Considering the Ionic Strength and pH of Process Water on Bubble-Particle Attachment of Sulfide Minerals: Implications for Froth Flotation in Saline Water

L. L. October[1], K. C. Corin[1], M. S. Manono[1], N. Schreithofer[2], J. G. Wiese[1]

[1]*Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa, Kirsten.Corin@uct.ac.za*

[2]*Department of Bioproducts and Biosystems, Clean Technologies Research Group, Aalto University, Vuorimiehentie 1, 02150 Espoo, Finland*

Abstract

Due to the current climate of water scarcity in mining areas and the fact that water treatment is costly; the recirculation of process water seems to be a viable option in mineral processing. A consequence of the recirculation of water is the build-up of ions such as Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-} and NO_3^{-} as well as increases in pH. This study thus considers the combined effect of increasing ionic strength and pH of process water on the froth flotation process. These parameters are important to study simultaneously because complex water systems at high pH values, may result in the formation of various hydroxo complexes compromising the flotation efficiency.

Both fundamental bubble-particle attachment tests and microflotation show decreases in attachment and sulfide recovery as the pH is increased to 11. However, at the elevated pH the recovery increases as the ionic strength (water recycles) is increased. This could be due to the compression of the electrical double layer by the indifferent ions as seen by the zeta potential measurements. Zeta potential measurements also show steep increases in the potential of the sulphide minerals at pH 11.

Although this work suggests that process water with a pH as high as 11 will result in decreased mineral recoveries, it has been shown that at increased levels of ionic strength (increased recirculation of process water) higher recoveries can be obtained. Thus, it can be concluded that if the pH of process water was to reach a pH of 11, the combined effect of recirculation of process water would not necessarily have detrimental effects on sulfides flotation performance.

Introduction

Froth flotation takes advantage of a minerals surface properties as a means of separating valuable minerals from non-valuable gangue. When air is introduced into the mineral slurry, the hydrophobic particles (most often valuables) attach to the air bubbles and rise into the froth phase where they are eventually collected. Whereas the hydrophilic, (most often non-valuable) particles stay in the pulp zone (Wills and Finch, 2016).

This process thus depends on the attachment of particles to air bubbles; which makes the bubble-particle attachment sub-process critical in achieving the separation of valuables from non-valuables (Albijanic *et al.*, 2010).

Water scarcities in parts of the world with massive mining industries have led to recycled process water and sea water usage gaining huge interest in the mining industry. These water types are of high ionic strength and therefore their water chemistry is very different to that of fresh water and may negatively affect the froth flotation process (Rao and Finch, 1989). Recycled process water is a combination of varying water streams from the process thus the proportions of dissolved solids will vary and affect the pH of the system (Levay et al., 2001). It is therefore valuable to understand how a change in pH in recycled process water will affect the flotation process.

It has been proposed that upon the addition of electrolytes, the electrical double layer is compressed which lead to the accelerated rupturing of the wetting film at the air-water and solid-water interface and in turn assists in faster bubble-particle attachment (Laskowski and Iskra, 1970; Li and Somasundaran, 1993; Harvey *et al.*, 2002; Laskowski and Castro, 2015).

Manono *et al.* (2017) and Tadie *et al.* (2016) both reported a decrease in solids recovery with process water at elevated pH values in a flotation system and attributed this to the hydroxo complexes and its possible precipitation on the mineral surface, hence imparting hydrophilicty on the particles. This study thus looks at the simultaneous effect of increasing ionic strength and pH from both a flotation and fundamental bubble-particle attachment perspective in a chalcopyrite and galena system respectively.

Materials and Methods

Mineral Sample

1 kg of Galena and 1 kg of Chalcopyrite obtained from Ward’s Science was crushed using a hammer to 100% passing 1000 microns. The respective sulphide mineral particles were then pulverized and sieved through 75 and 38 micron sieves to obtain a size fraction between 38 and 75 microns for the microflotation and attachment time tests. The fraction below 38 microns was sieved through a 25 micron sieve and the particles below 25 microns were used for the zeta potential measurements. The two minerals in the 2 size fractions of interest (38-75 microns and <25 microns) split, purged with nitrogen and refrigerated.

