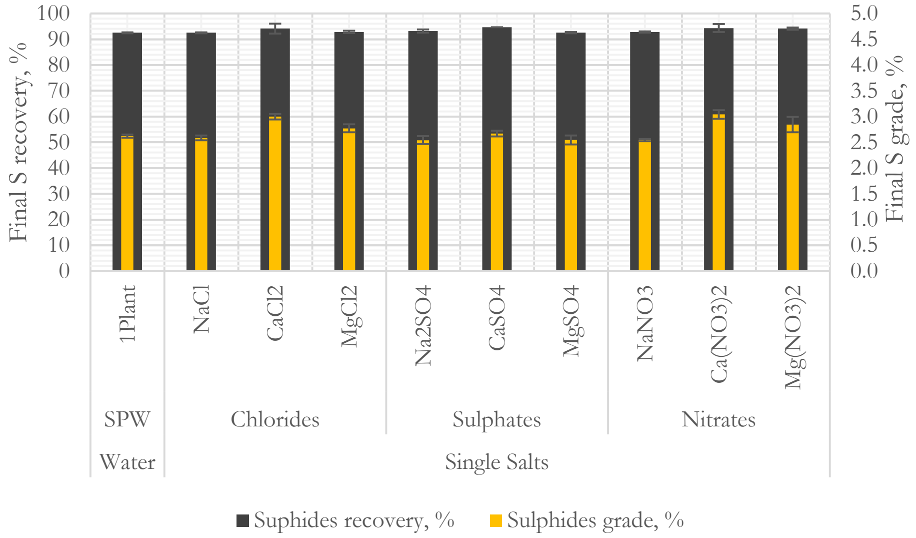


Figure 8.4: Total sulphides recoveries and grades for all single salts and synthetic plant water.

Figure 8.4 shows the total sulphide recoveries and grades for all tested singles salts and synthetic plant water. It is clear that the %S recovery remained unaffected by changes in the inorganic electrolyte solution type whereas the %S grade proved susceptible to changes in the quality of the ionic solution. $Ca(NO_3)_2$ and $CaCl_2$ resulted in significantly higher concentrate grades compared to all the other single salts. It is also interesting to note that the Na^+ containing solutions resulted in the %S grades slightly lower than the grand mean.

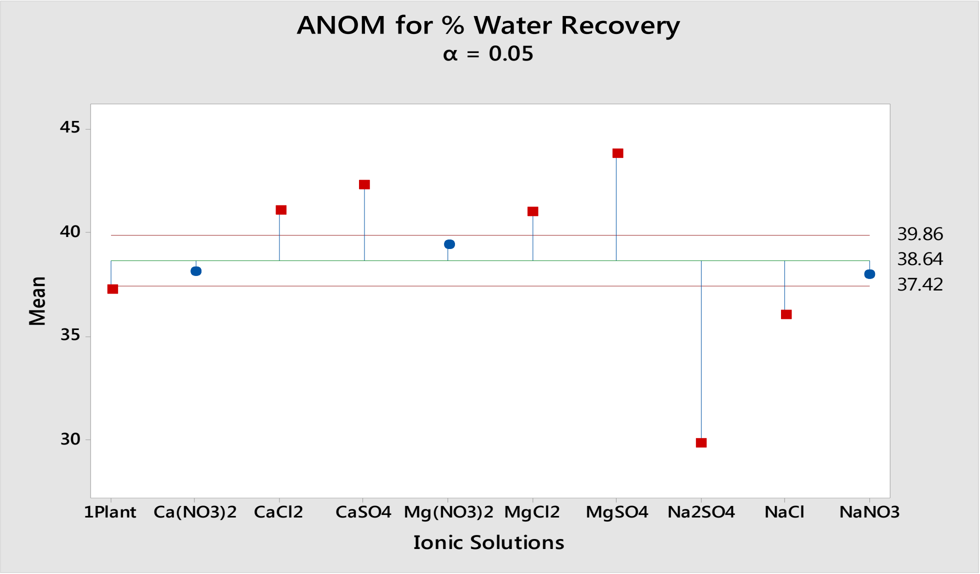


Figure 8.5: ANOM of water recoveries in grams for all single salts and synthetic plant water.

Figure 8.5 shows a clearly discernable difference in the water recoveries in various single salts The synthetic plant water, Na_2SO_4 and NaCl resulted in a significant decrease in the water recovery compared to the total mean of 38.64 % with Na_2SO_4 resulting in the greatest decrease in water recoveries. Conversely $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$ led to a significant increase in water recoveries whereas $Ca(NO_3)_2$, $Mg(NO_3)_2$ and $NaNO_3$ yielded water recoveries which were within the total mean.

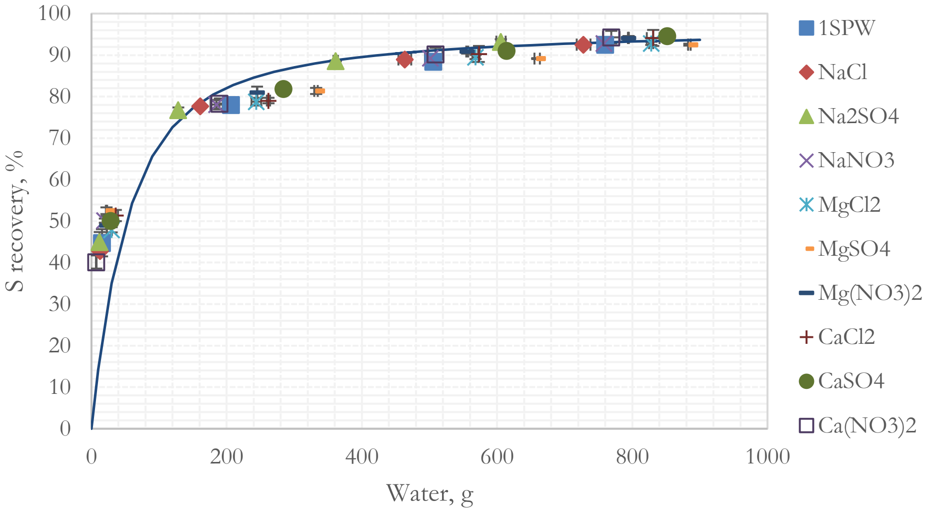


Figure 8.6: The %sulphides recovery vs. water for all single salts and synthetic plant water.

Figure 8.6 shows the %S recovery as a function of the amount of water recovered for all tested single salts. According to Figure 8.6, all tested single salt solutions and synthetic plant water, generally followed the same trend of a 1st order model. It is shown that there was no difference in the rate at which the flotation of sulphides occurred and that also the maximum attainable total sulphides recovery remained within 94% regardless of the inorganic electrolytic solution used.

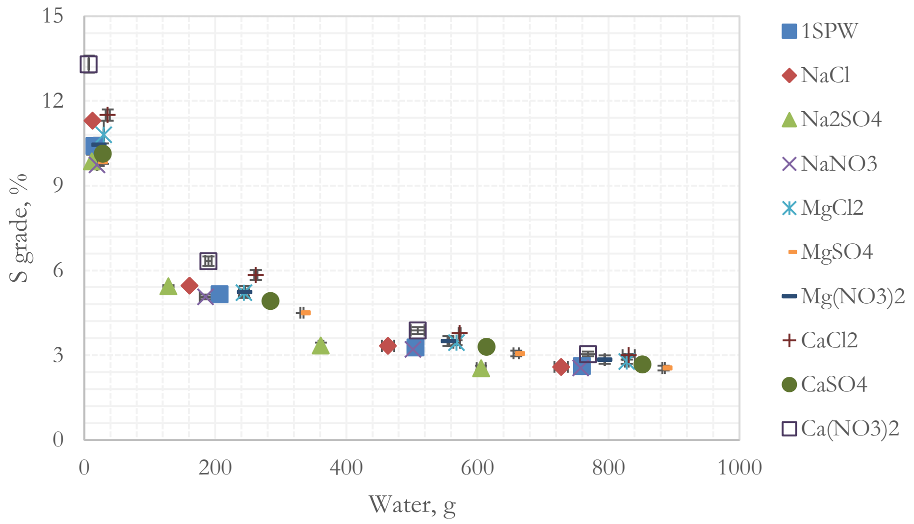


Figure 8.7: The %sulphides grade vs. water for all single salts and synthetic plant water.

Figure 8.7 depicts the %S grade against the amount of water reporting to the concentrate for all tested single salts. A closer inspection into Figure 8.7 shows a clear difference in the total sulphides grade between single salts solutions. The total sulphides grade for Na_2SO_4 is lower than all the single salts tested whereas $Ca(NO_3)_2$ and $CaCl_2$ resulted in higher total sulphides grade. Moreover, it is interesting to note that the %S grade followed an exponential decay trend with increasing unit mass of water.

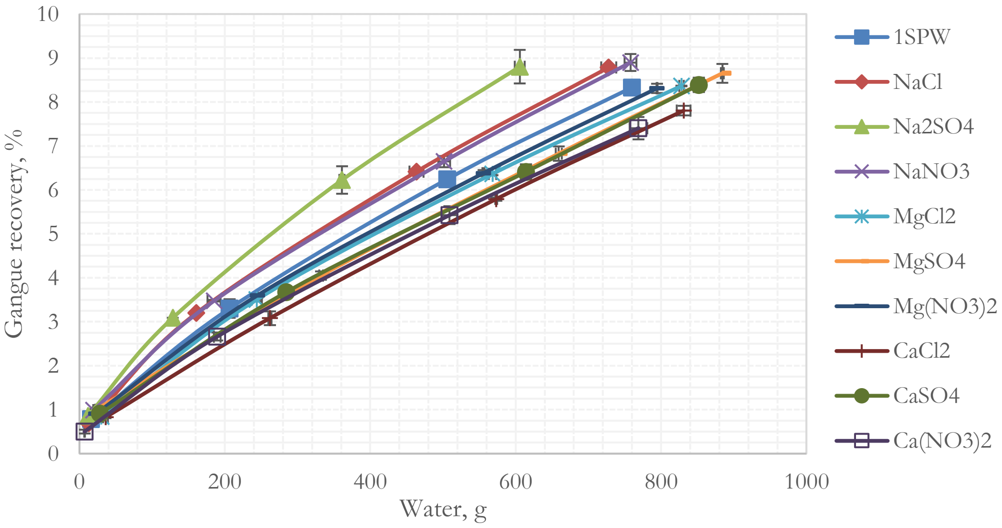


Figure 8.8: Gangue recovery vs. water for all single salts and synthetic plant water.

Figure 8.8 depicts the recovery of gangue per g of water for the various single salts and synthetic plant water. It is evident that all single salt solutions containing the monovalent Na^+ resulted in a higher total gangue recovery per g of water compared to plant water and the divalent cations (Ca^{2+} and Mg^{2+}) containing single salt solutions. Also, for the Na^+ single salts, gangue recovery per g of water was higher in the SO_4^{2-} solution than with the Cl^- and NO_3^- containing solutions. Moreover, of the divalent cation containing single salts, Ca^{2+} resulted in lower gangue recovery per unit mass of water compared to Mg^{2+}.

8.7.2 *Single Salt Solutions on Two-phase Froth Stability*

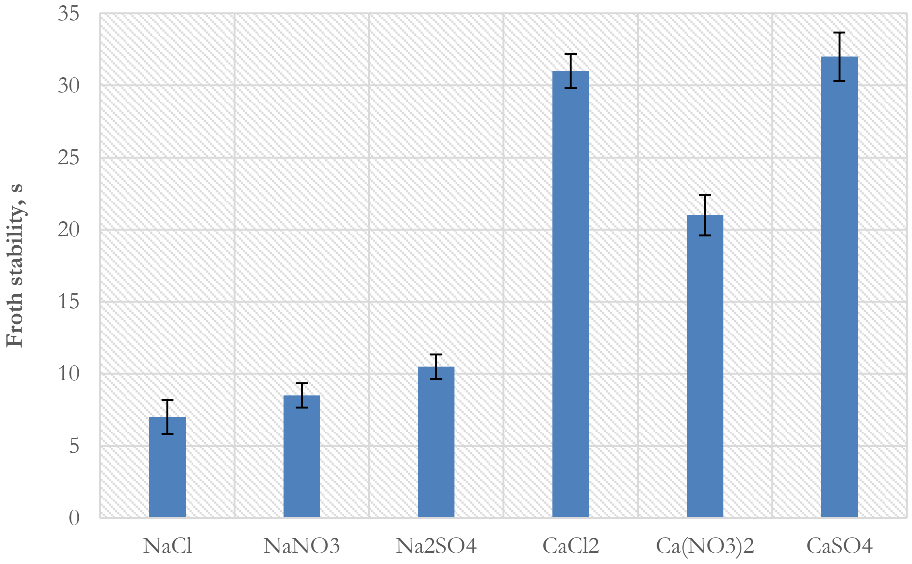


Figure 8.9: Froth stability for various single salts.

Figure 8.9 depicts the froth stability for the selected salts. The monovalent Na^+ containing single salts resulted in lower froth stabilities compared to the divalent Ca^{2+} containing single salt solutions. Also, for the Na^+ salts, froth stability increased such that $Cl^- < NO_3^- < SO_4^{2-}$ in the presence of a frother whereas with Ca^{2+}, NO_3^- resulted in the lowest froth stability compared to Cl^- and SO_4^{2-}.

8.7.3 Single Salt Solutions on the Coagulation of a Merensky ore

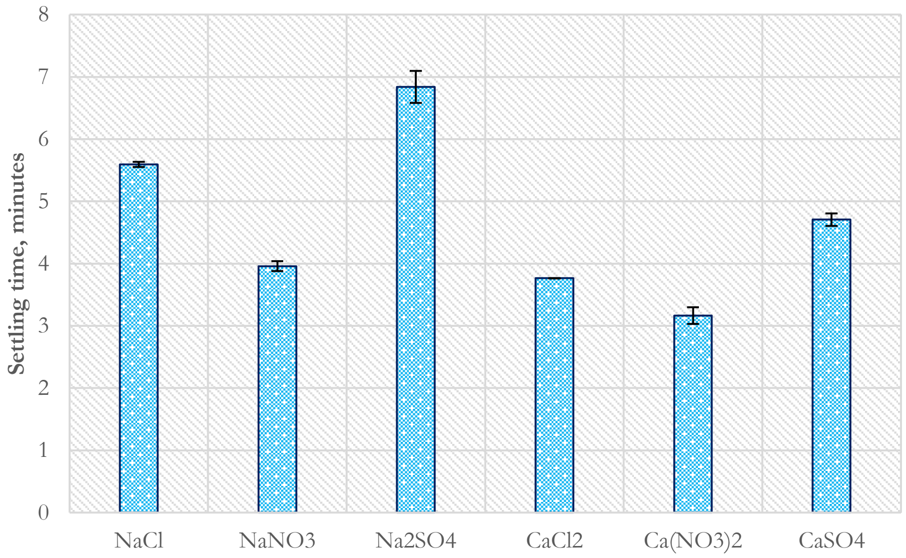


Figure 8.10: Merensky ore solids settling time as a function of the single salts.

Figure 8.10 shows the settling time of solids for a Merensky ore for various single salts as a proxy to cationic and anionic effect on coagulation. The Na^+ containing solutions resulted in longer settling times compared to the Ca^{2+} containing solutions for every corresponding anion suggesting a cation effect on coagulation with the divalent cation having a stronger coagulative effect than the monovalent cation. Moreover, for a fixed cation, SO_4^{2-} resulted in the longest settling time followed by Cl^- whilst the NO_3^- anions resulted in the lowest settling time.

8.7.4 Effect of Single Salts on the Zeta Potential of Talc

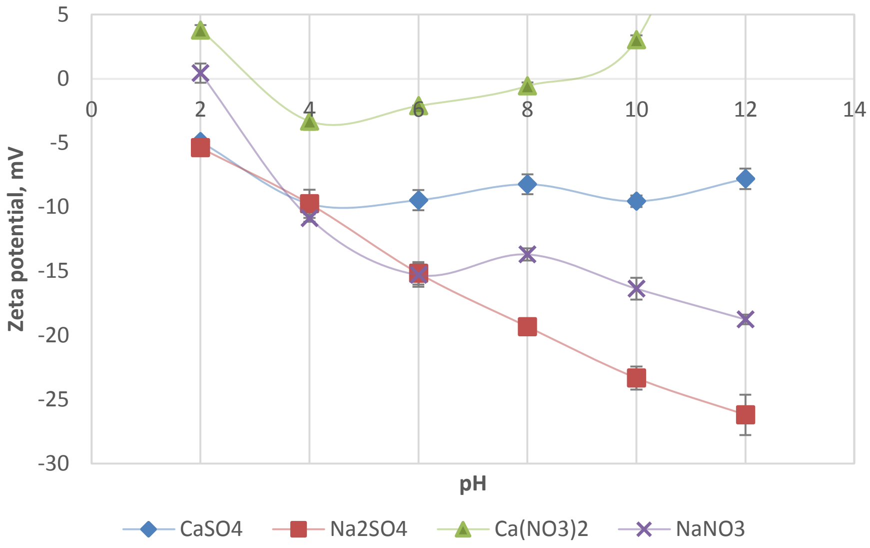


Figure 8.11: Zeta potential of talc in 0.0213 M ionic strength single salt solutions as a function of pH.

