

Article

Simulating the Effect of Water Recirculation on Flotation through Ion-Spiking: Effect of Ca^{2+} and Mg^{2+}

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Abstract: Froth flotation is a multifaceted complex process which is water intensive. The use of recycled water as an alternative source of water to meet water demands of the process may introduce deleterious inorganic ions that affect the mineral surface, pulp chemistry, and reagent action, hence the need to establish whether threshold ion concentrations exist beyond which flotation performance will be adversely affected. This is of paramount importance in informing appropriate recycle streams and allowing simple, cost-effective water treatment methods to be applied. Here we report that increasing ionic strengths of synthetic plant water (SPW); 3, 5, and 10 SPW respectively, resulted in an increase in water recovery in the order $0.073 \text{ mol}\cdot\text{dm}^{-3}$ (3 SPW) $<$ $0.121 \text{ mol}\cdot\text{dm}^{-3}$ (5 SPW) $<$ $0.242 \text{ mol}\cdot\text{dm}^{-3}$ (10 SPW), indicating an increase in froth stability as higher water recoveries are linked to increased froth stabilities. This behavior is linked to the action of inorganic electrolytes on bubble coalescence which is reported in literature. There was, however, no significant effect on the valuable mineral recovery. Spiking 3 SPW to 400 mg/L Ca^{2+} resulted in higher copper and nickel grades compared to 3 SPW, 5 SPW, and 10 SPW and was deemed to be the Ca^{2+} ion threshold concentration for this study since 3 SPW spiked with further Ca^{2+} to a concentration of 800 mg/L resulted in a decrease in the concentrate grade. The spiking of 3 SPW with Mg^{2+} resulted in higher copper and nickel grades compared to all other synthetic plant water conditions tested in this study.

Keywords: froth flotation; ion accumulation; ion concentration spiking; ionic strength; water recycling

1. Introduction

In froth flotation, reagents are added to a milled ore slurry so as to manipulate the physicochemical nature of minerals present in the ore. These reagents are added to enhance the differences in hydrophobicity between valuable minerals and gangue [1–3]. This facilitates the separation of gangue from valuable minerals [4]. Reagent suites for flotation typically consist of collectors, depressants, frothers, and occasionally activators [5,6]. It is worth mentioning that recent literature acknowledges that water should also be considered as a reagent in flotation [7].

Different ores bear different minerals and therefore behave differently in the presence of chemical reagents. This understanding led Bradshaw et al. [4] to assert that it is difficult to isolate and quantify the interaction of each reagent with minerals present in an ore. Due to the complexity of flotation and its dependence on chemical reagents, more and more specialized chemicals are being developed with a specific focus on altering the surface properties of mineral particles of interest and enhance their recovery [8]. The question of how process water constituents such as ions will affect reagent–mineral interactions and therefore flotation is however often barely addressed when new reagents are developed.

It is known that reagents such as collectors and depressants are affected by the ionic nature of the solution in their interaction with mineral particles [9–15]. These ion–reagent–particle interactions could in turn impact both the pulp and froth phase phenomena. Therefore, it stands to reason that the inorganic electrolytes present in process water may affect interactions occurring in the pulp phase and in turn the implications of these effects could be seen in the froth phase. As such, process operational changes affecting process water quality are a critical matter of importance and are worthy of being investigated.

Water scarcity and environmental degradation are global threats. The mining sector has become the central focus on these global threats as it contributes greatly to environmental degradation by waste disposal processes caused by tailings disposal and process water seepage into the water-table [16]. A closed water circuit is a key engineering process design consideration of green mining whose main focus is on recycling water, minimizing effluent discharge, while meeting production targets. In order to address process water issues, closed water circuits are being considered by many operations and in some cases they are already in use [17,18].

The recycling of water in mining processes may however cause ions and other water components to accumulate [15,19]. Recycled water is usually obtained from tailings dams where the typical contaminating species are SO_4^{2-} , Cl^- , F^- , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , base metals, collectors, frothers, activators, depressants, colloidal materials such as iron hydroxides, and natural organic material. It is worth noting that some ions exist naturally in water. There are some advantages to recycling process water, these include: the reduction of potable water usage and discharge from the plant, and the retention of some reagents, therefore lowering the consumption and costs of reagents [19]. It is however reported that some of these ions may be deleterious to the flotation process owing to their effects on the sub-processes of flotation [2,10]. However, there is limited literature regarding the concentration thresholds beyond which ions common in process water would result in adverse effects on flotation.

The influence of specific inorganic ions on mineral flotation is multifaceted and different ions may play various roles, that are either beneficial or detrimental to the flotation process [20]. As aforementioned, the interaction of flotation reagents with mineral particles is affected by the ionic nature of the solution, therefore water quality plays an important role in driving the ion–reagent–particle interactions occurring in the pulp phase and these also determine the nature and characteristics of the froth phase [9–12,14,15]. While using methyl iso-butyl carbinol (MIBC), Gungoren [21] developed a novel technique to investigate the effect of bubble coalescence in the presence of salts, such as NaCl and CaCl_2 , it was found that despite bubble coalescence being controlled by frothers, dissolved ions had a tendency to inhibit bubble coalescence. Cho and Laskowski [2] showed that at high ionic strength, there was possible inhibition of bubble coalescence. As bubble coalescence decreased, the gas hold-up in the froth phase decreased and this led to higher water recovery due to increased bubble interfacial area and increased water–gas bonding forces resulting in more water being recovered to the concentrate. In line with these findings, Manono et al. [22] showed that bubble size diameter decreased with synthetic plant water (SPW) in the order $d_{10\text{SPW}} < d_{5\text{SPW}} < d_{3\text{SPW}}$.

Bubble coalescence inhibition may also presumably be due to the concentration of the ions at the bubble surface. Earlier studies have also shown that increases in the ionic strength of synthetic plant water resulted in increases in water and solids recoveries [9,13,23], while a more fundamental study into increased ionic strength of plant water on froth stability showed bubble diameter reductions and increases in froth height and froth collapse time [22]. These studies came to the conclusion that process waters of high salinity such as seawater are froth stabilising. While a review into the effect of ions on frothing properties is important to this study, a more detailed and comprehensive review into the influence of inorganic electrolytes in plant water on the froth phenomena is presented in Manono et al. [14]. Although bubble size changes as the ionic concentration changes [22] and this consequently affects the interfacial surface area available for particle–bubble attachment and mineral recovery, bubble size was not tracked in this study. Alternatively, pulp and froth electrical conductivities were measured.

As water recycling results in recirculation and accumulation of ions which are known to stabilize the froth [22,23], the presence of these ions at high concentrations in flotation concentrators may negatively impacting reagent adsorption on valuable metal [10,24]. Additionally, the behaviour of gangue may very well be impacted by water quality changes as the salinity of process water could change the efficacy of depressants as well as the entrainment of gangue. Corin et al. [9] showed that as the ionic strength of plant water increased, the water and solids recovery also increased. They suggested that the increase in ionic strength increased the gangue recovery by entrainment as valuable mineral recoveries remained unaffected, increasing the froth stability and consequently increasing water recovery.

