

Article

The Electrochemical Response of Chalcopyrite and Galena to Degrading Water Quality

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Abstract: Water is used as a liquid medium as well as a means of transportation during mining operations. Flotation, in particular, is a water intensive process where water makes up about 80–85% of the pulp phase. Process water contains organic and inorganic species which accumulate as they are recycled. To avoid the treatment costs of removing these contaminants, many mining operations allow the quality of their water to degrade over time. When this water is introduced into flotation circuits, the pulp chemistry is altered. Ionic species that accumulate in recycled process water have been shown by previous studies to be especially deleterious to flotation performance. Such ions include Ca^{2+} , Cu^{2+} , Mg^{2+} , Pb^{2+} , SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$, amongst others. The flotation sub-process of collector adsorption which is responsible for inducing hydrophobicity on valuable mineral surfaces may be influenced by water chemistry. Accumulating ionic species have been shown to hinder collector adsorption which may reduce recovery of valuable minerals to the concentrate. Consequently, degrading water quality may threaten the economic viability of mining operations that make use of closed water circuits. Electrochemical techniques such as mineral rest potentials can be used to monitor the impact of changing water quality on collector–mineral interactions. Microflotation was used to determine whether mineral floatability was affected by changing water quality. This study therefore aimed to investigate whether electrochemical techniques such as rest potential measurements can be used to predict flotation performance under changing water quality. No definable relationship was found between the rest potential differences and the microflotation initial recoveries, however, rest potential measurements did identify the negative impact that thiosulphate ions may have on flotation processes.

Keywords: flotation water quality; electrochemical adsorption; xanthate collectors; mineral rest potential



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1. Introduction

Water is a transport and processing medium in mineral processing operations. In flotation, water makes up about 80–85% of the pulp phase [1]. Due to the ever-increasing scarcity of fresh water, as well as strict environmental regulations, many mining operations have adopted a zero-water discharge policy. This means that any process water that would otherwise be released as effluent is recycled back into the process [2]. This strategy not only reduces the amount of fresh and potable water consumed but limits the amount of potentially hazardous process water released into the environment. An additional benefit is a reduction in reagent consumption as residual reagents are recycled back to concentrators which reduces the amount of fresh reagent required [3].

Mining operations in arid countries are under pressure to reduce their freshwater consumption and effluent discharge. Process water can be reclaimed from tailings dams; tailings thickeners; concentrate dewatering processes; treated sewage effluent water; underground mine water and water from leaching; and milling and roasting processes [4–6]. In

addition to where the water is sourced from; the composition of recycled process water will also depend on ore mineralogy and the type of reagents used. Water quality deterioration is noted to be due to the accumulation of both organic and inorganic species as they are recycled. Several studies have found that the quality of process water deteriorates over time and that poor water quality has a negative impact on flotation performance [7–10]. Ionic species have also been seen to alter the structure of water in aqueous solutions. Ions are characterized by their ability to facilitate or disrupt the hydrogen bonds between water molecules. Classification of ions is therefore either structure makers, the ions that maintain hydrogen bonds, or structure breakers, which weaken them. Variations in water structure have been shown to alter pulp viscosity and salt–collector interactions [11–18].

Flotation separation efficiency is dependent on pulp chemistry, and the presence of accumulating ionic species in process water alters this chemistry significantly. Changes in the pulp chemistry affects flotation sub-processes such as bubble–particle attachment, bubble coalescence, and collector adsorption [19,20]. Separation efficiency depends on mineral hydrophobicity which is enhanced by collectors. Collector adsorption onto sulphide mineral surfaces has been shown to be inhibited by the presence of ionic species such as Mg^{2+} , Ca^{2+} , SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ [7,8,10,21–24].

Owing to the fact that water chemistry changes as soon as water is removed from its source, synthetic plant water recipes have been created to replicate, as far as possible, the composition of on-site plant water in an effort to study the effects of changing water quality on flotation performance in the laboratory [20,25,26]. The composition of synthetic plant water is case-specific and must be tailored to each individual plant. Parameters such as total dissolved solids (TDS), ionic strength (IS), and dissolved ion concentrations are considered when generating site-specific synthetic process water recipes.

Electrochemistry is an important concept in sulphide mineral flotation because collectors, in this case xanthates, adsorb onto mineral surfaces via oxidation and reduction reactions. This is possible because most sulphide minerals are semi-conductors which allows redox reactions to take place on their surfaces [27–31]. Electrochemistry techniques such as rest potential measurements can therefore be used to gain insight into collector–mineral interactions. Studies show that when the measured potential is above the equilibrium potential of xanthate oxidation, the xanthate ions are likely oxidizing to form dixanthogen [31–34]. When the measured potentials are below this equilibrium potential, it is likely that metal xanthate species are forming on the mineral surface [31,32]. These surface species are highly insoluble with the dixanthogen species, inducing the greatest hydrophobicity.

