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Water quality effects on a sulfidic PGM ore: Implications for froth stability and gangue management

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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

1. 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, Ca²⁺ and Mg²⁺, 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 Ca²⁺ 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⁺, Ca²⁺ and Mg²⁺ 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 Ca2+ 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 are negatively charged, and calcium adsorbs readily by electrostatic attraction. The presence of Ca2+ ions hinders the collector to mineral reaction on the pyrite surface. Also, it has been established that in the presence of cations such as Ca²⁺ and Mg²⁺, 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 NO₃- had a depressing effect in flotation as it resulted in superior Cu and Ni grades compared to Cl- and SO₄²⁻ (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.

2. Materials and Methods

2.1. Bench scale 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 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 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 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 Fig. 5.

Mineral	Weight %				
Pentlandite	0.31				
Chalcopyrite	0.25				
Pyrrhotite	0.44				
Pyrite	0.08				
Other sulfides	0.02				
TOTAL sulfides	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 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

2.2. 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 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).

2.3. 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 μ m. 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.

3. Results

3.1. The effect of ionic strength of plant water and depressant dosage on sulfides floatability and 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. Fig. 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.



Fig. 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

Fig. 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 Fig. 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.



Fig. 2. The amount of solids reporting to the concentrate for all conditions tested



Fig. 3. Final total sulphide recoveries and grades for all synthetic plant water types and depressant dosages

Fig. 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).

Fig. 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.



Fig. 4. Three-phase froth collapse time as a function of water type and CMC depressant dosages.

3.2. The 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 Fig. 5 and Fig. 6 respectively.

The data presented in Fig. 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 Fig. 2.

Fig. 6 shows the settling time of the Merensky ore solids for each water type in the presence and absence of CMC. Fig.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.



Fig. 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)



Fig. 6. Settling time as a function of water type and CMC dosages

4. Discussion

4.1. The effect of ionic strength and depressant dosage on froth stability

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 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 Fig. 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 Fig. 2 and Fig. 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 Fig. 2. The froth collapse time results presented in Fig. 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 bubbleparticle 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 talcdepressant 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 Fig. 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 Fig. 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.

4.2. The effect of the ionic strength of plant water and CMC 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 Fig. 1 and Fig. 2.



Fig. 7. A schematic summarising the counter-active relationship between increases in ionic strength and CMC dosage on the stability of the froth

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 theentrained gangue with increasing CMC dosage. Increases in ionic strength gave rise to decreases in tsulfide 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 Fig. 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 Fig. 7

5. 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.

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References

- BARKER, L.M., 1986. *The Effect of Electrolytes on the Flotation of Pyrite*. MSc.Eng Thesis, University of Cape Town, Chemical Engineering.
- BECKER, M., HARRIS, P.J., WIESE, J.G., BRADSHAW, D.J., 2009. *Mineralogical characterisation of naturally floatable gangue in Merensky reef ore flotation*. International Journal of Mineral Processing, 93, 246-255.
- BRADSHAW, D.J., HARRIS, P.J., O'CONNOR, C.T. 1998. *Synergistic interactions between reagents in sulphide flotation*. The Journal of the South African Institute of Mining and Metallurgy, 189-194.
- BRADSHAW, D.J., OOSTENDORP, B., O'CONNOR, C.T., 2004. Development of methodologies to improve the assessment of reagent behaviour in flotation with particular reference to collectors and depressants. Minerals Engineering, 18, 189-194.
- BRADSHAW, D.J., HARRIS, P.J., O'CONNOR, C.T., 2005. *The effect of collectors and their interactions wih depressants on the behaviour of the froth phase in flotation*. Proceedings of Centenary of Flotation Symposium. Brisbane.
- BURDUKOVA, E., 2007. Surface properties of New York talc as a function of pH, polymer adsorption and electrolyte concentration. PhD Thesis, University of Cape Town, Faculty of Engineering and the Built Environment, Chemical Engineering Department, Cape Town, South Africa.

