

Water Quality in PGM Ore Flotation: The effect of Ionic Strength and pH

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Abstract Water and its chemistry are important variables in froth flotation. The presence of electrolytes in water may form either hydroxo species or precipitates in the flotation pulp when the process pH is altered. This may alter the chemical interactions that enable the process.

This study investigates the interactive effect of plant water ionic strength and pH in the flotation of a sulphidic PGM bearing ore.

Results suggest that water quality variations may have effects at both the air-water interface as well as the mineral air interface.

Key words Froth stability, Ionic strength, pH, Water quality, Water recovery

Introduction

The quest for a cleaner and safer environment with clean surface and ground water has led to increased recycling of process water within the minerals processing industry. Since the chemistry of process water is entirely different from fresh water and changes as water is recycled, there is a concern about the possible effects of its constituents (ion type, ionic strength etc.) on the efficiency of the flotation process (Rao and Finch, 1989). Studies have shown that recycled process water in mineral processing has a high salinity, contains potentially toxic metals ions, flotation reagents, organics and other pollutants (Slatter et al. 2009). Therefore, process water treatment and reuse has much academic and industrial relevance (Chen et al. 2008).

In response to the scarcity of fresh water, and the tight environmental legislation on water usage, PGM bearing ore flotation circuits make use of recycled process water. However, the chemistry of recycled process water may alter the performance of the flotation system. It is therefore required to understand the effects of these elements on the flotation process. Electrolytes in recycled process water can hinder the collector from adsorbing onto the mineral surface (Wang et al, 2014; Hancer et al. 2001). It has been reported that ions such as Ca^{2+} , $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} may activate pentlandite and pyrrhotite mineral surfaces at normal process pH 9 while $\text{S}_2\text{O}_3^{2-}$ and Ca^{2+} compete with xanthate for adsorption on pentlandite surfaces (Hodgson and Agar, 1989). Shackleton et al. (2003) stated that Ca^{2+} ions can chemisorb onto the pentlandite surface, replacing metal ions at the surface and possibly reducing particle surface hydrophobicity. Metal ions hydrolyze in alkaline pH and may deposit as hydrophilic metal hydroxides, sulphates or carbonates on the mineral surfaces (Fuerstenau et al. 1999). The reduction in mineral surface hydrophobicity could compromise the efficiency of the particle – bubble attachment sub-process

and consequently the performance of the flotation system (Koh et al. 2009, Schwarz and Grano, 2005). Ionic strength and the type of cations in solution can have an influence on the extent of activation. The presence of divalent cations in solution like Mg^{2+} or Fe^{2+} can compete with metal ions like Cu^{2+} on the mineral surface (Lascelles et al. 2001). Studies by Parolis et al. (2008) and Shortridge et al. (2003) showed that the depression of naturally floatable gangue and the efficacy of carboxymethyl cellulose (CMC) were very much dependent upon the type and ionic strength of the electrolytes present in solution. They showed that when divalent cations (Ca^{2+} and Mg^{2+}) were present, depression was greater than when monovalent cations were present (K^+); and that increasing the ionic strength of the electrolytic conditions resulted in even greater depression of the naturally floatable gangue.

The presence of electrolytes can improve particle-bubble attachment efficiency through compressing the electric double layer and thus reducing the electrostatic repulsion between particles and bubbles (Kurniawan et al. 2011). Electrolytes are favourable to the formation of smaller more stable bubbles due to the influence of electrolytes on gas dispersion properties (bubble size, gas hold-up etc.). Smaller bubbles increase the particle-bubble collision probability (Pugh et al. 1997; Bićak et al. 2012) and thereby improve particle-bubble attachment efficiency (Hewitt et al. 1994). An increase in electrolyte concentration increases the density of ions in the bulk solution resulting in counter-ion diffusion into the Stern layer, which increases attraction forces and decreases repulsion forces (Wang et al. 2014). The impact of ionic strength on bubble size is attributed to the fact that inorganic ions in water seem to slow inter-bubble drainage and thereby inhibit bubble coalescence and promote stability in the froth phase (Barker, 1986; Craig et al. 1993).

However, whether there is an interactive effect of ionic strength of plant water and pH is not well understood. In literature these two parameters have been studied individually. pH has been investigated mostly on single salt electrolytes in order to simplify the complex water chemistry. This approach does not truly represent the complex water chemistry in flotation circuits and would not allow plant operators to predict the impact of ionic strength and pH when more than one hydroxo species, inorganic complex or precipitate is present in the system. Therefore, the purpose of this study is to investigate the interactive effect of ionic strength and pH on the floatability of a PGM containing ore with a keen focus on the depression of gangue as well as froth stability.

