# Water Quality Effects on Bubble-Particle Attachment of Pyrrhotite

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Abstract

In froth flotation, separation between the valuable and the gangue minerals comes as a result of the attachment of hydrophobic minerals to air bubbles. Considering the importance of bubble formation and bubble-particle attachment, it is evident that the pulp phase facilitates the events for the most crucial requirements of successful flotation. Water forms the bulk of the pulp phase; and as a result of water scarcities in countries like South Africa, the need to recycle process water within mining operations is increasing. Hence it is of great importance to understand the effects of water quality on the vital sub-processes within the flotation process, particularly bubble-particle attachment. A novel attachment timer was used for attachment probability measurements with different water qualities. The study presented thus evaluates the propensity for attachment of pyrrhotite to bubbles under water of increasing ionic strength.

## Introduction

With the current water scarcity in countries like South Africa, the need to recirculate process water within mining operations is becoming greater. The ionic strength of the process water however increases with each recirculation and this will affect the flotation process (Slatter, *et al.*, 2009). Considering that the most basic requirement for an effective separation is the attachment of hydrophobic particles to air bubbles, it is essential to understand how changes in water chemistry affects the bubble-particle attachment sub-process.

When a bubble and a particle approach one another and come into close contact, a wetting film between the air water and solid water interfaces forms. The bubble-particle attachment process begins with the thinning of the wetting film at the air water and solid water interfaces to critical thickness; followed by the rupturing of the wetting film as it becomes unstable, leading to the establishment of a three phase contact line and the occurrence of bubble-particle attachment. This process is concluded when the bubble-particle contact line spreads across the surface, forming a stable wetting perimeter with equilibrium contact angles (Albijanic *et al.*, 2010).

The attachment time is defined as the time it takes for the entire process described above to occur and the induction time is the time it takes for the wetting film to thin to critical thickness; the latter is generally used to predict the susceptibility of a particle to float (Albijanic *et al.*, 2010).

The effect of water quality on induction time with a bitumen system was studied by Gu *et al.* (2003) and it was shown that the induction time decreased upon the addition of $Ca^{2+}$ to clear process water compared

to without $Ca^{2+}$. Yoon and Yordan (1991) showed a decrease in induction time (and hence increase in floatability) with increasing KCl concentration in a quartz-dodecylammonium hydrochloride (DAH collector) system at low DAH dosage. This was attributed to the compression of the electrical double layer in the presence of ions leading to the acceleration of the rupturing of the wetting film between the bubble and particle; ultimately decreasing the bubble-particle attachment time. An opposite trend in floatability was observed by these authors with an increase in collector dosage under constant water conditions; this was said to be as a result of the collector ions associating with one another and its subsequent adsorption on the mineral surface in bimolecular layers. Thus from previous studies conducted in this area it is clear that there is little knowledge regarding the effect of plant water of increasing ionic strength on the bubble-particle attachment process in sulphide minerals.

Platinum bearing ores from the Merensky reef consists of approximately 1% sulphides and about 45% of these sulphides are pyrrhotite (Liddel et al., 1986); making pyrrhotite the main sulphide mineral in the Merensky reef. Pyrrhotite however readily oxidizes to ferric hydroxide under conventional flotation conditions, pH 9 and open to the atmosphere (Miller *et al.,* 2005). Both the natural and induced hydrophobicity of pyrrhotite have been widely studied and factors such as oxidation potential, pH and activation have shown to have significant effects on pyrrhotite flotation (Miller *et al.,* 2005; Hodgson and Agar, 1984; Peters, 1977; Montalti, 1994).

The aim of this study was thus to assess the bubble-particle attachment probability of pyrrhotite under synthetic plant water of increasing ionic strength both in the presence and absence of a collector. This was done by means of a novel attachment timer.

Equipment commonly used to measure either induction or attachment time consists of a particle bed and a bubble generated at the tip of a single needle. The bubble is then put in contact with the particle bed for a set contact time at several locations on the particle bed and this process is repeated for a range of contact times. Commonly 10 different locations are used on the particle bed and the attachment time is defined as the contact time at which the attachment probability is a certain percentage determined prior to the experiment (Yoon and Yordan, 1991; Gu *et al.*, 2003; Albijanic *et al.,* 2012).

The attachment time equipment used in this investigation has been described by Jávor *et al* (2016); Aspiala *et al.* (2017) elsewhere and a brief description will be given in the next sections.

## 2. Experimental

The attachment timer housed at Aalto University was used to perform the bubble-particle attachment measurements. This instrument, shown in Figure *1* was used to assess the effect of ionic strength of plant water on the bubble-particle attachment probability for pyrrhotite both in the absence and presence of a collector.