Water Quality

Standard synthetic plant water (1 SPW) as described by Wiese *et al.* (2005) was used as the baseline synthetic plant water for the test programme. In order to simulate the recycle, the amount of dissolved solids was increased five and ten times making up 5 SPW and 10 SPW respectively. The ionic concentrations of the three synthetic plant waters are depicted in Table 1.

Attachment Time Tests

The attachment timer (ACTA) used in this investigation was developed at Aalto University and has been described by Aspiala *et al.* (2018) and October *et al.* (2019). A detailed description of the experimental procedure in terms of particle bed building and running measurements is documented in October *et al.* (2019). Measurements were taken for each of the water qualities in Table 1. Further, these tests were performed in duplicate for each condition to minimise experimental error.

Microflotation Tests

The microflotation cell developed by Bradshaw and O’Connor (1996) was used to perform the microflotation tests in this work. 3 g of the respective sulphide minerals was mixed with 50 mL of the particular water quality under study; the mixture was then ultra-sonicated for 5 minutes to allow for good dispersion of the mineral mixture.. The suspension was then transferred to the microflotation cell and the pulp was circulated by a peristaltic pump at 90 rpm. Air was then introduced at the base of the cell at a flow rate of 7 mL/min and concentrates were collected at 2, 6, 12 and 20 minutes of flotation. The tailings and four concentrates were then filtered, dried and weighed. The microflotation tests were performed in duplicate to minimise error.

Zeta Potential Measurements

Very dilute mixtures of the particular water type and particles were made up; the dilute mixtures were then equally divided in six

Table 1: *Concentrations of ions for the various water qualities*

Water type	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+} mg/L	Cl^{-} mg/L	SO_4^{2-} mg/L	NO_3^{-} mg/L	CO_3^{2-} mg/L	TDS mg/L	Ionic Strength mol/L
1SPW	80	70	153	287	240	176	17	1023	0.0241
5 SPW	400	350	765	1435	1200	880	85	5115	0.1205
10 SPW	800	700	1530	2870	2400	1760	170	10230	0.241

containers and the pH was adjusted to 2, 4, 6, 8, 10 and 12 with dilute HCl or dilute NaOH. After 15 minutes on the magnetic stirrer the pH was measured again and adjusted where needed. 1 mL of the suspension was then transferred to the Malvern Dip Cell and inserted in the Malvern ZetaSizer where measurements were taken. All zeta potential measurements were performed in triplicate to reduce experimental error.

Results and Discussion

Figure 1 shows the recovery of galena in the microflotation cell for with the various synthetic plant waters at both the natural pH as well as at a pH 11. In terms of the galena recovery at the natural pH it is clear that the recovery increases as the ionic strength of the plant water increases, this can be attributed to the fact that an increase in ions result in the compression of the electrical double layer at the air-water and solid-water interface. This in turn will cause the accelerated rupturing of the film at the air-water and solid-water interface; increasing the attachment of particles to air bubbles (Laskowski and Iskra, 1970; Li and Somasundaran, 1993; Harvey *et al.*, 2002; Laskowski and Castro, 2015). The recovery of galena at the elevated pH reduced drastically compared to at the natural pH. With 1 SPW at a pH of 11 resulting in the poorest galena recovery. Similar results were obtained by Tadie *et al.* (2016) and this was said to be as a result of the precipitation of hydroxide species on the mineral surface. The recovery does however increase as the ionic strength increases even at the high pH.

Attachment time tests were further done to understand the effect of increasing pH and ionic strength on the bubble-particle attachment from a fundamental perspective, examining both the probability of attachment and the mass recovered through particle-bubble contacts. It is important to note, that the attachment probability is calculated by dividing the amount of bubbles with one or more attached particles by the total number of bubbles, but does not take into consideration how many particles are actually attached to one particular bubble. In certain experimental conditions particles tend to attach to each other and get recovered as clusters. In these cases relatively large mass of particles can be recovered, even when the quantified attachment probability is low.