The presence of divalent cations in the pulp phase results in the precipitation of hydroxides especially at $\text{pH} > 9$, these may adsorb on the metal surface thereby reducing the hydrophobicity of the valuable metal, meaning a compromise in bubble–particle attachment efficacy [24]. More recently, October et al. [25] investigated the effect of increasing ionic strength of plant water and increasing alkaline pH on the bubble–particle attachment of chalcopyrite and galena and showed that the attachment probability and microflotation recoveries of the two sulfide minerals decreased significantly at pH 11 compared to pH 9. This behaviour was attributed to the presence of calcium and magnesium hydroxo species as the potential of the sulfide minerals and therefore their surface charge increased with increasing ionic strength and pH of plant water [25]. These findings were in line with Manono et al. [26] who showed decreases in copper and nickel recoveries at pH 11 for a Cu-Ni-PGM (Platinum Group Mineral) bearing Merensky ore, indicating that the presence of hydroxo species were depressive to base metal sulfides. Generally, metal recovery is directly related to froth stability, increases in froth stability may result in increased gangue entrainment, consequently water and solids recoveries may increase too [2,9,19,20,23,24]

Ikumapayi et al. [27] investigated the effect of varying concentrations of Ca^{2+} and SO_4^{2-} on the flotation of pure galena and chalcopyrite, using CaCl_2 as a source of Ca^{2+} and K_2SO_4 as a source of SO_4^{2-} ions, they showed that 400 mg/L Ca^{2+} and 1400 mg/L SO_4^{2-} were the maximum concentrations of the ions beyond which the flotation recoveries were affected. On site process water from a New Boliden operation containing 186 mg/L Ca^{2+} and 153 mg/L SO_4^{2-} was used as the complex background. It was reasoned that Ca^{2+} could form complexes with the SO_4^{2-} ion in the bulk solution or on the surface of the mineral. These species, forming at the mineral surface, lower the surface area of the mineral available for hydrophobic bonding, leading to inhibited collector adsorption and reduced floatability of the mineral. In a study by Muzenda [15] in which total dissolved solids (TDS), total suspended solids (TSS), and conductivity (EC) were varied; an increase in the TDS, resulting from high Ca^{2+} ion concentration, resulted in a decrease in recoveries and grades. It was concluded by Hirajima et al. [28] using sea water that Ca^{2+} ions have a marginally negative effect on the flotation of chalcopyrite and suggested that this marginal decrease is owing to the presence of other ions such as Mg^{2+} , NO_3^- , SO_4^{2-} , etc. in the saline environment that cause preferential collector attachment to the sulfide mineral. Kirjavainen and Heiskanen [29] emphasized that the presence of ions at high concentration beyond a certain threshold results in modified pulp viscosity which leads to entrainment and reduced grade of the recovered sulfide mineral.

Solution pH, ionic strength, and the type of cations in solution may have an influence on the extent of gangue activation [13,30,31]. Manono et al. [32] found that divalent ions, specifically Ca^{2+} , Mg^{2+} , and SO_4^{2-} resulted in higher water recoveries than monovalent ions (Na^+ , Cl^- , and NO_3^-) in the presence of DOW 200. This implies that divalent ions stabilised the froth more than the monovalent ions as it was shown that water recovery can be used as a measure of froth stability. It is postulated in literature that the presence of Ca^{2+} and Mg^{2+} may compete with xanthate for adsorption onto the sulfide minerals, including pyrrhotite, which is considered as gangue in the ore used in this study [7,28,33]. Ca^{2+} ions may adsorb and may partially precipitate as CaOH^+ while Mg^{2+} forms MgOH^+ on the mineral surface during the flotation process. CaOH^+ , CaCO_3 , MgCO_3 , and MgOH^+ which are considered colloidal species, possibly attach to the mineral surface forming a hydrophilic

coating and the presence of such coating on the sulfide mineral surface hinders mineral–collector interaction and inevitably the mineral hydrophobicity decreases; this in turn compromises the efficiency of the bubble–particle attachment process [7,25].

Sea water is also being considered as an alternative to freshwater in mineral processing, it however contains water hardening ions such as Ca^{2+} and Mg^{2+} in high concentrations [24]. It was shown by Hirajima et al. [28] that sea water has detrimental effects in alkaline conditions when the flotation of molybdenum (Cu-Mo) was considered. The presence of Ca^{2+} and Mg^{2+} from sea water impacted the floatability of Cu-Mo and chalcopyrite at pH values higher than 9, with the results showing that Mg^{2+} exacerbates chalcopyrite flotation due to the adsorption of metallic precipitates onto the mineral surface. Laskowski and Castro [11] suggested in a later study that Ca^{2+} and Mg^{2+} should be removed prior to flotation by precipitates decantation method, as high saline environments at alkaline conditions promote the formation of precipitates that deposit onto the valuable mineral surface.

These concerns have led to the proposed novel spiking method used in this study which aims at ascertaining the impact that individually selected ions have on flotation performance, while maintaining a complex water chemistry background as would be found on site. This study therefore considers the selective spiking of plant water with specific ions of interest to simulate recycling within mineral processing concentrators and the impact that these ions will have on the flotation performance of a low-grade Cu-Ni-PGM ore. Copper and nickel grades and recoveries as well as solids and water recoveries were used as indicators for performance.

2. Materials and Methods

2.1. Synthetic Plant Water Preparation

SPW in this study stands for “synthetic plant water” while I.S stands for “ionic strength”. Wiese et al. [34] developed a standard SPW recipe with a total dissolved solids (TDS) concentration of 1023 mg/L, more recently referred to as 1 SPW [13]. This was designed to represent a typical water analysis of a PGM concentrator. This water recipe is achieved by adding various chemical salts to de-ionised water. The slurry had a constant pH of ~9, no pH modification was done throughout this study. The influence of ionic strength on flotation is thus studied by multiplying 1 SPW by 3, 5, and 10 times as shown in Table 1.

Table 1. Concentrations of ions for the various water qualities

| Water Type | Ca^{2+} (mg/L) | Mg^{2+} (mg/L) | Na^+ (mg/L) | Cl^- (mg/L) | SO_4^{2-} (mg/L) | NO_3^- (mg/L) | CO_3^{2-} (mg/L) | TDS (mg/L) | I.S [M] |
|-----------------------------------|----------------------------|----------------------------|-------------------------|-------------------------|------------------------------|---------------------------|------------------------------|---------------|---------|
| 1 SPW | 80 | 70 | 153 | 287 | 240 | 176 | 17 | 1023 | 0.021 |
| 3 SPW | 240 | 210 | 459 | 861 | 720 | 528 | 51 | 3069 | 0.073 |
| 5 SPW | 400 | 350 | 765 | 1435 | 1200 | 880 | 85 | 5115 | 0.121 |
| 10 SPW | 800 | 700 | 1530 | 2870 | 2400 | 1760 | 170 | 10,230 | 0.242 |
| Spiked Waters | | | | | | | | | |
| 3 SPW + 160 mg/L Ca^{2+} | 400 | 210 | 459 | 1141 | 720 | 528 | 51 | 3509 | 0.085 |
| 3 SPW + 560 mg/L Ca^{2+} | 800 | 210 | 459 | 1851 | 720 | 528 | 51 | 4619 | 0.115 |
| 3 SPW + 140 mg/L Mg^{2+} | 240 | 350 | 459 | 1050 | 720 | 528 | 51 | 3398 | 0.087 |
| 3 SPW + 490 mg/L Mg^{2+} | 240 | 700 | 459 | 1531 | 720 | 528 | 51 | 4229 | 0.123 |

3 SPW was considered best to represent average current on-site TDS levels and was thus used as the baseline experiment. The levels of Ca^{2+} and Mg^{2+} were increased from their 3 SPW concentration to their 5 SPW and 10 SPW equivalents respectively, for the different flotation test conditions shown in Table 1. Experimental runs were conducted separately using water of ionic strength; 3, 5, and 10 SPW before spiking commenced.

