

Article

# Considering Specific Ion Effects on Froth Stability in Sulfidic Cu-Ni-PGM Ore Flotation

Malibongwe S. Manono \*  and Kirsten C. Corin 

Centre for Minerals Research, Department of Chemical Engineering, Faculty of Engineering & the Built Environment, University of Cape Town, Rondebosch, Cape Town 7700, South Africa; kirsten.corin@uct.ac.za  
\* Correspondence: malibongwe.manono@uct.ac.za; Tel.: +27-21-650-1679

**Abstract:** The mining and mineral processing of Cu-Ni-PGM sulfide ores in South Africa occurs in semi-arid regions. The scarcity of water resources in these regions has become one of the biggest challenges faced by mineral concentrators. As a result, concentrators are forced to find ways through which they can manage and control their water usage. The recycling and re-use of process water in mineral concentration plants has therefore become a common practice. This practice is beneficial in that it reduces reliance on municipal water and harnesses compliance to stringent environmental regulations on freshwater usage. This approach also offers a better response to the Sustainable Development Goals (SDGs) for the mining industry, as water and its preservation form part of the SDGs. This practice could, however, be somewhat concerning to a process operator because recirculated water often has higher concentrations of ions compared to fresh or potable water. This is because an unintended change in the process water quality may affect critical aspects of flotation such as the stability of the froth. This issue has led to the need for both the mining industry and researchers in the field to find the ions in process water that have the greatest impact on froth stability. Thus, the authors of this study investigated the effects of various ions common in the process water of a typical Cu-Ni-PGM ore on froth stability using a 3 L bench scale flotation cell. Solids and water recoveries were used as proxies for froth stability. These were further complemented by bubble size, water recoveries, foam height, and dynamic foam stability from two-phase flotation systems. A two-phase foam study resulted in observations that supported findings from a three-phase study. Generally, single salt solutions containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions resulted in higher water recoveries both in the two-phase foam and three-phase froth studies, increases in foam heights and dynamic foam stability, and a decrease in bubble size compared to the solutions that contained  $\text{Na}^+$ .  $\text{SO}_4^{2-}$  also resulted in increased foam stability compared to  $\text{Cl}^-$  and  $\text{NO}_3^-$ . These results showed that the divalent inorganic electrolytes— $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ —were more froth- and foam-stabilizing than the monovalent inorganic electrolytes— $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{Na}^+$ . This finding was in agreement with previous research. The findings of this study are deemed crucial in the development of a process water management protocol in sulfidic Cu-Ni-PGM ore concentrators. However, more comparative three-phase froth stability tests are needed as subjects of future investigative work to further ascertain specific ion effects on froth stability in sulfide ores.

**Keywords:** bubble diameter; inorganic electrolytes; flotation; froth stability; water quality



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## 1. Introduction

### 1.1. Measures of the Stability of the Froth

Flotation, as a physicochemical separation process, consists of two distinct zones: the pulp zone where mineral recovery takes place and the froth zone where concentrated mineral particles are separated from the bulk [1]. The pulp zone, which promotes bubble–particle collision, is crucial in flotation because within the pulp, valuable minerals of a certain hydrophobicity are attached to air bubbles and are ultimately transported to the surface while gangue minerals with a measurable level of hydrophilicity are inhibited from

attaching to the bubbles. These gangue minerals are not recovered to the concentrate by “true flotation”; instead, they are removed into the tailings or recovered into the concentrate by non-selective transport mechanisms, namely entrainment and entrapment. It is therefore important to limit these two mechanisms [2,3].

The froth zone is crucial in ensuring maximum froth recovery, in that there needs to be a certain level of froth stability to ensure the maximum recovery or collection of the particles recovered from the pulp zone [1,3]. The dynamics of the froth zone, however, are controlled by the flow of air bubbles from the pulp through to the froth surface and by bubble coalescence. Froth stability is therefore determined by the ability of the air bubbles to resist coalescence and bursting, so a more stable froth is characterised by a decrease in bubble coalescences [1].

Several studies have shown that froth stability plays a major role in flotation performance, but there is no single specific criterion to quantify froth stability [4–13]. There are, however, many parameters available to indicate froth stability; Farrokhpay [8] listed the following parameters for use as indicators for froth stability: froth half-life time [14,15], maximum froth equilibrium height [4,16,17], bubble growth across the froth phase [18], air recovery, amount of solids loaded onto the bubbles [17], froth velocity, and froth rise velocity [4,19]. Most of these parameters are affected by a plant’s operating conditions such as ore mineralogy, reagents chemistry, and air velocity. Therefore, any working criterion for the best froth stability and therefore froth flotation performance would need to account for major operating fluctuations in order to develop froth control strategies. Water quality has become one such fluctuating variable in most sulfides concentrators, especially in water-scarce regions. Previous research has shown that the rupturing of rising bubbles results in the falling back of solid mineral particles and liquid film drainage, so the amount of water recovered in the flotation cell concentrate launder can be used to quantify froth stability. This research led to the proposal that the larger the amount of water recovered, the more stable the froth. Similar proposals have been made by several researchers, as mentioned in Farrokhpay [8].

Multiple methods have been developed to assess foam and or froth stability [8,16]. They are generalized into dynamic and static tests, but there are questions regarding their consistency since the presence of solids affects foam stability. Foam refers to a two-phase system comprising air bubbles and liquid, while froth refers to a three-phase system consisting of air bubbles, liquid particles, and solid particles [8]. Foam is the dispersion of gas bubbles stabilised by surfactants that adsorb onto the liquid–gas interphase and are separated by thin liquid film [8,20]. Foam stability is linked to liquid drainage in the foam and the rupture of liquid films [8].

Dynamic tests are conducted for a system that is in a dynamic equilibrium between the rates of formation and of decay of foam. Static tests are conducted by allowing the foam to drop from the maximum height without regeneration by agitation or air input. The dynamic test is the most used test in flotation since it is believed to closely approximate real flotation system dynamics [4,16,17]. The dynamics in flotation are such that air is continually introduced into the pulp, generating bubbles that move from the pulp zone to the interface between the pulp and froth zones while the liquid drains downwards; accordingly, the quality of the formed froth varies with height, and the top of the froth can reach a breaking condition that leads to the collapse of the top layer [12]. One other advantage of the dynamic test is that it is reproducible, accurate and convenient to apply [16].

Bikerman [21] originally proposed a dynamic froth stability column for non-overflowing froth columns, and this technique has been used, modified and applied in many areas. One such application was on mineral flotation on a laboratory scale by Barbian et al. [16] for measuring the froth performance. With this set-up, measurements are carried out using a vertical column that is inserted through the froth to far enough below the pulp–froth interface in the flotation cell to avoid froth leakage from the bottom. The froth rises inside the column, and froth height ( $H$ ) is measured as a function of time,  $t$ , until the equilibrium maximum height ( $H_{max}$ ), which is measured using pulp–froth interface as a reference,

is achieved. The equilibrium maximum height is dependent on the froth stability and operating conditions. It is worth noting that at the equilibrium height, the rates of growth and bursting are equal. This method was well-described by Barbian et al. [4] and allows for the determination of, e.g., the dynamic foam stability factor, the froth rise rate, the froth rise velocity, and the froth retention time.

In linking froth height to froth flotation performance, industries have experienced increases in grade and recovery with increases in froth height, though recovery may also decrease with increasing froth height [4,8,16,17]. Froth height is one of the factors that can be changed to maximise flotation performance. As previously discussed, the literature suggests that there are many other correlations and parameters that can be used to quantify froth stability, and these continue to be topics of future investigative research.