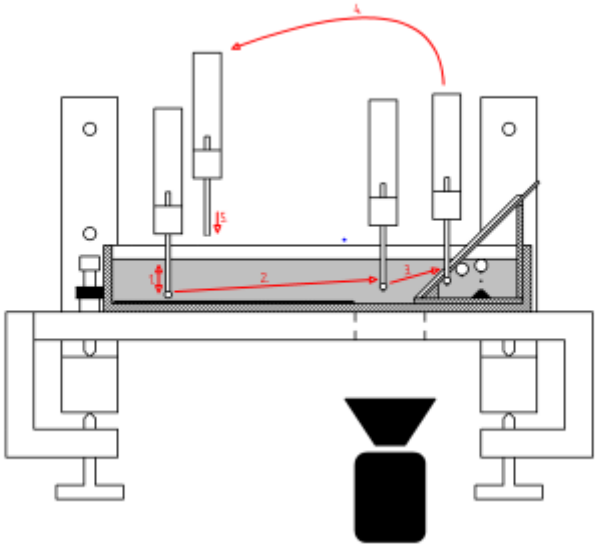


Figure 1: Schematic of the attachment timer (Aspiala *et al.* 2017)

2.1 Operation of the Attachment Timer

The instrument consists of six needles which each generate a bubble of a set diameter; once the bubbles are generated they are brought into contact with the particle bed for a set contact time. The needles are then automatically lifted and moved to the area where an image of the bubble-particle aggregates is taken. After the image is taken the needles with the bubble-particle aggregates are automatically transferred to the particle collection bin, where additional air is pumped through the needles to release the bubble-particle aggregates. After this deposition the needles then automatically move to the next 1 mm of the particle bed. This process is repeated such that the complete length of the particle bed is given an opportunity for bubble-particle attachment; resulting in a total of 66 cycles with 396 bubble-particle contacts per experiment.

2.2 Materials and Sample Preparation

2.2.1 Mineral Sample

The pyrrhotite used in this investigation was obtained from Ward's Science. 1 kg of pyrrhotite sample was hammered manually to 100% passing 1000 micron. The crushed sample was then pulverized and subsequently sieved through 75 and 38 micron sieves. The fraction of particles greater than 75 micron was then re-pulverized such that size fraction of the entire sample was less than 75 micron. This sample was purged with nitrogen and refrigerated. Upon arrival at Aalto University the pyrrhotite particles of -75+38 micron were split into 10 samples using a rotary splitter. The samples were purged with argon and stored in bottles in refrigerator.

2.2.2 Water Quality

Both purified water and synthetic plant waters were used for the attachment timer measurements. Synthetic plant water (1 SPW) as described by Wiese *et al.* (2005) was used as the water quality with low ionic strength

and to simulate a recirculation of this synthetic plant water, the content of dissolved solids was increased 5 and 10 times, referred to as 5 SPW and 10 SPW respectively. Table *1* gives an account of the concentrations of the various ions in the synthetic plant waters tested.

Table 1: Concentrations of ions for the various water qualities

| Plant Water Type | $Ca^{2+}$ (ppm) | $Mg^{2+}$ (ppm) | $Na^{+}$ (ppm) | $Cl^{-}$ (ppm) | $SO_4^{2-}$ (ppm) | $NO_3^{-}$ (ppm) | $CO_3^{2-}$ (ppm) | Total Dissolved Solids (mg/L) | Ionic Strength (mol/L) |
|---|---|---|---|---|---|---|---|---|---|
| **1 SPW** | 80 | 70 | 153 | 287 | 240 | 176 | 17 | 1023 | 0.0213 |
| **5 SPW** | 400 | 350 | 765 | 1435 | 1200 | 880 | 85 | 5115 | 0.0977 |
| **10 SPW** | 800 | 700 | 1530 | 2870 | 2400 | 1760 | 170 | 10230 | 0.186 |

2.2.3 Sample Preparation

A slurry was made with 9 g pyrrhotite and 100 ml of the particular water type under investigation. Experiments were performed both in presence and absence of collector. When collector was utilised, the slurry was conditioned for 2 minutes with 100 g/t sodium isobutyl xanthate collector (SIBX), thereafter it was allowed to settle for approximately 3 minutes. The liquid at the top was removed with a pipette and filtered with a glass funnel and filter paper such that a clear water was obtained and only a thin layer of liquid above the settled particles was left in the flask. The clear liquid was transferred to the cell of the attachment timer and the settled particles were used to make the particle bed.

2.3 Particle Bed Preparation

Once the pool was ¾ full with water, a heap of particles was introduced into the pool. An automated shovel attached to the linear actuator then ensured for a flat particle bed of a pre-set bed height. More particles were to fill the length of the pool; and between each addition of particles the shovel controller was employed until a flat particle bed of 2 mm was obtained. The particle collection bin was inserted into the cell.

2.4 Bubble-Particle Attachment Measurements

Prior to the start of the 66 measurement cycles certain parameters were set on the experimental controller programme. These parameters included the contact time, approach distance, approach velocity, detachment velocity, retreat distance, bubble size, compression and pumping time. Although the bubble size was set, this parameter was largely dependent on the chemical environment within the cell such as the ionic strength of the water investigated. Consequently, parameters such as the compression, approach and retreat distance which are dependent on bubble size may also differ slightly from what was set. However the actual values of these parameters for each cycle were given upon the completion of the 66 cycles.

The digital camera situated below the cell takes two images of the bubble-particle aggregate at the tip of the needle for each cycle. All the images of the 66 cycles are saved. The first image with white light illumination

is used to determine the bubble size, while the second image allows for the detection of whether particles were attached to the bubbles or not.

## 3. Results and Discussion

The images were studied to establish the bubble-particle attachment probability for the different water qualities tested. Figure *2* shows an example of an image from before attachment and after a measurement cycle.