Ion spiking was informed by actual on-site water compositions. All spiking tests were performed with the 3 SPW baseline. The selected cations, Ca^{2+} and Mg^{2+} were spiked to represent the accumulation of that specific cation over and above all other ions present in the complex background process water

matrix. Each ion was spiked to its concentration level of 5 and 10 SPW, respectively. It must be noted that for the single cation spiked synthetic plant waters, chloride salts were used. Cl^- was shown to have minimal impact in a previous study [32]. In line with the previous study, Cl^- ions are therefore deemed not to compete with the cations of interest [32].

2.2. Ore Preparation

A low-grade Cu-Ni-PGM sulfide sample was obtained and used for this study. The bulk sample was crushed, blended, riffled, and split using a rotary splitter into 1.3 kg samples. The 1.3 kg ore samples were finely ground in synthetic water (at the required ionic strength) using a laboratory scale stainless steel rod mill, to achieve a grind of 70% passing 75 μm as this represents the typical on-site grind size of the selected ore.

2.3. Batch Flotation

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 synthetic plant water (as given in Table 1). 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 constantly corrected to 2 cm by the addition of synthetic plant water of the relevant composition (Table 1). Concentrates were collected at 5, 10, 17.5, 25, 37.5, and 50 min respectively by scraping the froth into a collecting pan every 15 s. A feed sample was taken before and two tails samples after each flotation test. Water usage was monitored throughout.

All batch flotation tests were conducted in duplicate and reproducibility was found to be within 5% standard error. The gangue component of the ore self-buffered the system to a pH of 9 which is a natural pH typical of a low-grade Cu-Ni-PGM sulfide ore. 50 g/t of Aerophine 3184A as the copper collector (Univar, Van Horne, BC, Canada), 35 g/t of a Carboxy Methyl Cellulose (CMC) depressant meant to depress non-sulfide gangue (NSG) and pyrrhotite, and 20 g/t of Nasfroth 240 frother were used for the first 10 minutes to recover copper, immediately after 10 minutes of copper flotation, 50 g/t of sodium iso-propyl xanthate (SIPX with 97% purity) was added into the cell as nickel collector, 15 g/t of CMC depressant and 10 g/t Nasfroth 240 frother were added, and at 25 minutes, 30 g/t SIPX was added to collect the final two concentrates. Each reagent was conditioned for 2 minutes and used as supplied. Feeds, concentrates, and tails were filtered, dried, and weighed before copper and nickel analysis by a Bruker S4 Explorer XRF Spectrophotometer (Bruker AXS GmbH, Karlsruhe, Germany).

2.4. Electrical Conductivity Measurements

Electrical conductivity (EC) in water is a measure of its ability to conduct current. Current can be carried by ions in an electrolyte solution, the more ions there are in solution the higher the EC. In this study, the froth was removed using a vacuum pump into a collecting flask. The electrical conductivity was measured for the pulp and the collected froth. EC was measured using a HANNA Instruments' conductivity multiprobe (HI7634-00, HANNA[®] Instruments, JHB, South Africa). The measured EC was used as proxy for ionic strength.

3. Results

3.1. Effect of Increased Ca^{2+} and Mg^{2+} Concentration in Process Water on Solids and Water Recoveries: Implications on the Stability of the Froth

Figure 1 shows that as ionic strength increased the water recovery also increased from 3 SPW to 10 SPW. Water recovery increases with increase in Ca^{2+} spiking concentration (in comparison to the baseline experiment, 3 SPW) and follows the order: 10 SPW > 800 mg/L Ca^{2+} > 400 mg/L Ca^{2+} > 5 SPW > 3 SPW, while, water recovery with respect to Mg^{2+} spiking also increased with increase

in spiking concentration above 3 SPW and followed the order: 10 SPW > 700 mg/L Mg²⁺ > 5 SPW > 350 mg/L Mg²⁺ > 3 SPW. There is no direct correlation between the solids recovered when using 3 SPW, 5 SPW and 10 SPW. The solids recovery with regards to the Ca²⁺ spiking follows the order: 800 mg/L Ca²⁺ > 10 SPW > 400 mg/L Ca²⁺ > 3 SPW > 5 SPW and that of Mg²⁺ spiking follows the order: 10 SPW > 3 SPW > 5 SPW > 350 mg/L Mg²⁺ > 700 mg/L Mg²⁺. The descending order of the solids recovery, considering both increases in the ionic strength of SPW and spiked concentrations of the selected cations is: 800 mg/L Ca²⁺ > 10 SPW > 400 mg/L Ca²⁺ > 3 SPW > 5 SPW > 350 mg/L Mg²⁺ > 700 mg/L Mg²⁺. That of water recovery follows the order: 10 SPW > 800 mg/L Ca²⁺ > 400 mg/L Ca²⁺ > 700 mg/L Mg²⁺ > 5 SPW > 350 mg/L Mg²⁺ > 3 SPW. It is therefore clear that Ca²⁺ has a greater influence on solids and water than Mg²⁺.