### *1.2. Current Understanding into Electrolytes on Froth Stability*

It is known that pulp chemistry in mineral flotation has important roles in not only froth stability but also mineral recoveries and grades as a result of interactions taking place at the air–water, air–mineral, and water–mineral interfaces [3,22–33]. These interactions may affect critical aspects of flotation such as the hydrophobicity or hydrophilicity of mineral particles, bubble coalescence, froth stability, and entrainment. Understanding reagent or chemical effects on any of these critical aspects of flotation can be a complex challenge because these various interfacial interactions are interrelated (e.g., any effects on the hydrophobicity of mineral particles may have serious implications on froth stability, which would also need to be studied so as to have a holistic view of how certain parameters—whether chemical, physical or operational—affect flotation performance) [34]. It is thus argued that any change effected by flotation control variables on the pulp chemistry could bring about significant step-changes to flotation performance.

In general, until recent years, the effect of ions during flotation on mineral recovery, especially on complex and polymetallic sulphide ores, was not well-documented in the literature [35,36]. However, the effect of calcium and magnesium ions on a select few sulphide minerals such as pyrite and sphalerite was reported on as early as the 1980s [37,38]. The sources of ions in flotation cells are mainly salts dissolved in the flotation water and other flotation reagents such as pH modifiers. It was reported that an apparent consequence of a high salt content is that a flotation circuit can operate without the addition of a frother [39]. This observation was in agreement with previous evidence suggesting that flotation in saline water presented in lower reagent consumption [40]. It is speculated that salts could have some similar capabilities as frothers, such decreasing bubble size and consequently increasing froth stability due to a decrease in surface tension that prevents bubbles from coalescing [39]. There are, however, significant differences between inorganic salts and frothers. High salt concentrations are required for coalescence inhibition. Previously, it was reported that inorganic ions are usually not able to form froth (foam) in a two-phase system [41]. It was reported that only in the presence of hydrophobic particles could salt solutions form a stable froth since salts are categorised as surface-inactive agents whereas frothers are surface-active agents [41]. However, recent studies have shown that inorganic ions, despite being surface-inactive agents, are easily able to form a stable foam in a two-phase system [42]. These findings agree with those of Craig et al. [43], who showed that although salts are surface-inactive surfactants, their addition to solutions containing frothers brought about great reductions in surface tension and bubble coalescence than when the frothers were added to solutions of de-ionised water. Researchers have attempted to determine a transition concentration at which salts inhibit bubble coalescence [43,44]. An important similarity between frothers and salts is the ability to produce bubbles with small size. However, bubble size is not the primary factor causing changes in bubble coalescence, as bubble coalescence mainly occurs at the frit surface where the momentum of the gas stream is high and can overcome the resistance of liquid film between the gas–liquid interfaces [45,46]. Evidently, the gas velocity is the primary factor in determining and or

inhibiting bubble coalescence. Zieminski and Whittemore [47] showed that many ions of high valence have a greater effect on hindering bubble coalescence than monovalent ions.

Recently, it has been acknowledged that water should be considered a reagent in flotation, and as such, its quality is an important factor to consider because it may alter the pulp chemistry and thereby affect the froth phenomena and overall flotation performance [38,48–52]. Although flotation research in the past has considered electrolyte–reagent–mineral interactions on mineral hydrophobicity and therefore pulp chemistry, there seems to have been very little or no consideration of the consequences and implications that such interactions would have on the froth phase despite existing evidence in literature on the impact of inorganic electrolytes on gas dispersion properties [43,52,53].

The research gap begs the question of how reagents' chemistry and the tripartite electrolyte–reagent–mineral interactions could affect the bubble size and water recoveries within flotation and other above-mentioned froth-stability-determining factors. The authors of this paper argue that meaningful research into water quality in flotation should consider this identified gap. Thus, building on the work published by Manono et al. [42], in which the effects of increasing ionic strength of synthetic plant waters on gas dispersion properties were considered with the use of complex water matrices, the current study was aimed at decoupling specific ion effects in order to understand which ions are detrimental or beneficial for froth stability. It is known that certain electrolytes present in process water exhibit frother-like gas dispersion properties in that they inhibit bubble coalescence [10,42,54–58]. Castro et al. [56] reported that water with an increased concentration of electrolytes showed a significant degree of frothing ability, hence the need for more investigations into this topic.

A few investigative studies have been published in this regard. Biçak et al. [59] suggested that the sensitivity of flotation to water quality is such that an accumulation of both organic and inorganic ions in the process water may also affect froth stability. Corin and Wiese [49] also reported that process water quality, specifically that of increased ionic strength, affected froth stability in that the frother dosage and ionic strength of plant water could be interchangeably used to increase froth stability, proving that ions in process water could cause the required step changes in froth stability and flotation performance without further increases in the dosage of the frother. These effects were supported Quinn et al. [39], who showed that certain concentrators processing sulphides in Western Australia and some parts of Chile did not add frothers in their flotation circuits due to the high salinity (from ~40,000 to 60,000 mg/L) of their process water and yet achieved the desired froth stability.

An earlier study conducted at the University of Cape Town (UCT) by Barker [37] showed that divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in solution resulted in an increase in the kinematic viscosity compared to the monovalent  $\text{Na}^+$  and  $\text{K}^+$ , and froth stability concurrently increased. As a mechanism, Barker [37] proposed that the increase in the kinematic viscosity caused an increase in the liquid film thickness of the bubble, causing a slower drainage and thus a more stable froth. Biçak et al. [59] corroborated Barker's proposal by showing that at high electrolyte concentrations, bubbles became more stable and did not coalesce even in the absence of a frother. A similar investigation carried out by Kurniawan et al. [60] on froth properties in coal flotation, using  $\text{MgCl}_2$ ,  $\text{NaCl}$  and  $\text{NaClO}_3$  solutions in the absence and presence of Dowfroth 250, showed that in the presence of Dowfroth 250,  $\text{MgCl}_2$  led to the generation of smaller bubbles, more stable froths, and higher recoveries than  $\text{NaCl}$ .  $\text{NaClO}_3$ , however, resulted in the lowest froth stability and mineral recoveries. Their findings could be linked to the differences in the cation–anion combinations for the three different single salts used.

On the mechanism of the impact of ions at the air–water interface and froth stability, Biçak et al. [59] concluded that the rate of coalescence of air bubbles decreased due to either the frother molecules absorbed at the air–water interface or the presence of a stable liquid film layer on the surface of the bubbles. Biçak et al.'s work was in agreement with that of Yousef et al. [61], who stated that flotation plants that use seawater and process water with high salinity are likely to experience voluminous and stable froths due to the frothing properties of dissolved ions. These findings corroborated the work by Quinn et al. [39]. On

the impact of specific ions in process water, Biçak et al. [59] argued that dissolved metal ions and sulphide oxidation products, mainly in the form of  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ , had the most influence on both froth stability and surface chemistry. It was then hypothesized that increased froth stability in concentrated electrolytes was caused by an increased stability of the water layer between air bubbles [59]. Corin et al. [48] reported higher solids and water recoveries in increasing ionic strengths of synthetic plant water and suggested that these were caused by increased froth stability. These results supported the findings of Schwarz and Grano [37] and Tao et al. [38], who linked water recovery with froth stability in flotation as more stable froths were accompanied by an increase in water recovery.

Bournival et al. [62] investigated NaCl and MIBC as bubble coalescence inhibitors in relation to froth stability. It was found that NaCl at higher concentrations was as effective as MIBC in preventing bubble coalescence in a dynamic environment. The unbundling of such an effect may not be easy, as Castro et al. [56] purported that “the coalescence of bubbles in flotation is a particularly complex phenomenon especially when it takes place in saline or seawater, since both a surface-active compound (frother) and a surface-inactive compound (inorganic salt) are able to stabilise bubbles against coalescence and therefore reduce bubble size giving rise to stable froths”. Castro et al. [56] were preceded by Grau et al. [54] and Laskowski et al. [63], who showed that bubble coalescence could be completely prevented at frother concentrations exceeding a certain concentration known as the critical coalescence concentration (CCC). Laskowski et al. [62] also showed that inorganic electrolytes inhibited bubble coalescence and that inorganic electrolytes had a critical concentration beyond which their ability to inhibit coalescence was exhausted. Such an idea was not entirely new, as Zieminski et al. [64] and Lessard and Zieminski [44] had previously proposed such a phenomenon with specific salts that they had examined. A mechanism to the interaction of frothers and inorganic electrolytes at the air–water interface had been proposed by Castro et al. [56] after it was seen that increasing frother concentration resulted in a decrease in the solution surface tension, as can be expected for a surface-inactive agent, but they more interestingly showed that the ability of a frother to decrease the surface tension of a solution was increased in the presence of a coalescence-inhibiting inorganic electrolyte.