Figure 2 shows the attachment probability of galena particles to air bubbles with plant water of increasing ionic strength at both the natural pH and elevated pH so as to complement the microflotation results. The attachment contact time apparatus also collects the particles that have successfully attached to the bubbles, the mass recovered of these particles are also depicted in Figure 2.

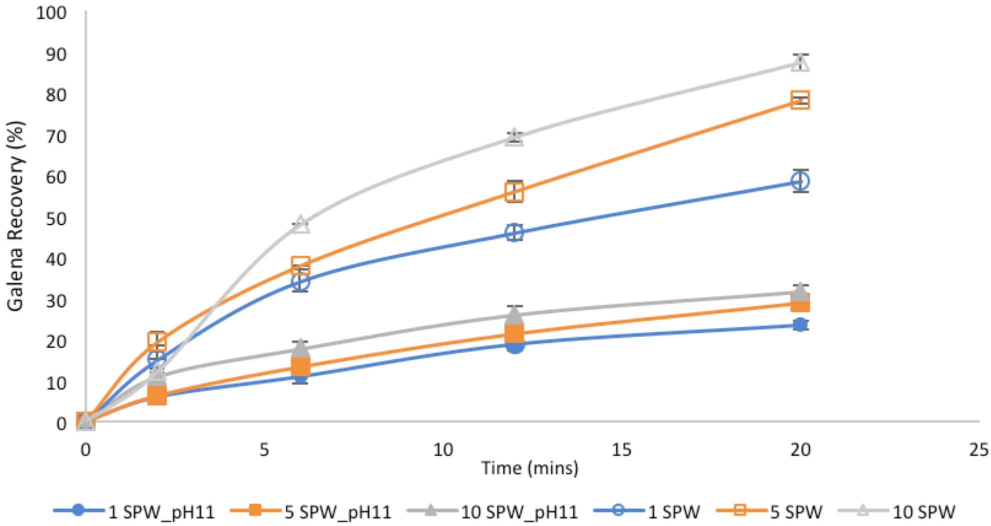


***Figure 1:** Microflotation of Galena with various water qualities*

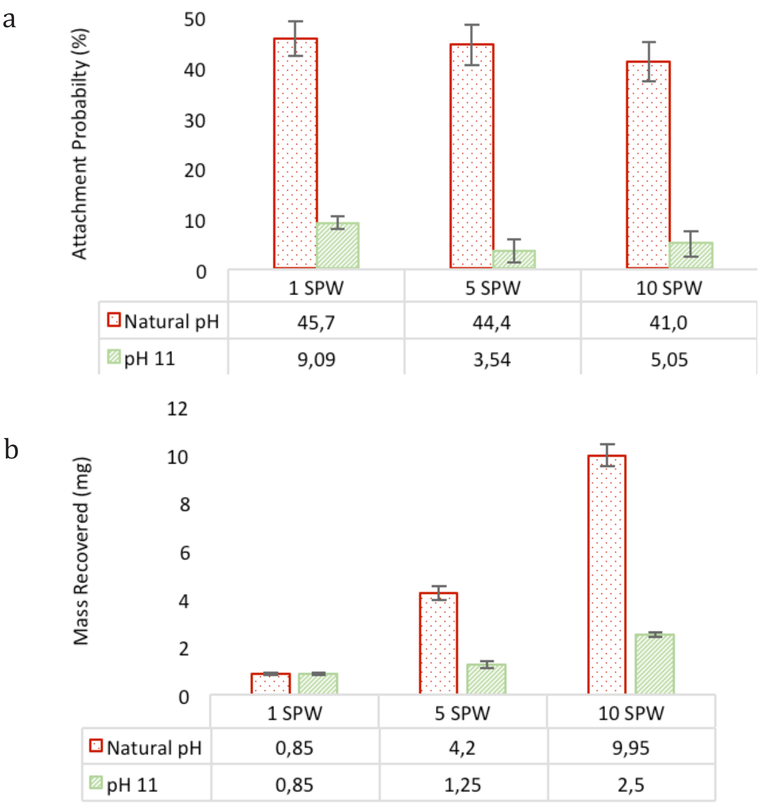


Figure 2: *Attachment Probability (a) and Mass Recovered of Galena particles under various water qualities*