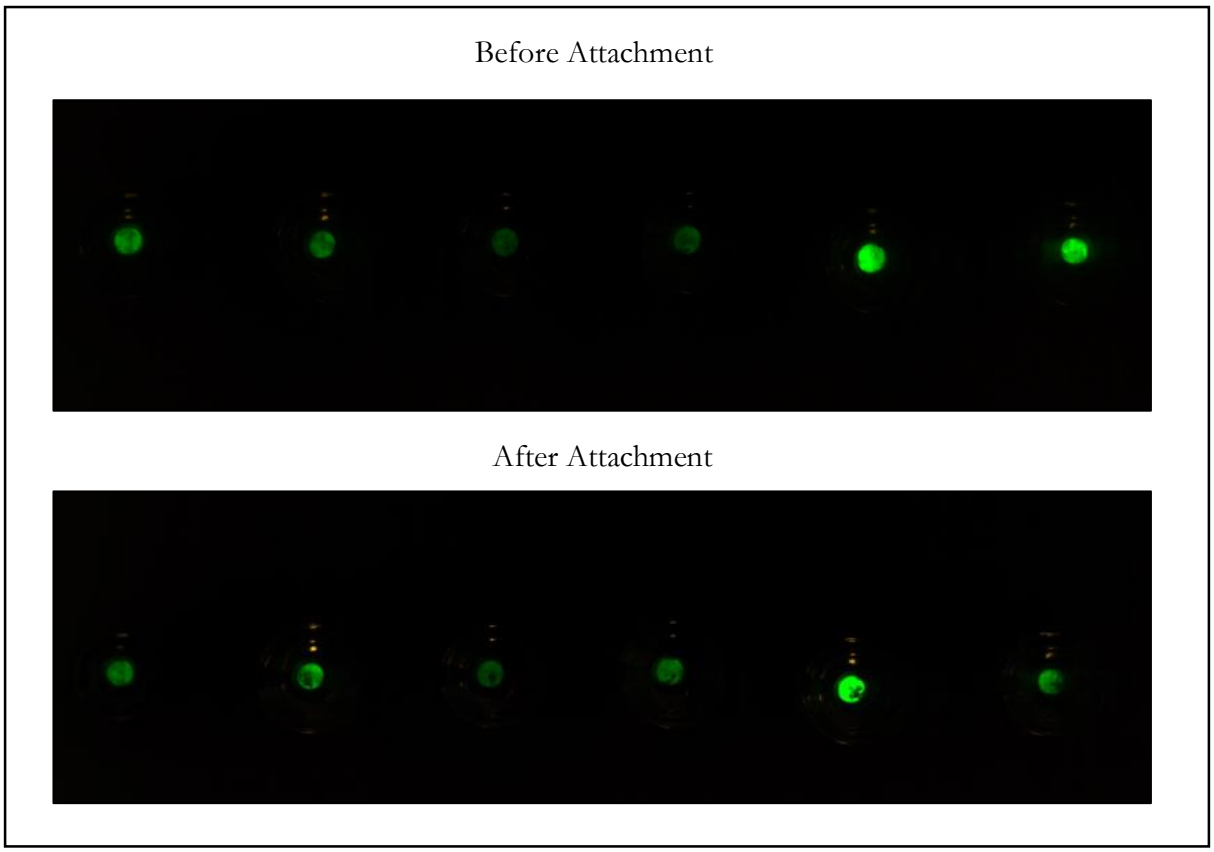



Figure 2: Image of the array generated for bubble-particle attachment detection

Figure *2* shows that there was attachment of particles occurring at five of the six needles (needles two to six, from left to right). The 66 images obtained per condition investigated were studied in this way to quantify the probability of bubble-particle attachment under water of increasing ionic strength.

### 3.1 The Effect of Water Quality on Attachment Probability in the Presence of a Collector

The actual bubble sizes generated by each needle for the 66 cycles was returned by the experimental programme. Figure *3* depicts the bubble size distribution averaged across the two contact times for every water quality tested.