Methods

1 kg ore samples were milled at 66% solids in synthetic plant water for 15 minutes in order to obtain a grind of 60% passing $75\mu m$. The milled slurry was transferred into a 3L Denver flotation cell. The volume of the cell was made up to generate 35% solids using synthetic plant water (at the required ionic strength). The cell was fitted with a variable speed drive and the pulp level was controlled manually. The impeller speed was set at 1200 rpm. An air flow rate of 7 L/min was maintained for all flotation experiments and a constant froth height of 2 cm was sustained throughout. Reagents were dosed and

allowed to condition as shown in Table 1. Concentrates were collected at 2, 6, 12 and 20 minutes respectively by scraping the froth into a collection pan every 15 seconds. A feed sample was taken before each flotation test and a tails sample after each flotation test. Water usage and pH were monitored throughout the tests. Feeds, concentrates and tails were filtered, dried and weighed before analysis. The flotation test work was carried out at pH 9 and pH 11. The addition of reagents and sequence thereof is shown in Table 1. Synthetic plant water (Table 2) of various ionic strengths (IS) and total dissolved solids (TDS) was used throughout the test work. All the reagents were supplied by Senmin. Copper and nickel assays were conducted at UP (University of Pretoria) using X-Ray Fluorescence (XRF) and Leco was used for determination of sulphur. For the 2-phase batch flotation test work only the water type and pH were varied. Prepared plant water solutions were transferred directly to a 3 L Barker flotation cell. The operating conditions of the cell were maintained as in the 3-phase test work with the frother, DOW 200, dosed at 40 ppm. The collection of (foam) concentrates was done at 2, 6, 12 and 20 minutes respectively by scraping the foam into a collecting pan every 15 seconds. Two phase froth column tests were conducted for all the water types as presented in Table 2 and pH 9 and pH 11) with a frother dosage of 5 ppm DOW 200. A full experimental set up and operation of the University of Cape Town (UCT) Centre for Minerals Research (CMR) froth column which was used to obtain the foam height and collapse time presented in this study is given in Manono et al. (2013). All tests were conducted in duplicate in order to ensure reproducibility and reliability of the tests data. Standard error bars are shown in each graph presented and the standard error was well below 5 % for each data presented.

Table 1: Reagents addition and sequence

Reagent	Type	Dosages (g/t)	Conditioning time (min)
Collector	SIBX	150	15
Depressant	Sendep 30E	0, 100, 500	3
Frother	DOW200	40	1

Table 2: Concentration of ions present in synthetic plant water (SPW)

Water type	Ca ²⁺ (ppm)	Mg ²⁺ (ppm)	Na ⁺ (ppm)	Cl ⁻ (ppm)	SO ₄ ²⁻ (ppm)	NO ₃ ⁻ (ppm)	NO ₂ ⁻ (ppm)	CO ₃ ²⁻ (ppm)	TDS mg/L	Ionic Strength [mol/L]
1SPW	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	0.1860

Results and Discussion

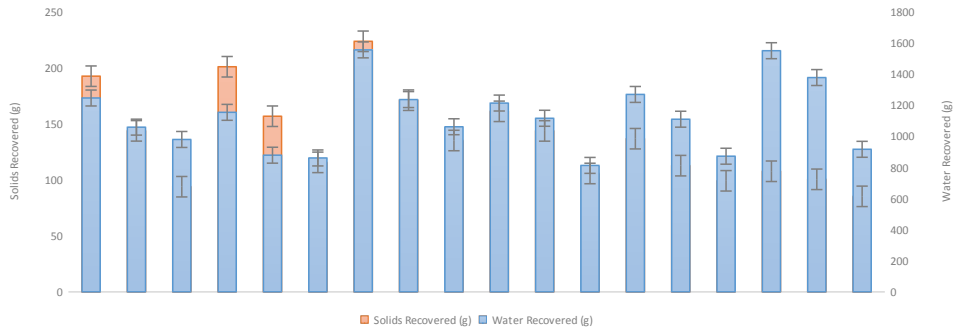


Figure 1: Final solids and water recovery for all tested conditions.

From Figure 1, it is evident that at pH 9, both the solids and water recoveries decreased with an increase in depressant dosage for all ionic strength conditions. Further to this, it can be seen that with increasing ionic strength (at pH 9), the recovery of solids and water was higher compared to lower ionic strengths. Interestingly, at pH 11 an opposite trend was observed regarding the effect of ionic strength on solids recovery. Here, the solids recovery decreased as the ionic strength of plant water increased. The water recovery however increased at increasing ionic strengths as is the case at pH 9.