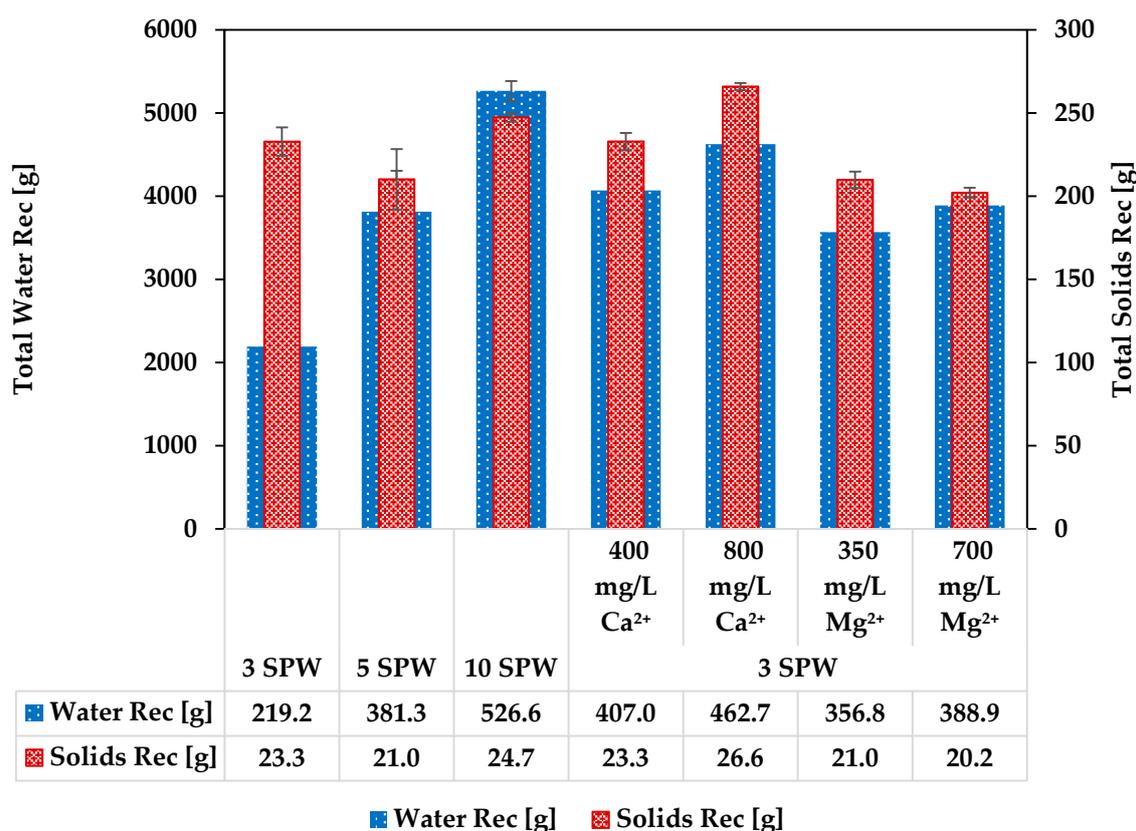


Figure 1. Final water recovery vs. solids recovery at different levels of cationic spiking.

3.2. Effect of Increased Ca²⁺ and Mg²⁺ Concentration in Process Water on Copper Recoveries and Grades

Figure 2 shows the impact of increasing ionic strength of SPW and cation ion spiking on the recovery and grade of copper. It can be seen that the increase in ionic strength of SPW from 3 to 10 SPW has a marginal effect on copper grade. From 3 SPW to 5 SPW, a 2% decrease in copper recovery is seen, however 10 SPW results in a 2% increase in copper recovery compared to 3 SPW. Thus, 5 SPW results in the lowest copper recovery compared to 3 and 10 SPW. Spiking 3 SPW to 400 mg/L Ca²⁺ results in slightly higher copper grade than 3 SPW, however the copper grade decreases as the Ca²⁺ ion concentration increases from 400 to 800 mg/L. At 400 mg/L Ca²⁺ spiking, copper recovery is lower than 3 SPW and 10 SPW but similar to that of 5 SPW. For 800 mg/L Ca²⁺ spiking, copper recovery is higher than 3 and 5 SPW. 400 mg/L Ca²⁺ was the maximum concentration beyond which the copper flotation performance was negatively impacted with respect to grade. Beyond 400 mg/L Ca²⁺ the copper grade decreased. For Mg²⁺; copper recovery is the same for both 350 mg/L and 700 mg/L Mg²⁺ spiking as well as the baseline synthetic plant water (3 SPW). At 350 and 700 mg/L, the copper grades

are comparable and higher than that at 3 SPW. The Mg^{2+} effects on this specific ore are superior to those of Ca^{2+} , as increases in Mg^{2+} concentration resulted in improved copper grades.

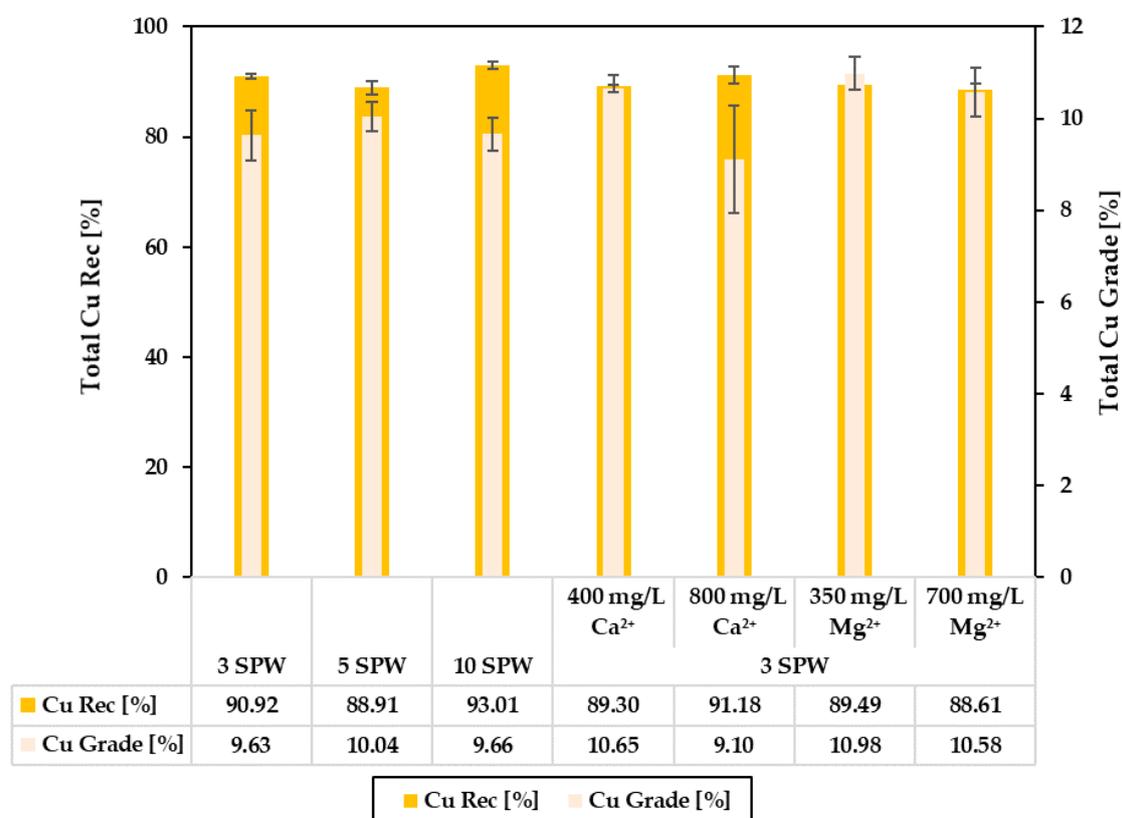


Figure 2. Copper recovery and grade recovered at different cationic concentrations.

3.3. Effect of Increased Ca^{2+} and Mg^{2+} Concentration in Process Water on Nickel Recoveries and Grades

Figure 3 shows the impact of increasing ionic strength and cationic spiking on the recovery and grade of nickel. From 3 SPW to 5 SPW, ~4% decrease in nickel recovery is seen, however 10 SPW results in an 8% increase in nickel recovery compared to 3 SPW. Thus, 5 SPW results in the lowest nickel recovery compared to 3 and 10 SPW. 3 SPW has the lowest nickel grade, however at higher ionic strengths of 5 and 10 SPW the nickel grades are comparable. As the spiking concentration of Ca^{2+} increases from 400 to 800 mg/L, the grade of nickel increased significantly above the baseline experiment, 3 SPW. Ca^{2+} ion spiking resulted in significantly higher nickel grade compared to 3, 5, and 10 SPW. Spiking Mg^{2+} from 350 to 700 mg/L Mg^{2+} resulted in a 1.87% decrease in nickel recoveries. As the Mg^{2+} ionic concentration increases from 350 to 700 mg/L, the nickel grade increased much higher above 3, 5, and 10 SPW and even higher than Ca^{2+} spiking. As the overall ionic strength increases, the nickel grade also increases substantially above the baseline experiment. The lowest nickel recovery is at 700 mg/L Mg^{2+} spiking.