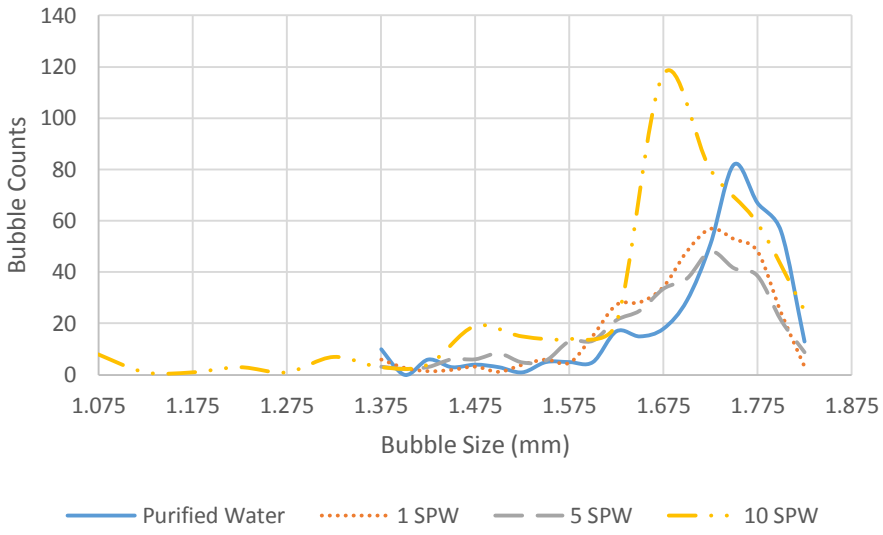



Figure 3: Bubble size distribution for the various water qualities

The bubble size distribution in Figure *3* shows that the largest mean bubble size was generated with purified water (1.75 mm), while the smallest mean bubble size was generated with 10 SPW (1.65 mm). This decrease in bubble size as the ionic strength of the plant water increased was expected as it has been shown that salts have a bubble size reduction ability (Quinn et al. 2007; Corin and Wiese 2014; Manono *et al.* 2013).

With the acquisition of the actual bubble size generated by each of the needles for an experimental run and the probability of attachment which was provided by the images, the attachment probability per bubble size was determined. *Figures 4, 5* and *6* provide illustrations of the attachment probability per bubble size for 1, 5 and 10 SPW respectively at contact times of 100 ms and 200 ms.