Previous work has indicated that it may be possible to link electrochemical collector–mineral interactions to flotation performance via rest potential measurements. This is due to the ability of rest potential measurements to determine the extent of collector–mineral interactions by measuring the extent of potential change after collector addition [35–39]. Rest potential measurements can also indicate which collector oxidation species is present and responsible for inducing mineral hydrophobicity. The measured potential relative to the collector oxidation potential indicates whether the dixanthogen of metal xanthate species forms on the mineral surface [19,31,36,37,40–42]. This means that rest potential measurements may be able to provide insights into how the presence of ionic species affects collector adsorption, and suggests that electrochemical techniques could be used to predict flotation performance with changing water quality. In this paper, an analysis of the rest potentials of chalcopyrite and galena and their floatability in different ionic solutions simulating variable concentration in plant waters is presented. While a number of previous studies have considered the electrochemistry of minerals within flotation systems, none consider the water chemistry, which will change as water is recycled on site. The work attempts to find a relationship between electrochemistry and microflotation, and suggests a meaningful way in which such measurements can be applied to understanding flotation performance.

2. Materials and Methods

In order to isolate the impact of specific ions, pure galena and chalcopyrite electrodes were exposed to single salt synthetic plant water solutions within an electrochemical cell. Table 1 shows the ionic compositions of the single salt synthetic plant water solutions considered in this study. The salt solutions were prepared in 2 L volumetric flasks with ultra-pure water as the solvent. The single salt solutions had the ionic strengths that corresponded to synthetic plant water (SPW) concentrations of 1, 3, 5 and 10 times standard 1SPW [25,26]. The pH of the SPW solutions was not modified in order to limit the introduction of additional ions that might affect the responses measured. Consequently, no pH modifiers and buffers were used during this study.

Table 1. Composition of single salt ion concentrations (adapted from [25,26,38]).

| Water Type | Cl ⁻ in NaCl (ppm) | Cl ⁻ in MgCl ₂ (ppm) | Mg ²⁺ in MgSO ₄ ·7H ₂ O (ppm) | Mg ²⁺ in MgCl ₂ (ppm) | SO ₄ ²⁻ in MgSO ₄ ·7H ₂ O (ppm) | SO ₄ ²⁻ in Na ₂ SO ₄ (ppm) | S ₂ O ₃ ²⁻ in Na ₂ S ₂ O ₃ (ppm) |
|------------|-------------------------------|--------------------------------------------|----------------------------------------------------------------|---------------------------------------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| 1SPW | 1414 | 4609 | 5965 | 2304 | 5965 | 2325 | 2714 |
| 3SPW | 4242 | 13,827 | 17,895 | 6912 | 17,895 | 6975 | 8142 |
| 5SPW | 7070 | 23,045 | 29,825 | 11,520 | 29,825 | 11,625 | 13,570 |
| 10SPW | 14,140 | 46,090 | 59,650 | 23,040 | 59,650 | 23,250 | 27,140 |

A three-electrode system consisting of a reference, counter and working electrode were used for rest potential measurements. The double junction Ag/AgCl reference electrode containing 3 M KCl solution was sourced from Metrohm SA, a subsidiary of Metrohm AG (Herisau, Switzerland). The reference electrode carries a potential of -0.207 V vs. Standard Hydrogen Electrode (SHE). The working electrodes consisted of pure mineral samples of galena and chalcopyrite manufactured as described in Tadie [43] and Ndamase, et al. [38]. A Metrohm Model 60301100 platinum electrode was used as a baseline working electrode and to monitor the standard potential of the system. Before each electrochemical test, the mineral electrodes were polished, first with 600 grit silica carbide paper and then with alumina powders with particle sizes of 1, 0.3 and 0.05 μm . Before and after each polishing step, the mineral electrodes were rinsed using ultra-pure water.

Rest potential tests were conducted in a 500 mL double-jacketed electrochemical cell placed on a magnetic stirring plate. The temperature of the cell was maintained at 25 ± 1 °C using a circulating water bath. The cell was filled with 450 mL of synthetic plant water and the electrodes were placed in the solution under thorough stirring to eliminate mass transfer limitations. A Gamry (Warminster, PA, USA) 600 potentiostat connected to a computer recorded the measured potentials using the Gamry Framework software. The rest potential measurements were conducted over a period of 1200 s where 4 mL of the 1% collector solution was dosed at 600 s. The collector concentration was maintained at 6.24×10^{-4} M in order to compare results from this study with previous studies [36,40,41]. The natural pH values of the SPW solutions during rest potential measurements remained neutral and averaged a pH of 8.0. Each test was conducted in duplicate to ensure repeatability.