Figure 8.11 depicts the zeta potential of talc as a function of pH in various single salt solutions in an attempt to investigate whether there are any ion (anion or cation) specific effects on the zeta potential of talc. Firstly, it is evident that the monovalent Na^+ resulted in a highly negative zeta potential across the studied pH range compared to solutions containing the divalent Ca^{2+}. Secondly, for both cations, NO_3^- resulted in a less negative zeta potential compared to SO_4^{2-} across the studied pH.

8.7.5 Effect of Single Salts on the Zeta Potential of Pyrrhotite

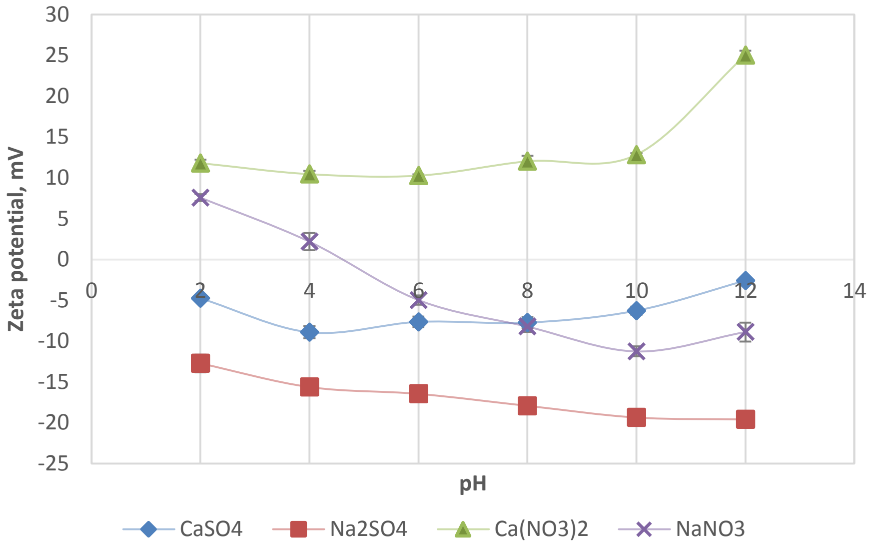


Figure 8.12: Zeta potential of pyrrhotite in 0.0213 M ionic strength single salt solutions as a function of pH.

Figure 8.12 demonstrates the zeta potential of pyrrhotite in inorganic electrolytes over pH 2-12. The results show that the zeta potential of pyrrhotite was less negative in Ca^{2+} solutions compared to Na^+ with $Ca(NO_3)_2$ resulting in a positive zeta potential across the studied pH range. Also, the pyrrhotite zeta potential was less negative in solutions containing NO_3^- compared to SO_4^{2-}.

8.7.6 Single Salt Solutions Speciation

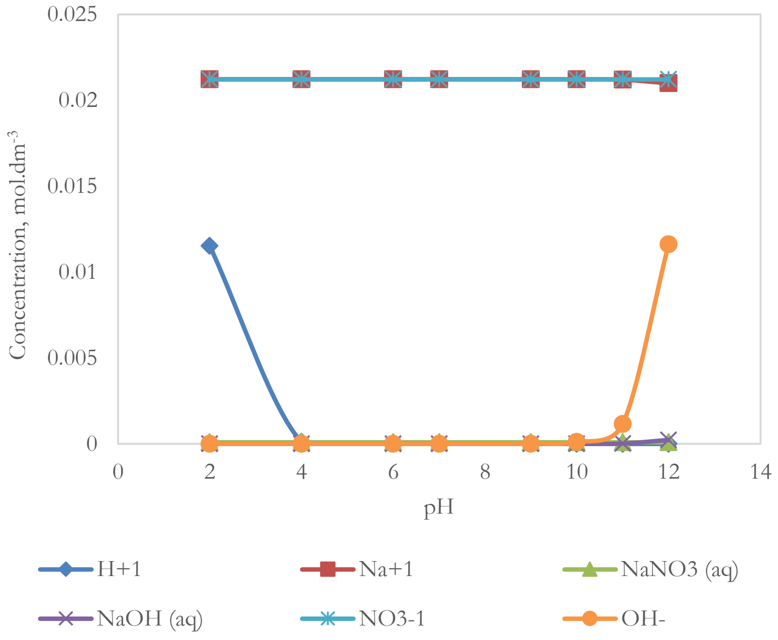


Figure 8.13: $NaNO_3$ speciation for a solution of 0.0213 mol.dm^{-3} ionic strength.

Figure 8.13 depicts the speciation of a $NaNO_3$ solution, with an ionic strength of 0.0213 mol.dm^{-3}, generated through Visual MINTEQ 3.1software. The speciation of $NaNO_3$ shows that at pH 4 and below, the dominant species are Na^+, NO_3^- and H^+ whilst the other species exist at comparably insignificant concentrations. At the pH range of 4-10, only Na^+ and NO_3^- are dominant and present in solution. Beyond pH 10, the concentration of OH^- rises.

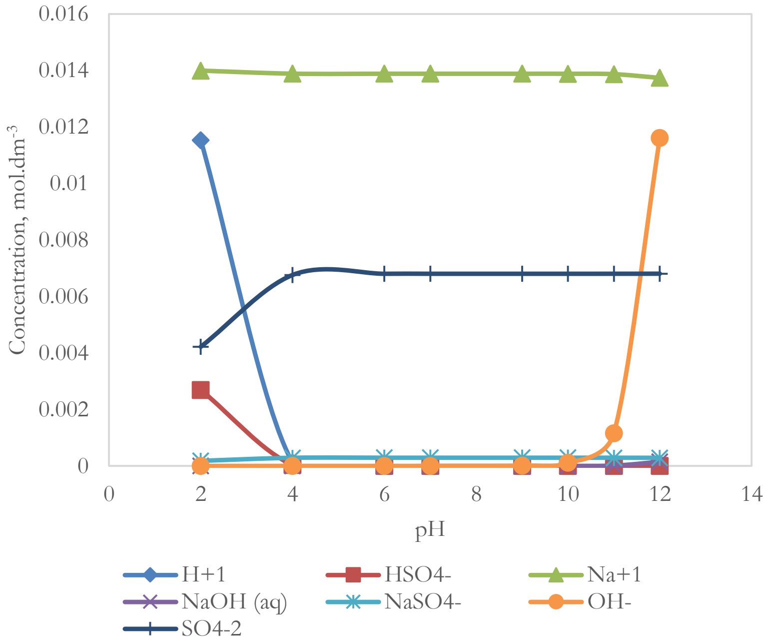


Figure 8.14: Na_2SO_4 speciation for a solution of 0.0213 mol.dm^{-3} ionic strength.

Figure 8.14 depicts the speciation of a Na_2SO_4 solution, with an ionic strength of 0.0213 mol.dm^{-3}, generated through Visual MINTEQ 3.1software. The speciation of Na_2SO_4 shows that below pH 4, contrary to the $NaNO_3$ speciation, the dominant species are Na^+, H^+ and SO_4^{2-}, HSO_4^- and a partial presence of $NaSO_4^-$. The concentration of these species remains fairly constant in the pH 4-10 range except for HSO_4^- and H^+ which become virtually insignificant whilst the concentration of OH^- rises when the pH is increased beyond pH 10. It is important to note that the specific Na^+ concentration in Na_2SO_4 is roughly 0.014 mol.dm^{-3}, relatively lower than that of 0.021 mol.dm^{-3} in $NaNO_3$ reported in Figure 8.13 although both single salts have a fixed similar ionic strength of 0.021 mol.dm^{-3} NO_3^- is also present in higher concentrations than SO_4^{2-}.

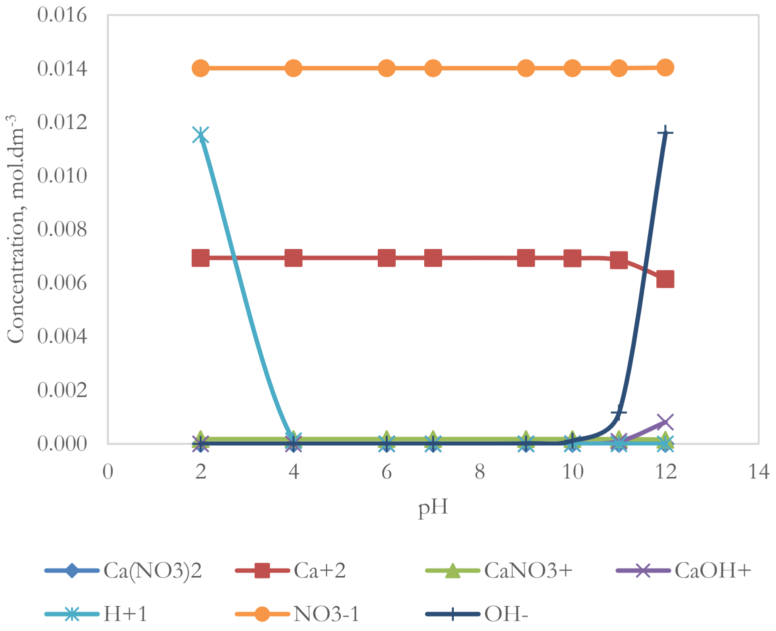


Figure 8.15: $Ca(NO_3)_2$ speciation for a solution of 0.0213 mol.dm^{-3} ionic strength.

Figure 8.15 depicts the speciation of a $Ca(NO_3)_2$ solution, with an ionic strength of 0.0213 mol.dm^{-3}, generated through Visual MINTEQ 3.1. The speciation of $Ca(NO_3)_2$ shows that below pH 4, the dominant species are Ca^{2+}, NO_3^- and H^+ with all the other species existing at comparably insignificant concentrations. At the pH range of 4-10 only Ca^{2+} and NO_3^- are dominant and present in solution with a concentration of 0.014 mol.dm^{-3} for the NO_3^- anions compared to other species. It is also shown that above pH 10, the concentration of OH^- rises, however that concentration is still relatively lower than the nitrate anions.

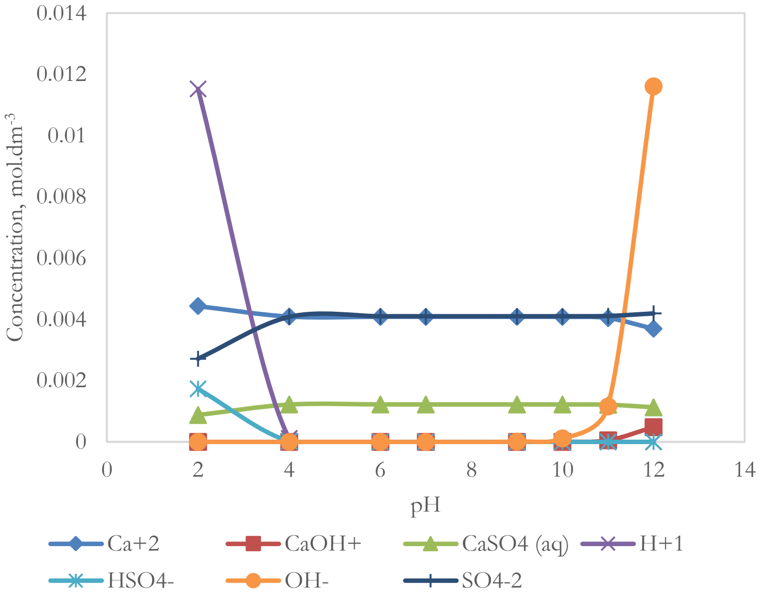


Figure 8.16: $CaSO_4$ speciation for a solution of 0.0213 mol.dm^{-3} ionic strength.

Figure 8.16 depicts the speciation of a $CaSO_4$ solution, with an ionic strength of 0.0213 mol.dm^{-3}, generated through Visual MINTEQ 3.1. The speciation of Na_2SO_4 shows that below pH 4, contrary to the $NaNO_3$ speciation and similarly with Na_2SO_4, the dominant species are Ca^{2+}, $H^+$and SO_4^{2-}, HSO_4^- and $CaSO_4$. The concentration of these species remains fairly constant in the pH 4-10 range whilst H^+ becomes obsolete. The concentration of OH^- and $CaOH^+$ increase with an increase in the solution alkalinity whilst the concentration of Ca^{2+} decreases with an increase in pH beyond pH 10. It is worth noting that the specific Ca^{2+} concentration in $CaSO_4$ is roughly 0.004 mol.dm^{-3} which is relatively lower than that of 0.014 mol.dm^{-3} in $Ca(NO_3)_2$ reported in Figure 8.15 although both single salts have a fixed similar ionic strength of 0.0213 mol.dm^{-3}. NO_3^- is also present in higher concentrations (0.062 mol.dm^{-3}) compared to SO_4^{2-} (0.003 mol.dm^{-3}).

8.7 Discussion

8.7.1 Specific Ion Effects on Froth Stability

It is generally accepted that water recovery in flotation is a good indicator of the stability of the froth (Wiese *et al*., 2011). The results of this work have shown higher water recoveries in the presence of the divalent cations Ca^{2+} and Mg^{2+} compared to the monovalent Na^{+}. Also, it became apparent that the divalent SO_4^{2-} anion had an increasing effect on the water recoveries and thus in froth stability compared to the monovalent Cl^{-} and NO_3^{-}. This was in line with Farrokhpay and Zanin (2012) who showed that froth stability was higher in the presence of multivalent metal ions compared to monovalent metal ions. This was also supported and confirmed by the froth stability test results shown in Figure 8.9 which clearly showed that Ca^{2+} resulted in higher froth stabilities compared to the monovalent Na^{+} containing single salt solutions across anion types. The observations from Figure 8.9 also confirmed the specific anion effect observed in Figure 8.5 in that, generally, SO_4^{2-} resulted in a higher froth stability compared to Cl^{-} and NO_3^{-} with an even lower froth stabilising effect observed for NO_3^{-}. There findings of this work are in line with Kurniawan *et al.* (2011) who showed that Mg^{2+} resulted in increased froth stability and smaller froth bubble size and thus higher mineral recovery compared to Na^{+} when single salt solutions of $MgCl_2$, NaCl and $NaClO_3$ were investigated during coal flotation in the absence and presence of Dowfroth 250, their findings were also in line with Castro *et al.* (2013), Henry and Craig (2010), Henry *et al.* (2007), Pugh *et al.* (1997) and Quinn *et al.* (2007) who showed that water with an increased concentration of electrolytes exhibited an increased frothing ability. Biçak *et al.* (2012) attributed this effect to the presence of a stable layer on the surface of the bubbles. Biçak *et al.* (2012) showed higher froth stabilities in the presence of SO_4^{2-} and $S_2O_3^{2-}$ than any other anions and the findings of this paper also showed similar findings in that the SO_4^{2-} containing solutions had the highest water recoveries and froth stability compared to the Cl^{-} and NO_3^{-}, this trend was particularly noticeably in the presence of Ca^{2+} and Mg^{2+}. Lessard and Zieminski (1971) investigated the effects of various inorganic electrolytes, viz., $AlCl_3$, $MgSO_4$, Na_2SO_4, $CaCl_2$, $MgCl_2$, NaCl, LiCl, and NaBr on bubble coalescence and the interfacial gas transfer in aqueous solution. 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. These are shown in Table

8.3. It is important to note that from Table 8.3, the monovalent cations (Na^+ and K^+) exhibited a higher transition concentration compared to the multivalent cations Al^{3+}, Ca^{2+} and Mg^{2+}. This lower transition concentration achieved by the multivalent cations is indicative of their superior ability to retard bubble coalescence and thus their froth stability enhancing behaviour compared to monovalent cations. Also considering the transition concentration of $MgSO_4$ in comparison to $MgCl_2$ and that of Na_2SO_4 in comparison with NaCl, it is evident that the SO_4^{2-} had a lower transition concentration of 0.032 $mol.dm^{-3}$ and 0.061 $mol.dm^{-3}$ in Mg^{2+} and Na^+ respectively compared to Cl^-. Lessard and Zieminski's findings could explain why higher froth stabilities were obtained in SO_4^{2-} containing solutions than in Cl^- and NO_3^- solutions.

Table 8.3: Bubble Coalescence Transition Concentration in Different Electrolytes (Lessard and Zieminski, 1971).