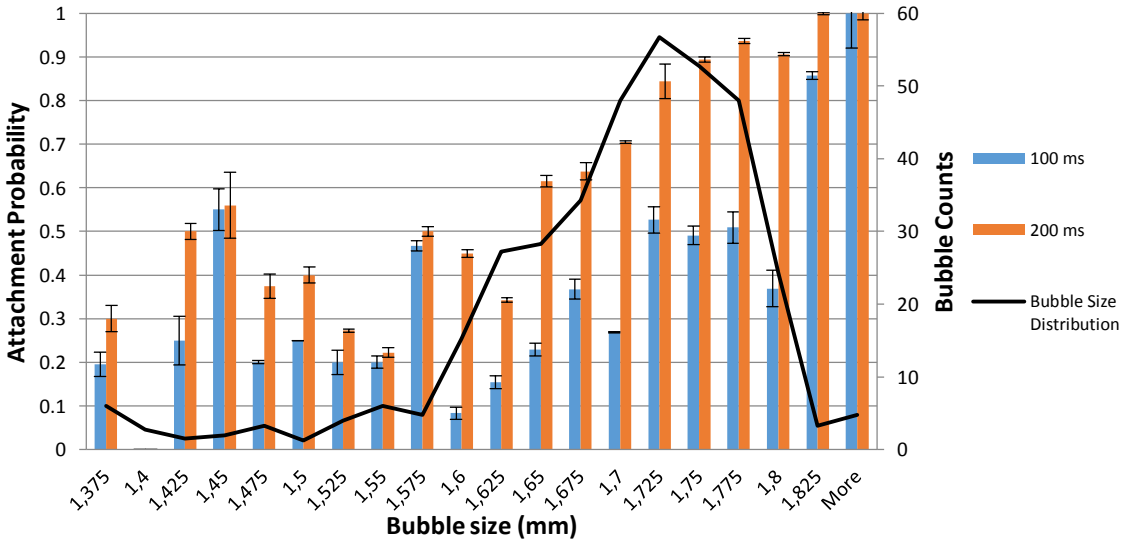


Figure 4: Attachment probability per bubble size for 1 SPW

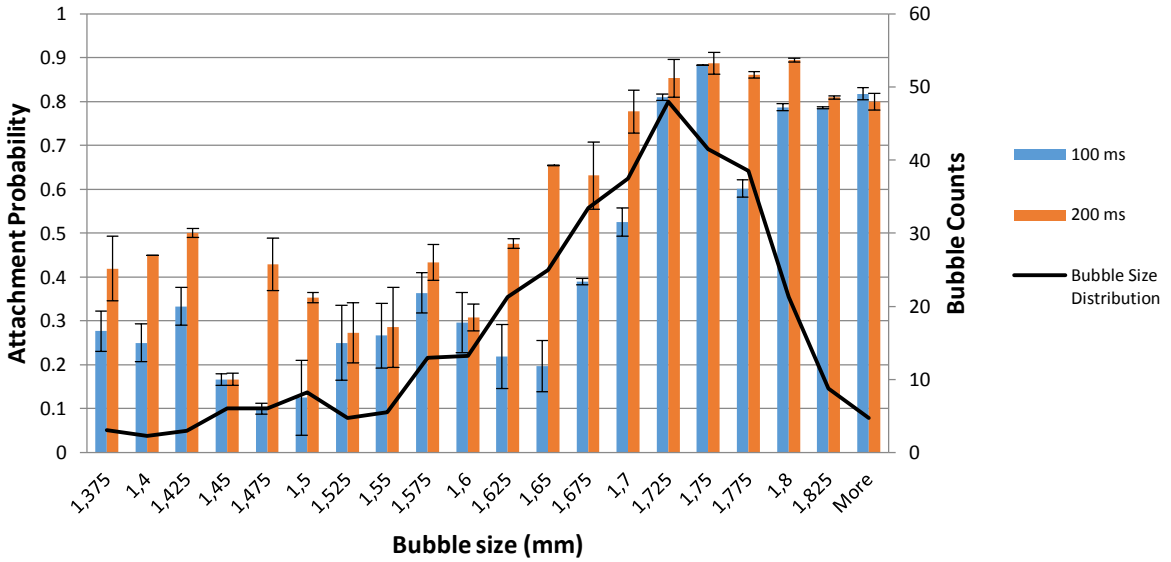



Figure 5: Attachment probability per bubble size for 5 SPW

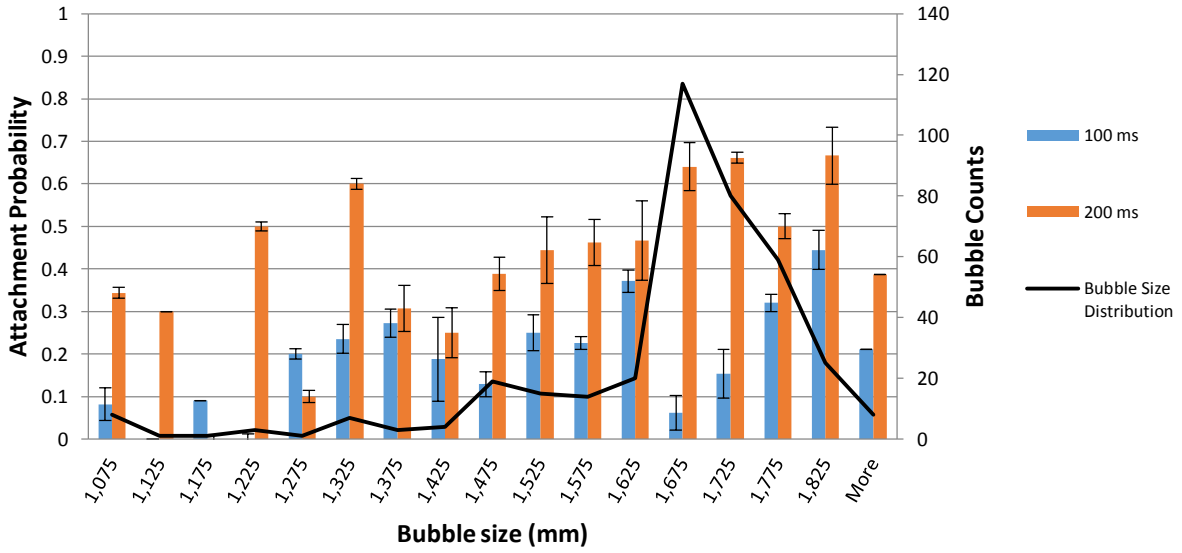
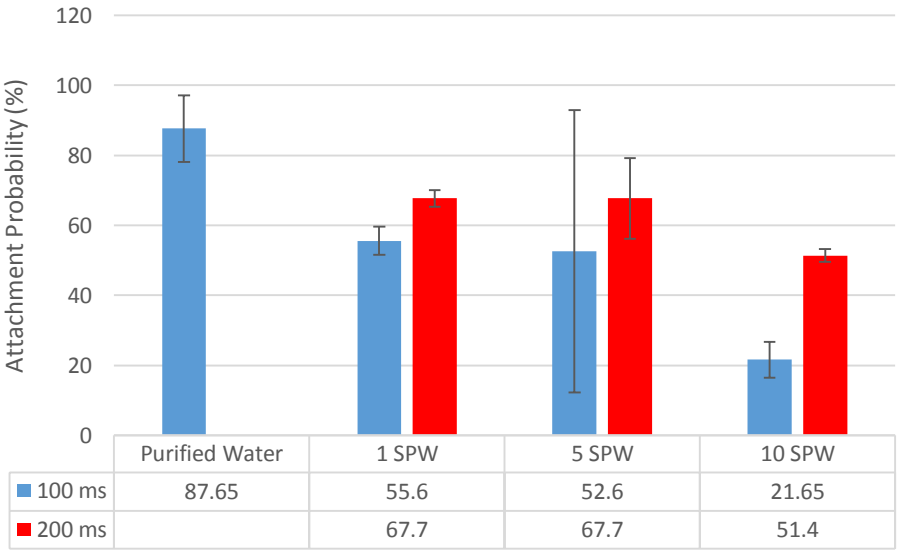



Figure 6: Attachment probability per bubble size for 10 SPW

*Figures 4, 5* and *6* show that the attachment frequency was greater at a contact time of 200 ms across all bubble sizes for all the water qualities investigated, this result was expected as the longer the bubble is in contact with the particle bed the greater the opportunity for particles to attach to the bubbles. Additionally it was evident that the attachment frequency was higher around the mean bubble size and greater compared to the attachment frequency when smaller bubbles were generated. Previous studies have shown that smaller bubble sizes yielded lower induction times and consequently increased a particles' susceptibility to float (Yoon and Yordan, 1991; Gu *et al.*, 2003; Wang e*t al.*, 2005). This phenomenon was attributed to the fact that it takes longer to displace the wetting film between the bubble and the particle with bubbles of

larger diameter. This was not observed in this system but was anticipated as the bubble size was pre-set for a sufficient compression; the compression is dependent on the bubble size and smaller bubble sizes may not make sufficient contact with the bed. This further explains the higher attachment frequency around the mean bubble size which was close to the pre-set bubble size of 1.77 mm. *Figures 4, 5* and *6* show that the attachment frequency at the mean bubble size decreased as the ionic strength of the water was increased. Figure *7* further gives an account of the overall average attachment probability for each of the water qualities investigated at contact times 100 ms and 200 ms respectively.