For microflotation, high purity samples of galena and chalcopyrite were obtained from Mineral World, Cape Town South Africa and Ward's Science, respectively. Both samples were crushed manually in a stainless-steel laboratory mill using a single stainless-steel rod until 500 g of crushed mineral was obtained. The sample was then pulverized for 10 s at a time in a stainless-steel ring mill. The pulverized samples were dry sieved using 75 μm and 38 μm sieves. Microflotation tests were conducted in a 250 mL UCT microflotation cell [44]. Prior to each test, 3 g of pure mineral, ground to $-75 + 38$ μm , was mixed with 50 mL of each single salt SPW solution in a beaker. This slurry was sonicated for 5 min to scatter any fine particle agglomerations. The slurry was transferred to the microflotation cell using a funnel. The funnel was rinsed with a wash bottle containing SPW to wash any remaining slurry into the cell. The cell was filled with single salt SPW to the point just above the pump

recycle point. The equivalent of 50 g/ton of sodium ethyl xanthate (SEX) was added to the slurry using a micropipette. The first peristaltic pump, set at 65 rpm, was switched on to condition the pulp for 2 min. The cell was then filled to just below the 250 mL mark with single salt SPW. A microsyringe with an air flowrate of 7 mL/min was introduced at the base of the cell to deliver air. Once the syringe was inserted, a stopwatch was used to collect concentrates after 2, 4, 6 and 8 min. After a total of 20 min the cell was drained to collect the tailings. The concentrates and tailings were then filtered, air dried overnight, and weighed to determine mineral recovery. The pH was not controlled during microflotation tests and the natural pH values of the chalcopyrite and galena slurries during microflotation averaged a pH of 6.6. Microflotation tests for each single salt SPW were performed in duplicate to ensure repeatability.

3. Results and Discussion

3.1. Rest Potential Measurements

Rest potential measurements were used to assess the extent of xanthate–mineral interactions with changing water quality. Collector oxidation to form dixanthogen or metal xanthate is an essential process during the electrochemical adsorption of xanthate onto sulphide minerals. The magnitude of potential change after collector addition during Open Circuit Potential (OCP) measurements can give an indication of the extent of collector oxidation and xanthate–mineral interactions [42]. Positive values of potential change show that the measured rest potentials on the mineral after collector addition are more cathodic (negative) than those prior to collector addition, which is indicative of collector oxidation reactions contributing to the potential. Conversely, when the potential change values are negative, it indicates that the measured potentials after collector addition are more anodic than those prior to xanthate addition, suggesting increased rates of reduction on the mineral surface. Consequently, a highly positive value of potential change suggests a greater extent of xanthate–mineral interaction.

Figures 1 and 2 show the extent of potential change after collector addition to the rest potentials of chalcopyrite and galena in different SPW water with different ions.

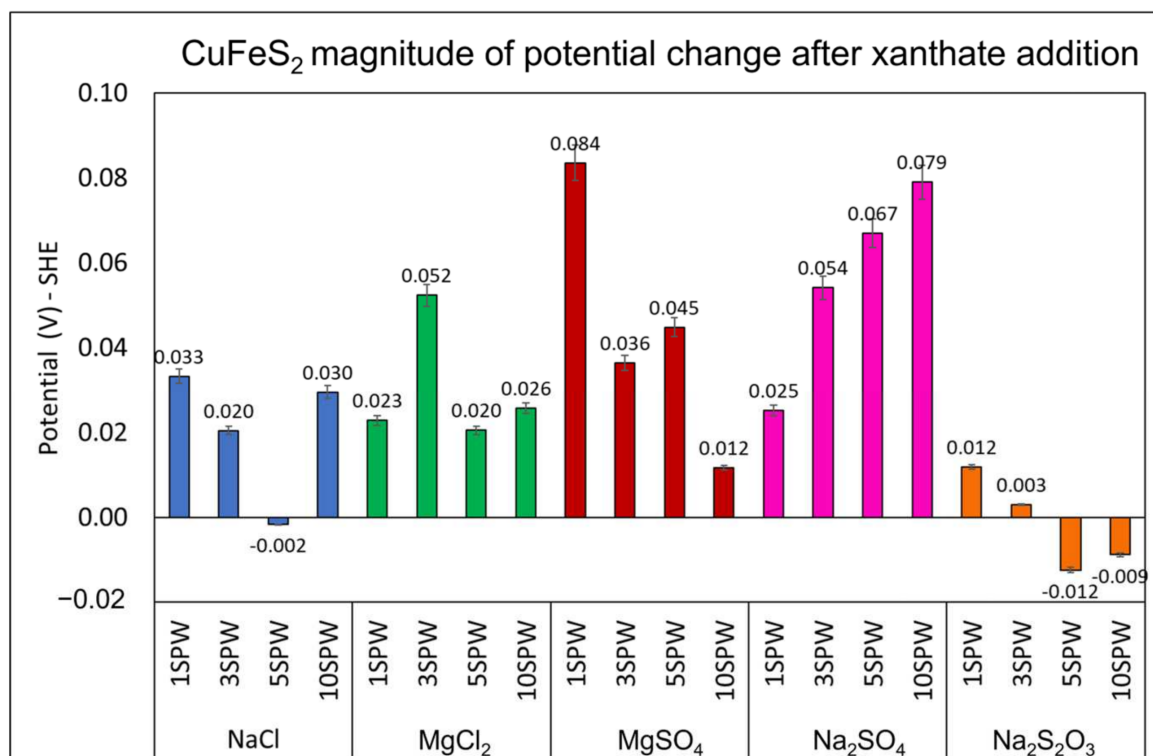


Figure 1. Extent of potential change after SEX addition for chalcopyrite with changing water quality.