### 1.3. Gap in the Literature and Basis for Future Studies

Based on the presented literature, several mechanisms have been proposed to better understand the action of inorganic electrolytes in flotation. These range from the action of inorganic ions in (i) disrupting the hydration layers surrounding the particles and enhancing bubble–particle attachment, (ii) reducing the electrostatic interactions between bubbles and particles, and (iii) increasing the charge on the surface of the bubbles to prevent primary bubble coalescence [37,65]. However, as previously mentioned by Manono et al. [45], there is little or no information in the literature on the action of electrolytes on bubble coalescence and froth stability in relation to the action of ions on interactions occurring in the pulp phase that affect valuable mineral hydrophobicity, the hydrophilicity of gangue, and the resulting impact on froth stability. Such research should bring about a better understanding of the effects that the tripartite electrolyte–reagent–mineral interactions occurring in the pulp phase have on the froth phase phenomena. Thus, research is required to consider the impact of common process water ions on the pulp chemistry and froth stability in Cu-Ni-PGM sulphide ores, since recent work showed that for such ores, many of the effects seen have more significant implications on gangue management rather than on the recovery of sulfides due to the ores’ sulfides content being relatively low compared to gangue [66]. The management of gangue against varying flotation process control measures requires an understanding of how process variables affect the stability of the froth, as the stability of the froth has grave implications regarding whether the operators limit or promote entrainment [67,68].

Current understanding suggests that investigative research into the influence of each specific process water constituent on flotation could result in both technical and financial

benefits, i.e., costs could be saved in process water treatment if research proves that flotation circuits could still perform at their best in recycled process water containing constituents that would have previously been removed (as long as key aspects of flotation such as the froth behaviour are well-understood and controlled against varying process water quality). This would allow for an implementation of closed water circuits in flotation processes and a contribution to the sustainability of the flotation process if flotation process water is screened for inorganic electrolytes that would be detrimental to the process. It is proposed that if such implementation were to take place, there would be minimal process water discharge to the environment, minimal make-up water requirements, a reduction in process water treatment before reuse, savings in treatment costs, and a reduction in fresh reagent dosing. Thus, the aim of this study was to ascertain whether there are ions in flotation with dominant effects on froth stability using various single salts such as CaCl<sub>2</sub>, CaNO<sub>3</sub>, CaSO<sub>4</sub>, MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, NaCl, NaNO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>. Froth stability was examined using a three-phase batch flotation system with, solid and water recoveries being used as proxies for froth stability. To complement the three-phase study, gas dispersion properties were measured using two-phase batch flotation and column studies to generate experimental data on bubble size, water recoveries, foam height and foam collapse time.

## 2. Materials and Experimental Methods

### 2.1. Water Preparation

Synthetic plant water (hereafter referred to as SPW) and various single salt solutions of the ionic strength and compositions shown in Table 1 were prepared. The synthetic plant water and single salt solutions comprised de-ionised water and inorganic salts of analytical grade supplied by Merck to ensure that the water contained the required total dissolved solids (TDS) and ionic strength. The ionic strength ( $I$ ) was calculated using Equation (1). The preparation of the single salts was such that these solutions had a fixed ionic strength equivalent to that of SPW (0.0213 M). It is worth mentioning that the composition of synthetic plant water was based on the onsite process water quality of a typical Cu-Ni-PGM ore concentrator [3].

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (1)$$

where  $I$  is the total ionic strength,  $a$  is a measure of the electrical intensity of a solution,  $c_i$  represents the concentration of the  $i$ th species for an ideal or dilute solution, and  $z_i$  is the ionic valency of the  $i$ th species in the solution, the summation being taken over all positive and negative ions ( $n$ ) present in solution [69].

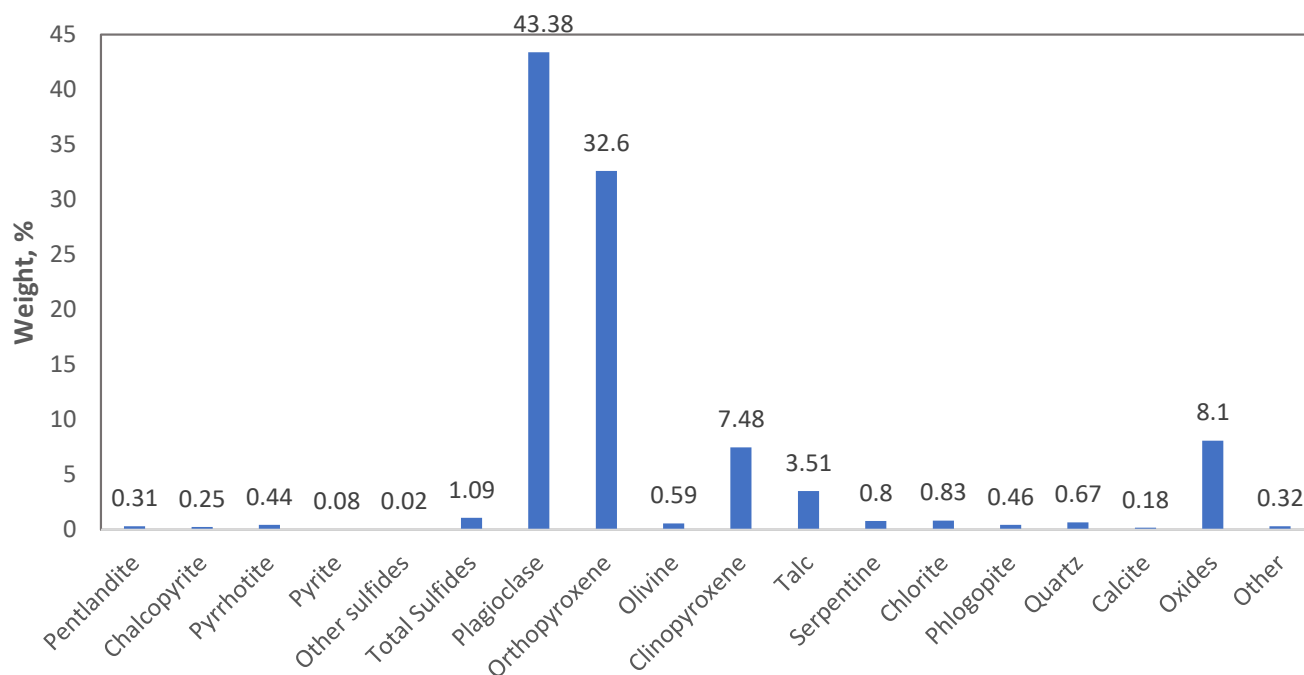
**Table 1.** Chemical compositions of synthetic plant water and the various single salt solutions tested in this study.