| | Purified Water | 1 SPW | 5 SPW | 10 SPW |
|---|---|---|---|---|
| 100 ms | 87.65 | 55.6 | 52.6 | 21.65 |
| 200 ms | | 67.7 | 67.7 | 51.4 |

Figure 7: Overall attachment probability of different water qualities at 2 contact times

Figure *7* shows the attachment probability using purified water and the three synthetic plant waters of increasing ionic strength when a contact time of 100 ms and 200 ms was employed; purified water was not tested with a contact time of 200 ms. The overall average attachment probability also decreased with deteriorating water quality.

It was expected that with an increase in ionic strength of plant water the floatability of the mineral would increase, as explained by the electrical double layer theory (Laskowski and Iskra, 1970; Yoon and Yordan, 1991). Hodgson and Agar (1989) indicated that $Ca^{2+}$ increased the amount of xanthate necessary to create a hydrophobic pyrrhotite surface; suggesting that the presence of $Ca^{2+}$ induces hydrophilicity. Moreover, Ikumapayi *et al.* (2012) described the decrease in galena recovery with increasing $Ca^{2+}$ to be as a result of $Ca^{2+}$ inhibiting the adsorption of xanthate on the mineral surface. Additionally, Kirjavainen *et al.* (2002) found that calcium and thiosulfate ions had a declining effect on the floatability of sulphides in the absence of iron ions that is leached into solution during milling. It was thus speculated that the reduction in attachment probability as the ionic strength of water was increased as observed in Figure *7* was as a result of the increasing concentration of ions such as calcium, which inhibited the adsorption of xanthate on the mineral surface. This could further be supported by the fact that the attachment probability was highest in

purified water. It should be noted that the collective effect of ions existing in plant water is complex and requires further investigation.

The pH of the pyrrhotite-SIBX-purified water system was 6.52, being close to the iso-electric point of pH 6.5 in a pyrrhotite-ethyl xanthate system (Montalti, 1994) and could thus explain the high attachment probability observed. The natural pH of the pyrrhotite-SIBX-synthetic water systems was measured to be between 5.8 and 6.7; thus it was also close to the iso-electric point. It would therefore be of interest to investigate the change in potential of the pyrrhotite surface with plant waters of increasing ionic strength.

3.2 The Effect of Water Quality on Attachment Probability in the Absence of a Collector

*Figure 8* depicts the bubble size distribution averaged across the two contact times for every water quality tested.

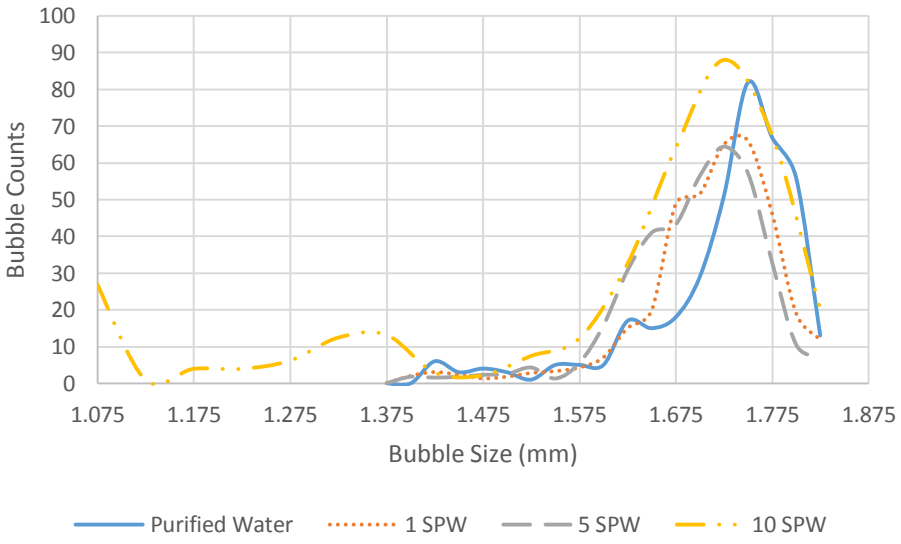



Figure 8: Bubble size distribution for the various water qualities for the collectorless system

Similarly as in *Figure 4* the mean bubble size tended to decrease as the ionic strength of plant water increased.

*Figures 9, 10* and *11* provide illustrations of the attachment probability per bubble size for 1, 5 and 10 SPW respectively at contact times of 100 ms and 200 ms.