The extents of xanthate–mineral interactions varied notably with changing water quality as shown in Figure 1. For chalcopyrite in Na_2SO_4 , the potential change became increasingly positive with increasing salt concentration, indicating that xanthate–chalcopyrite interactions improved with increasing ionic strength. Upon closer inspection, these are the only conditions where xanthate–mineral interactions were improved by increasing ionic strength. This improvement could be due to mineral surface activation where these conditions resulted in the precipitation or the adsorption of surface species which form a conducting layer that further aids electron transfer reactions [45]. Contrastingly, Figure 2 for galena indicates that increasing the concentration of the SO_4^{2-} ion, in both MgSO_4 and Na_2SO_4 , decreased the extent of xanthate–galena interactions, a result that is in line with previous work that showed that the presence of SO_4^{2-} hinders collector adsorption [23].

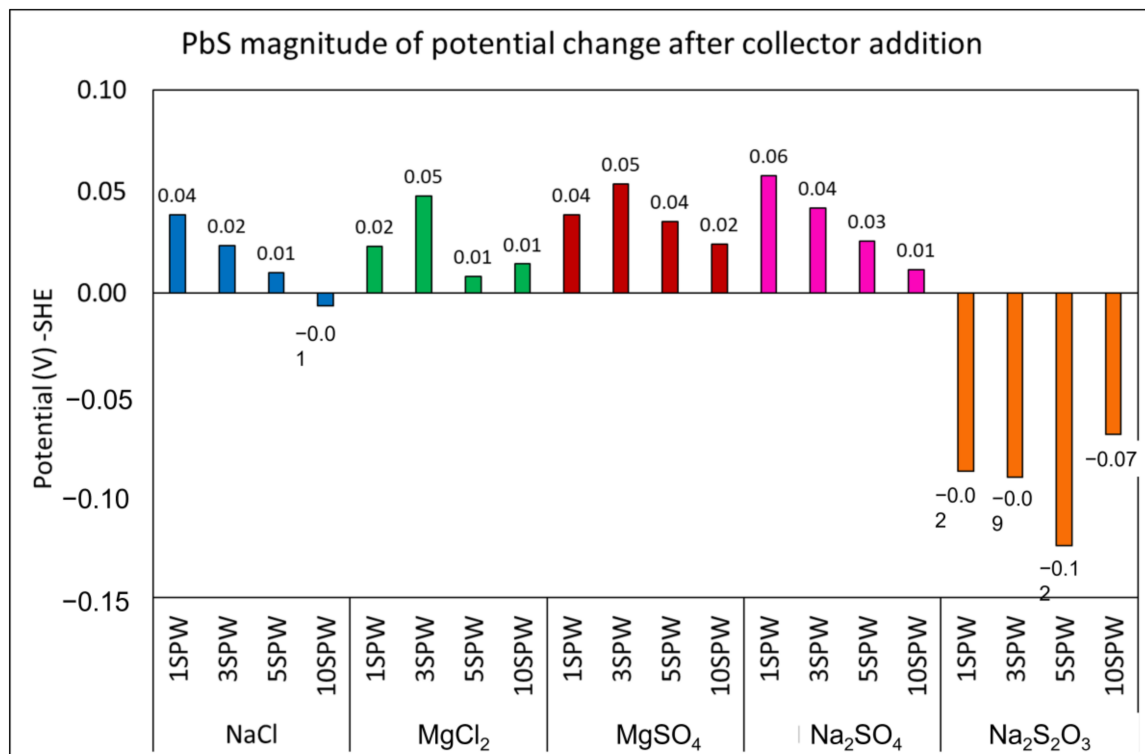


Figure 2. Extent of potential change after SEX addition for galena with changing water quality.

Figure 1 shows that increasing the concentration of the $\text{S}_2\text{O}_3^{2-}$ ion decreased the extent of xanthate–chalcopyrite interactions; the magnitude of the potential change decreased from 1SPW to 3SPW, after which the potential changes became negative in value, indicating that the average potentials after collector addition were more anodic than the average potentials prior to collector addition. This negative potential change was also observed in NaCl at 5SPW. Similarly, Figure 2 indicates that galena in $\text{Na}_2\text{S}_2\text{O}_3$ yielded negative potential changes at all ionic strengths, while galena in NaCl had a negative potential change at 10SPW only. The data suggest that xanthate–mineral interactions were limited in the conditions resulting in negative changes in potential. These anodic measured potentials after collector addition could be due to unstable xanthate species formed on both mineral surfaces.