Water Type	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	CO <sub>3</sub> <sup>2-</sup> (mg/L)	TDS (mg/L)	Ionic Strength [M]
SPW	80	70	153	287	240	176	17	1023	0.0213
NaCl	-	-	490	755	-	-	-	1245	0.0213
Na <sub>2</sub> SO <sub>4</sub>	-	-	326	-	682	-	-	1009	0.0213
NaNO <sub>3</sub>	-	-	490	-	-	1321	-	1810	0.0213
CaCl <sub>2</sub>	285	-	-	503	-	-	-	788	0.0213
CaSO <sub>4</sub>	213	-	-	-	512	-	-	725	0.0213
Ca(NO <sub>3</sub> ) <sub>2</sub>	285	-	-	-	-	880	-	1165	0.0213
MgCl <sub>2</sub>	-	173	-	503	-	-	-	676	0.0213
MgSO <sub>4</sub>	-	129	-	-	512	-	-	641	0.0213
Mg(NO <sub>3</sub> ) <sub>2</sub>	-	173	-	-	-	880	-	1053	0.0213

### 2.2. Ore Preparation and Milling

A sulfidic Cu-Ni-PGM containing ore from the Merensky Reef found within the Bushveld Igneous Complex of South Africa, with the mineralogical composition shown in

Figure 1, was used throughout the bench scale flotation tests. It can be seen from Figure 1 that only ~1.09% constituted sulphide minerals and the rest were gangue, with talc (which is a naturally floatable gangue and therefore problematic for flotation) notably comprising 3.51% of this ore. A bulk sample of the selected ore was crushed, riffled, and split into 1 kg samples using a rotary splitter. The 1 kg ore samples were milled in a stainless-steel tumbling mill at 66% solids in the presence of synthetic plant water or a single salt solution with Sodium Iso-Butyl Xanthate (SIBX) as the collector dosed into the mill at a dosage of 150 g/t. The addition of synthetic plant water or a single salt solution was such that after milling, a target grind of 60% passing 75  $\mu\text{m}$  was attained. This grind size is typical of industrial concentrator rougher circuits for Merensky ores. The grinding media used inside the tumbling mill were 20 rods of stainless steel with varying diameters: 6  $\times$  25 mm, 8  $\times$  20 mm, and 6  $\times$  16 mm.



**Figure 1.** QEMSCAN modal composition of sulfides and gangue minerals of the selected Merensky ore.

### 2.3. Batch Flotation

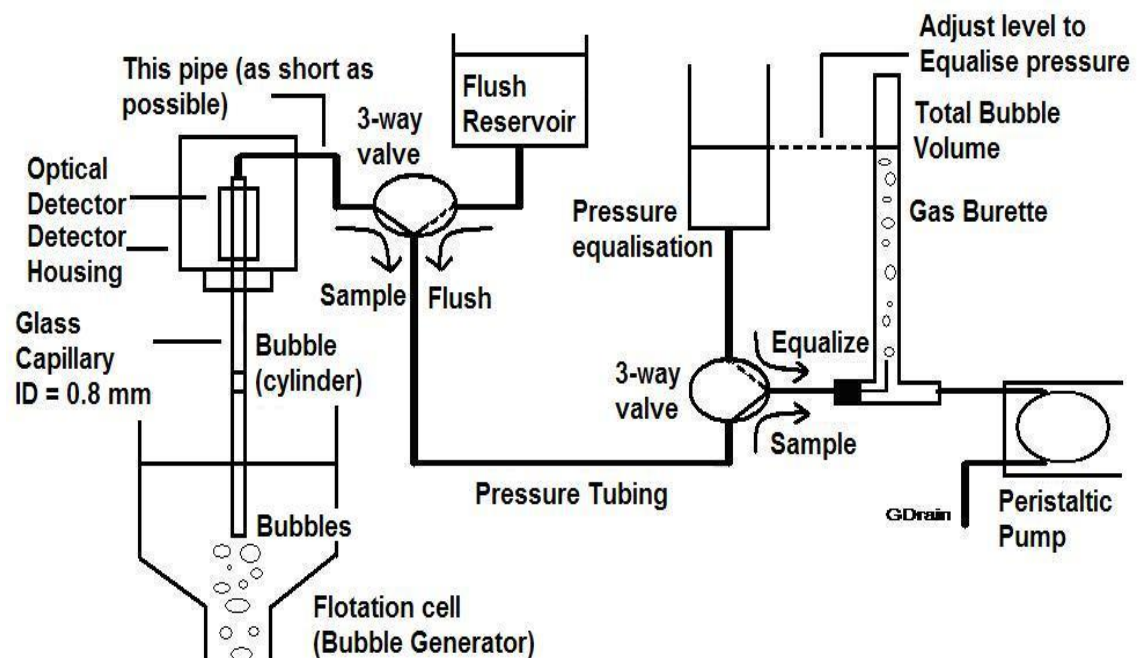
For the three-phase batch flotation procedure, after milling, the milled Merensky ore slurry was transferred to a 3 L UCT Barker flotation cell, and the specific water or single salt solution under investigation was added to the cell to ensure a pulp density of 35%. Then, the impeller was set to an agitation speed of 1200 rpm, and a feed sample was taken. DOW 200 frother at 40 g/t was allowed to condition for 1 min, after which air was introduced to the cell at 7 L/min. A constant froth height of 2 cm was maintained. The pH of the flotation experiments was measured and found to be ~9. This was unadjusted and uncontrolled because it was found to represent the acceptable and natural operating flotation pH for ores typical of the selected ore. Four concentrates were collected for 2, 4, 6, and 10 min, and they were scraped at 15 s intervals. At the end of flotation, a tails sample was taken. All feed, tail, and concentrate samples were filtered, dried, weighed, and analysed for S in the UCT Chemical Engineering Analytical Services Laboratory using an in-house Leco. Total S assays were conducted to determine the sulphide gangue fraction of the solids reporting to the concentrate because previous investigations showed strong correlations between froth stability and gangue recoveries, which is important for the management of gangue and the concentrate grade [66]. All tests were performed in duplicate for reproducibility. The two-phase batch flotation procedure was described by Manono et al. [42].

#### 2.4. Two-Phase Foam Column Procedure

Specific ion effects on foam stability were investigated using a two-phase foam column test rig. The test rig was discussed in detail by Manono et al. [42]. Two-phase foam column tests were conducted for various single salts in distilled water at pH 9, representing the pH at which the batch floats were conducted. These foam studies were conducted in the presence of a frother (DOW 200) at a dosage of 5 ppm. The pH was adjusted using a stock solution of NaOH to achieve the desired pH before the solution was added into the column, where the initial air–water interface height was measured. Air was pumped into the column at a flow rate of 2 L/min. This allowed for the development of the foam phase until an equilibrium height was reached. This equilibrium condition was reached after approximately 3 min for selected single salt solutions, namely  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ . The equilibrium condition is defined as the state at which the bubble collapse rate at the top of the foam is equal to the air flow rate through the sparger at the bottom of the column. Once equilibrium was reached, air was stopped and the foam collapse time (i.e., the time taken for the foam to collapse to the initial air–water interface) was immediately measured. All experiments were performed in duplicate to minimise error.

#### 2.5. Two-Phase UCT Bubble Size Analyser

The UCT Bubble Sizer (Randall et al. [70]), a schematic of which is shown in Figure 2 was used for all bubble sizing tests. This apparatus consists of a capillary tube that passes between two pairs of photo-cell-diode detectors. The detectors are mounted 5 mm apart at right angles to one another. Bubbles drawn up the capillary by vacuum are transformed into cylinders, so as they pass the detectors, a change in light intensity is monitored. This change occurs because of the different refractive indices and optical densities of the air–glass and liquid–glass boundaries. To obtain an accurate bubble size distribution, 3000 bubbles are sized in any one test. The bubbles are then drawn from the capillary into a burette so that the volume of bubbles can be determined [71].



**Figure 2.** A schematic representation of the UCT bubble size analyser (adapted from the work of Randall et al. [70] and Goodall [71]).

The bubble sizer was used with a 1 L glass column fitted with a frit in the base. This column was attached to a gas sparger to allow for the generation of bubbles. To study the effect of different ions in water, SPW and selected single salt solutions were used.