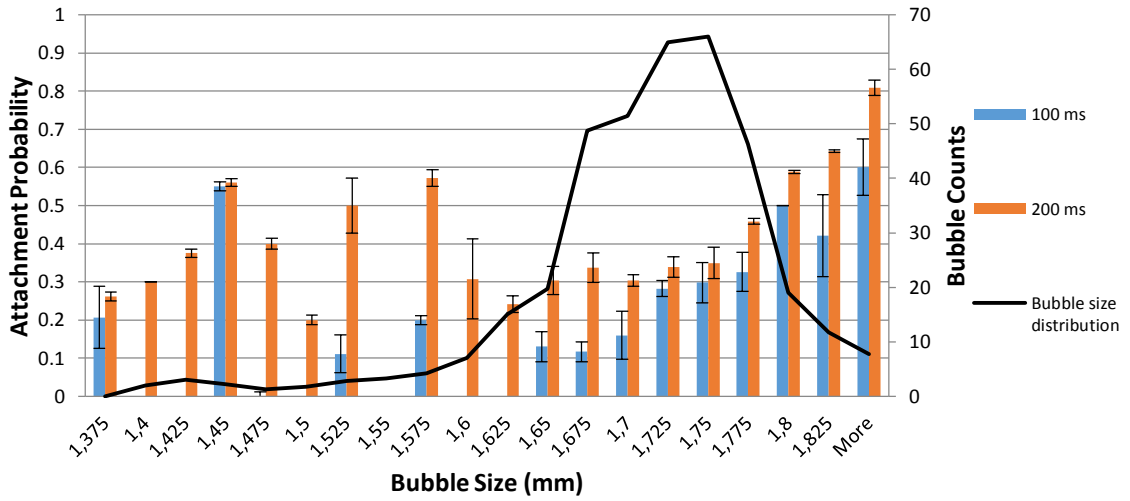



Figure 9: Attachment probability per bubble size for 1 SPW - collectorless

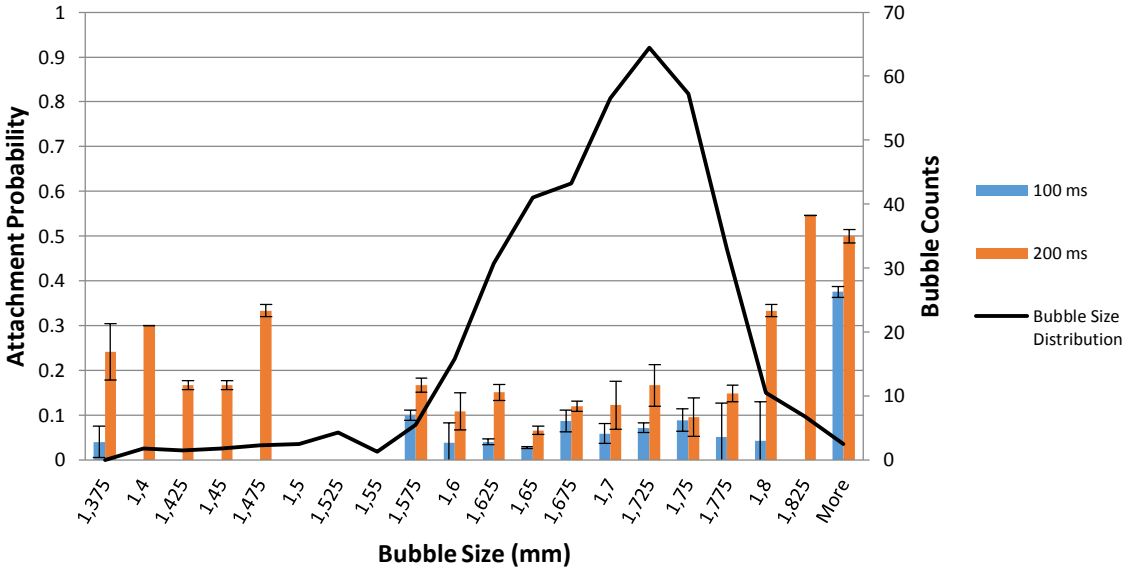



Figure 10: Attachment probability per bubble size for 5 SPW - collectorless

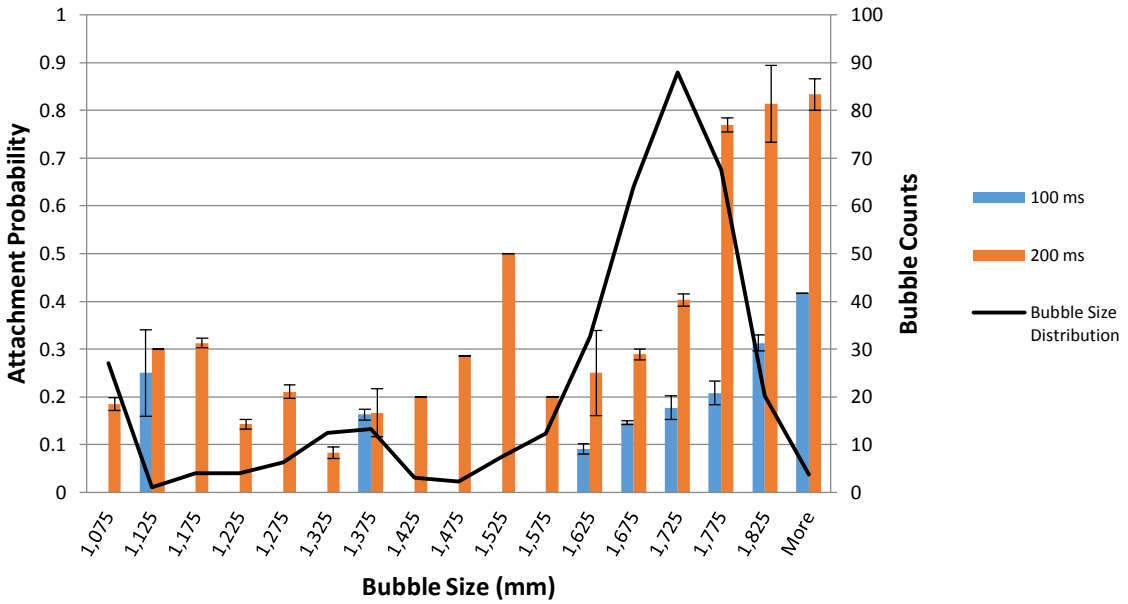



Figure 11: Attachment probability per bubble size for 10 SPW - collectorless

The overall picture presented by *Figures 9* to *11* shows a decrease in attachment frequency comparing purified water to 1 SPW; further a dramatic decrease in attachment frequency was noted for 5 SPW compared to 1 SPW. The attachment frequency then shows a slight increase at 10 SPW compared to that of 5 SPW. Figure *12* summarises the attachment probability at the mean bubble size for each of the water qualities investigated.

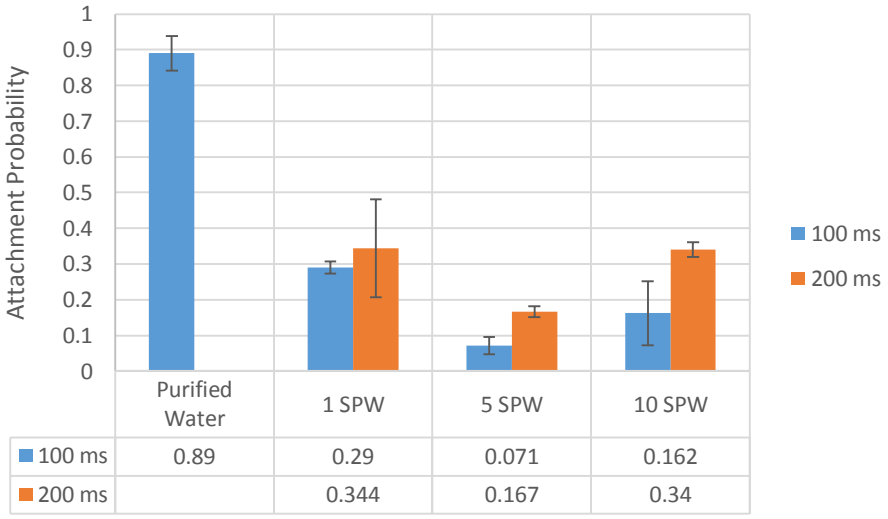



Figure 12: Attachment probability at the mean bubble size in the absence of a collector

The natural pH of this system was measured to be between 6.27 and 6.61 and it is evident that attachment does indeed occur in this pH range. This result was contrary to the findings of Miller *et al.* (2005) where

contact angle measurements showed that the hydrophilic state of pyrrhotite stabilized (contact angle of zero) at pH values above 4.5 in the absence of collector. However, it has been reported that elemental sulphur, which is hydrophobic forms at the surface of pyrrhotite in the absence of a collector and can remain stable for long periods (Peters, 1977). The formation of sulphur could thus be the reason for the observed floatability of pyrrhotite in this pH range.

According to the electrical double layer theory previously stated, an increase in ionic strength of the solution should increase the floatabilty of the mineral but Figure *12* shows a general decrease in the probability of attachment of pyrrhotite particles to air bubbles with an increase in the concentration of dissolved solids.