Figure 1 suggests that the presence of $\text{S}_2\text{O}_3^{2-}$ ion resulted in the lowest xanthate–chalcopyrite interactions, and that the extent of interaction decreased with increasing ionic strength. Figure 2 indicates that a similar effect was observed for xanthate–galena interactions in $\text{S}_2\text{O}_3^{2-}$ ion solution. A similar study by Mhonde, et al. [19] found that the presence of tetrathionate ions, which are known to oxidize to thiosulphate ions, significantly decreased xanthate–chalcopyrite and xanthate–galena interactions, and that this deleterious

effect increased with increasing ionic strength. The authors attributed this to the formation of stable metal–thiolate complexes that passivated the mineral surfaces and prevented collector adsorption. These authors also found that the presence of thiosalts was especially detrimental to xanthate–galena interactions, which is corroborated in the current study.

Although Figure 2 indicates that MgCl_2 and MgSO_4 had critical concentrations at 3SPW, after which the extent of xanthate–galena interactions decreased, it is evident that increasing the ionic strengths of all the salts, except $\text{Na}_2\text{S}_2\text{O}_3$, decreased the extent of collector–mineral interaction after xanthate addition. This finding is in line with several studies that have previously shown that the presence of accumulating ionic species such as Mg^{2+} , SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ hinders collector adsorption [7,8,10,22].

In summary, increasing the concentration of the ions of interest decreased the extent of xanthate–galena interactions. The effect of changing water quality on xanthate–chalcopyrite interactions were less consistent with salts such as $\text{Na}_2\text{S}_2\text{O}_3$ improving them, while the effect of the other salts with changing ionic strength was variable. The $\text{S}_2\text{O}_3^{2-}$ ion was found to be the ion of interest that was the most significantly detrimental to collector–mineral interactions for both minerals. This hindrance of collector adsorption by ionic species can manifest in different ways. Some ions are active on the mineral surface and thus reduce the number of active sites available for collector adsorption, while other ions form precipitates that passivate the mineral surface, thus limiting collector–mineral interactions.

3.2. Microflotation Responses of Minerals

Although previous investigations have shown that rest potential measurements can be a useful tool to study collector–mineral interactions with changing water quality [19,36,37,42], it is important to conduct floatability tests such as microflotation measurements to demonstrate the effect of changing water quality on flotation performance. In froth flotation, mineral floatability is strongly dependent on collector adsorption, which has been shown to be affected by the presence of ionic species [7,8,10,22–24].

Apart from galena in $\text{Na}_2\text{S}_2\text{O}_3$ solution, the cumulative recoveries at the end of 20 min of flotation time for both minerals studied, regardless of changing water quality, were greater than 90%. For galena in $\text{Na}_2\text{S}_2\text{O}_3$, the cumulative recoveries were no greater than 35%. Therefore, the cumulative recoveries at the end of flotation time are not shown, rather flotation recovery in the first 2 min of microflotation were used to determine the impact of changing water quality on floatability by single salt variation.

Figure 3 shows the initial chalcopyrite recoveries with changing water quality. This figure indicates that the initial chalcopyrite recoveries in NaCl increased with increasing ionic strength, where an increase from 1SPW to 10SPW improved the initial recovery by about 15%. Similarly, the initial chalcopyrite recoveries yielded by Na_2SO_4 showed an increase of about 10% when the ionic strength was increased from 1SPW to 3SPW, 5SPW, and 10SPW. MgCl_2 and MgSO_4 also produced their lowest initial chalcopyrite recoveries at 1SPW. This indicates that, although the relationship between ionic strength and initial chalcopyrite recovery was not linear for these salts, it can be said that higher ionic strengths yielded greater initial recoveries in NaCl , MgCl_2 , MgSO_4 and Na_2SO_4 . This is in keeping with literature findings, where increasing the ionic strength likely compressed the electrical double layer which destabilized the mineral–air and air–water interfaces resulting in faster bubble particle attachment [46]. Additionally, previous studies have suggested that increasing the concentration of ions such as Cl^- and SO_4^{2-} inhibits bubble coalescence which improves solids recovery [47,48].

MgSO_4 had a critical concentration at 5SPW; the recovery increased with increasing ionic strength from 58.4% to 79.4% between 1SPW and 5SPW but decreased to 70.1% at 10SPW. This critical concentration effect has been observed by Dzingai, et al. [49] who studied the effects of ions in recirculated water on flotation performance. The authors found that the critical concentration of Ca^{2+} ions in synthetic plant water used to treat low grade Cu–Ni–PGM ore was 400 ppm, beyond which the flotation performance of copper was negatively affected. It is worth noting that this critical concentration effect was not

observed in MgCl_2 and Na_2SO_4 bearing waters, indicating that it is possibly a combined effect of the Mg^{2+} and SO_4^{2-} ions, or perhaps the conditions of this study did not fall under the critical concentrations of the other salts.

