MECHANISMS RESPONSIBLE FOR PARTICLE FORMATION DURING METAL SULPHIDE PRECIPITATION PROCESSES

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ABSTRACT

The use of novel biological processes, based on the activity of SRB, has been introduced as viable alternatives for AMD treatment. However, a number of challenges exist, particularly with respect to the metal sulphide precipitation step of these processes. Metal sulphide precipitation processes are inherently driven by high degrees of supersaturation and a large number of small particles, with unfavourable solid-liquid separation characteristics are formed during the process. In this study, the effect of metal to sulphide molar ratio and operating pH on the nature and settling behaviour of the copper and zinc sulphide precipitates formed during sulphide precipitation process was investigated. It was shown that a large number of small particles with highly charged surfaces and poor settling characteristics were formed when copper sulphide precipitation was conducted at pH 6 with excess amount of sulphide present in solution. However, when the process was conducted with excess amount of sulphide present in solution using operational pH below 6, the size and the settling characteristics of the copper sulphide particles were significantly improved while the number and zeta potential of the particles was decreased. By comparison, for zinc sulphide precipitation a small change in the number and size of the particles was obtained for all the different metal to sulphide molar ratios and operating pH conditions. However, a decrease in the metal to sulphide molar ratio resulted in an increase in the zeta potential of the particles when the zinc sulphide precipitation process was operated at pH 6. When the precipitation process was conducted using excess amount of sulphide in solution at operational pH below 6, the zeta potential of the particles was decreased and the settling and dewatering characteristics of the precipitate were improved. From all the results obtained, it was found that the amount of reactive sulphide species (HS^- and S^{2-} ions) available in solution was important in determining the nature and surface characteristics of the particles produced and this was dependent on the pH-dependent on aqueous hydrogen sulphide speciation.

1. INTRODUCTION

Many industrial processes, especially the mining and metallurgical process industry, produce acidic wastewater effluents containing significant amounts of metals. When these metal contaminated wastewaters are exposed to the environment, they can cause serious and sometimes permanent ecological damage (Micera and Dessi, 1988). Acid mine drainage (AMD), has been identified as one of the most important environmental problems facing the mineral industry globally (Ribet et al, 1995). AMD is caused by chemical or biologically catalysed oxidation of sulphide minerals upon exposure to atmospheric oxygen and moisture. It is characterised by low pH and elevated concentrations of dissolved heavy metals and sulphate. Several treatment technologies have been developed for the treatment of AMD prior to discharge into the environment (Johnsonn and Hallberg, 2005). Traditionally, chemical precipitation by addition of lime is employed as the primary method for metal removal and neutralisation. In recent years the use of biological treatment processes, based on the activity of sulphate reducing bacteria (SRB), have become more prominent. In these treatment processes, sulphide and bicarbonate alkalinity are produced by SRB through the oxidation of a suitable electron donor and carbon source. The bicarbonate alkalinity is employed to neutralise acidic effluents while the sulphide ions are used to effect precipitation of dissolved metal ions (Bhagat et al, 2004). The SRB based treatment technology has been established and applied successfully both at laboratory and full scale (Dvorak et al, 1992; Hulshoff Pol et al, 2001; Kaksonen et al, 2003; van Houten et al, 2006; Huismann et al, 2006). However, a number of challenges exist around the precipitation step, particularly where the recovery of valuable metals is desired. Due to the low solubility of metal sulphides and the high affinity between the reactants, metal sulphide precipitation reactions are inherently driven by high levels of supersaturation. As a result, metal sulphide precipitation reactions are difficult to control and a large number of small particles are formed during the process. This leads to significant technical challenges with respect to solid-liquid separation and subsequent recovery of the precipitate. Despite the theoretically high metal removal, due to the low solubility of the resulting metal precipitate the practical efficiency is often significantly lower.

Most of the studies carried out on metal sulphide precipitation in relation to removal of metal ions from solution have focused on metal sulphide precipitation kinetics and/or the selective precipitation of metal ions from solution (Bryson and Bijsterveld, 1991; Rickard, 1995; Jandova et al, 2005, Sampaio et al, 2009) without investigating the effect of processing conditions on the nature of the resulting precipitates and their processing characteristics.