Salt	***Transition concentration, $mol.dm^{-3}$ (50 % coalescence)***
$MgSO_4$	0.032
$AlCl_3$	0.035
$MgCl_2$	0.055
$CaCl_2$	0.055
Na_2SO_4	0.061
LiCl	0.160
NaCl	0.175
NaBr	0.220
KCl	0.230

8.7.2 Specific Ion Effects on Gangue Recovery, Sulphides Grade, Zeta potential & Coagulation: Implications for Gangue Management

As discussed, froth stability findings showed that the SO_4^{2-} had resulted in the greatest froth stabilisation compared to Cl^- and NO_3^-; also the divalent cations (Ca^{2+} and Mg^{2+}) also exhibited a superior froth stabilising effect compared to the monovalent Na^+. It is important to relate these findings to the behaviour of gangue and thus froth flotation performance of the selected ore. Thus henceforth the results of gangue recovery, sulphides recoveries and grades, zeta potential and coagulation are discussed so as to ascertain whether these showed any evidence of specific ion effects on gangue behaviour.

Figure 8.1, 8.2 and 8.4 showed no evidence of specific ion effects on the sulphide recoveries for the given ore. Also the recovery of sulphide per unit mass of water did not change with ion type as shown in Figure 8.6. However specific ion effects are observed on the recovery of gangue in that

$Ca(NO_3)_2$ and $CaCl_2$ resulted in the lowest amount of gangue reporting to the concentrate compared to all the other single salts with $NaNO_3$, Na_2SO_4 and NaCl as shown in Figure 8.3 (whilst those of Mg^{2+} were about average as reported in Figure 8.3. $Ca(NO_3)_2$ and $CaCl_2$ resulted in the highest sulphide grades with all the Na^+ salts resulting in the lowest sulphide grades compared to the Ca^{2+} and Mg^{2+} single salt solutions. Thus, it can be said that some ions depressed gangue more effectively. It was apparent that NO_3^- depressed gangue more readily than Cl^- and SO_4^{2-}. This effect was stronger in the presence of Ca^{2+} than when a combination of Na^+ and NO_3^- was present in solution. These findings suggested a reason to conduct further investigative work into the mechanism of the gangue depression effects seen. Thus settling tests, zeta potential tests and single salt speciation calculations were carried out. Talc and pyrrhotite were selected as proxies for the minerals common in the selected ore as naturally floatable gangue and floatable sulphides respectively for the zeta potential tests. Single salts with the greatest impact on froth stability and gangue depression were selected for further investigative work. NO_3^- resulted in a shorter settling time compared to Cl^- and SO_4^{2-}. Also the divalent cation Ca^{2+} resulted in the shortest settling time compared to the monovalent Na^+. This implies that NO_3- resulted in increased coagulation of solids compared to Cl^- and SO_4^{2-}. It can also be said that it was easier for coagulation to occur in Ca^{2+} than in Na^+ containing solutions. These results are in line with the lower gangue recovery in Ca^{2+} and NO_3^- compared to solutions containing Na^+, Cl^- and SO_4^{2-}. However it needs to be stated that cation and anion pairs were important in that $NaNO_3$ resulted in less gangue depression compared to $Ca(NO_3)_2$. It was then proposed that the specific ion effects were evident in gangue depression and did so through coagulation as can be seen in Figure 8.10. Ca^{2+} resulted in the lowest gangue recovery per unit mass of water compared to Na^+ and a similar behaviour was observed with NO_3^- in comparison with Cl^- and SO_4^{2-}. The specific ion effects observed on gangue depression as seen on the decreased gangue recoveries can be ascribed to the coagulation of gangue particles. The decrease in gangue recoveries occurred through mineral particle surface passivation by the presence of species such as Ca^{2+}, $CaOH^+$ and $CaNO_3^+$ as can be seen though the single salts speciation diagrams shown in Figure 8.13-8.16. These show that beyond pH 9, hydroxo species and metal complexes become dominant and thus their surface chemistry can affect flotation performance. These species are thought to impart a more hydrophilic nature and thus cause a greater depression of gangue. These findings are supported by the zeta potential for both talc and pyrrhotite which was less negative with Ca^{2+} than Na^+. Thus the mineral surface was passivated by the presence of the divalent cations and its hydroxo species such that the surface of the mineral particle would become hydrophilic and thereby enhancing its depression. A similar finding was observed for the anions which resulted in less gangue recovery and greater coagulation in the NO_3^- containing solutions which resulted in a more positive zeta potential particularly at the natural flotation pH 9 compared to the SO_4^{2-} containing solutions.

Literature also suggests that zeta potential changes occur as a result of the influence of an adsorption of ions onto the mineral surface. This is said to occur either by electrostatic attraction, chemisorption or chemical reaction. Changes in the potential determining ion concentration or increases in the ionic strength of an inorganic electrolyte solution can cause a reduction in the zeta potential (Gaudin, 1932; Gaudin and Charles, 1953). Furthermore a qualitative parallel between flocculation and zeta potential is said to exist in the pulp phase and the findings of this paper have shown a direct correlation (Fuerstenau and Mishra, 1980; Fuerstenau *et al.*, 1988).

Dishon *et al.* (2009) found that in highly concentrated electrolyte solutions, the adsorption of cations onto the mineral surface changed the surface charge of the particles and resulted in strong attractive forces between particles which consequently formed hydrophilic agglomerates. An investigation into the role of Ca^{2+} ions on the surface properties of molybdenite in copper porphyries showed that the floatability of fine molybdenite particles decreased significantly when Ca^{2+} ions and silica coexisted in the flotation pulp this which suggested depression; similar to what has been shown in this present work (Li *et al.*, 2015). According to Raghavan and Hsu (1984), this phenomenon is attributed to the adsorption of Ca^{2+} ions on molybdenite and quartz, reducing the magnitude of the negative surface charge and therefore causing heterocoagulation of molybdenite and quartz. In this paper, it has been shown that mineral particles were also coagulated in Ca^{2+} containing solutions. Ikumapayi *et al.* (2012) also observed that Ca^{2+} present in process water adsorbed onto the mineral surface and reduced the negative surface charge and therefore the xanthate adsorption onto galena resulting in the depression of galena. It is thus evident that the presence of divalent Ca^{2+} in process water causes an adsorption of these electrolytes into the mineral surface, these in turn reduce the negative surface charge of the mineral as shown by the less negative positive zeta potential. This in turn led to coagulation of the passivated mineral surfaces.

8.8 Conclusions

The findings of this work have shown that the monovalent Na^+ did not promote froth stability nor did it promote coagulation. However in Ca^{2+}, froth stability and coagulation were favoured as less gangue was recovered into the concentrate indicating an increased gangue depression in the presence of Ca^{2+} compared to Na^+. This trend was more pronounced when Ca^{2+} was in combination with NO_3^-. The zeta potential results showed a less negative zeta potential on Ca^{2+} compared to Na^+ showing the passivation of the mineral surface. The depression by NO_3^- claim was confirmed by the less negative zeta potential, the lower gangue recoveries, shorter settling time and lower froth stabilities. Thus key findings of this work are:

- SO_4^{2-} and Ca^{2+} proved to have a greater froth stabilising action compared to Cl^-, NO_3^- and Na^+.
- Both NO_3^- and Ca^{2+} increased the depression of gangue as shown by the lower gangue recoveries.
- Coagulation and zeta potential tests indicated Ca^{2+} and NO_3^- would mostly likely create a pulp chemistry environment that promotes gangue depression.

This work has also shown that in terms of the depressive action of inorganic electrolytes together with their implied action on froth stability, is effected on gangue whilst maintaining valuable sulphides recoveries for this specific ore.

8.9 Acknowledgements

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CHAPTER 9 CONCLUDING DISCUSSION & FUTURE WORK

9.1 Introduction

The recycling and re-use of process water in flotation circuits has become a common practice owing to the scarcity and availability of fresh water. This practice is certainly beneficial in that it reduces reliance on municipal water and promotes compliance to stringent environmental regulations on water usage. However, it may have adverse effects on flotation performance owing to the salinity of recycled process water which alters the physico-chemical interactions of the flotation process. Previous studies on the flotation of a PGM ore have speculated that there may well be ionic strength effects as well as specific ion effects on flotation performance. It is thought that the influence of a particular ion type may depend on its ability to enhance or retard gangue activation as well as its ability to change the stability of the froth. Thus, this study investigated the effect of ion type and concentration contained in plant water on froth stability and gangue depression. Specific ion effects on froth stability and gangue depression were also considered. Water recovery, froth height and froth collapse time were used as measures of froth stability in both 2-phase and 3-phase flotation systems as previous studies showed that these can be used as key performance indicators or proxies for froth stability (Craig, 2004; Kracht *et al.*, 2016; Quinn *et al.*, 2007). Sulphide recoveries and grades, gangue recoveries, coagulation of gangue and zeta potential measurements were used to ascertain whether there existed any ionic strength and or specific effects of ion type or concentration ion effects on gangue depression.

9.2 Consolidated Discussion

This study considered the effects of ionic strength of plant water and specific inorganic electrolytes common in process water on the froth phase. Froth stability was used as a key indicator of the influence of inorganic electrolytes and their ionic strength on the froth. Regarding the pulp phase phenomenon, of interest to this study was how inorganic electrolytes and their ionic strengths affected the hydrophilicity of gangue with a keen focus on the depression of gangue in the absence and presence of CMC. The study aimed at gaining a better understanding of the proposed simultaneous enhancement of froth stability and hydrophilicity of gangue. The mechanisms through which these phenomena occur needed to be investigated. This study was deemed necessary in responding to water quality challenges facing sulphidic Cu-Ni-PGM ore concentrators since physicochemical problems arising from water recirculation necessitate such responses as enablers to the development of water management protocols in Cu-Ni-PGM ore flotation circuits. The study was designed in such a way that key questions developed would consider the froth phase and the pulp phase in order to identify dominant or controlling inorganic electrolytic conditions in process water, the impact of which would be the most dominant on froth stability and hydrophilicity on a Merensky ore. Thus, concluding remarks, hereafter, are presented as answers to key questions posed in Chapter 3, based on the results presented in Chapters 4 to 8.

9.2.1 How Does Ionic Strength Affect Froth Stability?

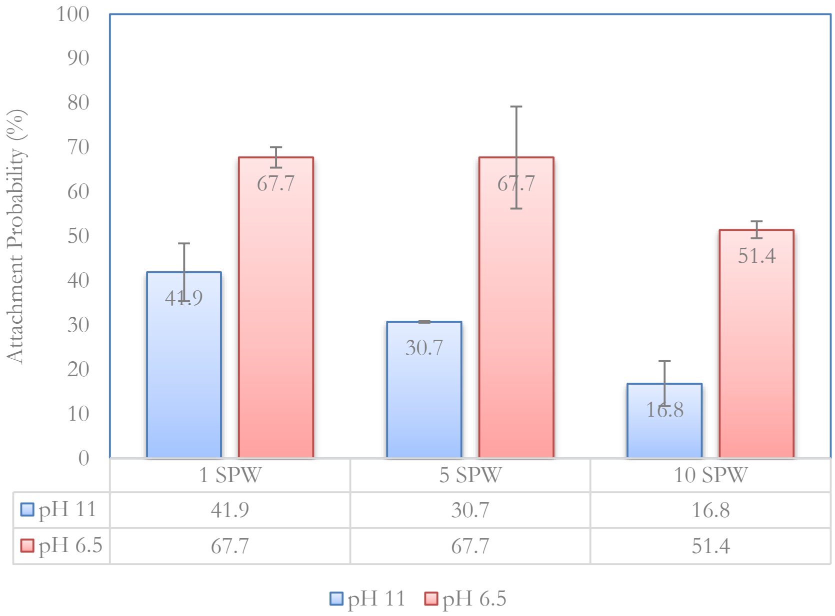
The first key questions, as laid out in Chapter 3, sought to assess the impact of changes in process water ionic strength on froth stability. After investigative tests, results showed that increases in the ionic strength of plant water increased the stability of the froth owing to increased concentrations of inorganic electrolytes which are said to be as effective as frothers in inhibiting bubble coalescence of the bubbles in the pulp phase (Craig, 2004; Henry *et al.*, 2007; Lessard and Zieminski, 1971; Quinn *et al.*, 2014, 2007).

The investigation to assess the effect of ionic strength on froth stability involved the use of various bench scale flotation tests; the results of which are discussed in detail hereafter. Batch flotation tests were conducted using a Cu-Ni-PGM bearing ore from the Merensky reef. These tests were conducted in process water of increasing ionic strengths, namely, 0.0242, 0.0727, 0.1212 and 0.2426 mol.dm^{-3} at CMC dosages of 0, 100, and 500 g/t whilst all other parameters were kept constant at the natural flotation pH 9. These results showed increases in water and solids recoveries with increasing ionic strength of process water whilst the addition of CMC decreased both the water and solids recoveries. The increase in water and solids recoveries was undoubtedly a result of an increase in froth stability as 2-phase and 3-phase froth column studies showed increases in the froth collapse time and maximum froth height with increasing ionic strength as reported in Chapter 4 and Chapter 5. The mechanism proposed for this is the ability of electrolytes to compress the electrical double layer between the thin film surrounding the bubble and the mineral surface, thereby allowing for an increase in bubble-particle attachment due to a decrease in the electrostatic repulsive forces (Bournival *et al.*, 2012; Espinosa-Gomez et al., 1987; Quinn *et al.*, 2014, 2007; Quinn and Finch, 2017; Ramos *et al.*, 2013; Weissenborn and Pugh, 1996, 1995). This was also attributed to an increase in the concentration of ions which inhibit bubble coalescence as shown by Lessard and Zieminski (1971). An earlier study which investigated pulp phase bubble size showed decreases in bubble diameter in increasing ionic strength (Manono *et al.*, 2013). It is proposed that increased ionic strength decreased bubble coalescence owing to increased concentrations of inorganic electrolytes which inhibit bubble coalescence (Lessard and Zieminski, 1971). This in turn allowed for the formation of smaller bubbles which in turn allowed for an increased bubble surface area. The increase in bubble surface area would in turn increase bubble-particle attachment and thus enhance solids and water recoveries in a 3-phase system.

The addition of CMC destabilised the froth as indicated by the decrease in water and solids recoveries. This is in agreement with the 3-phase froth stability tests which showed decreases in the froth collapse time and maximum froth height in increasing CMC dosages. It is proposed that the addition of CMC disrupted the attachment of froth stabilising NFG onto the bubbles increasing the repulsive forces between NFG particles and the bubbles as indicated by the decrease in the recovery of NFG per unit water with increasing ionic strength as reported in Chapter 4.

This was also supported by the microflotation recoveries of talc reported in Chapter 6 which showed a significant decrease in talc recovery with increasing CMC dosage. The increased CMC adsorption onto talc, reported in Figure 6.4, in increased ionic strength further confirms the inhibition of NFG attachment onto bubbles, suggesting that the hydrophobicity of NFG decreased in increased ionic strengths, and thereby decreasing bubble particle attachment which resulted in indirect froth destabilisation in the batch flotation study. In short, the ions act at both the air-water and water-mineral interfaces, changing both the bubble surface character as well as the mineral surface character, hindering the ability of the NFG to attach to the bubbles and be recovered to the concentrate

Further work to investigate the effect of process water ionic strength on froth stability, was carried out. This investigation, incorporated the variation of pH from its natural pH 9 to pH 11 as process water speciation diagrams presented in Chapter 2 and Chapter 8 (Figure 2.2 and Figure 8.13-16) showed that beyond natural pH 9, hydroxo species were observed. These may result in differing froth stabilities and mineral hydrophobicities owing to the ionic species which may be present at the higher pH such as hydroxo species and their precipitates. At pH 9, increases in both water and solids recoveries were observed as the ionic strength of plant water increased. However, at pH 11, increasing the ionic strength resulted in an increase in water recoveries and a decrease in solids recoveries. At pH 11 the solids and water recoveries were relatively lower than those at pH 9 for the same ionic strength and CMC dosage. The addition of CMC led to an even greater decrease in both solids and water recoveries under both pH conditions. The decrease in solids recoveries with increasing ionic strength despite increases in water recovery was attributed to the presence of hydroxo species such as those of $CaOH^+$ which hinder bubble-particle attachment by increasing the hydrophilicity of the surface of the minerals. This was strongly supported by the zeta potential results presented in Chapter 6 where for both talc and pyrrhotite, the zeta potential at pH 11 was less negative compared to the zeta potential values at pH 9, showing that at pH 11 the presence of hydroxo species seen in Figure 2.2 passivated the surface of the mineral, creating a more hydrophilic nature at the mineral surface and thereby causing depression. This was further supported by bubble-particle attachment tests performed on a novel bubble particle attachment timer known as the Automated Contact Time Apparatus housed at Aalto University (Aspiala *et al.*, 2018). These tests showed that for each corresponding ionic strength, the bubble particle attachment probability for pyrrhotite decreased with increasing pH as shown in Figure 9.1.