A direct correlation between changing ionic strength and chalcopyrite initial recovery was observed in $\text{Na}_2\text{S}_2\text{O}_3$ water with the chalcopyrite recoveries decreasing linearly with increasing ionic strength. This means that a longer residence time would be required to achieve high cumulative recoveries when chalcopyrite is floated in the presence of the $\text{S}_2\text{O}_3^{2-}$ ion. Overall, from Figure 3 it is evident that the relationship between ionic strength and chalcopyrite recovery is not consistent across all the salts and, therefore, depends on the ions present.

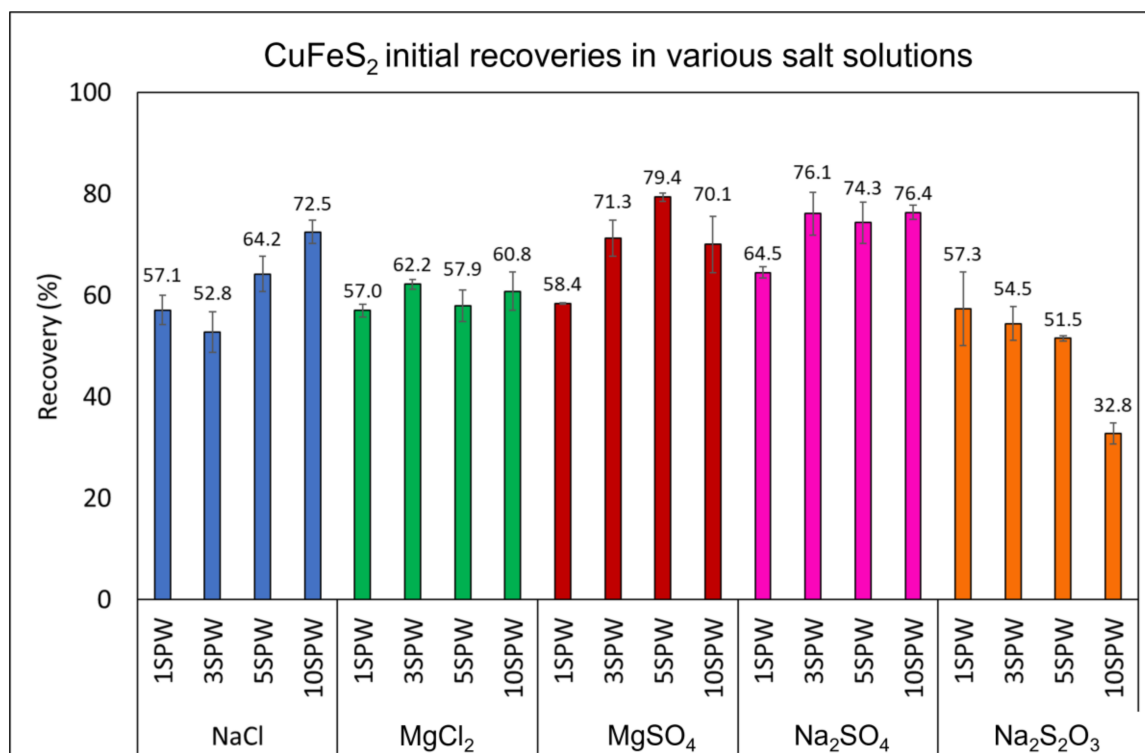


Figure 3. CuFeS_2 1st concentrate recovery in single salt solutions at varying ionic strengths.

The initial galena recoveries in various salts with changing ionic strength are shown in Figure 4. It can be observed that the galena initial recoveries only had a direct correlation with changing ionic strength in the MgSO_4 solution, as the recoveries increased linearly with increasing ionic strength. The rest of the salts did not exhibit this linear relationship. NaCl and MgCl_2 yielded their highest initial galena recoveries at 1SPW, which indicates that increasing the ionic strengths of these salts negatively affected galena floatability. Contrastingly, Na_2SO_4 yielded its lowest initial galena recoveries at 1SPW, indicating that increasing the ionic strength of this salt improved galena floatability. Figure 4 also shows that Na_2SO_4 exhibited a critical concentration at 5SPW, after which the galena recovery decreased. A similar study by Bulut and Yenil [50] also observed this critical concentration effect for galena recovery in the presence of the SO_4^{2-} ion. $\text{Na}_2\text{S}_2\text{O}_3$, on the other hand, consistently yielded dramatically lower initial recoveries than the other salts. This is evidently an effect caused by the presence of the $\text{S}_2\text{O}_3^{2-}$ ion, as the recoveries achieved using Na_2SO_4 were significantly higher.