All solutions were set to the specified ionic strength in de-ionised water. For all tests, the addition of a frother (DOW 200) was kept constant at 5 ppm. Tests were conducted for 10–20 s each. A peristaltic pump was used to draw the samples through the capillary and into the measuring burette; this pump was set at 790 rpm. All bubble sizes measured were Sauter mean diameters. Bubble size measurements were repeated for each condition, and the results were shown to be reproducible. The reproducibility of this system was also demonstrated by Tucker et al. [72].

### 3. Results and Discussion

#### 3.1. Specific Ion Effects on Water Recoveries

Figure 3 shows clearly discernible differences in the water and gangue recoveries in various single salts, though sulphide recoveries remained constant despite changes in single salts. Therefore, it could be said that changes in the stability of the froth did not affect the flotation recovery of sulphides, as the amount of sulphides reporting to the concentrate was well within an average of ~6.5 g. SPW, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaNO<sub>3</sub> resulted in significantly lower water recoveries compared to the Ca<sup>2+</sup>- and Mg<sup>2+</sup>-bearing single salt solutions. Conversely, CaCl<sub>2</sub>, CaSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>, and Mg(NO<sub>3</sub>)<sub>2</sub> resulted in significantly higher water recoveries. It is worth mentioning that for Ca<sup>2+</sup>, Ca(NO<sub>3</sub>)<sub>2</sub> yielded lower water recoveries than CaCl<sub>2</sub> and CaSO<sub>4</sub>. A similar trend was observed with Mg<sup>2+</sup>, as Mg(NO<sub>3</sub>)<sub>2</sub> yielded lower water recoveries than MgCl<sub>2</sub> and MgSO<sub>4</sub>. SO<sub>4</sub><sup>2-</sup>, however, yielded larger water recoveries than Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in Ca<sup>2+</sup> and Mg<sup>2+</sup>. Furthermore, for Ca<sup>2+</sup> and Mg<sup>2+</sup>, gangue recoveries followed similar trends as water recoveries. However, Na<sup>+</sup>-containing salts resulted in higher gangue recoveries than Ca<sup>2+</sup> and Mg<sup>2+</sup>. This behaviour was not in line with the lower water recovery trend with Na<sup>+</sup> salts, as the lower water recoveries could be used to infer that the stability of the froth in Na<sup>+</sup> was somewhat poorer. Therefore, higher gangue content in Na<sup>+</sup> salts could be attributed to the poor passivation of gangue particles by monovalent cations, which was reported by Manono et al. [73], who showed that the zeta potential of talc and the coagulation of a Merensky ore were lower than when single salt solutions of Ca<sup>2+</sup> and Mg<sup>2+</sup> were used.

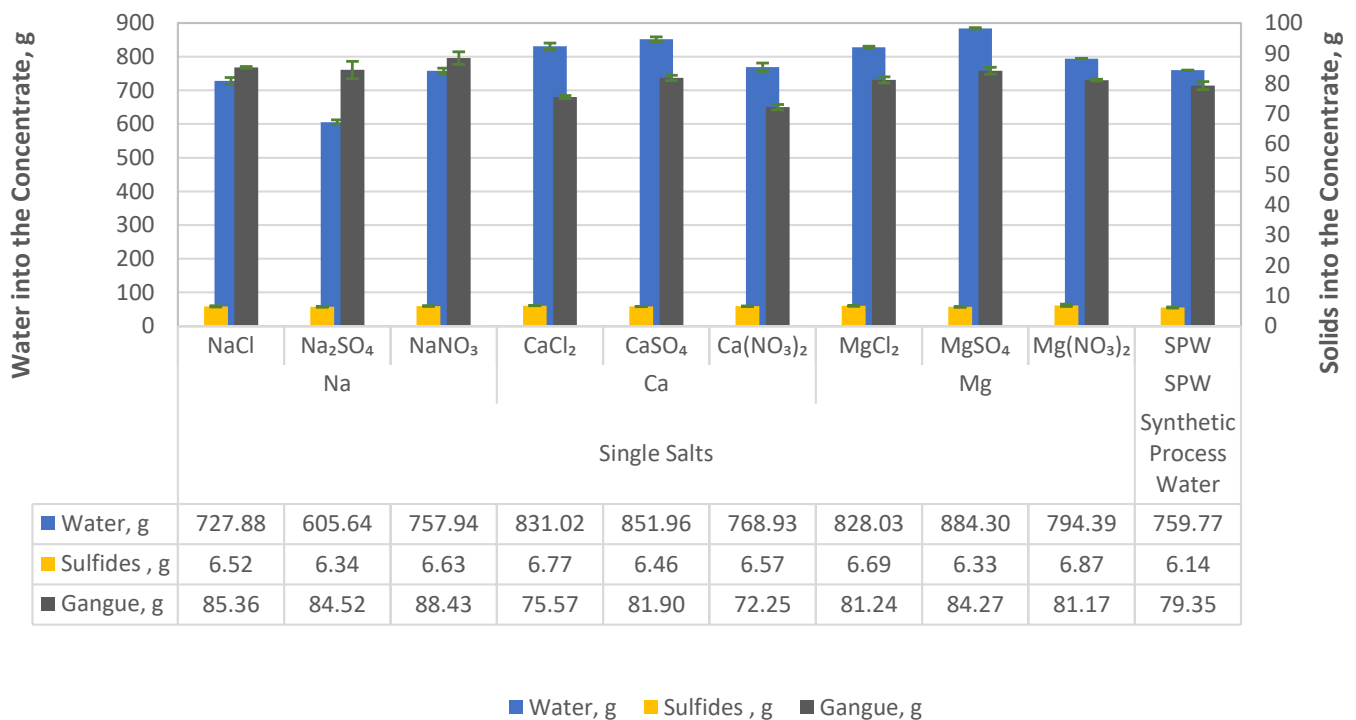
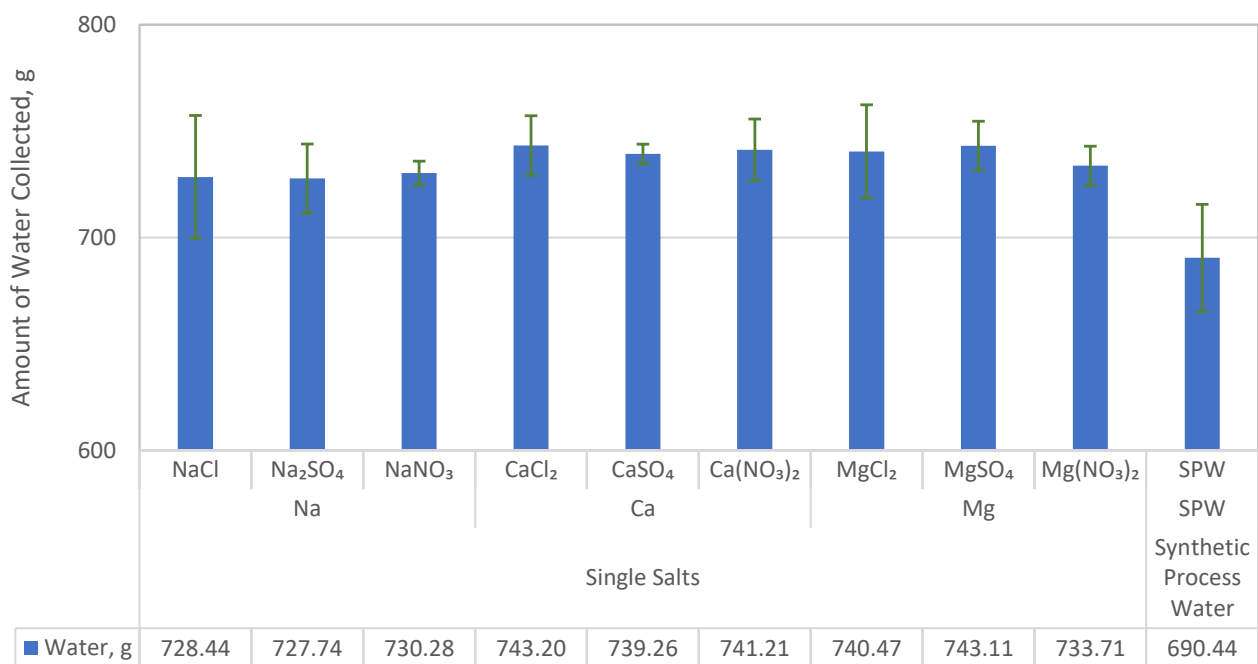


Figure 3. Amounts of water, total sulphides, and total gangue reporting to the concentrate for all single salts and SPW in a three-phase system.