In terms of the attachment probability, it is clear that the probability of galena particles attaching to air bubbles are dramatically reduced at the high pH. However, the result of the combined effect of increasing ionic strength at pH 11 on the attachment probability is not clear. Therefore, the result showing the mass of particles that successfully attached to the bubbles prove to be useful. As with the microflotation tests, the mass of galena recovered in the ACTA increases with increasing ionic strength at the natural pH. In addition, at pH 11 the mass recovered is also substantially lower than at the natural pH but the mass recovered does increase with water of high ionic strength even at pH 11. Thus, matching the microflotation results.

Figure 3 shows the recovery of chalcopyrite in the microflotation cell for with the various synthetic plant waters at both the natural pH as well as at a pH of 11. The recovery of chalcopyrite at the natural pH is relatively similar with the three water qualities, this is possibly due to the floatable nature of chalcopyrite. However, the recovery of chalcopyrite with the highest ionic strength plant water does give a better recovery, as with galena this is attributed to the compression of the electrical double layer in waters of high ionic concentration. Similarly, as with galena the chalcopyrite recovery at the elevated pH is reduced drastically compared to at the natural pH. With 1 SPW at a pH of 11 resulting in the poorest chalcopyrite recovery. The recovery does however increase as the ionic strength increases even at the high pH.

Figure 4 shows the attachment probability of chalcopyrite particles to air bubbles with plant water of increasing ionic strength at both natural pH and elevated pH as well as the mass of particles recovered at the conditions under study. Both the attachment probability and mass recovered perfectly matches the results of the microflotation. Thus, reinforcing the trend of a decrease in bubble-particle attachment at an increased pH but at a higher

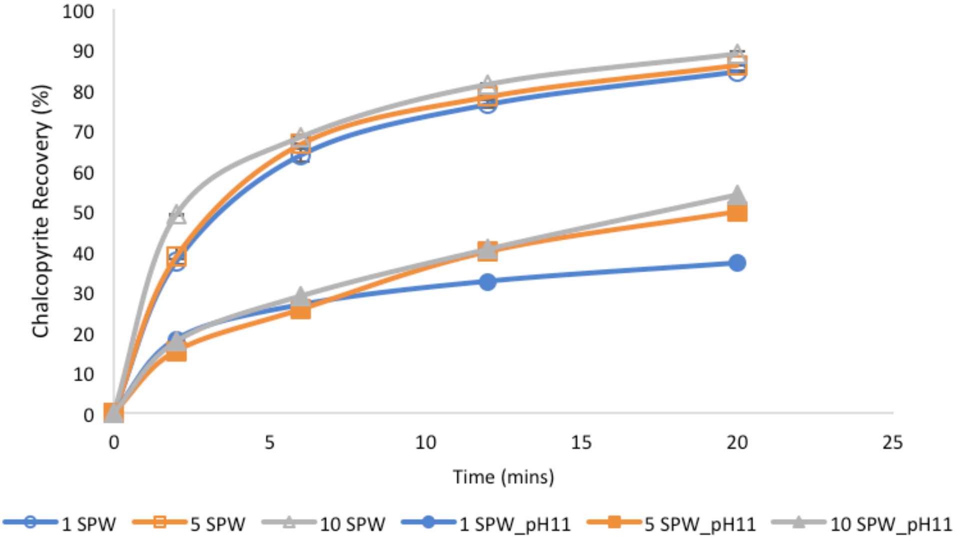
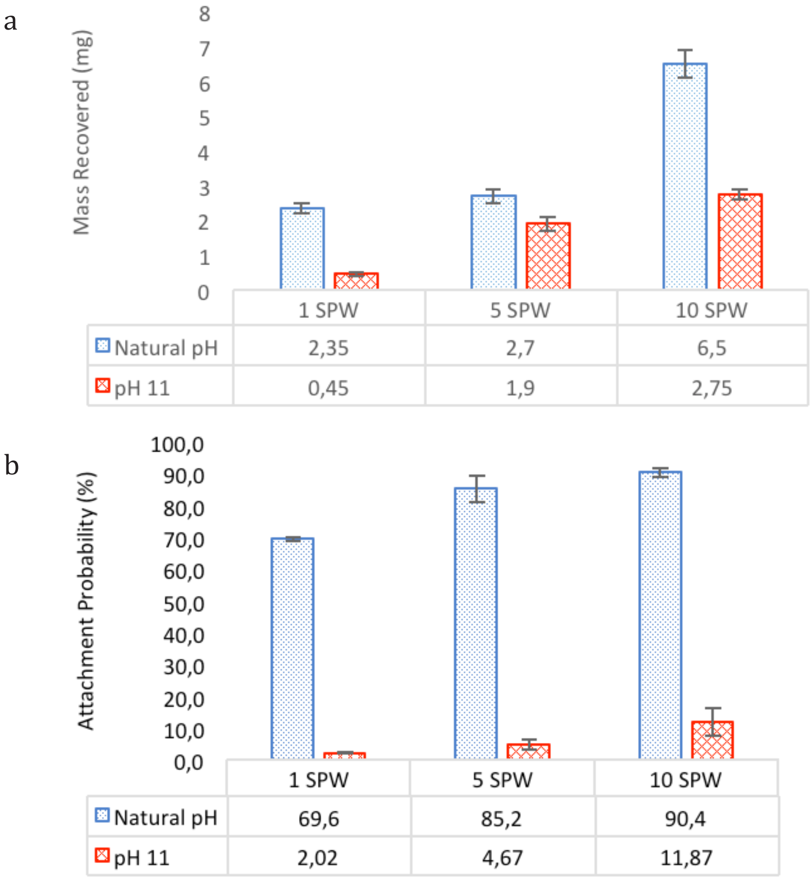