Al-Tarazi (2004) studied the effect of operating conditions on the particle rate processes involved in metal sulphide precipitation under different regimes of pH, metal to sulphide ratio and residence time using an MSMPR. They showed that all these factors had an effect on the particle rate processes. However, the investigation did not take into account the colloidal nature of the precipitates formed during the process. The correlation between the processing conditions and product characteristics during precipitation is determined and controlled by the solid-liquid equilibria, precipitation kinetics, colloid-surface chemistry and reactor selection and design (Demopolous, 2009). In this study, an investigation into the effect of processing conditions on the mechanisms responsible for particle formation during metal sulphide precipitation processes was conducted. The effect of metal to sulphide molar ratio and operating pH on the nature of the particles produced during metal sulphide precipitation process and their settling characteristics was determined. The particle size distribution (PSD) related information and surface characteristics of the produced particles was used to relate the effect of processing conditions on the nature and solid-liquid separation characteristics of the precipitates.

2. MATERIALS AND METHODS

Reagents

All the reagents ($CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $Na_2S.9H2O$, NaOH and HCl) used in this investigation were analytical grade chemicals obtained from Merck. The solutions were made up to required concentrations using Millipore de-ionised water. The pH electrode was calibrated using pH buffer solutions from Merck before every experiment.

Experimental Set-Up

Experiments were performed in a 1.0 L glass vessel with a working volume of 900 mL. The reactor was operated as a continuously stirred tank reactor (CSTR) equipped with four baffles and an outlet for the effluent outflow. Mixing was achieved using an overhead stirrer fitted with a Rushton turbine which was agitated at 620 rpm in all the experiments. The top of the reactor was covered with a lid that had ports for pH electrode, reagent inlet, impeller shaft and nitrogen gas inlet.

The metal and the sulphide solutions were pumped into the reactor using pre-calibrated Watson Marlow 520S (Falmouth, UK) pumps. The flow rate of the reagents was kept at 50 $mL.min^{-1}$ for each reagent and the total flow rate (100 $mL.min^{-1}$) was kept constant in all the experiments. A pH stat device (Metrohm 800 Dosino, Switzerland), auto dosing 0.5 M HCl/1.0 M NaOH, in combination with a sulphide resistant pH electrode (Metrohm AG, Switzerland) was used for reading and controlling the pH at a desired value. The dosing device was connected to a computer unit equipped with the control software (tiamo^{TM} version 1.2, Metrohm AG, Switzerland) for data logging and data was logged every 2s.

Experimental Design

The experimental programme was divided into two phases. In the first phase, the effect of metal to sulphide ratio (i.e. metal to sulphide molar ratio) on the precipitation process at a constant operational pH was investigated. For all the experiments in this investigation, the pH was kept constant at 6 and the effect of different metal to sulphide ratio (2.0, 1.0 and 0.67) on the metal sulphide precipitation behaviour was investigated. In the second part of the work, an investigation into the effect of operating pH on the precipitation process was conducted. The investigation was carried out by operating the precipitation process at different pH levels while keeping the metal to sulphide ratio (0.67) constant. For copper sulphide precipitation, the investigated pH was 2, 4 and 6 and for zinc sulphide precipitation pH 3, 4, 6 and 8 were investigated. The process was characterised by studying the PSD of the precipitate, the surface charge carried by the particles, the settling rate of the precipitate and the amount of metal ions precipitated from solution.

Experimental Procedure

The reactor was first filled with 900 mL of Millipore water and the water was de-oxygenated by bubbling with nitrogen gas for 20 minutes. After 20 minutes, the nitrogen gas flow rate was adjusted to a lower level to minimise bubble formation and possible particle flotation. The reagents were then pumped into the reactor at the same flow rate. The pH was controlled at a desired level by adding required amounts of 0.5M HCl or 1.0 M NaOH using the dosing device (Metrohm 800 Dosino, Switzerland).