It is clear from Figures 3 and 4 that the $\text{S}_2\text{O}_3^{2-}$ ion had an especially adverse effect on both chalcopyrite and galena floatability, as well as their interactions with SEX. Figure 3 indicated that the chalcopyrite initial recoveries in $\text{Na}_2\text{S}_2\text{O}_3$ decreased significantly with increasing ionic strength. A similar trend was observed by Petrus, et al. [51] where the

presence of the $S_2O_3^{2-}$ ion depressed chalcopyrite, even in the presence of dithiophosphate. The authors also observed that this depressant effect was strongly dependent on the pH.

Literature suggests that the mechanism behind mineral depression in the presence of thiosalts is the formation of metal and xanthyl thiosulphate complexes. Petrus, et al. [51] suggested that the mechanism behind the depression of chalcopyrite by $Na_2S_2O_3$ in alkaline conditions is the formation of a copper thiosalt complex, $[Cu(S_2O_3)_2]^{3-}$, which passivates the mineral surface and hinders collector adsorption. Another study by Mhonde, et al. [19] stated that the presence of thiosalts not only forms xanthyl thiosulphate complexes, but reduces the amount of residual xanthate available to induce hydrophobicity on the mineral surface as well. Another study echoes this observation by suggesting that dioxanthogen decomposes in the presence of thiosulphate ions to form xanthate and xanthyl thiosulphate [52]. The depression of both minerals in the presence of $S_2O_3^{2-}$ ions can therefore be attributed to this simultaneous consumption of dioxanthogen and the formation of passivating species. The consumption of xanthate and dioxanthogen suggests that higher collector dosages would be required to induce sufficient hydrophobicity on the mineral surfaces in the presence of thiosalts.

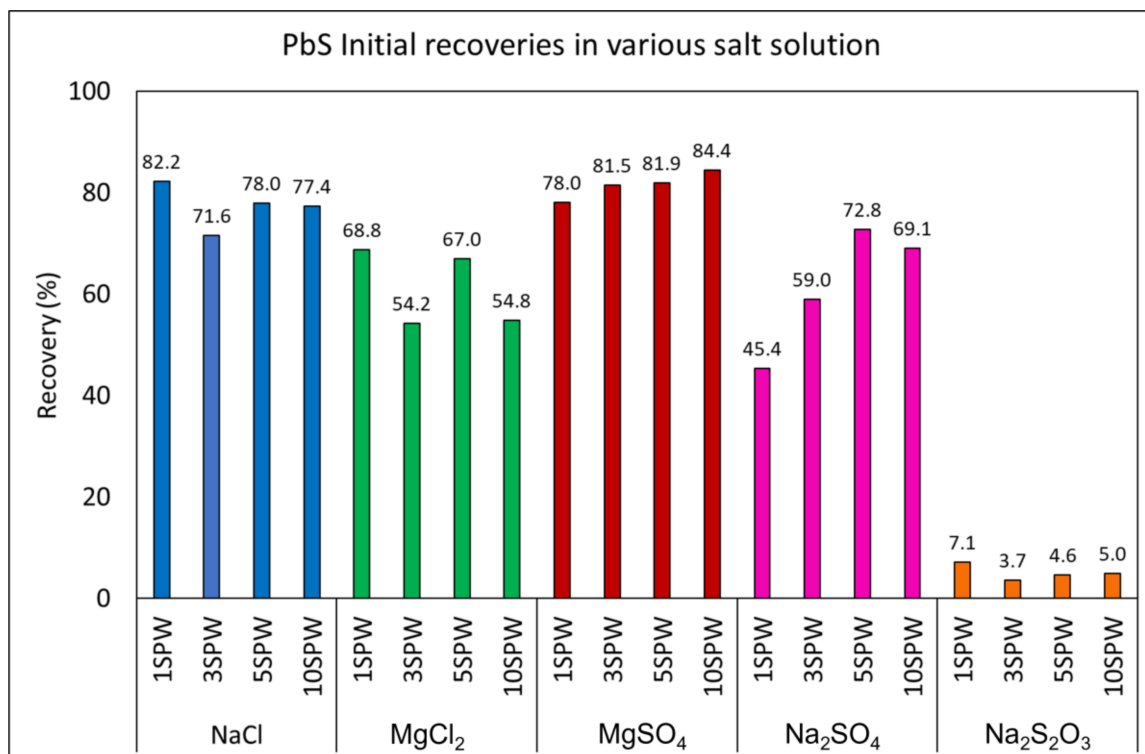


Figure 4. PbS 1st concentrate recovery in single salt solutions at varying ionic strengths.