3.4. Relating the Effect of Spiking Ca^{2+} and Mg^{2+} on the Electrical Conductivity (EC) to Flotation Performance

Figures 4 and 5 show the electrical conductivity of the froth and pulp in increasing ionic strength of SPW to 3, 5, and 10 SPW with each ion spiked to 5 and 10 times its normal concentration in 1 SPW in a background matrix of 3 SPW in comparison with copper and nickel grades respectively. It can be seen that the EC increased with increasing ionic strength of SPW for both the froth and pulp. The EC of the froth is lower compared to the EC of the pulp except for 5 SPW.

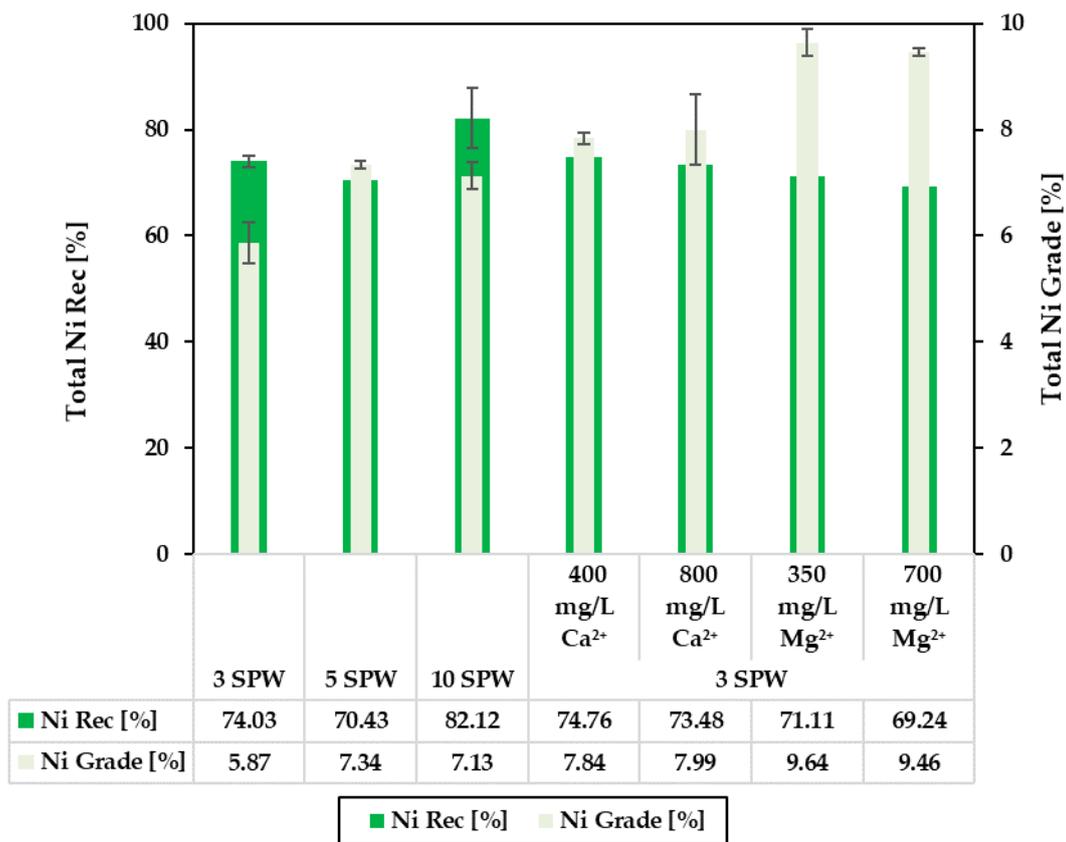


Figure 3. Nickel recovery and grade at different cationic concentrations.

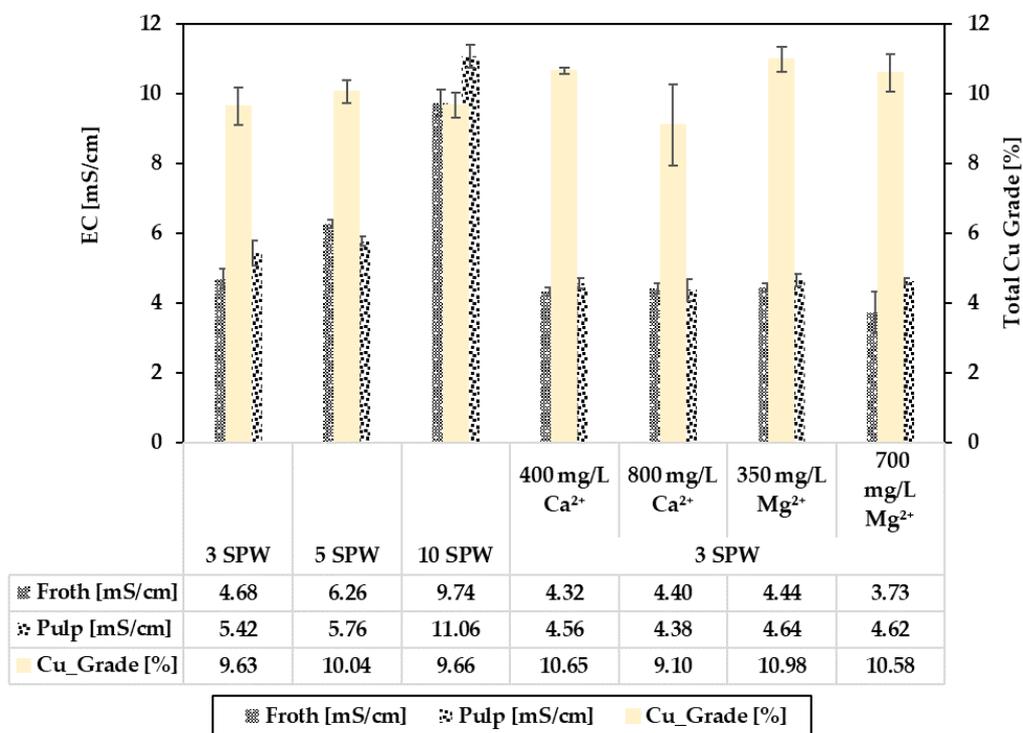


Figure 4. Relating the electrical conductivity to Cu grade.

Figure 4 shows the effect of EC in both the pulp and the froth phase on total copper grade. The EC between the froth and pulp from 3 to 10 SPW increases along with the IS. However, there is no marked

trend in EC upon spiking with the cations, where most conditions show very similar ECs. Notable at 800 mg/L Ca²⁺, the EC between the froth and pulp phase is practically the same and the copper grade decreases to a minimum in comparison to other experimental conditions. In this case, it is not possible to correlate the EC with the copper grade.