- CORIN, K.C., & WIESE, J.G., 2014. *Investigating froth stability: A comparative study of ionic strength and frother dosage.* Minerals Engineering.
- CORIN, K.C., REDDY, A., MIYEN, L., WIESE, J.G., HARRIS, P.J. 2011. *The effect of ionic strength of plant water on valuable mineral and gangue recovery in a platinum bearing ore from the Merensky reef.* Minerals Engineering, 24, 131-137.
- CRAIG, V.S., 2004. *Bubble coalescence and specific-ion effect*. Current opinion in Colloid and Interface Science, 9, 178-184.
- DHLIWAYO, E.C., 2005. *The interactive effect of depressant type and dosage with frother dosage in the flotation of a PGM ore*. MSc.Eng Thesis, University of Cape Town, Chemical Engineering, Cape Town.
- DISHON, M., ZOHAR, O., SIVAN, U., 2009. From repulsion to attraction and back to repulsion: the effect of NaCl, KCl and CsCl on the force between silica surfaces in aqueous solution. Langmuir, 25 (5), 23, 2831-2836.
- ENGELBRECHT, WOODBURN, E.I., 1975. *The effects of froth height, aeration rate and gas precipitation of flotation*. Journal of the South African Institute of Mining and Metallurgy, 125-132.
- GEORGE, C., 1996. *The Mt. Keith operation*. In: Grimsey, E.J., & Neuss, I. (eds.) Nickel. Melbourne Australasian Institute Mining and Metallurgy, Melbourne, 9-23.
- GLEMBOTSKII, V.A., KLAASEN, V.I., PLAKSIN, I.N., 1972. Flotation. New York: Primary Sources.
- HAIG-SMILLIE, L.D. (1974). Sea water flotation. Proceedings Canadian Mineral Processors Conference,
- 263-281.
- IKUMAPAYI, F., MAKITALO, M., JOHANSSON, B., RAO, K. H., 2012. Recycling of process water in sulphide flotation: effect of calcium and sulphate ions on flotation of galena. Minerals Engineering, 39, 77-88.
- IWASAKI, I., SMITH, K. A., LIPP, R. J., SATO, H., 1980. *Effect of calcium and magnesium ions on selective desliming and cationic flotation of quartz from iron ores.* (P. Somasundaran, Ed.) Fine Particles Processing.
- KIRJAVAINEN, V., SCHREITHOFER, N., HEISKANEN, K., 2002. The effect of calcium thiosulphate ions on flotation selectivity of nickel-copper ores. Minerals Engineering, 15, 1-5.
- KLAASEN, V., MOKROUSOV, 1963. An introduction to the theory of flotation. London: Butterworths.
- KLIMPEL, R.D. (1984). Froth flotation: The kinetic approach. Mintek 5. Johannesburg, South Africa.
- KRACHT, W., OROZCO, Y., & ACUÑA, C. (2016). Effect of surfactant type on the entrainment factor and selectivity of flotation at laboratory scale. Minerals Engineering, 92, 216-220.
- KURNIANWAN, A.U., OZDEMIR, O., NGUYEN, A.V., OFORI, P., FIRTH, B., 2011. Flotation of coal particles in MgCl₂, NaCl, and NaClO₃ solutions in the absence and presence of Dowfroth 250. International Journal of Mineral Processing, 98, 137-144.
- LASKOWSKI, J.S., CHO, Y.S., DING, K., 2003. *Effect of frothers on bubble size and foam stability in potash ore flotation systems*. Canadian Journal of Chemical Engineering, 81:63–69.
- LASKOWSKI, J.S., LIU, Q., O'CONNOR, C.T., 2007. Current understanding of the mechanism of polysaccharide adsorption at the mineral/aqueous solution interface. International Journal of Mineral Processing, 84, 59-68.
- LEVAY, G., SMART, R.S., SKINNER, W.M., 2001. *The impact of water quality on flotation performance*. Journal of the South African Institute for Mining and Metallurgy, 69-76.
- LIDDELL, K.S., MCRAE, L.B., DUNNE, R.C., 1986. Process routes for beneficiation of noble metals from Merensky and UG-2 ores. Mintek Review No.4, Randburg.
- LIU, L.R., FINCH, J.A., 1993. Technical note laboratory study of effect of recycle water on flotation of a Cu/Zn sulphide ore. Minerals Engineering, 6, 1183-1190.
- LIU, W., MORAN, C.J., VINK, S., 2013. A review of the effect of water quality on flotation. Minerals Engineering, 53, 91-100.
- MAILULA, T.S., 2004. An investigation into chemical factors that affect the behaviour of gangue minerals in the flotation of *PGM ores*. MSc.Eng Thesis, University of Cape Town, Faculty of Engineering and the Built Environment, Chemical Engineering Department, Cape Town, South Africa.
- MANONO, M.S., CORIN, K.C., WIESE, J.G., 2012. An investigation into the effect of various ions and their ionic strength on the flotation performance of a platinum bearing ore from the Merensky reef. Minerals Engineering, 36-38, 231-236.
- 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.
- MANONO, M.S., CORIN, K.C., WIESE, J.G., 2013. The effect of ionic strength of plant water on foam stability: A 2-phase flotation study. Minerals Engineering, 40, 42-47.