The increase in water recovery with increasing ionic strength of process water is speculated to have been caused by an enhancement in froth stability due to the presence of high amounts of ions (Corin et al. 2011; Ejtemaei et al. 2016; Wiese et al. 2007). The increase in water recovery at a pH 11 is attributed to the excessive presence of hydroxyl ions which may have caused an increase in the mobility of the froth. It is believed that increasing the ionic strength of plant water and pH inhibits bubble coalescence retarding inter – bubble drainage (Craig et al. 1993; Manono et al. 2013; Wiese, 2009; Yousef et al. 2003).

The decrease in solids recovery at pH 11 with increasing ionic strength is believed to have been as a result of the presence of ions, hydroxo species and precipitates that can influence the mineral surface by changing the hydrophobicity of the mineral and hindering the collector from adsorbing onto the mineral surfaces (Bićak et al. 2012; Bickerman, 1953). This in agreement with Ikumapayi et al. (2012) who showed that the adsorption of calcium and sulphate ions led to the reduction of the negative surface charge and the xanthate adsorption to the mineral surface resulting in less solids recovery. These findings are also in agreement with Tadie et al. (2016) who investigated the application of potential control to the flotation of galena under varying pH who showed that at pH 11.8, the recovery of galena dropped significantly compared to pH 9.2, indicating the depressing effect of hydroxyl ions at higher pH.

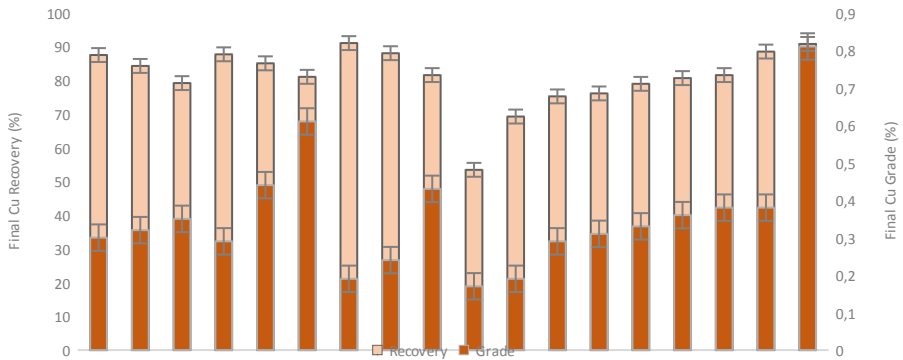


Figure 2: Final Cu recovery and grade of all tested conditions.

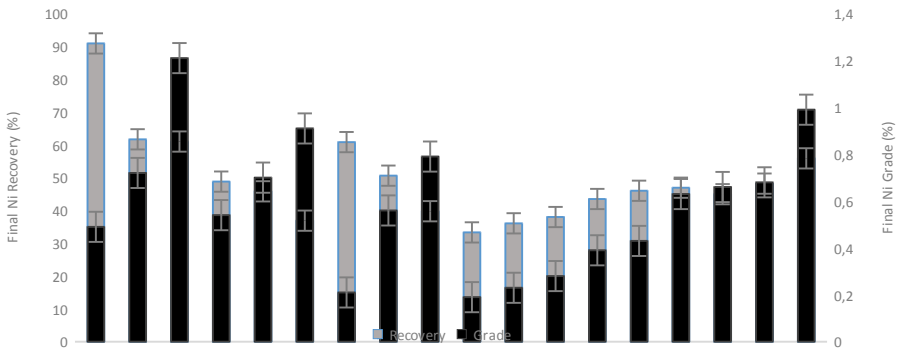


Figure 3: Final Ni recovery and grade for all tested conditions.

Figure 2 and Figure 3 depicts the final Cu and Ni recovery and grade respectively. At pH 9, it is shown that an increase in depressant dosage resulted in a decrease in mineral recovery, as expected. However, an increase in ionic strength resulted in a slight increase in mineral recovery, which agrees with the increased solids recoveries. Cu and Ni grades increased with an increase in depressant dosage, as expected, however there was a decrease in mineral grades with increasing ionic strength. Mineral recoveries are lower when the pH is increased from 9 to 11. It is also worth noting that at pH 11 mineral grades tend to increase with increasing ionic strength. It must be noted that the 91 % recovery of Ni for 1SPW at 0 g/t could be due to an experimental error from the elemental assays.