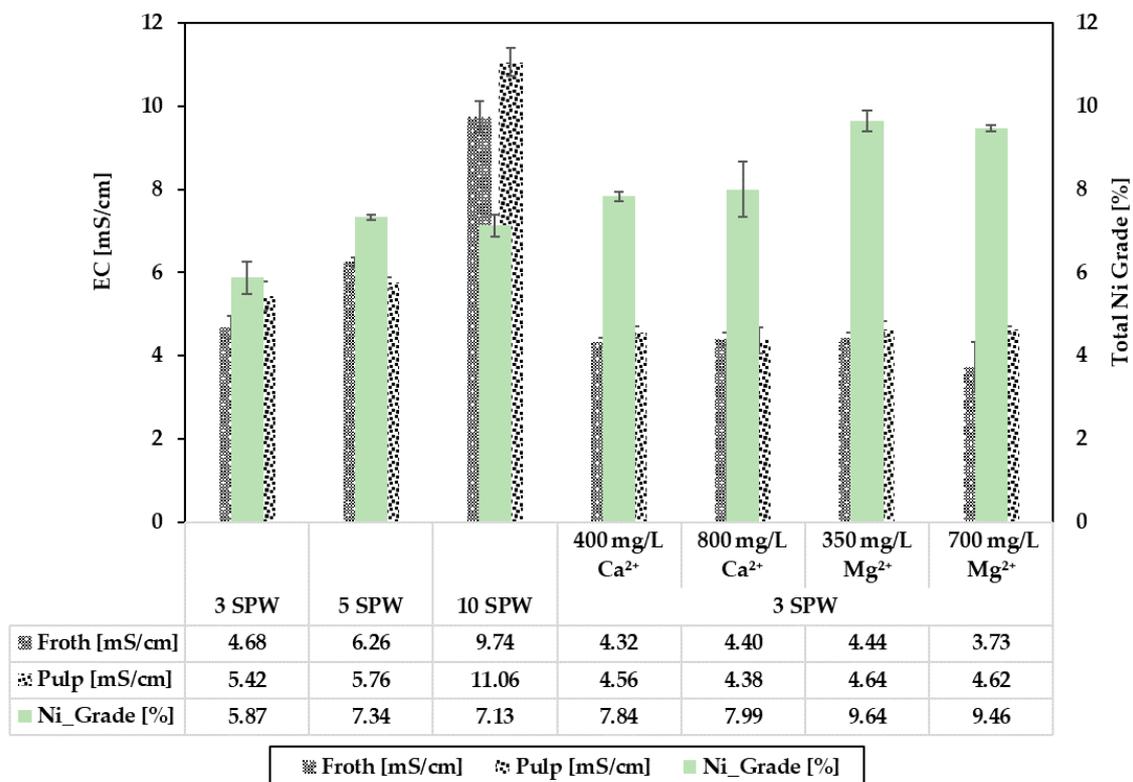


Figure 5. Relating the electrical conductivity to Ni grade.

Figure 5 shows the distribution of EC between the froth and pulp phase and the effect EC has on total nickel grade. When the froth phase EC is higher compared to that of the pulp phase EC at 5 SPW, the grade is higher than that of the baseline experiment of 3 SPW. As the ionic strength increases to 10 SPW, the froth and pulp EC also increases. Spiking with Ca²⁺ and Mg²⁺ results in a decrease in the froth and pulp EC, this shift in EC however results in an increase in total nickel grades above what was seen in 3 SPW.

4. Discussion

4.1. Effect of Increased Ca²⁺ and Mg²⁺ Concentration in Process Water on Flotation Performance

Figure 1 shows that as ionic strength increased, the water recovery also increased. This agrees with findings from Manono et al. [32] that bubble diameter decreased in the order $d_{3SPW} > d_{5SPW} > d_{10SPW}$ hence water recovery increased with increasing ionic strength as smaller bubbles recover more water. Divalent ions at high enough concentrations, e.g., 285 mg/L Ca²⁺ and 173 mg/L Mg²⁺ [32] have been shown to inhibit bubble coalescence, slow inter-bubble drainage, promote froth mobility and thereby enhance the stability of the froth [10,23,28,32], increasing water recovery. Cation spiked synthetic plant waters resulted in higher water recoveries and therefore more stabilised froths compared to the baseline experiment of 3 SPW, this finding is also in line with published literature on the effects of polyvalent cations on froth stability [10,23,28,32].

Corin et al. [9] showed that as the ionic strength increases, water recovery increases, however solids recovery may decrease, as a consequence of entrainment per gram of water decreasing. Although

total entrained material/solids may appear to increase, owing to the much higher water recoveries, or in the case of 5 SPW, which appears to decrease, the proportion of solids per gram of water recovered decreases as ionic strength increases. As a demonstration of this, from this study (as in Figure 1), the solids percentage (w/v) of the combined concentrate decreases as IS increases; 3 SPW 10.6%, 5 SPW 5.5%, 10 SPW 4.7%. Hence, while 5 SPW appears to be an outlier giving a lowest solids recovery of the SPW test, it, in fact, fits the solids percentage trend as shown.

Copper recovery is almost constant throughout the flotation conditions, including when changing the water types as shown in Figure 2. Corin et al. [9] observed similar trends from a Merensky reef ore and attributed the invariant copper recovery while total solids increased to an increase in naturally floatable gangue (NFG) as the ionic strength of water increased. Previous studies, [9,13,14,23], have shown that an increase in ionic strength increases the froth stability and NFG recovery, and a decrease in grade is likely to be observed, and is seen in this study. The decrease in copper grade at higher Ca^{2+} ion concentration results from the action of Ca^{2+} ions on the stability of the froth. At 800 mg/L Ca^{2+} , the grade is lower than that for 3 SPW. This may suggest that 400 mg/L Ca^{2+} is the threshold for copper grade and beyond this Ca^{2+} concentration, the copper grade may be affected negatively.

For the conditions used in this study, spiking Mg^{2+} resulted in increased grades of copper and nickel in comparison to the baseline experiment, 3 SPW, and this suggested that any detrimental threshold for Mg^{2+} concentration for the selected ore may lie outside of the boundary concentrations used in this study. There was no significant nickel recovery difference when the system was spiked with Mg^{2+} at either 350 or 700 mg/L Mg^{2+} , however, the nickel grade was significantly impacted as it showed an increase of approximately 3.65% from 3 SPW to 350 mg/L Mg^{2+} . This shows that increased Mg^{2+} concentrations enhanced the depression of gangue for the ore type used in this investigation.

These findings are in agreement with Hirajima et al. [28] who investigated the effect of Ca^{2+} and Mg^{2+} as divalent seawater cations on the floatability of molybdenite and chalcopyrite and found that both Mg^{2+} and Ca^{2+} had a depressing nature on chalcopyrite while Mg^{2+} had a less dominant effect compared to Ca^{2+} . At ~pH 9, Ca^{2+} and Mg^{2+} are known to chemisorb onto the sulfide mineral surface, thereby reducing the hydrophobicity of the mineral [7,27]. Due to the different ionic strengths of 3, 5, and 10 SPW, the concentration of Ca^{2+} and Mg^{2+} are different, meaning that the Ca^{2+} and Mg^{2+} species act on the mineral surface differently. The findings of this study are in agreement with the postulation that metallic hydrophilic hydroxides present in solution at alkaline pH, would act differently on the mineral surface. Laskowski and Castro [11] investigated the hydrolysis of metallic ions in flotation and also found that Mg^{2+} forms hydrolysis products such as MgOH^+ and $\text{Mg}(\text{OH})_2$ that strongly depress sulfide minerals such as molybdenite over typical plant pH ranges (8–12). The metallic ions under alkaline conditions hydrolyse and deposit in the form of metallic hydrophilic hydroxides which passivate the mineral surface [7,25,27]. Such mineral surface passivation would have a negative impact on the bubble–particle attachment efficacy [11,25], leading to a decrease in the floatability of the valuable minerals as well as an enhanced depression of naturally floatable gangue minerals [13,25,26]. Susceptibility to xanthate collector adsorption is also reduced as has been shown by species formations and zeta potential studies by Manono et al. [14] and October et al. [25].