	1 SPW	5 SPW	10 SPW
🟦 pH 11	41.9	30.7	16.8
🟥 pH 6.5	67.7	67.7	51.4

Figure 9.1: Attachment probability under varying ionic strengths of plant water and pH for pyrrhotite (October, 2018).

The increase in water recoveries at pH 11 was further examined by conducting 2-phase batch flotation tests and froth column tests where water recoveries and foam collapse time were investigated under varying ionic strength and pH. The findings, reported in Chapter 5 (Figure 5.1, 5.4-5.5), showed higher water recoveries with increasing ionic strength and increasing pH. It was also shown that foam collapse time and foam height increased with increasing ionic strength and pH. This was attributed to the presence of OH^- ions which, through hydrogen bonding, increased the stability of the liquid between the bubbles. In this present study, it was suggested that this increase was caused by an increase in ionic strength upon pH modifier addition. It was thought that the increase in water recoveries was as a result of the contribution of the ions added to the system by the pH modifier itself. These may have increased the ionic strength and in turn increased foamability as shown by Figure 5.5.

9.2.2 How Does Ionic Strength Affect The Depression of Gangue?

A mass balance was performed on the batch flotation results reported in Chapter 4. The mass balance considered that, for this specific ore, at 500 g/t CMC dosage, all NFG had been depressed and would thus not report to the concentrate for this specific ore (Wiese, 2009). Figure 4.1 showed an increase in the total amount of solids reporting to the concentrate with increasing ionic strength and a decrease upon the addition of CMC. This was shown as a split of the solids recovered into three fractions, viz., the mass of sulphides, the mass of NFG, and the mass of entrained gangue. Sulphide recoveries and grades were also determined with the recoveries not following a defined trend for ionic strength and CMC dosage while there was a direct relationship shown for the concentrate grades. At a fixed CMC dosage, the increase in solids recoveries was largely a result of an increase in entrained gangue. The increase in entrained gangue is associated with the increase in water recovery (Corin *et al.*, 2011). A more stable froth resulted in increased amounts of entrained gangue reporting to the concentrate. While total NFG recovered was constant, the recovery of NFG per g of water decreased with increasing ionic strength, which was attributed to an increase in the coagulation of solid particles (Corin *et al.*, 2011). At higher ionic strengths, the recovery of both floatable gangue and entrained gangue decreased upon the addition of CMC. In order to corroborate coagulation claims, settling tests were performed for the same ore at various ionic strengths of plant water and changing CMC dosages. Increasing both the ionic strength and CMC dosage resulted in a shorter settling time supporting the claims of coagulation of gangue. Using talc as a proxy for NFG, further settling tests were performed and the results are presented in Chapter 6 (Figure 6.5). A similar trend was found, viz., the coagulation of talc particles increased under high ionic strength and CMC dosages. Furthermore, the rate of recovery for talc decreased with increasing ionic strength and CMC dosage as shown by the microflotation results in Figure 6.2. Therefore, at increased ionic strength of electrolyte solution, gangue minerals are depressed and this is ascribed to the coagulation behaviour seen in Chapter 4 and Chapter 6. These findings were in agreement with Yarar and Kitchener (1970) who investigated the flocculation of quartz under varying pH and ionic conditions. They showed that increases in NaCl concentration decreased the electrostatic repulsion between particles, resulting in particle aggregates and consequently causing coagulation of particles (size -37µm). They also found that coagulation increased with increasing pH. Salts of divalent ions such as Ca^{2+} were found to coagulate quartz readily. Owing to these findings, it was further hypothesised that this coagulation behaviour was due to enhanced CMC adsorption onto gangue at increased ionic strengths. As a result, adsorption tests were performed on both pure talc and pure pyrrhotite. The results presented in Figure 6.4 showed that for both talc and pyrrhotite, more CMC adsorbed onto the mineral particles at increased ionic strengths. This agrees with the work of Burdukova *et al.* (2008) and Laskowski *et al.* (2007) who showed that the adsorption of CMC onto talc increased with increasing ionic strength of electrolyte solution, although this only considered Ca^{2+}. With regards to the mechanism by which increased ionic strengths improve CMC adsorption, it was hypothesised that the electrolytes present in process water adsorb onto the mineral surface passivating the surface of the mineral and CMC would adsorb onto the passivated mineral surface. Zeta potential measurements were performed on talc and pyrrhotite at varying ionic strengths and pH. De-ionised water resulted in the most negative potential of both minerals followed by 1SPW, 5SPW and 10SPW which resulted in the least negative potential, indicating cation adsorption on the mineral surface (Figure 6.6). Also, in the more alkaline conditions above pH 9, the zeta potential was the least negative and this is attributed to the presence of hydroxo species and complexes such as $CaOH^+$, $CaNO_3^+$, $CaSO_4^+$, $MgOH^+$, $MgNO_3^+$ and $MgSO_4^+$ at pH values above 11 which would reduce the negative charge of the mineral. The prevalence and occurrence of these species is clearly shown in the speciation diagram shown in Figure 2.2.

9.2.3 Which Ions Have The Greatest Impact On Froth Stability?

The question of "which ions have the greatest impact on froth stability?" was examined through batch flotation and 2-phase foam column studies with various single salts. The results showed that generally divalent cations of Ca^{2+} and Mg^{2+} led to greater water recoveries compared to the monovalent Na^+. SO_4^{2-} containing salts resulted in the highest water recoveries compared to NO_3^- and Cl^-. NO_3^- had the least froth stabilising effect compared to SO_4^{2-} as indicated by the decrease in water recoveries reported in Figure 8.4. Foam column studies were performed using $CaCl_2$, $CaSO_4$, $CaNO_3$, NaCl, Na_2SO_4 and $NaNO_3$ at an ionic strength of 0.0213 $mol.dm^{-3}$ equivalent of 1SPW. The foam collapse time was the longest for Ca^{2+} containing solutions compared to those which contained Na+ for each corresponding anion type. SO_4^{2-} resulted in the longest foam collapse time compared to Cl- and NO_3^-. NO_3^- resulted in the lowest froth stability. The trend reported in Figure 8.12 was in agreement with that of the water recoveries reported in Figure 8.4. In line with the work of Lessard and Zieminski (1971), this was attributed to the ability of the ions to retard bubble coalescence. Table 9.1 depicts the molar concentrations of the single salts studied in this work.

Table 9.1: A molarity based composition of the single salts used in this study.

Water type	Ca^{2+} [M]	Mg^{2+} [M]	Na^{+} [M]	Cl^{-} [M]	SO_4^{2-} [M]	NO_3^{-} [M]	CO_3^{2-} [M]	Total Molarity [M]	TDS (mg/L)	Ionic Strength [M]
NaCl	-	-	0.0213	0.0213	-	-	-	0.0213	1245	0.0213
Na_2SO_4	-	-	0.0142	-	0.0071	-	-	0.0071	1009	0.0213
$NaNO_3$	-	-	0.0213	-	-	0.0213	-	0.0213	1810	0.0213
$CaCl_2$	0.0071	-	-	0.0124	-	-	-	0.0071	788	0.0213
$CaSO_4$	0.0053	-	-	-	0.0053	-	-	0.0053	725	0.0213
$Ca(NO_3)_2$	0.0071	-	-	-	-	0.0142	-	0.0071	1165	0.0213
$MgCl_2$	-	0.0071	-	0.0142	-	-	-	0.0071	676	0.0213
$MgSO_4$	-	0.0053	-	-	0.0053	-	-	0.0053	641	0.0213
$Mg(NO_3)_2$	-	0.0071		-	-	0.0142	-	0.0071	1053	0.0213

From Table 9.1 it can be seen that although all the single salts were studied at a fixed ionic strength of 0.0213 mol.dm^{-3} equivalent to the ionic strength typical of process water in Merensky concentrators (Wiese, 2009), concentration differed with each salt and so did the specific ion molar concentrations. For the monovalent Na^{+}, a higher amount of the salt needed to be dissolved in solution compared to the divalent Ca^{2+} and Mg^{2+} containing single salts as shown by the higher TDS and total molarity for Na^{+} salts compared to both Ca^{2+} and Mg^{2+}. Specific species concentrations or molarities are presented in an attempt to make a comparison with Lessard and Ziemanski (1971) who reported bubble coalescence for single salts in the form of a 50% transition concentration presented in Table 2.1 and Table 8.6. Lessard and Ziemanski (1971) showed that for a fixed cation (e.g. $MgSO_4$ vs. $MgCl_2$ and NaCl vs. Na_2SO_4) the concentration required to retard 50% bubble coalescence was lower for SO_4^{2-} compared to Cl^{-}, while for a fixed anion type, the required concentration to retard half of the coalescence occurring between bubbles was lower for Mg^{2+} and Ca^{2+} compared to Na^{+}. This is in agreement with the findings of this study. From Table 9.1 it can also be seen that for all single salts, a lower specific anion concentration was required for the SO_4^{2-} in producing a total ionic strength of 0.0213 mol.dm^{-3} compared to Cl^{-} and NO_3^{-}. Although all the single salts tested for impact on froth stability were present at molarities lower than their concentrations required to retard 50% bubble coalescence. It is evident that specific ion concentration and specific ion valency are important aspects in considering froth stability as shown by the fact that Ca^{2+} in combination with SO_4^{2-} has a concentration of 0.0053 mol.dm^{-3} which is lower than that of Ca^{2+} (0.0071 mol.dm^{-3}) in combination with Cl^{-} and NO_3^{-} but still resulted in the highest froth stability. This is attributed to the divalent nature of the SO_4^{2-} anion compared to the monovalent Cl^{-} and NO_3^{-} anions and hence lower concentrations would be required for the SO_4^{2-} anion compared to the Cl^{-} or NO_3^{-} anion to achieve the same effect on bubble coalescence (Lessard and Zieminski, 1971). This specific ion trend is sustained across cation types as shown in Table 9.1.

9.2.4 Which Ions have The Greatest Impact on The Depression of Gangue?

Specific ion effects on gangue behaviour were investigated in order to **identify whether any ions had a more pronounced impact on the depression of gangue**. In order to satisfy this objective, sulphide recoveries and grades, gangue recoveries, coagulation and zeta potential measurements were considered under varying single salt solutions. No impact was seen or observed on sulphide recoveries. However, the mineral grades were affected since specific ions affected froth stability and therefore, as discussed above, gangue recovery. Na^+ containing single salts resulted in an increase in gangue recovery which resulted in the concentrate grade being compromised. This was confirmed by the fact that Na^+ recovered far more solids to the concentrate compared to the divalent Ca^{2+} and Mg^{2+} despite the lower water recoveries in Na^+ containing single salt systems. This behaviour is attributed to entrainment as Figure 8.9 showed that in Na^+, the recovery of gangue per g of water was higher as indicated by the slope of the lines which is similar to the trend shown in Figure 4.5 where the less froth stabilising 1SPW resulted in a higher gangue recovery per unit water compared to the more froth stabilising 3SPW, 5SPW and 10SPW. This behaviour also suggests that in Na^+ there was less of a coagulation of gangue than in Ca^{2+}. Fuerstenau (1982) showed a greater depression of quartz with Ba^{2+} compared to Na^+. Iwasaki *et al.* (1980) investigated the zeta potential and flocculation of quartz in increased concentrations of $MgCl_2$ and $CaCl_2$ under varying pH. They showed that increases in both electrolyte concentration and pH resulted in the least negative zeta potential and the most coagulation of quartz particles compared to deionised water even at molar concentrations of 10^{-4} mol.dm^{-3}. They concluded that calcium adsorbed as $CaOH^+$ and magnesium as $Mg(OH)_2$ precipitate and that these species were responsible for the coagulation of quartz suspensions. Furthermore, they linked the depression of quartz in alkaline pulp solution with the proposed coagulation. Gaudin and Charles (1953) also showed that increases in Ca^{2+} concentration and pH resulted in increased Ca^{2+} adsorption onto pyrite as well as increases in the zeta potential, thereby decreasing pyrite recoveries. Fuerstenau (1982) proposed that Ca^{2+} adsorbed onto negatively charged pyrite particles through electrostatic attraction, thus hindering the action of a xanthate collector. With regards mechanisms proposed in the literature, the effects of specific ions on coagulation were further tested by zeta potential measurements which showed that for both talc and pyrrhotite the zeta potential was less negative in Ca^{2+} compared to Na^+. This trend was even more pronounced in alkaline conditions. This was indicative of the less hydrophilic nature of the mineral particles in the monovalent Na^+ compared to the divalent Ca^{2+} It can thus be said that there existed a stronger electrostatic interaction between the divalent Ca^{2+} and the negatively charged talc and pyrrhotite resulting in higher Ca^{2+} adsorption onto the mineral surface, thereby reducing the negative surface charge compared to the monovalent Na^+.

Concerning specific anion effects, NO_3^- resulted in the most gangue depression as lower gangue recoveries were found when compared to SO_4^{2-} and Cl^- for all cation types. This was further confirmed by the higher coagulation and higher zeta potential in NO_3^- compared to SO_4^{2-}. Considering the effect of Ca^{2+} on hydrophilicity, it is important to mention that the concentration of Ca^{2+} was higher in NO_3^- singles salts than in SO_4^{2-} and Cl^- solutions, and this could explain the greater hydrophilic impartation in NO_3^- containing solutions.

9.3 Summary of Findings

A number of questions were posed in Chapter 2 and discussed in Section 9.2. Investigations conducted have satisfied these questions and thus concluding remarks are given here below as answers to these key questions.

- ✓ **How does the ionic strength of plant water affect froth stability?**

Increasing the ionic strength of plant water resulted in an increase in froth stability as indicated by increases in water and solids recoveries, froth height and froth collapse time. This action is attributed to the presence of ions in process water which inhibit bubble coalescence and those inhibiting drainage in the lamellae. Increased ionic strengths resulted in the formation of smaller bubbles, increasing the bubble surface area which in turn created an environment conducive for bubble particle attachment necessary to stabilise the froth.

- ✓ **Which ions have the biggest impact on froth stability?**

Through water recoveries and froth collapse time studies it was shown that SO_4^{2-} and Ca^{2+} had the greatest froth stabilising effect compared to $Cl^{-,}$ NO_3^- and $Na^{+.}$ It was also shown that NO_3^- had the least froth stabilising effect. Furthermore, this work has shown that ions added for pH control result in increased water recoveries and frothability owing to the addition of bubble coalescence inhibiting inorganic electrolytes.

- ✓ **How does the ionic strength of plant water affect CMC adsorption onto selected minerals (talc and pyrrhotite) common to a Merensky ore?**

The findings of this work showed that an increase in the ionic strength of plant water resulted in an increase in the adsorption of CMC onto the selected minerals due to the action of inorganic electrolytes, particularly the divalent cations on the surface of the mineral. Their action modifies the surface chemistry of the mineral in a manner that favours the interaction between CMC and the mineral surface as was proposed by Laskowski *et al.* (2007). It was also shown that an increase in the ionic strength of plant water created an environment conducive for gangue depression as less NFG and entrained gangue reported to the concentrate per gram of water in increased ionic strengths. These findings were further supported by zeta potential analysis which showed that increased ionic strength resulted in an increases in zeta potential indicating that increased ionic strength created an environment conducive for CMC adsorption onto the mineral particle.

- ✓ **Which specific ions have the biggest impact on gangue depression?**

Adsorption, coagulation and zeta potential tests indicated an enhancement in depression of gangue with increasing ionic strength and in Ca^{2+} and NO_3^- containing solutions owing to the greater passivation effect divalent cations have on the mineral surface compared to monovalent cations Laskowski *et al.* (2007).

9.4 Concluding Remarks & Relevance of Findings

This work arose from a much larger project in collaboration with industry and academic partners, the aim of which was to develop a water management protocol for flotation given the increase in the occurrence of recirculated process water which leads to increased inorganic and organic substances in such closed water circuits. It became clear from the onset that fundamental work needed to be done to provide findings, through established bench scale techniques, to inform the protocol development part of the said project. It was decided that there was a need to investigate the inorganic electrolytes in process water on the aspects of flotation which are shown in Figure 9.2.