The increase in mineral recoveries with increasing ionic strength is evidence of the froth stabilizing effect of increased ionic strength which is also evident in the solids recovery shown in Figure 1 at pH 9 (Craig et al. 1993). A decrease in the Cu and Ni grade at pH 9 with increasing ionic strength could be an indication that the increase in froth stability resulted in more gangue being recovered to the concentrate as previously reported by Corin et al. (2011), Corin and Wiese (2014) and Manono et al. (2012). The trend of an increase in the Cu and Ni recoveries and grades with increasing ionic strength at pH 11 could be attributed to

a possibly enhanced depressant (CMC) selectivity or the hydroxyl species and precipitates which may have selectively deposited onto gangue minerals, inducing their hydrophilicity, enhancing their coagulative nature with the result of poor adsorption of the collector. These findings are in agreement with Parolis et al. (2008) who showed that the presence of di-valent ions such as Ca^{2+} improved the depressive nature of CMC.

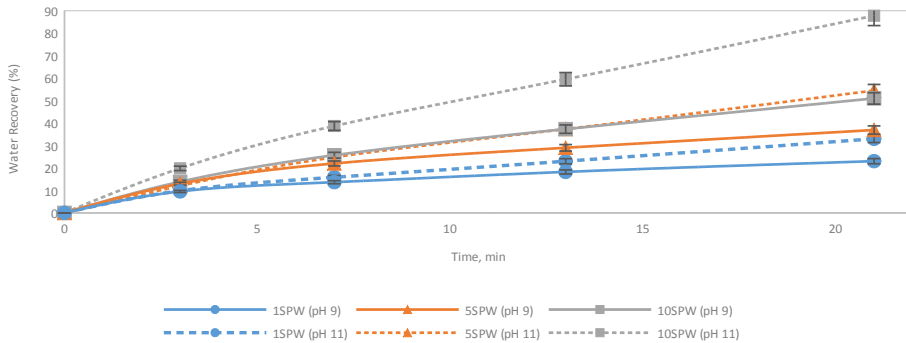


Figure 4. The effects of ionic strength and pH on water recovery as a function of time

Figure 4 illustrates the effect of ionic strength and pH on water recovery as a function of time. It is shown that the rate of water recovery increased with increasing ionic strength as well as with increasing pH.

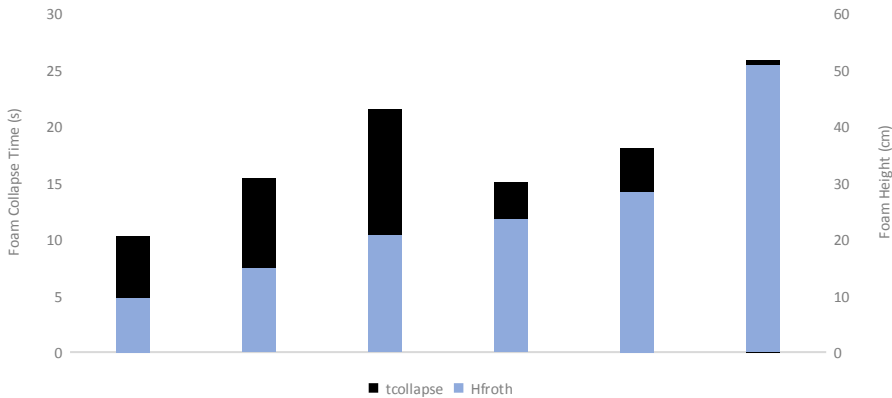


Figure 5. Effect of ionic strength and pH on foam height and foam collapse time.

Figure 5 illustrates the effects of ionic strength and pH on foam height and foam collapse time. Both foam height and foam collapse time increased with increasing ionic strength and pH. The higher pH resulted in higher foam height and longer foam collapse time compared to the lower pH.

A frother dosage of 5 ppm was chosen in the 2-phase experiments so as to elucidate frothing effects of ionic strength and pH as this dosage is below the selected frother’s critical

coalescence concentration. The results shown in Figure 4 and Figure 5 are indicative of an enhancement in froth stability with increased ionic strength and increased pH and are in agreement with the batch flotation performance given in Figure 1. It is postulated that this froth stabilising effect of ionic strength and pH is a result of a decrease in bubble size owing to an inhibition of bubble coalescence which is (mechanistically) attributed to a decrease in inter-bubble drainage rate and the stability of the inter-bubble film (Craig et al. 1993).

Conclusions

It is clear that the increase in both pH and ionic strength favour high water recoveries which indicates froth stabilisation. It was also shown that an increase in both pH and ionic strength resulted in a decrease in solids recovery despite an increase in water recovery. This finding was attributed to the enhancement of the depression of naturally floatable gangue minerals, which is a result of hydroxyl species and precipitates which selectively coated the gangue mineral surfaces as the ionic strength increased at pH 11.

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