3.3. Potential vs. Floatability

After conducting rest potential as well as microflotation tests, it is apparent that a direct correlation between rest potential trends and floatability cannot be drawn, as shown by Figure 5. This is because rest potential measurements do not consider other flotation subprocesses that affect mineral floatability, such as bubble–particle attachment. Results suggest that this technique cannot be considered in isolation of the other flotation sub-processes, but can be used as an indicator of the effect of solution conditions on the hydrophobicity of a mineral particle. In effect, the rest potential of a mineral can be used to identify the solution, Eh and pH conditions, or domains in which hydrophobicity will be induced. Considering Figure 5 and comparing Figures 1 and 3 for chalcopyrite and Figures 2 and 4 for galena, it can be observed that as long as the change in rest potential is above a minimum value, particle floatability can take place. In the case of

chalcopyrite minimal, changes in rest potential positively or negatively in the presence of Na_2SO_3 resulted in floatability of the mineral, although this is on average lower floatability compared to chalcopyrite in the presence of the other salts. For galena, Figure 5 indicates strongly negative potential changes that are complemented by very low floatability in terms of recovery, also shown in Figure 5, suggesting that the rest potential for the mineral has crossed a threshold for which hydrophobicity will not take place.

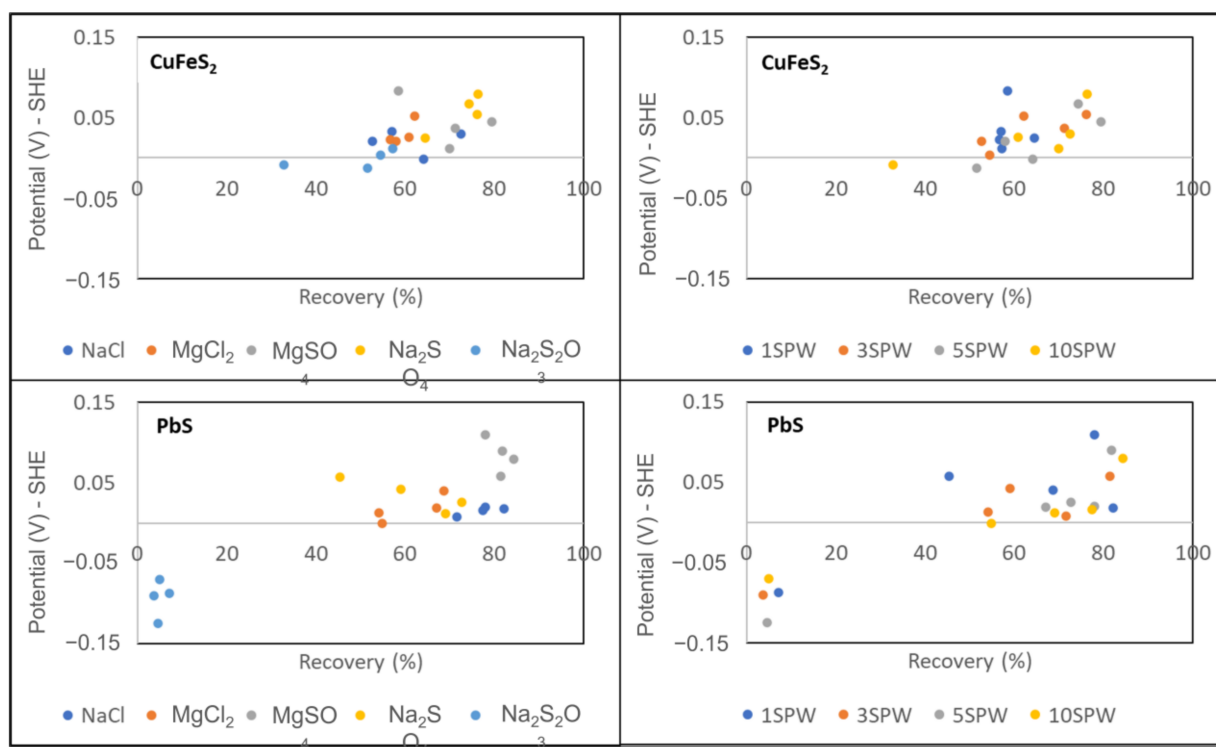


Figure 5. Plots of potential difference vs. initial recoveries for chalcopyrite (top) and galena (bottom) distinguishing between salt type (left) and water type (right).

4. Conclusions

In summary, the highest initial galena recoveries in NaCl , MgCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ were achieved at 1SPW, indicating that, even though the correlation was not linear, the galena initial recoveries in these salts decreased with increasing ionic strength. The highest chalcopyrite initial recoveries in NaCl , MgCl_2 and Na_2SO_4 were achieved at 10SPW, indicating that increasing the ionic strength improved chalcopyrite floatability. This suggests that the impact of changing ionic strength depends on the mineral under consideration as well as the ions present. Apart from the impact of the $\text{S}_2\text{O}_3^{2-}$ ion on the floatability of chalcopyrite and galena, predictions made by rest potential measurements regarding the extent of xanthate–mineral interactions with changing water quality did not translate well into actual flotation performance. This was probably because rest potential measurements do not consider other flotation sub-processes that affect mineral floatability, such as bubble–particle attachment. The introduction of other parameters, such as ore mineralogy, only stands to further complicate matters. Rest potential measurements had the potential to be a quick and easy technique to predict the effect of changing water quality on sulphide mineral flotation performance.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data is stored within the internal UCT CMR data repository.

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