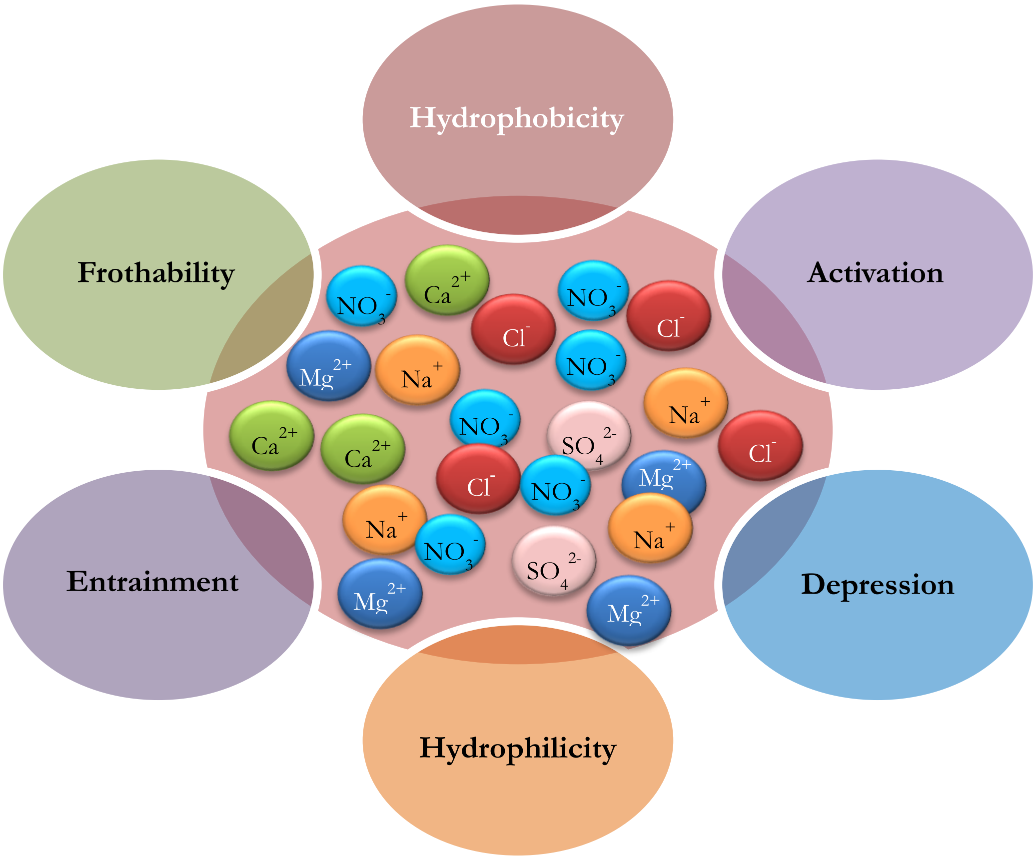


Figure 9.2: The effects of electrolytes in process water on the various aspects of froth flotation investigated in this study.

This study has investigated inorganic electrolytes on froth stability as well as their effects on depression of gangue (i.e. hydrophilicity). The efficacy of CMC as a depressant for naturally floatable gangue under various inorganic electrolytes and their ionic strength was also investigated.

This study showed that water recovery and froth and or foam collapse time can be used as indicators of froth stability. It was shown that increasing ionic strengths of plant water and concentrations of ions such as divalent ions such as Ca^{2+}, Mg^{2+} and SO_4^{2-} had a more pronounced effect on froth stability compared to monovalent ions. This thus means that in a plant environment excessive froth stabilisation should be expected if and when the process water consists of relatively high concentrations of these divalent ions. If the increase in froth stability is at the expense of the concentrate grades, a counter measure or action would be to either reduce the frother dosage or increase the depressant dosage.

Furthermore, the findings of this work have shown that the effect of water quality on the behaviour of gangue can be analysed and predicted at a bench scale level through gangue recovery, coagulation, zeta potential and adsorption studies. Data and findings obtained through such studies should be translatable to water quality effects at an industrial scale operations level. Process water with high concentrations of inorganic electrolytes such as Ca^{2+} and Mg^{2+} and their oxyhydroxo species is likely to affect the depression of gangue. The performance of polysaccharides such as CMC as depressants targeting NFG is enhanced in the presence of polyvalent cations.

9.5 Future Work

Recommendations for future work are presented below from ideas emanating from the findings of this PhD.

- Considering the cost benefit that may exist as a result of residual reagents in recirculated water. It is thus important to mimic water recycling by performing bench scale flotation tests under various CMC dosages; re-use the water from the tails and the concentrates with the necessary make-up amount required. The tails should be investigated for how long it takes the solids to settle before a supernatant of a recyclable quality appears in order to mimic and assess the recyclability of water from tailings ponds and thickener overflows. The du Bois method should be used to determine the amount of residual CMC in the liquid supernatant that is to be recycled. The clear liquid supernatant should also be analysed for electrical conductivity and pH as proxies for the inorganic content of the recycled water. It is anticipated that work of this nature will give an idea of the number of cycles necessary for CMC to be benign. This should enable the determination of those limits within which fresh reagent dosing would be necessary as well as limits that would prompt the need to treat the process water before further recirculation.
- It is proposed that on the basis of this work and literature, an in depth technical report could be developed regarding how flotation performance indicators (such as froth stability and grades) in Cu-Ni sulphidic concentrators can be linked to the various process water constituents. These linkages will assist in tailoring the quality of water and reagent regime towards the desired flotation performance.
- The activation of gangue by certain ions is known but the mechanism for the same is unknown. Therefore as this question was not addressed in this study. Future studies should thus consider investigating the mechanism by which certain ions activate gangue.

9.6 References

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APPENDICES

Appendix A: Raw Data for Chapter 4

Batch Flotation Tests

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Rec, %	Entrained gangue, g	Floating gangue, g
Test 1	1SPW	C1	3	14.42	14.42	65.44	116.80	8.10	38.96	3.46	7.75
		C2	7	17.27	31.69	196.14	192.10	6.06	64.07	10.38	16.04
	40 g/t D200	C3	13	18.85	50.54	371.44	218.11	4.32	72.75	19.65	24.91
		C4	21	19.75	70.29	606.90	235.45	3.35	78.54	32.11	31.73
	150 g/t SIBX	F		994.89							
		Tails		924.60							
Test 2	1SPW	C1	3	16.39	16.39	84.61	129.64	7.91	46.76	4.48	8.36
		C2	7	15.52	31.91	184.60	172.32	5.40	62.15	9.77	17.42
	40 g/t D200	C3	13	19.10	51.01	358.51	201.36	3.95	72.62	18.97	26.52
		C4	21	21.13	72.14	631.66	219.53	3.04	79.17	33.41	30.70
	150 g/t SIBX	F		1010.19							
		Tails		921.81							
Test 1	3SPW	C1	3	16.35	16.35	86.71	141.92	8.68	47.75	4.53	8.12
		C2	7	15.01	31.36	212.70	187.55	5.98	63.11	11.12	17.09
	40 g/t D200	C3	13	20.23	51.59	431.52	218.90	4.24	73.66	22.57	25.49
		C4	21	22.88	74.47	760.98	238.49	3.20	80.25	39.80	29.89
	150 g/t SIBX	F		1021.16							
		Tails		946.69							
Test 2	3SPW	C1	3	15.76	15.76	88.66	150.19	9.53	51.77	4.53	7.92
		C2	7	14.71	30.47	217.61	193.88	6.36	66.83	11.12	17.90
	40 g/t D200	C3	13	26.10	56.57	425.72	231.73	4.10	79.88	22.57	25.02
		C4	21	21.10	77.67	754.32	245.84	3.17	84.74	39.80	29.13
	150 g/t SIBX	F		1006.57							
		Tails		897.83							

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Rec, %	Entrained gangue, g	Floating gangue, g
Test 1	5SPW 40 g/t D200 150 g/t SIBX	C1	3	14.42	14.42	65.44	116.80	8.10	38.96	6.01	11.75
		C2	7	17.27	31.69	196.14	192.10	6.06	64.07	12.26	19.42
		C3	13	18.85	50.54	371.44	218.11	4.32	72.75	27.47	29.70
		C4	21	19.75	70.29	606.90	235.45	3.35	78.54	47.76	33.70
		F		994.89							
		Tails		924.60							
Test 2	5SPW 40 g/t D200 150 g/t SIBX	C1	3	16.39	16.39	84.61	129.64	7.91	46.76	5.91	13.49
		C2	7	15.52	31.91	184.60	172.32	5.40	62.15	12.27	21.37
		C3	13	19.10	51.01	358.51	201.36	3.95	72.62	27.59	26.59
		C4	21	21.13	72.14	631.66	219.53	3.04	79.17	47.93	28.02
		F		1010.19							
		Tails		921.81							
Test 1	10SPW 40 g/t D200 150 g/t SIBX	C1	3	16.35	16.35	86.71	141.92	8.68	47.75	6.93	11.63
		C2	7	15.01	31.36	212.70	187.55	5.98	63.11	17.06	23.21
		C3	13	20.23	51.59	431.52	218.90	4.24	73.66	40.13	32.94
		C4	21	22.88	74.47	760.98	238.49	3.20	80.25	70.05	33.31
		F		1021.16							
		Tails		946.69							
Test 2	10SPW 40 g/t D200 150 g/t SIBX	C1	3	15.76	15.76	88.66	150.19	9.53	51.77	7.08	13.31
		C2	7	14.71	30.47	217.61	193.88	6.36	66.83	17.07	20.92
		C3	13	26.10	56.57	425.72	231.73	4.10	79.88	40.50	30.66
		C4	21	21.10	77.67	754.32	245.84	3.17	84.74	70.07	28.10
		F		1006.57							
		Tails		897.83							

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Recovery, %	Entrained gangue, g	Floating gangue, g
Test 1	1SPW 40 g/t D200 100 g/t CMC 150 g/t SIBX	C1	3	5.06	5.06	20.27	99.68	19.70	34.67	1.50	0.82
		C2	7	12.76	17.82	144.03	204.82	11.49	71.24	10.67	3.53
		C3	13	9.80	27.62	248.63	224.42	8.13	78.06	18.42	4.04
		C4	21	13.92	41.54	419.68	240.43	5.79	83.63	31.10	5.23
		F		1001.00							
		Tails		959.46							
Test 2	1SPW 40 g/t D200 100 g/t CMC 150 g/t SIBX	C1	3	5.17	5.17	22.62	83.24	16.10	36.50	1.68	1.21
		C2	7	10.53	15.70	148.04	147.36	9.39	64.63	10.97	3.49
		C3	13	9.73	25.43	251.99	164.59	6.47	72.18	18.67	4.69
		C4	21	12.82	38.25	424.27	176.68	4.62	77.48	31.44	5.10
		F		1007.49							
		Tails		954.36							
Test 1	3SPW 40 g/t D200 100 g/t CMC 150 g/t SIBX	C1	3	5.92	5.92	27.11	137.94	23.30	45.76	1.81	1.05
		C2	7	10.33	16.25	149.92	217.48	13.38	72.15	10.00	3.28
		C3	13	11.81	28.06	320.47	240.74	8.58	79.87	21.38	4.08
		C4	21	14.58	42.64	566.15	254.61	5.97	84.47	37.76	5.21
		F		977.27							
		Tails		934.63							
Test 2	3SPW 40 g/t D200 100 g/t CMC 150 g/t SIBX	C1	3	5.89	5.89	29.32	104.84	17.80	38.25	1.96	1.06
		C2	7	10.64	16.53	146.01	109.71	11.54	69.58	9.74	3.10
		C3	13	11.58	28.11	310.70	215.60	7.67	78.66	20.72	4.69
		C4	21	15.31	43.42	560.38	231.37	5.33	84.41	37.38	5.25
		F		1013.82							
		Tails		953.69							

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Recovery, %	Entrained gangue, g	Floating gangue, g
Test 1	5SPW	C1	3	9.42	9.42	74.59	154.49	16.40	52.88	3.79	1.39
		C2	7	10.14	19.56	211.00	208.33	10.62	71.31	10.72	3.13
	40 g/t D200	C3	13	12.97	32.53	395.65	229.73	7.06	78.64	20.10	4.13
	100 g/t CMC	C4	21	15.87	48.40	683.46	242.59	5.01	83.04	34.72	5.51
	150 g/t SIBX	F		1352.36							
		Tails		1303.96							
Test 2		C1	3	9.57	9.57	63.28	222.98	23.30	55.58	3.21	1.92
	5SPW	C2	7	10.36	19.93	197.89	302.75	15.19	75.46	10.05	3.57
		C3	13	12.86	32.79	390.26	328.09	10.01	81.78	19.83	4.89
	40 g/t D200	C4	21	16.12	48.91	680.88	343.42	7.02	85.60	34.59	5.10
	100 g/t CMC	F		1218.26							
	150 g/t SIBX	Tails		1153.11							
Test 1	10SPW	C1	3	10.60	10.60	81.35	188.68	17.80	50.06	3.60	1.82
		C2	7	10.85	21.45	227.99	276.24	12.88	73.29	10.10	3.71
	40 g/t D200	C3	13	15.74	37.19	458.31	310.08	8.34	82.27	20.30	4.78
	100 g/t CMC	C4	21	21.39	58.58	932.43	332.11	5.67	88.11	41.31	5.59
	150 g/t SIBX	F		1058.60							
		Tails		1000.02							
Test 2		C1	3	10.09	10.09	80.99	165.48	16.40	56.04	3.59	1.96
	10SPW	C2	7	10.25	20.34	225.96	219.90	10.81	74.47	10.01	3.01
		C3	13	14.14	34.48	452.34	243.23	7.05	82.37	20.04	4.62
	40 g/t D200	C4	21	20.55	55.03	921.79	259.88	4.72	88.01	40.84	5.06
	100 g/t CMC	F		1002.49							
	150 g/t SIBX	Tails		931.71							

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Recovery, %	Entrained gangue, g	Floating gangue, g
Test 1	1SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	1.71	1.71	19.03	44.12	25.80	22.46	1.41	0.00
		C2	7	2.90	4.61	41.88	100.67	21.84	51.25	3.10	0.00
		C3	13	2.88	7.49	64.59	140.99	18.82	71.77	4.79	0.00
		C4	21	2.29	9.78	88.69	162.19	16.58	82.57	6.57	0.00
		F		982.43							
		Tails		972.65							
Test 2	1SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	1.67	1.67	20.94	42.59	25.50	25.17	1.55	0.00
		C2	7	2.69	4.36	43.74	92.62	21.24	54.75	3.24	0.00
		C3	13	2.89	7.25	66.69	122.96	16.96	72.68	4.94	0.00
		C4	21	2.24	9.49	90.26	136.78	14.41	80.85	6.69	0.00
		F		1010.89							
		Tails		974.27							
Test 1	3SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	2.71	2.71	22.84	65.31	24.10	27.54	1.52	0.00
		C2	7	4.62	7.33	47.64	145.70	19.88	61.45	3.18	0.16
		C3	13	2.89	10.22	75.23	181.25	17.73	76.44	5.02	0.23
		C4	21	2.85	13.07	109.56	200.63	15.35	84.61	7.31	0.26
		F		1023.73							
		Tails		1010.66							
Test 2	3SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	2.67	2.67	22.91	63.81	23.90	27.22	1.53	0.00
		C2	7	4.60	7.27	48.64	149.37	20.55	63.72	3.24	0.00
		C3	13	2.85	10.12	77.43	182.72	18.06	77.92	5.16	0.00
		C4	21	2.77	12.89	113.60	200.03	15.52	85.33	7.58	0.00
		F		1058.51							
		Tails		1020.75							

Run no.	Reagents	Sample	Time, min	Mass Pull, g	Cum Mass Pull, g	Cum Water Rec, g	Cum Sulphur Mass, 100 g	Sulphur Grade, %	Sulphur Recovery, %	Entrained gangue, g	Floating gangue, g
Test 1	5SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	5.75	5.75	43.29	123.05	21.40	56.45	2.20	0.18
		C2	7	2.18	7.93	89.51	145.07	18.29	66.55	4.55	0.00
		C3	13	3.14	11.07	127.68	167.17	15.10	76.69	6.49	0.00
		C4	21	2.80	13.87	165.01	181.40	13.08	83.21	8.38	0.51
		F		1033.20							
		Tails		1019.33							
Test 2	5SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	5.67	5.67	45.19	127.01	22.40	59.62	2.30	0.00
		C2	7	2.23	7.90	96.33	148.30	18.77	69.62	4.89	0.00
		C3	13	3.39	11.29	128.87	167.36	14.82	78.56	6.55	0.15
		C4	21	2.43	13.72	167.68	179.07	13.05	84.06	8.52	0.29
		F		1062.23							
		Tails		1018.25							
Test 1	10SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	8.27	8.27	110.53	132.32	16.00	60.25	4.90	0.00
		C2	7	3.41	11.68	177.40	160.55	13.75	71.39	7.86	0.00
		C3	13	2.40	14.08	217.62	174.71	12.41	77.68	9.64	0.00
		C4	21	3.51	17.59	275.63	189.84	10.79	84.41	12.21	0.00
		F		978.13							
		Tails		960.54							
Test 2	10SPW 40 g/t D200 500 g/t CMC 150 g/t SIBX	C1	3	8.29	8.29	110.20	128.50	15.50	60.25	4.88	0.00
		C2	7	3.53	11.82	180.32	152.75	12.92	71.62	7.99	0.00
		C3	13	2.65	14.47	219.18	166.98	11.54	78.29	9.71	0.18
		C4	21	3.49	17.96	277.75	179.96	10.02	84.38	12.30	0.72
		F		1020.99							
		Tails		972.89							