The surface of pyrrhotite is known to oxidize rapidly when exposed to air and results in the surface of the mineral being covered with ferric hydroxide (Miller *et al.,* 2005); rendering the mineral hydrophilic. This phenomenon will undoubtedly hinder any activation reaction from occurring on the surface of the mineral and could possibly obstruct the expected effect of the electrical double layer.

The flotation of pyrrhotite is recognised to be very complicated and is influenced mainly by oxidation potential and pH. The plant water with an intermediate level of ionic strength tends to show a lower probability for the attachment of pyrrhotite particles to the bubbles. This result could potentially be explained by a combined effect of pH, oxidation potential and electrolytes in the system yielding a minima in attachment probability.

Upon comparison it is clear that the attachment probability is higher in the presence of a collector as opposed to without a collector for all the synthetic plant water tested. This result was expected as the primary role of a collector is to induce hydrophobicity on the valuable mineral particles.

## 4. Conclusions

The results presented in this study generally show a decrease in the floatability of pyrrhotite as the ionic strength of synthetic plant water is increased both in the presence and absence of a collector. These findings were recognised to be as a result of the increase in concentration of $Ca^{2+}$ possibly having an inhibiting effect on the adsorption of xanthate as the ionic strength of plant water is increased. Furthermore, pyrrhotite readily oxidises when open to the atmosphere, resulting in ferric hydroxide formation on the mineral surface. In the absence of a collector this trend may possibly be due to the joint effects of oxidation, pH and ionic strength; individually these factors are known to affect the natural flotation of pyrrhotite. It should also be noted that the collective effect of ions existing in plant water is complex and require further investigation in terms of their effect on the potential of the mineral surface and their influence on xanthate adsorption.

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