Figure 3: *Microflotation of Chalcopyrite with various water qualities*



	1 SPW	5 SPW	10 SPW
▨ Natural pH	2,35	2,7	6,5
☒ pH 11	0,45	1,9	2,75

	1 SPW	5 SPW	10 SPW
▨ Natural pH	69,6	85,2	90,4
☒ pH 11	2,02	4,67	11,87

Figure 4: *Attachment Probability (a) and Mass Recovered Chalcopyrite particles under various water qualities*

pH the bubble-particle attachment increases with waters of higher ionic strengths in both a flotation system as well as a fundamental bubble-particle attachment system.

Figure 5 show the zeta potential of galena (a) and chalcopyrite (b) under the various water qualities. Both sulfide minerals display a similar trend in terms of charge on the mineral; with the zeta potential becoming less negative with increase in ionic strength of the synthetic plant water. This phenomenon is indicative of the compression of the electrical double layer as the ionic concentration of the water increases (Moignard *et al*., 1977). This result was also observed by October *et al*. (2019) in a pyrrhotite system as well as Ikumapayi *et al*. (2012) in a galena system. These authors attribute this to be due to the increased passivation of the mineral surface by the increasing cation concentration. Upon closer study of these zeta potential results, an increase in potential with all the synthetic plant water is observed between pH values of 10 and 12. Which is said to be because of metal hydroxide precipitation or oxidation at the mineral surface (Harvey *et al*., 2002; Ikumapayi *et al*., 2012; Hirajama *et al*., 2016). Speciation diagrams as shown by Manono *et al*. (2018) show that at this pH range for these waters, the content of hydroxo species increases substantially with the highest concentration of these species occurring in the 10 SPW plant water at pH values of 11 and above.