- MANONO, M.S., CORIN, K.C., WIESE, J.G., 2016. The influence of electrolytes present in process water on the flotation behaviour of a Cu-Ni containing ore. Minerals Engineering, 96-97, 99-107.
- MCFADZEAN, B., MAROZVA, T., WIESE, J., 2016. Flotation frother mixtures: decoupling the sub-processes of froth stability, froth recovery and entrainment. Minerals Engineering, 85, 72–79.
- MUZENDA, E., 2010. An investigation into the effect of water quality on flotation performance. World Academy of Science, Engineering and Technology, 69, 237-241.
- NESSET, J.E., FINCH, J.A., GOMEZ, C.O., 2007. *Operating variables affecting the bubble size in forced air mechanical flotation machines*. Ninth Mill Operators' Conference. Fremantle, WA.
- OZDEMIR, O., TARAN, E., HAMPTON, M. A., KARAKASHEV, S.I., NGUYEN, A.V., 2009. Surface chemistry aspects of coal flotation in bore water. International Journal of Mineral Processing, 92(3-4), 177-183.
- PAROLIS, L.A., GROENMEYER, G.V., HARRIS, P.J., 2008. The influence of metal cations on the behaviour of carboxymethyl celluloses as talc depressant. Colloids and Surfaces, (317), 109-115.
- PAULSON, O., PUGH, R.J., 1996. Flotation of inherently floatable particles in aqueous solutions of inorganic electrolytes. Langmuir, 12, 4808-4813.
- PENG, Y., SEAMAN, D., 2011. The flotation of slime-Fine fractions of Mt. Keith pentlandite ore in de-ionised and saline water. Minerals Engineering, 24(5), 479-481.
- PUGH, R.J., WEISSENBORN, P., PAULSON, O., 1997. Flotation in inorganic electrolytes; the relationship between recover of hydrophobic particles, surface tension, bubble coalescence and gas solubility. International Journal of Mineral Processing, 51, 125-138.
- QUINN, J.J., KRACHT, W., GOMEZ, C.O., GAGNON, C., FINCH, J.A., 2007. Comparing the effect of salts and frother (MIBC) on gas dispersion and froth properties. Minerals Engineering, 20, 1296-1302.
- ROBERTSON, C., 2003. Development of a methodology to decouple the effects of dispersion and depression in batch flotation. Masters Thesis, University of Cape Town, Faculty of Engineering and the Built Environment, Chemical Engineering Department, Cape Town, South Africa

SHENI, N., CORIN, K, WIESE, J., 2017. Considering the effect of pulp chemistry during flotation on froth stability. Minerals Engineering, 116, 15-23.

- SHORTRIDGE, P.G., HARRIS, P.J., BRADSHAW, D.J., 2003. The influence of ions on the effectiveness of polysaccharide depressants in the flotation of talc. Proceedings of the Third UBC-McGill International Symposium "Polymers in Mineral Processing", (pp. 155-169).
- SHORTRIDGE, P.G., HARRIS, P.J., BRADSHAW, D.J., KOOPAL, L.K., 1999. The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc. International Journal of Mineral Processing, 59, 215-224.
- SLATTER, K.A., PLINT, N.D., COLE, M., DE VAUX, D., PALM, N., OOSTENDORP, B., 2009. *Water management in Anglo Platinum process operations: Effects of water quality on process operations*. Abstracts of the International Mine Water Conference. Pretoria, South Africa.

SMITH, P.G., WARREN, L.J., 1989. Entrainment of particles in flotation. Mineral Processing and Extractive Metallurgy Review, 5 (1-4), 123-145.

STEENBERG, E., HARRIS, P.J., 1984. Adsorption of carboxymethyl cellulose, guar gum and starch onto talc, sulphides, oxides and salt type minerals. South African Journal of Chemistry, 37 (3), 85-90.

- WARREN, L.J., 1985. Determination of the contributions of true flotation and entrainment in batch flotation tests. International Journal of Mineral Processing, 14, 33-34.
- WIESE, J.G., HARRIS, P.J., BRADSHAW, D.J., 2010. The effect of increased frother dosage on froth stability at high depressant dosages. Minerals Engineering, 11-13, 1010–1017.
- WIESE, J.G., 2009. *Investigating depressant behaviour in the flotation of selected Merensky ores*. Master's Thesis, Faculty of Engineering and the Built Environment, University of Cape Town, Chemical Engineering, Cape Town.
- WIESE, J.G., HARRIS, P.J., BRADSHAW, D.J., 2005. The influence of the reagent suite on the flotation of ores from the *Merensky reef.* Minerals Engineering, 18(2), 189-198.
- YIANATOS, J.B., FINCH, J.A., LAPLANTE, A.R., 1988. Selectivity in Column Flotation Froths. International Journal of Mineral Processing, 15, 279-292.
- ZHANG, Q., XU, Z., BOZKURT, V., FINCH, J.A., 1997. *Pyrite flotation in the presence of metal ions and sphalerite*. International Journal of Mineral Processing, 52, 187-201.