4.2. Relating the Effect of Ca^{2+} and Mg^{2+} on the Electrical Conductivity (EC) to Flotation Performance

A decrease in the total EC means there are ions preferentially adsorbing onto the sulfide mineral surface. It was found that the presence of ions in the pulp phase may hinder froth mobility and froth stability. The influence of EC is not evident when looking at recoveries as they are quite similar for copper and nickel, however nickel shows differences in grade even with a slight difference between the froth and pulp EC, as illustrated by Figure 6.

Spiking 3 SPW from 400 to 800 mg/L Ca^{2+} results in a slight increase in EC in the froth phase while at 800 mg/L Ca^{2+} , the EC in the froth phase is the same as in the pulp phase. Increasing the ionic concentration of Mg^{2+} from 350 to 700 mg/L results in decreased froth phase EC. At 700 mg/L Mg^{2+} , the difference in EC is more pronounced compared 350 mg/L Mg^{2+} . The higher EC in the pulp

phase at 700 mg/L Mg^{2+} means there are more free ions in the slurry and this may hinder the collector interaction with the target mineral [28].

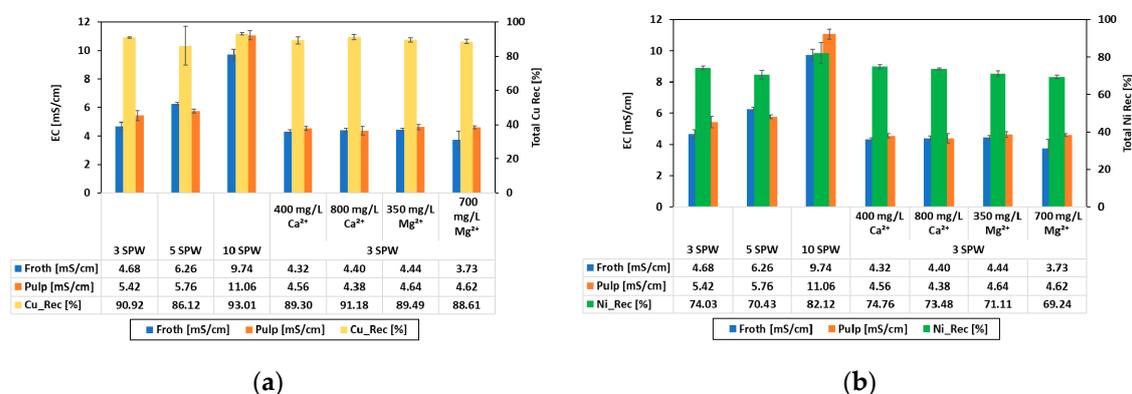


Figure 6. Effect of EC on metal recovery; copper (a) and nickel (b).

Spiking from 400 to 800 mg/L Ca^{2+} results in a slight increase in EC in the froth phase and at 800 mg/L Ca^{2+} the EC in the froth phase is the same as in the pulp phase. The presence of Ca^{2+} and Mg^{2+} ions depresses the gangue hence the increase in nickel grade upon spiking in comparison to 3 SPW. Increasing the ionic concentration of Mg^{2+} from 350 to 700 mg/L results in decreased froth phase EC and this in turn shows improved nickel grade in comparison to the baseline experiment 3 SPW. The EC could not be related to the metal recovery as it did not show any marked differences.

Bearing in mind that the outcomes of this study may be ore-dependent, when recycled water is being monitored for the amount of Ca^{2+} and Mg^{2+} present, it is imperative to operate at a maximum concentration of 400 mg/L Ca^{2+} , beyond this concentration the grades for copper will decrease owing to the impact of Ca^{2+} on frothing properties [10,32]. The trend for nickel recoveries and grades did not point to a Ca^{2+} concentration threshold. The threshold concentration for magnesium was not determined within the limits of this study.

5. Conclusions

While recycling of water on site might not have a large impact on the valuable mineral recoveries, there is a need to manage the quality of water, in order to maintain a suitable concentrate grade, particularly for the nickel circuit which may be operated at moderate ionic strengths such as that of 5 SPW. Overall, our study has shown minimal impact on the valuable mineral recovery however, a notable impact on grade was shown, upon spiking. This could be due to the behavior of gangue minerals as a result of bubble coalescence, changes in bubble sizes as the ionic strength of water changes and increases in water recovery upon spiking as well as the advent recovery of gangue material. It is this reason why the sulfide-based mineral is not notably changing but the grade has been impacted.

Below are notable conclusions from this study:

Ca^{2+} spiking: Copper and nickel recovery were insignificantly impacted while the copper grade decreased in the order 800 mg/L < 3 SPW < 10 SPW < 5 SPW < 400 mg/L. This showed that elevated concentrations of Ca^{2+} above 400 mg/L decreased the grade of copper, and this may be regarded as the threshold concentration above which the grade of the valuable minerals will drop, as higher Ca^{2+} concentrations result in increased froth stabilities which may complicate gangue management. While nickel grade followed the order 3 SPW < 10 SPW < 5 SPW = 400 mg/L Ca^{2+} = 800 mg/L Ca^{2+} there is no obvious trend noted.

Mg^{2+} spiking: Copper recoveries were insignificantly affected. A drop in nickel recoveries was seen compared to the baseline 3 SPW. Copper and nickel grade decreased in the order of 3 SPW < 10 SPW < 5 SPW < 700 mg/L Mg^{2+} = 350 mg/L. The threshold for Mg^{2+} was deemed to be outside the spiking boundaries for this study as the two Mg^{2+} spiked 3 SPW conditions resulted in similar

nickel recoveries and grades. The biggest benefit of spiking 3 SPW with Mg^{2+} is seen on the nickel concentrate grades across all tested water types.

Spiking with Ca^{2+} and Mg^{2+} had little impact on copper and nickel recovery, however the grade was impacted hence it is important to maintain a level of ions below the threshold concentrations, when possible, for manageable flotation performance. EC had no notable impact on the recoveries of copper and nickel, respectively. Upon increase in ionic strength, the bubble sizes would change hence the changes in bubble size affects the interfacial area available for bubble–particle similar to what Manono et al. [22] found.