A similar study by Manono *et al*. (2017) looking at the interactive effect of ionic strength and pH on a Merensky ore in a batch flotation system also showed a decrease in recovery at pH 11 and this was attributed to the increase in hydroxo complexes. While, Fuerstenau *et al*. (1999) proposed that in alkaline conditions metal ions hydrolyze and deposit hydrophilic metal hydroxides on the mineral surface. The decrease in sulfide mineral bubble-particle attachment at pH 11 from this more fundamental study considering pure minerals may also be attributed to the increase in hydroxo complexes deposited on the mineral surface as supported by the zeta potential measurements in Figure 5. This deposition of hydrophilic metal hydroxides on the mineral surface will also hinder the adsorption of the collector on the mineral surface, decreasing the bubble-particle attachment (Rao, 2004).

The bubble-particle attachment results both fundamental and microflotation shows how the attachment of sulfide mineral particles to air bubbles increases with waters of higher ionic strength which is due to the compression of the electrical double layer as reinforced by Figure 5. At a high pH the bubble-particle attachment decreases substantially but however still increases with increasing ionic strength. It would be expected that a high pH and high ionic strength water would result in the poorest performance as the hydroxide concentration is even higher, but this is not the case demonstrating the effect of the compression of the electrical double layer even in alkaline solutions.

Conclusions

Fundamental bubble-particle attachment tests and microflotation tests show a substantial decrease in the attachment of sulfide minerals to air bubbles with synthetic plant water at a pH of 11. This has been attributed to the

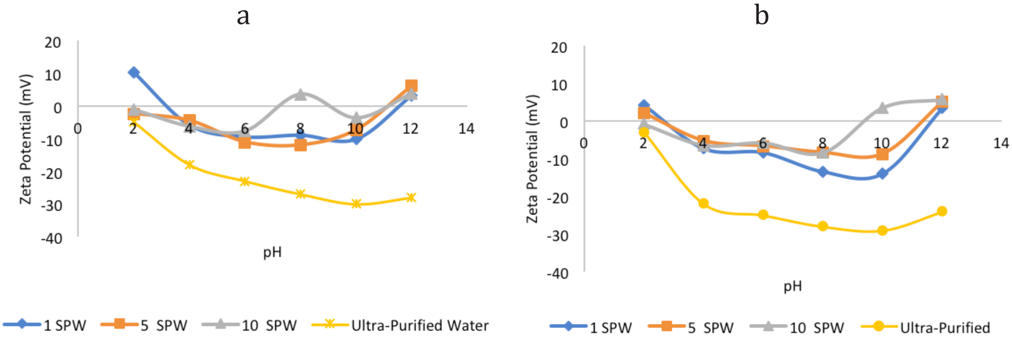


Figure 5: Zeta Potential of Galena (a) and Chalcopyrite (b) under various water qualities

increase in hydroxo complexes at this pH, inducing hydrophilicity upon the particles or hindering the action of the collector. This work does however show that increases in sulfide mineral recovery can be attained at a high pH with plant water of high ionic strengths.

Acknowledgements

This work is financed by the National Research Foundation of South Africa (NRF) [Grant number 103641] and this project has received funding from the European Union H2020 programme under grant agreement No 730480. Any opinion, finding and conclusion or recommendation expressed in this material is that of the authors and the NRF does not accept any liability in this regard. Further the financial and technical contributions from the South African Minerals to Metals Research Institute (SAMMRI) is also acknowledged.

References

Albijanic, B., Ozdemir, O., Nguyen, A. & Bradshaw, D. (2010). "A Review of Induction and Attachment Times of Wetting Thin Films between Air Bubbles and Particles and Its Relevance in the Separation of Particles by Flotation." *Advances in Colloid and Interface Science* 159 (1). Elsevier B.V.: 1–21. https://doi.org/10.1016/j.cis.2010.04.003.

Aspiala, M., Schreithofer, N., Serna-Guerrero, R. (2018). Automated contact time apparatus and measurement procedure for bubble-particle interaction analysis, Minerals Engineering, 121(1):77-82.

Bradshaw, D. & O'Connor, C. (1996) Measurement of the sub-process of bubble loading in flotation. Minerals Engineering. 9: 443-448.