It is generally accepted that water recovery in flotation is a good indicator of the stability of the froth [11]. The results in Figure 3 show higher water recoveries in the presence of divalent cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , compared to the monovalent  $\text{Na}^+$ . For example,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  resulted in water recoveries mostly within the range 770–880 g, while  $\text{Na}^+$  resulted in water recoveries within the range 600–750 g. Additionally, it is apparent that the presence of the divalent  $\text{SO}_4^{2-}$  anion increased the water recoveries and froth stability compared to the monovalent  $\text{Cl}^-$  and  $\text{NO}_3^-$ , except when combined with  $\text{Na}^+$ . This was in line with the work of Farrokhpay and Zanin [7], who showed that froth stability was higher in the presence of multivalent metal ions than monovalent metal ions.

Figure 4 shows the amount of water (foam) reporting to the concentrate for various single salts including SPW in the absence of solids. As synthetic plant water and  $\text{Na}^+$  resulting in only 690 and ~730 g of recovered water, respectively, it can be seen that  $\text{Na}^+$  and SPW resulted in lower water recoveries compared to the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  single salt solutions because these divalent cations,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , resulted in ~740 g of water recovered. The anion effects on water recoveries were not as apparent in the three-phase study, the results of which are reported in Figure 3; here, it can be seen that there were no significant difference between the water recoveries obtained for  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaNO}_3$ . The same can be said for  $\text{Ca}^{2+}$ , except for  $\text{Mg}^{2+}$  because  $\text{Mg}(\text{NO}_3)_2$  resulted in lower water recoveries than  $\text{MgCl}_2 = \text{MgSO}_4$ . This difference between the results shown in Figures 3 and 4 could be attributed to the role of the different species that form in solution with studied anions because these species may behave differently in solution in the presence of mineral particles, as was shown by the zeta potential results reported by Manono et al. [73].

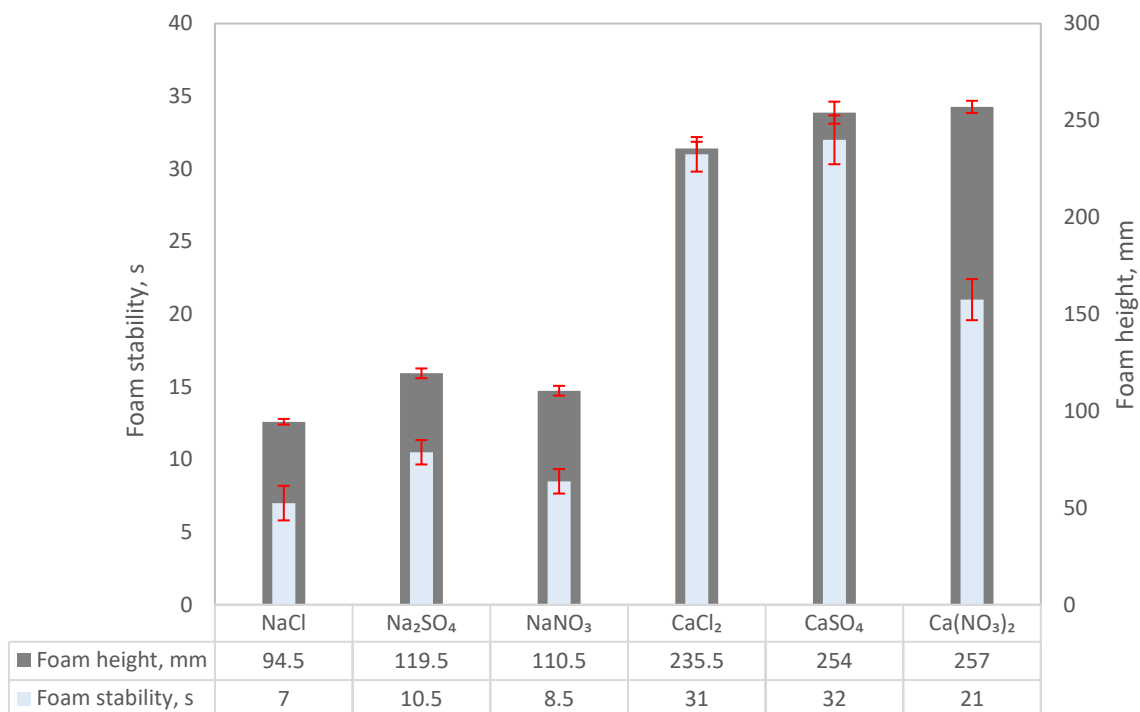


**Figure 4.** Amounts of water reporting to the concentrates for all single salts and SPW in a two-phase system.

In terms of the higher water recoveries in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  than in  $\text{Na}^+$ , Figure 4 shows a similar trend to that shown in Figure 3. The non-apparent effect on the anion effect on water recoveries per cation type seen in Figure 3 compared to the apparent anion effects shown in Figure 4 suggests that no direct correlation between the water recoveries in the three-phase studies and the water recoveries in two-phase studies can be made without considering pulp rheology and how specific anions combined with cations would form—possibly as different ionic complexes in solution that could act differently on the mineral surface and thus differently affect mineral hydrophobicity and froth stability. To further examine this, the results of foam studies regarding foam height, foam collapse time, and bubble size data are presented.

### 3.2. Specific Ion Effects on Foam Height and Foam Collapse Time

Figure 5 depicts the foam stability, measured as foam collapse time and the foam height for the selected single salts. The monovalent  $\text{Na}^+$ -containing single salt solution resulted in lower foam stabilities compared to the divalent  $\text{Ca}^{2+}$ -containing single salt solutions. For example,  $\text{Na}^+$  resulted in an average foam height and foam stability of  $\sim 108$  mm and  $\sim 8.6$  s, respectively, whereas these values for  $\text{Ca}^+$  were  $\sim 249$  mm and  $\sim 28$  s, respectively. Considering the impact of ion combinations, for  $\text{Na}^+$ -containing single salt solutions, the stability of the foam was greater with  $\text{SO}_4^{2-}$  ions in solution compared to  $\text{NaNO}_3$  and  $\text{NaCl}$ .  $\text{NaNO}_3$ , however, resulted in the lowest foam stability of all  $\text{Na}^+$  solutions, and this trend was similar to that shown in Figure 3 concerning water recoveries. For  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ -containing solutions resulted in higher foam stabilities compared to  $\text{Cl}^-$  and  $\text{NO}_3^-$ , whereas  $\text{NO}_3^-$  resulted in the lowest foam stability. Once again, this trend is similar to that of water recoveries results shown in Figure 3. The foam height for  $\text{Na}^+$ -containing salts was in the order of  $\text{Na}_2\text{SO}_4 > \text{NaNO}_3 > \text{NaCl}$ , and the foam height for  $\text{Ca}^{2+}$  was in the order of  $\text{CaSO}_4 = \text{Ca}(\text{NO}_3)_2 > \text{CaCl}_2$ .