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References

- Bradshaw, D.J. Synergistic Effects between Thiol Collectors Used in Flotation of Pyrite. Ph.D. Thesis, University of Cape Town, Cape Town, South Africa, 1997.
- Cho, Y.S.; Laskowski, J.S. Effect of flotation frothers on bubble size and foam stability. *Int. J. Miner. Process.* **2002**, *64*, 69–80. [[CrossRef](#)]
- Melo, F.; Laskowski, J.S. Fundamental properties of flotation frothers and their effect on flotation. *Miner. Eng.* **2006**, *19*, 766–773. [[CrossRef](#)]
- Bradshaw, D.J.; Harris, P.J.; Connor, C.T.O. Synergistic interactions between reagents in sulphide flotation. *J. S. Afr. Inst. Miner. Metall.* **1998**, *98*, 187–192.
- Davis, F.; Hyatt, D.; Cox, C. *Environmental Problems of Flotation Reagents in Mineral Processing Plant Tailings Water Mineral Processing Plant Tailings Water*; U.S. Department of the Interior: Washington, DC, USA, 1975.
- Wiese, J.G. Investigating Depressant Behaviour in the Flotation of Selected Merensky Ores. Master's Thesis, University of Cape Town, Cape Town, South Africa, 2009.
- Ikumapayi, F.; Rao, K.H. Recycling Process Water in Complex Sulfide Ore Flotation: Effect of Calcium and Sulfate on Sulfide Minerals Recovery. *Miner. Process. Extr. Metall. Rev.* **2014**, *36*, 45–64. [[CrossRef](#)]
- Bulatovic, S.M. *Handbook of Flotation Reagents*; Elsevier: Amsterdam, The Netherlands, 2007; pp. 1–6. [[CrossRef](#)]
- Corin, K.C.; Corin, K.C.; Reddy, A.; Miyen, L.; Wiese, J.G.; Harris, P.J. The effect of ionic strength of plant water on valuable mineral and gangue recovery in a platinum bearing ore from the Merensky reef. *Miner. Eng.* **2011**, *24*, 131–137. [[CrossRef](#)]
- Craig, V.; Ninham, B.; Pashley, R. The effect of electrolytes on bubble coalescence in water. *J. Phys. Chem.* **1993**, *39*, 10192–10197. [[CrossRef](#)]
- Laskowski, J.S.; Castro, S. Hydrolysis of metallic ions in mineral processing circuits and its effect on flotation. In Proceedings of the COM Conference of Metallurgists, Vancouver, BC, Canada, 27–30 August 2017. [[CrossRef](#)]
- Levay, G.; Smart, R.; Skinner, W. The impact of water quality on flotation performance. *J. S. Afr. Inst. Miner. Metall.* **2001**, *1*, 69–76. [[CrossRef](#)]
- Manono, M.S.; Corin, K.C.; Wiese, J.G. 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. *Miner. Eng.* **2012**, *36–38*, 231–236. [[CrossRef](#)]
- Manono, M.; Corin, K.; Wiese, J. Perspectives from literature on the influence of inorganic electrolytes present in plant water on flotation performance. *Physicochem. Probl. Miner. Process.* **2018**, *54*, 1191–1214.

15. Muzenda, E. An Investigation into the Effect of Water Quality on Flotation Performance. *World Acad. Sci. Eng. Technol.* **2010**, *70*, 237–241.
16. Haggard, E.L.; Sheridan, C.M.; Harding, K.G. Quantification of water usage at a South African platinum processing plant. *Water SA* **2015**, *41*, 279–286. [[CrossRef](#)]
17. Muzinda, I.; Schreithofer, N. Water quality effects on flotation: Impacts and control of residual xanthates. *Miner. Eng.* **2018**, *125*, 34–41. [[CrossRef](#)]
18. Schreithofer, N.; Muzinda, I. *Boliden Kevitsa Mine Report*; NI 43-101; New Boliden: Sodankylä, Finland, 2017.
19. Slatter, K.A.; De Vaux, D.; Plint, N.D.; Cole, M.; Dilsook, V.; Palm, Oostendorp, B. Water management in anglo platinum process operations: Effects of water quality on process operations. In Proceedings of the The International Mine Water Conference, Pretoria, South Africa, 19–23 October 2009; pp. 46–55.
20. Li, Y.; Li, W.; Xiao, Q.; He, N.; Ren, Z.; Lartey, C.; Gerson, A. The Influence of Common Monovalent and Divalent Chlorides on Chalcopyrite Flotation. *Minerals* **2017**, *7*, 111. [[CrossRef](#)]
21. Gungoren, C.; Islek, E.; Baktarhan, Y.; Unver, I.K.; Ozdemir, O. A novel technique to investigate the bubble coalescence in the presence of surfactant (MIBC) and electrolytes (NaCl and CaCl₂). *Physicochem. Probl. Miner. Process.* **2018**, *54*, 1215–1222, ISSN 1643-1049.
22. Manono, M.S.; Corin, K.C.; Wiese, J.G. The effect of ionic strength of plant water on foam stability: A 2-phase flotation study. *Miner. Eng.* **2013**, *40*, 42–47. [[CrossRef](#)]
23. Corin, K.C.; Wiese, J.G. Investigating froth stability: A comparative study of ionic strength and frother dosage. *Miner. Eng.* **2014**, *66–68*, 130–134. [[CrossRef](#)]
24. Liu, W.; Moran, C.J.; Vink, S. A review of the effect of water quality on flotation. *Miner. Eng.* **2013**, *53*, 91–100. [[CrossRef](#)]
25. October, L.; Corin, K.; Schreithofer, N.; Manono, M.; Wiese, J. Considering the Ionic Strength and pH of Process Water on Bubble-Particle Attachment of Sulfide Minerals: Implications for Froth Flotation in Saline Water. In *Mine Water-Technological and Ecological Challenges*; Khayrulina, E., Wolkersdorfer, C.H., Polyakova, S., Bogush, A., Eds.; Perm State University: Perm, Russia, 2019; pp. 437–445.
26. Manono, M.S.; Matibidi, K.; Thubakgale, C.K.; Corin, K.C.; Wiese, J.G. Water Quality in PGM Ore Flotation: The effect of Ionic Strength and pH. In Proceedings of the IMWA 2017—Mine Water & Circular Economy, Lappenranta, Finland, 25–30 June 2017; pp. 777–784.
27. Ikumapayi, F.; Makitalo, M.; Johansson, B.; Hanumantha, K. Recycling of process water in sulphide flotation. Effect of calcium and sulphate ions on flotation of galena. *Miner. Eng.* **2012**, *39*, 77–88. [[CrossRef](#)]
28. Hirajima, T.; Suyantara, G.P.W.; Ichikawa, O.; Elmahdy, A.M.; Miki, H.; Sasaki, K. Effect of Mg²⁺ and Ca²⁺ as divalent seawater cations on the floatability of molybdenite and chalcopyrite. *Miner. Eng.* **2016**, *96–97*, 83–93. [[CrossRef](#)]
29. Kirjavainen, V.; Heiskanen, K. Some factors that affect beneficiation of sulphide nickel—copper ores. *Miner. Eng.* **2007**, *20*, 629–633. [[CrossRef](#)]
30. Musuku, B.; Muzinda, I.; Lumsden, B. Cu-Ni processing improvements at First Quantum’s Kevitsa mine. *Miner. Eng.* **2016**, *88*, 9–17. [[CrossRef](#)]
31. Muzenda, E.; Afolabi, A.S.; Abdulkareem, A.S.; Ntuli, F. Effect of pH on the Recovery and Grade of Base Metal Sulphides (PGMs) by Flotation. In Proceedings of the World Congress on Engineering and Computer Science, San Francisco, CA, USA, 19–21 October 2011.
32. Manono, M.S.; Corin, K.C.; Wiese, J.G. The influence of electrolytes present in process water on the flotation behaviour of a Cu-Ni containing ore. *Miner. Eng.* **2016**, *96–97*, 99–107. [[CrossRef](#)]
33. Clarke, P.; Fornasiero, D.; Ralston, J.; Smart, R.S.C. A study of the removal of oxidation products from sulfide mineral surfaces. *Miner. Eng.* **1995**, *8*, 1347–1357. [[CrossRef](#)]
34. Wiese, J.; Harris, P.; Bradshaw, D. The influence of the reagent suite on the flotation of ores from the Merensky reef. *Miner. Eng.* **2005**, *18*, 189–198. [[CrossRef](#)]

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