Froth Column Tests

CMC=0 g/t, Dow 200=40 g/t, SIBX=150 g/t				
1SPW				
	Test 1	Test 2	Average	Stdev
H_i	453	448	450.5	3.54
H_f	470	475	472.5	3.54
$H_{i,new}$	460	463	461.5	2.12
$t_{collapse}$	6	4	5	1.41
H_{froth}	17	27	22	7.07
ΔH_i	7	15	11	5.66

CMC=500 g/t, Dow 200=40 g/t, SIBX=150 g/t				
1SPW				
	Test 1	Test 2	Average	Stdev
H_i	442	453	447.5	7.78
H_f	446	456	451	7.07
$H_{i,new}$	444	455	449.5	7.78
$t_{collapse}$	4	4	4	0.00
H_{froth}	2	2	2	0.00
ΔH_i	2	2	2	0.00

CMC= 0 g/t, Dow 200= 40g/t, SIBX=150 g/t				
5SPW				
	Test 1	Test 2	Average	Stdev
H_i	440	445	442.5	3.54
H_f	455	460	457.5	3.54
$H_{i,new}$	450	453	451.5	2.12
$t_{collapse}$	4	3	3.5	0.71
H_{froth}	15	15	15	0.00
ΔH_i	10	8	9	1.41

CMC=0 g/t, Dow 200=40 g/t, SIBX=150 g/t				
10SPW				
	Test 1	Test 2	Average	Stdev
H_i	453	452	452.5	0.71
H_f	540	544	542	2.83
$H_{i,new}$	475	480	477.5	3.54
$t_{collapse}$	20	21	20.5	0.71
H_{froth}	87	92	89.5	3.54
ΔH_i	22	28	25	4.24

CMC=100 g/t, Dow 200=40 g/t, SIBX=150 g/t				
1SPW				
	Test 1	Test 2	Average	Stdev
H_i	454	442	448	8.49
H_f	460	449	454.5	7.78
$H_{i,new}$	457	446	451.5	7.78
$t_{collapse}$	2	4	3	1.41
H_{froth}	6	7	6.5	0.71
ΔH_i	3	4	3.5	0.71

CMC=0 g/t, Dow 200=40 g/t, SIBX=150 g/t				
5SPW				
	Test 2	Test 1	Average	Stdev
H_i	457	460	458.5	2.12
H_f	485	490	487.5	3.54
$H_{i,new}$	462	470	466	5.66
$t_{collapse}$	8	9	8.5	0.71
H_{froth}	28	30	29	1.41
ΔH_i	5	10	7.5	3.54

CMC=0 g/t, Dow 200=40g/t, SIBX=150g/t				
5SPW				
	Test 1	Test 2	Average	Stdev
H_i	445	448	446.5	2.12
H_f	454	452	453	1.41
$H_{i,new}$	455	450	452.5	3.54
$t_{collapse}$	2	3	2.5	0.71
H_{froth}	9	4	6.5	3.54
ΔH_i	10	2	6	5.66

CMC=100 g/t, Dow 200=40 g/t, SIBX=150 g/t				
10SPW				
	Test 1	Test 2	Average	Stdev
H_i	455	460	457.5	3.54
H_f	490	500	495	7.07
$H_{i,new}$	465	468	466.5	2.12
$t_{collapse}$	12	11	11.5	0.71
H_{froth}	35	40	37.5	3.54
ΔH_i	10	8	9	1.41

CMC=500 g/t, Dow 200=40 g/t, SIBX=150 g/t				
10SPW				
	Test 1	Test 2	Average	Stdev
H_i	456	455	455.5	0.71
H_f	475	479	477	2.83
$H_{i,new}$	464	463	463.5	0.71
$t_{collapse}$	4	5	4.5	0.71
H_{froth}	19	24	21.5	3.54
ΔH_i	8	8	8	0.00

Coagulation Tests

1SPW			
CMC	0 g/t	100 g/t	500 g/t
SIBX	150 g/t	150 g/t	150g/t
$t_{settling,1}$	9.50	8.17	7.03
$t_{settling,2}$	10.00	8.83	7.08
$t_{settling,average}$	9.75	8.50	7.06

5SPW			
CMC	0 g/t	100 g/t	500 g/t
SIBX	150 g/t	150 g/t	150g/t
$t_{settling,1}$	9.58	7.83	6.33
$t_{settling,2}$	10.08	7.17	6.58
$t_{settling,average}$	9.83	7.50	6.46

10SPW			
CMC	0 g/t	100 g/t	500 g/t
SIBX	150 g/t	150 g/t	150g/t
$t_{settling,1}$	9.83	6.67	6.17
$t_{settling,2}$	10.00	6.52	6.57
$t_{settling,average}$	9.92	6.59	6.37

Appendix B: Raw Data for Chapter 7

Conditions	Test Number	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Copper Grade %	Copper Rec %	Nickel Grade %	Nickel Rec %
NaCl Dow 200 SIBX	1	C1	3	9.44	9.44	12.68	4.12	67.86	4.18	23.87
		C2	7	26.91	36.35	158.88	1.26	80.03	2.36	51.85
		C3	13	31.07	67.42	454.14	0.72	84.71	1.39	56.85
		C4	21	23.27	90.69	717.59	0.55	87.18	1.08	59.45
		F		966.07						
		T		840.16						
		T2		16.54						
		T3		18.68						
	2	C1	3	10.01	10.01	13.38	3.92	69.08	4.13	23.98
		C2	7	26.73	36.74	163.07	1.26	81.80	2.42	51.72
		C3	13	33.05	69.79	473.18	0.71	87.04	1.41	57.22
		C4	21	23.28	93.07	738.16	0.55	89.42	1.11	59.95
		F		989.85						
		T		862.89						
		T2		16.83						
		T3		17.06						
Na_2SO_4 Dow 200 SIBX	1	C1	3	10.32	10.32	11.26	3.68	66.44	3.88	23.36
		C2	7	24.68	35.00	127.50	1.29	79.01	2.46	50.20
		C3	13	28.02	63.02	357.74	0.76	83.57	1.50	55.04
		C4	21	24.50	87.52	598.76	0.56	86.26	1.13	57.71
		F		970.55						
		T		850.71						
		T2		16.35						
		T3		15.97						
	2	C1	3	12.34	12.34	12.84	3.32	71.74	3.96	29.45
		C2	7	22.46	34.80	129.51	1.33	81.29	2.41	50.59
		C3	13	33.80	68.60	364.79	0.72	86.09	1.36	56.11
		C4	21	25.60	94.20	612.52	0.54	88.58	1.04	58.97
		F		962.80						
		T		834.89						
		T2		17.18						
		T3		16.53						

Conditions	Test Number	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Copper Grade %	Copper Rec %	Nickel Grade %	Nickel Rec %
NaNO$_3$ Dow 200 SIBX	1	C1	3	13.22	13.22	20.18	3.48	72.20	4.31	33.72
		C2	7	26.80	40.02	194.45	1.30	81.76	2.12	50.23
		C3	13	31.37	71.39	509.74	0.77	86.56	1.34	56.36
		C4	21	22.10	93.49	766.06	0.61	88.91	1.07	59.40
		F		1004.44						
		T		870.01						
		T2		20.57						
		T3		20.37						
	2	C1	3	13.59	13.59	19.02	3.48	72.54	4.54	34.85
		C2	7	26.71	40.30	176.31	1.32	81.88	2.25	51.29
		C3	13	33.20	73.50	493.51	0.77	87.11	1.39	57.50
		C4	21	23.13	96.63	749.82	0.60	89.51	1.11	60.46
		F		996.36						
		T		862.51						
		T2		18.56						
		T3		18.66						
MgCl2 Dow 200 SIBX	1	C1	3	11.45	11.45	29.44	3.72	71.62	4.34	28.40
		C2	7	28.47	39.92	250.90	1.22	81.94	2.33	53.32
		C3	13	28.16	68.08	573.38	0.75	86.27	1.49	58.11
		C4	21	19.20	87.28	831.09	0.60	88.37	1.21	60.30
		F		967.86						
		T		845.17						
		T2		17.96						
		T3		17.45						
	2	C1	3	11.85	11.85	30.28	3.58	71.56	4.06	27.52
		C2	7	27.64	39.49	236.73	1.23	81.98	2.29	51.74
		C3	13	28.98	68.47	563.22	0.75	86.42	1.45	56.70
		C4	21	20.11	88.58	824.96	0.59	88.55	1.17	59.08
		F		987.86						
		T		864.24						
		T2		17.04						
		T3		18.00						

Conditions	Test Number	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Copper Grade %	Copper Rec %	Nickel Grade %	Nickel Rec %
MgSO4 Dow 200 SIBX	1	C1	3	14.03	14.03	23.22	3.29	73.55	3.95	32.09
		C2	7	32.49	46.52	334.95	1.13	83.56	2.05	55.21
		C3	13	25.28	71.80	655.10	0.76	87.03	1.43	59.34
		C4	21	17.68	89.48	882.39	0.62	88.89	1.18	61.33
		F		990.24						
		T		866.56						
		T2		16.39						
		T3		17.81						
	2	C1	3	12.58	12.58	21.51	3.34	71.57	4.07	30.53
		C2	7	31.01	43.59	329.77	1.10	81.78	2.05	53.30
		C3	13	29.79	73.38	663.43	0.69	86.45	1.32	57.91
		C4	21	18.34	91.72	886.21	0.57	88.47	1.10	59.96
		F		970.60						
		T		845.53						
		T2		16.55						
		T3		16.80						
Mg(NO3)2 Dow 200 SIBX	1	C1	3	12.57	12.57	22.73	3.38	70.83	3.92	28.39
		C2	7	28.43	41.00	244.79	1.19	81.27	2.19	51.91
		C3	13	27.63	68.63	554.46	0.75	85.49	1.43	56.69
		C4	21	19.27	87.90	793.72	0.60	87.59	1.16	59.03
		F		973.46						
		T		849.23						
		T2		18.74						
		T3		17.59						
	2	C1	3	12.30	12.30	22.80	3.60	67.81	4.11	26.47
		C2	7	28.90	41.20	245.35	1.28	80.69	2.49	53.72
		C3	13	28.09	69.29	557.19	0.81	85.64	1.63	59.09
		C4	21	18.89	88.18	795.06	0.65	87.73	1.33	61.32
		F		993.68						
		T		865.13						
		T2		19.04						
		T3		21.33						

Conditions	Test Number	Sample	Time min	Mass Pull g	Cum Mass g	Cum Water g	Copper Grade %	Copper Rec %	Nickel Grade %	Nickel Rec %
CaCl2 Dow 200 SIBX	1	C1	3	11.88	11.88	39.31	3.32	73.14	3.95	29.25
		C2	7	25.26	37.14	264.23	1.20	82.71	2.30	53.25
		C3	13	25.76	62.90	574.57	0.74	86.85	1.47	57.75
		C4	21	18.31	81.21	821.55	0.59	88.98	1.18	59.87
		F		974.34						
		T		857.91						
		T2		18.20						
		T3		17.02						
	2	C1	3	11.53	11.53	32.67	3.38	72.95	4.30	31.20
		C2	7	22.40	33.93	259.63	1.28	81.31	2.40	51.32
		C3	13	28.36	62.29	571.79	0.74	85.91	1.43	56.12
		C4	21	21.18	83.47	840.49	0.57	88.48	1.12	58.65
		F		976.26						
		T		859.17						
		T2		15.99						
		T3		17.63						
CaSO4 Dow 200 SIBX	1									
		C1	3	12.67	12.67	27.23	3.29	71.53	4.14	32.14
		C2	7	29.86	42.53	287.24	1.12	81.56	1.86	48.54
		C3	13	27.76	70.29	619.37	0.71	85.57	1.24	53.60
		C4	21	19.36	89.65	858.86	0.57	87.56	1.02	56.09
		F		979.67						
		T		854.76						
		T2		18.09						
		T3		17.17						
	2	C1	3	11.95	11.95	29.45	3.37	70.90	3.98	30.62
		C2	7	28.43	40.38	281.34	1.14	81.20	1.83	47.63
		C3	13	26.95	67.33	609.00	0.72	85.69	1.22	52.79
		C4	21	19.74	87.07	845.06	0.57	87.64	0.99	55.38
		F		985.64						
		T		861.06						
		T2		18.61						
		T3		18.90						

Conditions	Test Number	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Copper Grade %	Copper Rec %	Nickel Grade %	Nickel Rec %
Ca(NO3)2 Dow 200 SIBX	1	C1	3	8.34	8.34	7.61	4.52	65.04	4.48	22.38
		C2	7	22.54	30.88	184.80	1.48	78.96	2.74	50.67
		C3	13	26.92	57.80	498.33	0.85	84.31	1.64	56.76
		C4	21	19.36	77.16	756.67	0.65	86.57	1.28	59.20
		F		992.85						
		T		875.94						
		T2		19.85						
		T3		19.90						
	2	C1	3	7.03	7.03	6.53	5.04	63.14	4.28	18.11
		C2	7	24.98	32.01	194.33	1.39	79.22	2.65	51.03
		C3	13	28.60	60.61	519.48	0.78	84.46	1.58	57.57
		C4	21	19.87	80.48	781.18	0.61	87.28	1.24	60.24
		F		972.17						
		T		853.62						
		T2		18.65						
		T3		19.42						
1Plant Dow 200 SIBX	1	C1	3	11.59	11.59	16.63	3.93	73.81	4.00	29.02
		C2	7	27.28	38.87	209.91	1.32	83.30	2.02	49.29
		C3	13	27.68	66.55	504.03	0.81	87.22	1.31	54.69
		C4	21	20.40	86.95	759.21	0.63	89.28	1.05	57.46
		F		957.48						
		T		834.05						
		T2		17.36						
		T3		19.12						
	2	C1	3	9.31	9.31	14.91	4.09	66.94	4.18	25.48
		C2	7	25.11	34.42	203.07	1.30	78.95	2.02	45.58
		C3	13	29.72	64.14	507.47	0.74	83.64	1.24	51.91
		C4	21	19.89	84.03	760.33	0.58	85.91	1.00	54.79
		F		959.90						
		T		838.80						
		T2		18.16						
		T3		18.91						

Appendix C: Raw Data for Chapter 5

Batch flotation

Depressant dosage (g/t CMC)	Mass Recovery (g)	Water Recovery (g)	Ni Recovery (%)	Ni Grade (%)	Cu Recovery (%)	Cu Grade (%)
pH 9						
1 SPW						
0	192.11	1243.17	56.08	0.39	87.46	0.31
100	143.39	1056.21	52.96	0.62	84.23	0.35
500	134.81	977.30	50.64	1	79.14	0.25
5 SPW						
0	156.42	858.78	48.35	0.5	87.67	0.41
100	223.16	1151.22	44.96	0.62	81.46	0.19
500	115.33	876.43	39.75	0.91	88.05	0.61
10 SPW						
0	200.51	1551.69	36.99	0.21	82.17	0.19
100	170.72	1233.08	32.40	5.54	83.12	0.24
500	93.66	1058.75	28.89	0.79	81.51	0.43
pH 11						
1 SPW						
0	105.45	1113.22	55.88	0.19	80.62	0.38
100	143.33	869.84	48.17	0.23	81.51	0.19
500	160.8	1210.76	44.95	0.28	75.2	0.17
5 SPW						
0	85.07	810.95	46.93	0.39	76.08	0.4
100	136.4	1266.11	46.02	0.43	78.92	0.31
500	112.42	1107.14	43.48	0.63	69.22	0.38
10 SPW						
0	98.89	944.62	38.01	0.66	90.75	0.43
100	100.24	1546.54	36.07	0.68	88.49	0.81
500	107.41	1374.31	33.31	0.99	53.43	0.29

Two-phase Froth Column Tests

1 SPW pH 9					
	Test 1	Test 2	Test 3	Average	Stdev
H_i	36.7	36.5	36.6	36.60	0.10
H_f	46.3	46	46.2	46.17	0.15
$H_{i, new}$	44.3	44.3	44.3	44.30	0.00
$t_{collapse}$	10.1	10.3	10.4	10.27	0.15
H_{froth}	9.6	9.5	9.6	9.57	0.06
ΔH	7.6	7.8	7.7	7.70	0.10