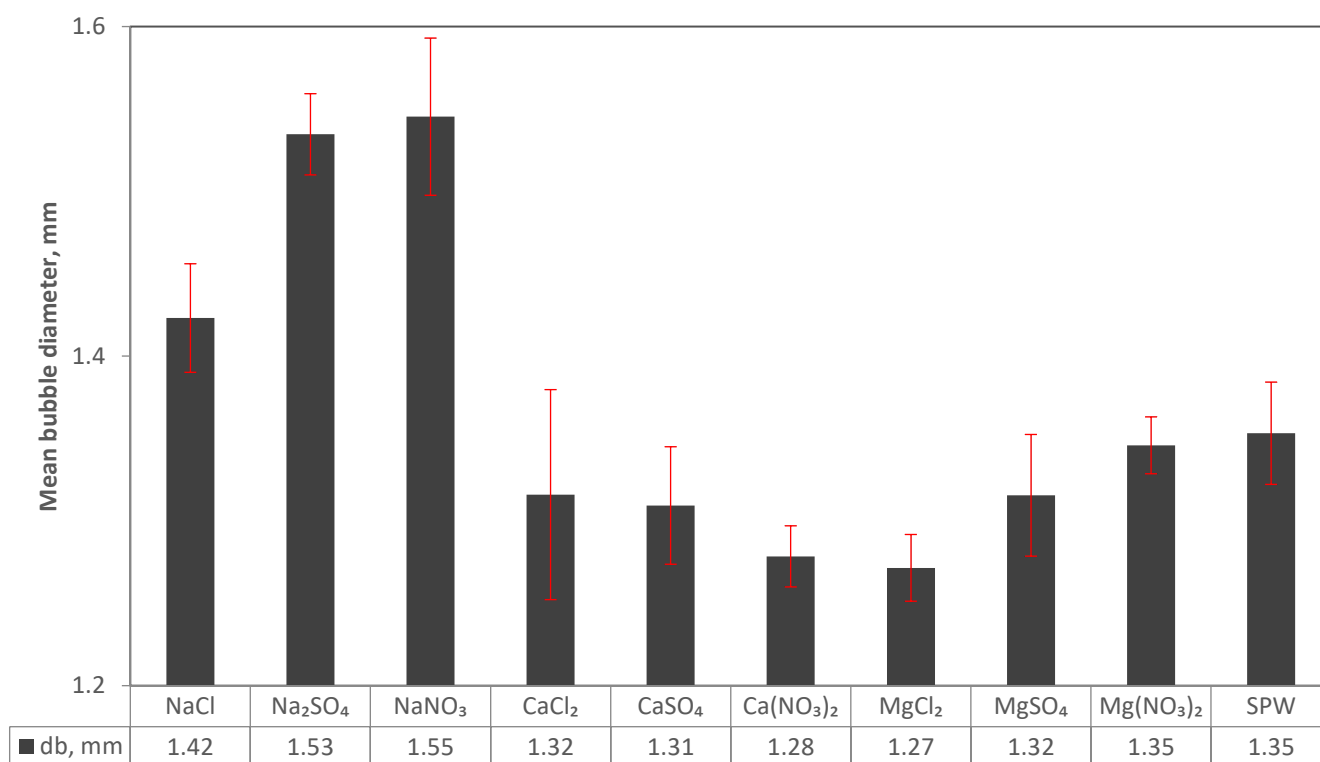
**Figure 5.** Specific ion effects on foam stability and foam height.

The results in Figure 3 on water recoveries for a three-phase system proved to be in line with the proposal that divalent ions would have a greater impact on the behaviour of the froth. Figure 4's foam stability results also support this proposal because the two-phase foam stability test results shown in Figure 5 clearly show that  $\text{Ca}^{2+}$  resulted in higher foam stabilities than the monovalent  $\text{Na}^+$ -containing single salt solutions across all anion types. The observations from Figure 5 also corroborate well with the specific anion effect trend observed in Figure 3, i.e.,  $\text{SO}_4^{2-}$  generally resulted in higher foam stabilities compared to  $\text{Cl}^-$  and  $\text{NO}_3^-$  and an even lower foam stability was observed for  $\text{NO}_3^-$ . The findings of this work are in line with those of Kurniawan et al. [60], who showed that  $\text{Mg}^{2+}$  resulted in increased froth stability and smaller froth bubble size and thus higher mineral recovery compared to  $\text{Na}^+$  when single salt solutions of  $\text{MgCl}_2$ ,  $\text{NaCl}$ , and  $\text{NaClO}_3$  were investigated during coal flotation in the absence and presence of Dowfroth 250. Their findings were also in line with those of other authors who showed that water with an increased concentration of electrolytes resulted in an increase in froth stability [33,36,59,60]. Biçak et al. [59] attributed this effect to the presence of a stable layer on the surface of the bubbles, and they

showed higher froth stabilities in the presence of  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  than any other anions; the findings of this paper were similar to ours in that the  $\text{SO}_4^{2-}$ -containing solutions had higher water recoveries and foam stability than  $\text{Cl}^-$  and  $\text{NO}_3^-$ , a trend that was particularly noticeably in the presence of the divalent  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It is important to mention that these previous studies do not seem to have been oriented towards understanding process water chemistry effects on froth stability in PGM ores. Thus, the findings of this paper should serve as a tool for two-phase foam stability studies as complements to three-phase studies considering the effects of specific ions on froth stability during the flotation of Cu-Ni-PGM ores.

### 3.3. Specific Ion Effects on Bubble Size

Figure 6 depicts the Sauter mean bubble diameter for SPW and various single salt solutions investigated in this study. The bubble diameter did not significantly change with ion type, although it was expected that the divalent  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  would result in smaller Sauter mean bubble diameters compared to the monovalent  $\text{Na}^+$ . It is worth noting the slight decreases in bubble diameter seen with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and SPW-containing solutions compared to  $\text{Na}^+$  (as expected), which is demonstrated by the fact that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  resulted in an average bubble diameter of  $\sim 1.31$  mm while  $\text{Na}^+$  resulted in an average of 1.50 mm. The slight decreases in bubble diameter in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  support the higher water recoveries observed in Figures 3 and 4 and are consistent with previous studies [39,43,58,65,74].



**Figure 6.** Specific ion effects on the mean bubble diameter.

### 3.4. Concluding Discussion

Lessard and Zieminski [44] investigated the effects of various inorganic electrolytes, shown in Table 2, on bubble coalescence and interfacial gas transfer in aqueous solutions. In their experiments, several pairs of bubbles were contacted, enabling the evaluation of the percentage degree of bubble coalescence as a function of the molar concentration of the inorganic electrolyte. Their findings showed a sharp transition concentration from higher degrees of coalescence to a 50% reduction on bubble coalescence. Thus, this concentration, which resulted in 50% bubble coalescence inhibition, was defined as the transition

concentration at which coalescence was sharply reduced. This enabled a comparison of the effectiveness of the salts in retarding bubble coalescence. Table 2 shows that the monovalent cations,  $\text{Na}^+$  and  $\text{K}^+$ , exhibited higher transition concentrations compared to the multivalent cations,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This lower transition concentration achieved by the multivalent cations was indicative of their superior ability to retard bubble coalescence and thus their froth-stability-enhancing behaviour compared to monovalent cations. Additionally, considering the transition concentration of  $\text{MgSO}_4$  in comparison to  $\text{MgCl}_2$  and that of  $\text{Na}_2\text{SO}_4$  in comparison with  $\text{NaCl}$ , it is evident that  $\text{SO}_4^{2-}$  had a lower transition concentration of  $0.032 \text{ mol}\cdot\text{dm}^{-3}$  and  $0.061 \text{ mol}\cdot\text{dm}^{-3}$  in  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , respectively, compared to  $\text{Cl}^-$ . Lessard and Zieminski's findings could explain why higher water recoveries and foam stabilities were obtained for  $\text{SO}_4^{2-}$ -containing solutions than  $\text{Cl}^-$  and  $\text{NO}_3^-$  solutions in this study.