Fuerstenau, DW, Herrera-Urbina, R, McGlashan, DW (1999) Studies on the applicability of chelating agents as universal collectors for copper minerals. International Journal of Mineral Processing 58, pp 15-33.

Harvey, P.A., Nguyen, A.V. & Evans, G.M. (2002). "Influence of Electrical Double-Layer Interaction on Coal Flotation." *Journal of Colloid and Interface Science* 250 (2): 337–43. https://doi.org/10.1006/jcis.2002.8367.

Hirajima, T., Pandhe, G., Suyantara, W., Ichikawa, O., Mohamed, A., Miki, H. & Sasaki, K. (2016). "Effect of Mg^{2+} and Ca^{2+} as Divalent Seawater Cations on the Floatability of Molybdenite and Chalcopyrite." *Minerals Engineering* 96–97. Elsevier Ltd: 83–93. https://doi.org/10.1016/j.mineng.2016.06.023.

Ikumapayi, F., Makitalo, M., Johansson, B. & Hanumantha, K. (2012). "Recycling of Process Water in Sulphide Flotation : Effect of Calcium and Sulphate Ions on Flotation of Galena." *Minerals Engineering* 39. Elsevier Ltd: 77–88. https://doi.org/10.1016/j.mineng.2012.07.016.

Laskowski, J., and Castro, S. (2015). "Flotation in Highly Concentrated Electrolyte Solutions," 1–12.

Laskowski, J. & Iskra, J. (1970). Role of capillary effects in bubble-particle collision in flotation. Transactions of the Institution of Mining and Metallurgy. 79, C6.

Levay, G., Smart, RStC, & Skinner, W. M. 2001. The impact of water quality on flotation performance. Journal of the South African Institute of Mining and Metallurgy, 101, 69-75.

Li, C. & Somasundaran, P. (1993). "Role of Electrical Double Layer Forces and Hydrophobicity in Coal Flotation in NaCl Solutions." *Energy and Fuels* 7 (2): 244–48. https://doi.org/10.1021/ef00038a014.

Manono, M.S., Matibidi, K., Thubakgale, C.K., Corin, K.C., Wiese, J.G. (2017). Water Quality in PGM Ore Flotation: Depressing and Frothing Effects Of The Ionic Strength Of Plant Water And pH. In Proceedings of 13th International Mine Water Association Congress, Paper 1125, Finland, Lappeenranta, 25-30 June

Manono, M.S, Corin, K.C. and Wiese, J.G. (2018). "Perspectives from Literature on the Influence of Inorganic Electrolytes Present in Plant Water on Flotation Performance." *Physicochemical Problems of Mineral Processing* 54 (4): 1191–1214. https://doi.org/10.5277/ppmp18157.

Moignard, M.S., James, R.O., Healy, T.W. (1977). Adsorption of calcium at the zinc sulphide–water interface. Australian Journal of Chemistry 30, 733–740.

October, L.L., Corin K.C., Schreithofer, N., Manono, M.S., Wiese, J.G. (2019). "Water Quality Effects on Bubble-Particle Attachment of Pyrrhotite" *Minerals Engineering* 131. Elsevier Ltd: 230–236. https://doi.org/10.1016/j.mineng.2018.11.017.

Rao, S.R., Finch, J.A. (1989). A review of water re-use in flotation. Minerals Engineering 2 (1), 65–85.

Tadie, M, Corin, K, Wiese, J, O'Connor, C, (2016) Application of potential control to the flotation of galena by varying dissolved oxygen, pH and ionic strength levels. Presented at the XXVIII Mineral Processing Congress (IMPC2016), Quebec City, Canada.

Wiese, J., Harris, P., Bradshaw, D., (2005) The influence of the reagent suite on the flotation of ores from the Merensky reef. Miner. Eng. 18, 189–198. doi:10.1016/j.mineng.2004.09.013.

Wills, B.A. & Finch, J.A. (2016). WILLS' Mineral Processing Technology, An introduction to the practical aspects of ore treatment and mineral recovery. Eighth Edition. Butterworth-Heinemann Elsevier.