5SPW pH 9					
	Test 1	Test 2	Test 3	Average	Stdev
H_i	36.7	36.6	36.4	36.57	0.15
H_f	51.3	51.6	51.1	51.33	0.25
$H_{i, new}$	44.5	44.3	44.2	44.33	0.15
$t_{collapse}$	15.3	15.1	15.6	15.33	0.25
H_{froth}	14.6	15	14.7	14.77	0.21
ΔH	7.8	7.7	7.8	7.77	0.06

10SPW pH 9					
	Test 1	Test 2	Test 3	Average	Stdev
H_i	36.7	36.7	36.5	36.63	0.12
H_f	57.5	57.2	57	57.23	0.25
$H_{i, new}$	44.5	44.3	44.1	44.30	0.20
$t_{collapse}$	21.3	21.6	21.4	21.43	0.15
H_{froth}	20.8	20.5	20.5	20.60	0.17
ΔH	7.8	7.6	7.6	7.67	0.12

Two-phase Batch Flotation Tests

	pH 9			pH 11		
t (min)	**1SPW**	**5SPW**	**10SPW**	**1SPW**	**5SPW**	**10SPW**
min	**R_{water} (%)**	**R_{water} (%)**	**R_{water} (%)**	**R_{water} (%)**	**R_{water} (%)**	**R_{water} (%)**
0	0	0	0	0	0	0
3	9.55	12.97	13.82	9.82	12.02	19.82
7	13.65	21.99	25.66	15.84	24.77	38.68
13	18.23	28.97	37.27	22.99	37.30	59.49
21	23.01	36.88	50.95	32.95	54.45	87.77

Appendix D: Raw Data for Chapter 6

Microflotation of Pyrrhotite with CMC at 300 g/t

1 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.38	0.31	0.07	0.07	4.79		pyrrhotite:	C1	0.37	0.31	0.06	0.06	3.75
CMC	6	C2	0.38	0.31	0.07	0.14	9.59		CMC	C2	0.41	0.3	0.11	0.17	10.63
	12	C3	0.46	0.3	0.16	0.3	20.55			C3	0.48	0.32	0.16	0.33	20.63
	20	C4	0.44	0.29	0.15	0.45	30.82			C4	0.45	0.31	0.14	0.47	29.38
		Tails	5.65	4.64	1.01					Tails	5.81	4.68	1.13		
					1.46								1.6		

5 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.34	0.3	0.04	0.04	3.48		pyrrhotite:	C1	0.41	0.32	0.09	0.09	5.56
CMC	6	C2	0.41	0.3	0.11	0.15	13.04		CMC	C2	0.42	0.31	0.11	0.2	12.35
	12	C3	0.41	0.31	0.1	0.25	21.74			C3	0.48	0.32	0.16	0.36	22.22
	20	C4	0.49	0.32	0.17	0.42	36.52			C4	0.56	0.33	0.23	0.59	36.42
		Tails	5.28	4.55	0.73					Tails	5.61	4.58	1.03		
					1.15								1.62		

10 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.43	0.3	0.13	0.13	7.83		pyrrhotite:	C1	0.44	0.33	0.11	0.11	6.25
CMC	6	C2	0.49	0.32	0.17	0.3	18.07		CMC	C2	0.49	0.3	0.19	0.3	17.05
	12	C3	0.56	0.32	0.24	0.54	32.53			C3	0.57	0.33	0.24	0.54	30.68
	20	C4	0.58	0.31	0.27	0.81	48.80			C4	0.62	0.31	0.31	0.85	48.30
		Tails	5.44	4.59	0.85					Tails	5.59	4.68	0.91		
					1.66								1.76		

Microflotation of Pyrrhotite without CMC

1 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.47	0.34	0.13	0.13	4.36		pyrrhotite:	C1	0.31	0.26	0.05	0.05	1.77
CMC	6	C2	0.58	0.29	0.29	0.42	14.09		CMC	C2	0.45	0.27	0.18	0.23	8.13
	12	C3	0.72	0.3	0.42	0.84	28.19			C3	0.65	0.25	0.4	0.63	22.26
	20	C4	0.51	0.26	0.25	1.09	36.58			C4	0.49	0.29	0.2	0.83	29.33
		Tails	20.04	18.15	1.89					Tails	11.84	9.84	2		
					2.98								2.83		

5 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.48	0.34	0.14	0.14	6.76		pyrrhotite:	C1	0.49	0.34	0.15	0.15	7.77
CMC	6	C2	0.52	0.31	0.21	0.35	16.91		CMC	C2	0.6	0.34	0.26	0.41	21.24
	12	C3	0.59	0.32	0.27	0.62	29.95			C3	0.59	0.38	0.21	0.62	32.12
	20	C4	0.5	0.33	0.17	0.79	38.16			C4	0.46	0.34	0.12	0.74	38.34
		Tails	12.05	10.77	1.28					Tails	11.92	10.73	1.19		
					2.07								1.93		

10 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.73	0.46	0.27	0.27	10.27		pyrrhotite:	C1	0.75	0.6	0.15	0.15	5.32
CMC	6	C2	0.84	0.48	0.36	0.63	23.95		CMC	C2	0.98	0.65	0.33	0.48	17.02
	12	C3	0.83	0.31	0.52	1.15	43.73			C3	1.09	0.54	0.55	1.03	36.52
	20	C4	0.69	0.51	0.18	1.33	50.57			C4	0.84	0.54	0.3	1.33	47.16
		Tails	16.83	15.53	1.3					Tails	9.9	8.41	1.49		
					2.63								2.82		

Microflotation of Talc with CMC at 300 g/t

1 SPW															
	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
Conditions	2	C1	0.89	0.32	0.57	0.57	23.08		pyrrhotite:	C1	0.9	0.34	0.56	0.56	22.86
pyrrhotite:	6	C2	0.76	0.34	0.42	0.99	40.08		CMC	C2	0.79	0.34	0.45	1.01	41.22
CMC	12	C3	0.71	0.34	0.37	1.36	55.06			C3	0.72	0.34	0.38	1.39	56.73
	20	C4	0.7	0.32	0.38	1.74	70.45			C4	0.67	0.34	0.33	1.72	70.20
		Tails	5.66	4.93	0.73					Tails	5.59	4.86	0.73		
					2.47								2.45		

5 SPW															
	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
Conditions	2	C1	0.58	0.33	0.25	0.25	9.51		pyrrhotite:	C1	0.68	0.33	0.35	0.35	15.35
pyrrhotite:	6	C2	0.95	0.35	0.6	0.85	32.32		CMC	C2	0.75	0.34	0.41	0.76	33.33
CMC	12	C3	0.88	0.34	0.54	1.39	52.85			C3	0.77	0.35	0.42	1.18	51.75
	20	C4	0.76	0.33	0.43	1.82	69.20			C4	0.62	0.33	0.29	1.47	64.47
		Tails	5.34	4.53	0.81					Tails	5.34	4.53	0.81		
					2.63								2.28		

10 SPW															
	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
Conditions	2	C1	0.69	0.34	0.35	0.35	12.41		pyrrhotite:	C1	0.72	0.33	0.39	0.39	16.12
pyrrhotite:	6	C2	0.8	0.34	0.46	0.81	28.72		CMC	C2	0.79	0.33	0.46	0.85	35.12
CMC	12	C3	0.75	0.32	0.43	1.24	43.97			C3	0.71	0.32	0.39	1.24	51.24
	20	C4	0.87	0.32	0.55	1.79	63.48			C4	0.7	0.34	0.36	1.6	66.12
		Tails	5.98	4.95	1.03					Tails	5.76	4.94	0.82		
					2.82								2.42		

Microflotation of Pyrrhotite without CMC

1 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.88	0.32	0.56	0.56	29.32		pyrrhotite:	C1	0.97	0.32	0.65	0.65	27.20
CMC	6	C2	0.81	0.32	0.49	1.05	54.97		CMC	C2	0.88	0.33	0.55	1.2	50.21
	12	C3	0.71	0.32	0.39	1.44	75.39			C3	0.81	0.33	0.48	1.68	70.29
	20	C4	0.51	0.32	0.19	1.63	85.34			C4	0.73	0.31	0.42	2.1	87.87
		Tails	0.59	0.31	0.28					Tails	0.62	0.33	0.29		
					1.91								2.39		

5 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	0.74	0.32	0.42	0.42	29.58		pyrrhotite:	C1	0.78	0.32	0.46	0.46	27.88
CMC	6	C2	0.8	0.33	0.47	0.89	62.68		CMC	C2	0.72	0.3	0.42	0.88	53.33
	12	C3	0.66	0.33	0.33	1.22	85.92			C3	0.72	0.3	0.42	1.3	78.79
	20	C4	0.51	0.34	0.17	1.39	97.89			C4	0.62	0.34	0.28	1.58	95.76
		Tails	4.71	4.68	0.03					Tails	4.73	4.66	0.07		
					1.42								1.65		

10 SPW

Conditions	Time		sample + fp	fp	mass	Cum mass	%		Conditions		sample + fp	fp	mass	Cum mass	%
pyrrhotite:	2	C1	2.01	0.32	1.69	1.69	64.75		pyrrhotite:	C1	2.03	0.32	1.71	1.71	59.17
CMC	6	C2	1.12	0.32	0.8	2.49	95.40		CMC	C2	1.25	0.3	0.95	2.66	92.04
	12	C3	0.39	0.34	0.05	2.54	97.32			C3	0.45	0.3	0.15	2.81	97.23
	20	C4	0.36	0.32	0.04	2.58	98.85			C4	0.35	0.34	0.01	2.82	97.58
		Tails	4.56	4.53	0.03					Tails	4.73	4.66	0.07		
					2.61								2.89		

Adsorption Studies

Data for Calibration Curve

		Absorbance				***Stdev***	***Stder***
point		**1**	**2**	**3**	**Average**		
1	0	0	0	0	0.000	0.000	0.008
2	5	0.068	0.072	0.094	0.078	0.014	0.027
3	25	0.352	0.334	0.424	0.370	0.048	0.063
4	50	1.014	0.968	0.806	0.929	0.109	0.063
5	100	2.076	1.382	1.476	1.645	0.376	0.217
6	150	2.024	1.89	2.85	2.255	0.520	0.300

Adsorption of CMC onto Talc

TALC

	Absorbance									**average**	**conc (mg/l)**	**adsorbed CMC**		**stdev of data**	**stdev of mean**	**std error**
	Flask 1			Flask 2			Flask 3									
Test tube	1	2	3	4	5	6	7	8	9			**(mg/l)**	**%**			
Distilled water	0.004	0	0.007	0	0	0.004	0.003	0.004	0.001	0.003	0.2	29.841	99%	0.126	0.042	0.042
1 SPW	0.037	0.07	0.13	0.143	0.123	0.051	0.074	0.049	0.1655	0.094	5.8	24.186	81%	3.107	1.036	1.036
5 SPW	0.032	0.055	0.1054	0.075	0.019	0.047	0.133	0.056	0.077	0.067	4.1	25.863	86%	2.064	0.688	0.688
10 SPW	0.016	0	0.007	0.008	0.024	0.016	0.004	0	0.008	0.009	0.6	29.427	98%	0.446	0.149	0.149

Adsorption of CMC onto Pyrrhotite

PYRRHOTITE

	Absorbance									**average**	**conc (mg/l)**	**adsorbed CMC**		**stdev of data**	**stdev of mean**	**std error**
	Flask 1			Flask 2			Flask 3									
Test tube	1	2	3	4	5	6	7	8	9			**(mg/l)**	**%**			
Distilled water	0.01	0.011	0	0.002	0.019	0	0.014	0.001	-	0.007	0.4	29.6	99%	0.456	0.161	0.161
1 SPW	0.479	0.069	0.371	0.340	0.587	0.462	0.172	0.403	0.099	0.331	20.6	9.4	31%	11.784	3.928	3.928
5 SPW	0.063	0.019	0.059	0.059	0.078	0.090	0.217	0.094	0.063	0.082	5.1	24.9	83%	3.374	1.125	1.125
10 SPW	0.069	0.007	0.045	0.009	0.031	0.016	0.031	0.000	0.014	0.025	1.5	28.5	95%	0.903	0.301	0.301

Coagulation Tests

Mineral	Water type	CMC dosage (g/t)	CMC volume (ml)	pH	Settling time
Talc	1 SPW	0	0	9	16.9
Talc	1 SPW	0	0	9	16.5
Average					**16.7**
Talc	1 SPW	100	0.09	9	9.19
Talc	1 SPW	100	0.09	9	9.32
Average					**9.3**
Talc	5SPW	0	0	9	11.7
Talc	5SPW	0	0	9	11.4
Average					**11.6**
Talc	5SPW	100	0.09	9	5.31
Talc	5SPW	100	0.09	9	5.23
					5.3
Talc	10 SPW	0	0	9	10.8
Talc	10 SPW	0	0	9	10.6
Average					**10.7**
Talc	10 SPW	100	0.09	9	4.45
Talc	10 SPW	100	0.09	9	4.33
Average					**4.39**

Zeta Potential of Talc

	Ultra-Purified Water						
		1	2	3	4	5	Average Zeta Potential (mV)
pH	**2**	4.84	4.57	4.55			4.65
	4	-4.44	-4.81	-4.52			-4.59
	6	-11.6	-7.33	-8.97			-9.30
	8	-20.5	-20.3	-21			-20.60
	10	-35	-38.5	-37.5			-37.00
	12	-27.8	-29.4	-27.5			-28.23

	1 SPW						
		1	2	3	4	5	Average Zeta Potential (mV)
pH	**2**	2.76	2.57	2.76			2.70
	4	-10.3	-10.5	-9.34	-10	-9.16	-9.86
	6	-11	-10.1	-10.3	-10.6	-10.8	-10.56
	8	-11.4	-12.9	-11.9	-12.5	-12.4	-12.22
	10	-14.3	-14.8	-13.1			-14.07
	12	-14.9	-14.5	-13.5			-14.30

	5 SPW						
		1	2	3	4	5	Average Zeta Potential (mV)
pH	**2**	1.01	1.58	0.65			1.08
	4	-7.87	-7.4	-6.99			-7.42
	6	-8.54	-8.24	-8.78			-8.52
	8	-5.68	-5.82	-5.18			-5.56
	10	-5	-5.98	-5.1			-5.36
	12	6.33	5.51	5.72			5.85

	10 SPW						
		1	2	3	4	5	Average Zeta Potential (mV)
pH	**2**	-2.31	-1.19	-2.38			-1.96
	4	-6.02	-5.86	-6.91			-6.26
	6	-5.1	-5.02	-5.43			-5.18
	8	-4.97	-4.39	-4.85			-4.74
	10	-3.34	-2.62	-1.64			-2.53
	12	6.26	6.16	6.12			6.18

Zeta Potential of Pyrrhotite

	Ultra-Purified Water					
		1	2	3		Average Zeta Potential (mV)
pH	**2**	-19.5	-20.2	-19.1		-19.60
	4	-21.5	-21.4	-22.1		-21.67
	6	-25.5	-23.2	-23.3		-24.00
	8	-26.2	-25.7	-26.1		-26.00
	10	-28.9	-28.5	-28.1		-28.50
	12	-19.1	-19	-19.4		-19.17

	1 SPW					
		1	2	3		Average Zeta Potential (mV)
pH	**2**	-10.1	-9.44	-10.3		-9.95
	4	-4.85	-7.86	-10.5		-7.74
	6	-6.71	-7.91	-8.57		-7.73
	8	-7.92	-7.43	-9.36		-8.24
	10	-10	-10	-9.12		-9.71
	12	-4.22	-4.48	-3.82		-4.17

	5 SPW					
		1	2	3		Average Zeta Potential (mV)
pH	**2**	-2.38	-4.39	-6.2		-4.32
	4	-2.92	-3.23	-4.1		-3.42
	6	-2.66	-4.1	-3.75		-3.50
	8	-5.75	-11.1	-8.75		-8.53
	10	-6.4	-2.35			-4.38
	12	2.06	3.59			2.83

	10 SPW					
		1	2	3		Average Zeta Potential (mV)
pH	**2**	-4.03	-3.03	-4.39		-3.82
	4	-4.34	-4.33	-4.34		-4.34
	6	-4.06	-4.2	-7.58		-5.28
	8	-7.6	-7.58	-7.08		-7.42
	10	4.81	3.63	3.34		3.93
	12	8.8	8.15	9.79		8.91