**Table 2.** Bubble coalescence transition concentration in different inorganic electrolytes [44].

Salt	Transition Concentration ( $\text{mol}\cdot\text{dm}^{-3}$ ) (50 % Coalescence)
$\text{MgSO}_4$	0.032
$\text{AlCl}_3$	0.035
$\text{MgCl}_2$	0.055
$\text{CaCl}_2$	0.055
$\text{Na}_2\text{SO}_4$	0.061
$\text{LiCl}$	0.160
$\text{NaCl}$	0.175
$\text{NaBr}$	0.220
$\text{KCl}$	0.230

In this study, we aimed to answer the question of which ions have the greatest impact on froth stability through batch flotation and two-phase foam column studies with various single salts. The results showed that generally divalent cations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  led to greater water recoveries compared to the monovalent  $\text{Na}^+$ .  $\text{SO}_4^{2-}$ -containing salts resulted in higher water recoveries than  $\text{NO}_3^-$  and  $\text{Cl}^-$ .  $\text{NO}_3^-$  had a lesser froth-stabilising effect than  $\text{SO}_4^{2-}$ , as indicated by the lower water recoveries and foam stabilities reported in Figures 3 and 5, respectively. Foam column studies were performed using  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{CaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaNO}_3$  at an ionic strength of  $0.0213 \text{ mol}\cdot\text{dm}^{-3}$  equivalent of 1 SPW. The foam collapse time was longer for  $\text{Ca}^{2+}$ -containing solutions than those that contained  $\text{Na}^+$  for each corresponding anion type.  $\text{SO}_4^{2-}$  resulted in a longer foam collapse time than  $\text{Cl}^-$  and  $\text{NO}_3^-$ . The  $\text{NO}_3^-$  ion resulted in the lowest foam stability. The foam stability trend reported in Figure 5 agreed with that of the water recoveries reported in Figures 3 and 4, especially for the effect of the monovalent cation vs. divalent cations on foam stability and water recovery. In line with the work of by Lessard and Zieminski [44], this was attributed to the ability of the ions to retard bubble coalescence, although the results presented in Figure 6 do not demonstrate any strongly apparent effect on bubble diameter, possibly due to the low ion concentration used in this study compared to the bubble coalescence transition concentration proposed by Lessard and Zieminski [44]. The Sauter mean bubble diameters were, however, slightly smaller in divalent cations than in monovalent cations. Table 3 depicts the molar concentrations of the single salts studied in this work to further examine this behaviour.

From Table 3, it can be seen that although all the single salts were studied at a fixed ionic strength of  $0.0213 \text{ mol}\cdot\text{dm}^{-3}$  equivalent to the ionic strength of typical of process water in Merensky concentrators [75], solution concentration or molarity differed with each salt, as did the specific ion molar concentrations. For the monovalent  $\text{Na}^+$ , a higher amount of the salt needed to be dissolved in the solution compared to the divalent  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ -containing single salts, as shown by the higher TDS and total molarity for  $\text{Na}^+$  salts compared to both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Table 3, with specific species concentrations or molarities, is presented to enable comparison with the results of Lessard and Zieminski [44], who

reported bubble coalescence for single salts in the form of the 50% transition concentration presented in Table 2. Lessard and Zieminski [44] showed that for a fixed cation (e.g., MgSO<sub>4</sub> vs. MgCl<sub>2</sub> and NaCl vs. Na<sub>2</sub>SO<sub>4</sub>), the concentration required to retard 50% bubble coalescence was lower for SO<sub>4</sub><sup>2-</sup> than Cl<sup>-</sup>, while for a fixed anion type, the required concentration to retard half of the coalescence occurring between bubbles was lower for Mg<sup>2+</sup> and Ca<sup>2+</sup> than Na<sup>+</sup>. These results agree with the findings of this study. From Table 3, it can also be seen that for all single salts, a lower specific anion concentration was required for the SO<sub>4</sub><sup>2-</sup> to reach a total ionic strength of 0.0213 mol.dm<sup>-3</sup> compared to Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. However, all the tested single salts were present at molarities lower than their concentrations required to retard 50% bubble coalescence. It is evident that specific ion concentration and specific ion valency are important aspects in considering froth stability, as shown by the fact that Ca<sup>2+</sup> in combination with SO<sub>4</sub><sup>2-</sup> had a concentration of 0.0053 mol.dm<sup>-3</sup>, which is lower than that of Ca<sup>2+</sup> (0.0071 mol.dm<sup>-3</sup>) in combination with Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> but still resulted in the highest water recoveries and therefore highest froth stability. This is attributed to the divalent nature of the SO<sub>4</sub><sup>2-</sup> anion compared to the monovalent Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions; hence, lower concentrations would be required for the SO<sub>4</sub><sup>2-</sup> anion compared to the Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> anions to achieve the same effect on bubble coalescence [44]. This trend was sustained across cation type, as shown in Table 3. However, it is acknowledged that gas dispersion properties that enable the more robust characterisation of froth such, e.g., bubble size, froth collapse time, froth height, gas hold-up, and froth rise velocity, need to be determined in the presence of solids. This together with the findings of this study should form the basis for future investigative work.

**Table 3.** Molarity-based composition of the single salts used in this study.

Water Type	Ca <sup>2+</sup> [M]	Mg <sup>2+</sup> [M]	Na <sup>+</sup> [M]	Cl <sup>-</sup> [M]	SO <sub>4</sub> <sup>2-</sup> [M]	NO <sub>3</sub> <sup>-</sup> [M]	CO <sub>3</sub> <sup>2-</sup> [M]	Total Molarity [M]	TDS (mg/L)	Ionic Strength [M]
NaCl	-	-	0.0213	0.0213	-	-	-	0.0213	1245	0.0213
Na <sub>2</sub> SO <sub>4</sub>	-	-	0.0142	-	0.0071	-	-	0.0071	1009	0.0213
NaNO <sub>3</sub>	-	-	0.0213	-	-	0.0213	-	0.0213	1810	0.0213
CaCl <sub>2</sub>	0.0071	-	-	0.0124	-	-	-	0.0071	788	0.0213
CaSO <sub>4</sub>	0.0053	-	-	-	0.0053	-	-	0.0053	725	0.0213
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.0071	-	-	-	-	0.0142	-	0.0071	1165	0.0213
MgCl <sub>2</sub>	-	0.0071	-	0.0142	-	-	-	0.0071	676	0.0213
MgSO <sub>4</sub>	-	0.0053	-	-	0.0053	-	-	0.0053	641	0.0213
Mg(NO <sub>3</sub> ) <sub>2</sub>	-	0.0071	-	-	-	0.0142	-	0.0071	1053	0.0213

#### 4. Conclusions

Water recoveries and foam stability studies showed that SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> had greater froth stabilising effects than Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Na<sup>+</sup>. It was also shown that NO<sub>3</sub><sup>-</sup> had the least froth stabilising effect. This proves the importance of considering changes in froth stability with water quality variations, as this could have serious implications on the management of gangue and concentrate grades.

Thus, the following key conclusions can be drawn:

- SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> resulted in higher water recoveries in the three-phase systems compared to Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and Na<sup>+</sup>.
- Ca<sup>2+</sup> and Mg<sup>2+</sup> resulted in higher water recoveries in the two-phase systems compared to Na<sup>+</sup>. No apparent anion effect was observed.
- Ca<sup>2+</sup> resulted in increased foam stability compared to Na<sup>+</sup>.
- SO<sub>4</sub><sup>2-</sup> resulted in higher foam stability compared to Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> led to the lowest foam stability.
- Foam heights were far more increased in single salt solutions consisting of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> than those containing Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and Na<sup>+</sup>.
- There was no apparent effect on bubble diameter. However, slight decreases in bubble diameter were observed in the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> compared to Na<sup>+</sup>.

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