Appendix E: Raw Data for Chapter 8

Batch Flotation

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1											
		C1	3	9.44	9.44	12.68	106.67	11.30	42.77	0.86	5.65
		C2	7	26.91	36.35	158.88	195.21	5.37	78.26	10.84	20.16
		C3	13	31.07	67.42	454.14	221.27	3.28	88.71	30.97	30.38
	NaCl	C4	21	23.27	90.69	717.59	230.23	2.54	92.31	48.94	35.43
	Dow 200	F		966.07							
	SIBX	T		840.16							
		T2		16.54							
		T3		18.68							
2		C1	3	10.01	10.01	13.38	113.11	11.30	42.83	0.91	5.99
		C2	7	26.73	36.74	163.07	203.73	5.55	77.14	11.12	20.03
		C3	13	33.05	69.79	473.18	235.55	3.38	89.20	32.27	31.06
	NaCl	C4	21	23.28	93.07	738.16	244.89	2.63	92.73	50.34	36.01
	Dow 200	F		989.85							
	SIBX	T		862.89							
		T2		16.83							
		T3		17.06							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1	**Na$_2$SO$_4$** **Dow 200** **SIBX**	C1	3	10.32	10.32	11.26	104.23	10.10	42.61	0.77	6.69
		C2	7	24.68	35.00	127.50	189.38	5.41	77.42	8.70	21.11
		C3	13	28.02	63.02	357.74	217.06	3.44	88.74	24.40	32.67
		C4	21	24.50	87.52	598.76	229.46	2.62	93.81	40.84	40.39
		F		970.55							
		T		850.71							
		T2		16.35							
		T3		15.97							
2	**Na$_2$SO$_4$** **Dow 200** **SIBX**	C1	3	12.34	12.34	12.84	118.71	9.62	47.40	0.88	8.21
		C2	7	22.46	34.80	129.51	190.58	5.48	76.09	8.83	20.74
		C3	13	33.80	68.60	364.79	221.65	3.23	88.50	24.88	37.64
		C4	21	25.60	94.20	612.52	231.91	2.46	92.60	41.77	46.06
		F		962.80							
		T		834.89							
		T2		17.18							
		T3		16.53							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1	**$NaNO_3$** **Dow 200** **SIBX**	C1	3	13.22	13.22	20.18	128.50	9.72	49.62	1.38	8.32
		C2	7	26.80	40.02	194.45	199.25	4.98	76.94	13.26	21.29
		C3	13	31.37	71.39	509.74	230.09	3.22	88.85	34.76	30.31
		C4	21	22.10	93.49	766.06	239.83	2.57	92.61	52.25	34.66
		F		1004.44							
		T		870.01							
		T2		20.57							
		T3		20.37							
2	**$NaNO_3$** **Dow 200** **SIBX**	C1	3	13.59	13.59	19.02	132.43	9.75	50.61	1.30	8.66
		C2	7	26.71	40.30	176.31	207.22	5.14	79.19	12.02	22.59
		C3	13	33.20	73.50	493.51	234.68	3.19	89.68	33.66	33.40
		C4	21	23.13	96.63	749.82	243.47	2.52	93.04	51.14	38.81
		F		996.36							
		T		862.51							
		T2		18.56							
		T3		18.66							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1											
		C1	3	11.45	11.45	29.44	129.39	11.30	48.55	2.01	5.89
		C2	7	28.47	39.92	250.90	212.52	5.32	79.74	17.11	16.98
		C3	13	28.16	68.08	573.38	240.06	3.53	90.07	39.10	22.39
	$MgCl_2$	C4	21	19.20	87.28	831.09	248.51	2.85	93.24	56.68	23.78
	Dow 200	F		967.86							
	SIBX	T		845.17							
		T2		17.96							
		T3		17.45							
2											
		C1	3	11.85	11.85	30.28	122.06	10.30	47.27	2.07	6.44
		C2	7	27.64	39.49	236.73	201.11	5.09	77.88	16.14	17.83
		C3	13	28.98	68.47	563.22	229.88	3.36	89.03	38.41	23.75
	$MgCl_2$	C4	21	20.11	88.58	824.96	238.75	2.70	92.46	56.26	25.77
	Dow 200	F		987.86							
	SIBX	T		864.24							
		T2		17.04							
		T3		18.00							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1	**$MgSO_4$** **Dow 200** **SIBX**	C1	3	14.03	14.03	23.22	135.95	9.69	53.32	1.58	8.72
		C2	7	32.49	46.52	334.95	209.38	4.50	82.12	22.84	17.93
		C3	13	25.28	71.80	655.10	227.05	3.16	89.05	44.68	20.89
		C4	21	17.68	89.48	882.39	235.29	2.63	92.28	60.18	22.85
		F		990.24							
		T		866.56							
		T2		16.39							
		T3		17.81							
2	**$MgSO_4$** **Dow 200** **SIBX**	C1	3	12.58	12.58	21.51	125.80	10.00	51.71	1.47	7.66
		C2	7	31.01	43.59	329.77	196.19	4.50	80.64	22.49	15.72
		C3	13	29.79	73.38	663.43	217.22	2.96	89.28	45.25	22.17
		C4	21	18.34	91.72	886.21	225.72	2.46	92.78	60.44	25.09
		F		970.60							
		T		845.53							
		T2		16.55							
		T3		16.80							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1		C1	3	12.57	12.57	22.73	128.21	10.20	51.25	1.55	7.50
		C2	7	28.43	41.00	244.79	206.11	5.03	82.39	16.69	18.65
		C3	13	27.63	68.63	554.46	228.55	3.33	91.36	37.81	24.55
	$Mg(NO_3)_2$	C4	21	19.27	87.90	793.72	236.66	2.69	94.60	54.13	27.28
	Dow 200	F		973.46							
	SIBX	T		849.23							
		T2		18.74							
		T3		17.59							
		C1	3	12.30	12.30	22.80	131.61	10.70	46.71	1.55	7.13
		C2	7	28.90	41.20	245.35	224.38	5.45	79.63	16.73	18.31
		C3	13	28.09	69.29	557.19	254.72	3.68	90.39	38.00	24.30
	$Mg(NO_3)_2$	C4	21	18.89	88.18	795.06	264.09	2.99	93.72	54.22	26.71
	Dow 200	F		993.68							
	SIBX	T		865.13							
		T2		19.04							
		T3		21.33							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1											
		C1	3	11.88	11.88	39.31	134.24	11.30	49.99	2.68	5.52
		C2	7	25.26	37.14	264.23	210.53	5.67	78.40	18.02	13.34
		C3	13	25.76	62.90	574.57	237.32	3.77	88.38	39.19	17.20
	$CaCl_2$	C4	21	18.31	81.21	821.55	247.54	3.05	92.18	56.03	18.39
	Dow 200	F		974.34							
	SIBX	T		857.91							
		T2		18.20							
		T3		17.02							
2		C1	3	11.53	11.53	32.67	134.90	11.70	52.72	2.23	5.60
		C2	7	22.40	33.93	259.63	203.89	6.01	79.68	17.71	10.63
		C3	13	28.36	62.29	571.79	235.94	3.79	92.21	39.00	16.82
	$CaCl_2$	C4	21	21.18	83.47	840.49	245.75	2.94	96.04	57.32	19.41
	Dow 200	F		976.26							
	SIBX	T		859.17							
		T2		15.99							
		T3		17.63							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1											
		C1	3	12.67	12.67	27.23	123.79	9.77	50.06	1.86	7.42
		C2	7	29.86	42.53	287.24	203.81	4.79	82.42	19.59	17.35
		C3	13	27.76	70.29	619.37	225.63	3.21	91.24	42.24	21.86
	CaSO$_4$	C4	21	19.36	89.65	858.86	234.03	2.61	94.64	58.57	24.66
	Dow 200	F		979.67							
	SIBX	T		854.76							
		T2		18.09							
		T3		17.17							
2		C1	3	11.95	11.95	29.45	125.48	10.50	50.08	2.01	6.50
		C2	7	28.43	40.38	281.34	203.94	5.05	81.39	19.19	15.60
		C3	13	26.95	67.33	609.00	227.77	3.38	90.90	41.53	19.55
	CaSO$_4$	C4	21	19.74	87.07	845.06	237.08	2.72	94.62	57.63	22.93
	Dow 200	F		985.64							
	SIBX	T		861.06							
		T2		18.61							
		T3		18.90							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1	**Ca(NO$_3$)$_2$** **Dow 200** **SIBX**	C1	3	8.34	8.34	7.61	108.42	13.00	41.71	0.52	4.85
		C2	7	22.54	30.88	184.80	200.38	6.49	77.09	12.60	12.78
		C3	13	26.92	57.80	498.33	230.53	3.99	88.69	33.99	17.49
		C4	21	19.36	77.16	756.67	241.22	3.13	92.80	51.60	18.94
		F		992.85							
		T		875.94							
		T2		19.85							
		T3		19.90							
2	**Ca(NO$_3$)$_2$** **Dow 200** **SIBX**	C1	3	7.03	7.03	6.53	95.61	13.60	38.54	0.45	3.96
		C2	7	24.98	32.01	194.33	197.28	6.16	79.53	13.25	13.34
		C3	13	28.60	60.61	519.48	227.59	3.76	91.75	35.43	18.94
		C4	21	19.87	80.48	781.18	237.75	2.95	95.85	53.28	20.68
		F		972.17							
		T		853.62							
		T2		18.65							
		T3		19.42							

Run no.	Reagents	Sample	Time, min	Mass Pull g	Cum Mass g	Cum Water g	Cum Sulphur mass g	Sulphur Grade %	Sulphur Recovery %	Entrained Gangue g	Floating Gangue g
1	**1Plant Dow 200 SIBX**	C1	3	11.59	11.59	16.63	119.38	10.30	48.05	1.13	7.18
		C2	7	27.28	38.87	209.91	197.94	5.09	79.67	14.32	19.12
		C3	13	27.68	66.55	504.03	220.61	3.32	88.80	34.37	26.12
		C4	21	20.40	86.95	759.21	230.34	2.65	92.71	51.78	28.85
		F		957.48							
		T		834.05							
		T2		17.36							
		T3		19.12							
2	**1Plant Dow 200 SIBX**	C1	3	9.31	9.31	14.91	97.76	10.50	41.47	1.02	5.61
		C2	7	25.11	34.42	203.07	179.86	5.23	76.30	13.85	15.64
		C3	13	29.72	64.14	507.47	207.77	3.24	88.14	34.61	23.83
		C4	21	19.89	84.03	760.33	217.56	2.59	92.29	51.85	26.21
		F		959.90							
		T		838.80							
		T2		18.16							
		T3		18.91							

Coagulation

	Water type	CMC dosage (g/t)	CMC volume (mL)	pH	Settling time min
Ore	**1SPW**	**0**	0	9	5.30
Ore	**1SPW**	**0**	0	9	5.30
Average					**5.3**
Ore	**1SPW**	**100**	0.09	9	3.39
Ore	**1SPW**	**100**	0.09	9	3.02
Average					3.2
Ore	**NaCl**	**0**	0	9	5.63
Ore	**NaCl**	**0**	0	9	5.55
Average					5.59
Ore	**NaCl**	**100**	0.09	9	3.98
Ore	**NaCl**	**100**	0.09	9	3.71
Average					3.84
Ore	**Na_2SO_4**	**0**	0	9	6.58
Ore	**Na_2SO_4**	**0**	0	9	7.10
Average					6.84
Ore	**Na_2SO_4**	**100**	0.09	9	4.68
Ore	**Na_2SO_4**	**100**	0.09	9	4.70
Average					4.69
Ore	**$NaNO_3$**	**0**	0	9	3.88
Ore	**$NaNO_3$**	**0**	0	9	4.04
Average					3.96
Ore	**$NaNO_3$**	**100**	0.09	9	2.65
Ore	**$NaNO_3$**	**100**	0.09	9	2.57
Average					2.61
Ore	$CaCl_2$	**0**	0	9	3.77
Ore	$CaCl_2$	**0**	0	9	3.76
Average					3.77
Ore	$CaCl_2$	**100**	0.09	9	2.93
Ore	$CaCl_2$	**100**	0.09	9	2.85
Average					2.89
Ore	$CaSO_4$	**0**	0	9	4.81
Ore	$CaSO_4$	**0**	0	9	4.60
Average					4.71
Ore	$CaSO_4$	**100**	0.09	9	3.60
Ore	$CaSO_4$	**100**	0.09	9	3.42
Average					3.51

	Water type	**CMC dosage (g/t)**	**CMC volume (mL)**	**pH**	**Settling time min**
Ore	**$Ca(NO_3)_2$**	**0**	0	9	3.30
Ore	**$Ca(NO_3)_2$**	**0**	0	9	3.03
Average					3.16
Ore	**$Ca(NO_3)_2$**	**100**	0.09	9	2.21
Ore	**$Ca(NO_3)_2$**	**100**	0.09	9	2.17
Average					2.19

Two-phase Froth Column

NaCl+frother					
	Run1	Run2	Average	Stdev	Stder
H_i	301	304	302.5	2.12	0.00
H_f	394	400	397	4.24	2.06
$H_{i,new}$	368	369	368.5	0.71	0.84
$t_{collapse}$	8	6	7	1.41	1.19
H_{froth}	93	96	94.5	2.12	1.46
ΔH	67	65	66	1.41	1.19
$NaNO_3$+frother					
	Run1	Run2	Average	Stdev	Stder
H_i	305	306	305.5	0.71	0.84
H_f	420	412	416	5.66	2.38
$H_{i,new}$	375	361	368	9.90	3.15
$t_{collapse}$	8	9	8.5	0.71	0.84
H_{froth}	115	106	110.5	6.36	2.52
ΔH	70	55	62.5	10.61	3.26
Na_2SO_4+frother					
	Run1	Run2	Average	Stdev	Stder
H_i	306	305	305.5	0.71	0.84
H_f	424	426	425	1.41	1.19
$H_{i,new}$	365	355	360	7.07	2.66
$t_{collapse}$	10	11	10.5	0.71	0.84
H_{froth}	118	121	119.5	2.12	1.46
ΔH	59	50	54.5	6.36	2.52
$CaCl_2$+frother					
	Run1	Run2	Average	Stdev	Stder
H_i	301	303	302	1.41	1.19
H_f	545	530	537.5	10.61	3.26
$H_{i,new}$	358	355	356.5	2.12	1.46
$t_{collapse}$	32	30	31	1.41	1.19
H_{froth}	244	227	235.5	12.02	3.47
ΔH	57	52	54.5	3.54	1.88

$Ca(NO_3)_2$+frother

	Run1	Run2	Average	Stdev	Stder
H_i	302	305	303.5	2.12	1.46
H_f	566	555	560.5	7.78	2.79
$H_{i,new}$	356	359	357.5	2.12	1.46
$t_{collapse}$	22	20	21	1.41	1.19
H_{froth}	264	250	257	9.90	3.15
ΔH	54	54	54	0	0

$CaSO_4$+frother

	Run1	Run2	Average	Stdev	Stder
H_i	304	303	303.5	0.71	0.84
H_f	535	580	557.5	31.82	5.64
$H_{i,new}$	361	355	358	4.24	2.06
$t_{collapse}$	30	34	32	2.83	1.68
H_{froth}	231	277	254	32.53	5.70
ΔH	57	52	54.5	3.54	1.88

Zeta Potential of Talc

		Zeta potential (mV)				**Stdev of data**	**Stder of data**
Salt	**pH**	**1**	**2**	**3**	**Average**		
$CaSO_4$	2	-4.8	-4.72	-5.22	-4.9	0.3	0.2
	4	-7.93	-9.62	-11.7	-9.8	1.9	1.1
	6	-7.92	-9.98	-10.5	-9.5	1.4	0.8
	8	-7.33	-7.6	-9.77	-8.2	1.3	0.8
	10	-9.62	-8.74	-10.3	-9.6	0.8	0.5
	12	-6.3	-8.15	-8.96	-7.8	1.4	0.8
Na_2SO_4	2	-4.26	-5.53	-6.38	-5.4	1.1	0.6
	4	-9.42	-9.89	-9.94	-9.8	0.3	0.2
	6	-13.6	-15.3	-16.6	-15.2	1.5	0.9
	8	-18.2	-19.7	-20.1	-19.3	1.0	0.6
	10	-22.7	-22.2	-25.1	-23.3	1.6	0.9
	12	-23.3	-26.6	-28.7	-26.2	2.7	1.6
$Ca(NO_3)_2$	2	3.92	3.07	4.39	3.8	0.7	0.4
	4	-2.03	-3.6	-4.29	-3.3	1.2	0.7
	6	-2.08	-2.11	-2.16	-2.1	0.0	0.0
	8	-1.1	-0.443	-0.153	-0.6	0.5	0.3
	10	2.68	3.71	2.75	3.0	0.6	0.3
	12	24.3	23.8	26.6	24.9	1.5	0.9
$NaNO_3$	2	-1.03	1.47	0.888	0.4	1.3	0.8
	4	-11.2	-11.1	-10.3	-10.9	0.5	0.3
	6	-17	-13.9	-15	-15.3	1.6	0.9
	8	-14.6	-13	-13.5	-13.7	0.8	0.5
	10	-15.2	-18	-15.9	-16.4	1.5	0.8
	12	-19.4	-18.8	-18.1	-18.8	0.7	0.4