Sampling and Analytical Techniques

A 25 mL sample was collected from the effluent stream every 10 minutes over a period of 90 minutes. The sample bottles used for collecting the samples were cleaned with acid, rinsed several times with Millipore water and dried in an oven before use. A portion of the collected sample was used for PSD measurements using laser diffraction techniques (Malvern Mastersizer and Zetasizer Nano Series). All the PSD measurements were done within 5 minutes of collecting the samples. Another portion of the sample was used to measure the zeta potential of the non-settling particles using the Zetasizer (Malvern, Nano-ZS model) after all the settling particles were separated from the sample.

The remaining portion of the sample was then filtered through a 0.22 μm filter and used to analyse for the amount of metal ions remaining in solution using atomic absorption spectroscopy (Varian 110).

A technique based on moment transformation of the number density function n(L) described by Randolph and Larson (1988) was used to derive and describe PSD related information. This technique has been successfully used by Bramley et al (1996), Ntuli and Lewis (2007), and Hove et al (2008).

3. RESULTS AND DISCUSSION

The Effect of Metal to Sulphide Ratio on the Precipitation Behaviour

The results for the effect of metal to sulphide ratio on the amount of metals ions precipitated from solution are shown in Table 1. The results show that the amount of metal ions precipitated from solution increased with a decrease in the metal to sulphide ratio and the amount of copper ions removed was always higher than the amount of zinc ions removed. At high metal to sulphide ratio (i.e. metal to sulphide ratio of 2:1), 80 % of copper was removed from solution even though the amount of sulphide available in solution for copper sulphide precipitation was half the amount of the copper ions present in solution. According to thermodynamic modelling results (OLI StreamAnalyzer ver. 2.0), when copper is precipitated from solution as copper sulphide at pH 6 with excess amount of copper ions present in solution, copper hydroxysulphate (bronchantite) is also formed. Thus, the additional amount of copper removed from solution in this case can be attributed to copper hydroxysulphate formation. In the case of zinc, the formation of hydroxysulphate precipitates under similar conditions is not likely and therefore zinc was only removed from solution as zinc sulphide. Due to copper hydroxysulphate formation the assessment of the particle rate processes was difficult at 2:1 metal to sulphide ratio in the case of copper, since the precipitate was not only sulphide. However, only sulphide precipitates were formed at stoichiometric and excess sulphide concentrations.

Table 1. Percentage conversion for Cu^{2+} and Zn^{2+} ions using different metal to sulphide ratio at pH 6

M:S ratio	Cu^{2+} conversion (%)	Zn^{2+} conversion (%)
2.00 (1:0.5)	80.76 ± 1.70	57.48 ± 5.39
1.00 (1:1.0)	93.32 ± 1.61	71.54 ± 3.24
0.67 (1:1.5)	97.94 ± 0.29	93.54 ± 0.95

The change in zeroth moment (*m0* – equivalent to number of particles) and number based mean size ($\overline{L}_{1.0}$) for copper and zinc sulphide precipitates produced under the conditions of different metal to sulphide ratio at pH 6 are shown in Figure 1. For copper sulphide precipitation at metal to sulphide ratio of 2:1, the interpretation of the results is complicated due to the formation of copper hydroxysulphate. However, a large value for *m0* was obtained when low metal to sulphide ratio (i.e. metal to sulphide ratio of 0.67:1) was employed and this value decreased significantly when the process was conducted using higher metal to sulphide ratios (Figure 1(A)). This indicates that the number of copper sulphide particles produced when excess sulphide was used to precipitate copper ions from solution was very high compared to the case where stoichiometric, or lower sulphide concentrations were employed. Comparing the copper and zinc data, *m0* obtained for zinc sulphide was significantly lower at the low metal to sulphide ratio (i.e. metal to sulphide ratio of 0.67:1) and the change in *m0* for zinc sulphide precipitation was insignificant as higher metal to sulphide ratios were employed. The consistently higher value of *m0* for copper sulphide across the range of metal to sulphide ratios indicates that more copper sulphide particles were formed under these conditions.

In terms of the particle rate processes, a large *m0* represents dominant nucleation and/or breakage. However, breakage is typically negligible during the precipitation of sparingly soluble compounds, due to the high levels of supersaturation which characterise such processes. Thus, the high number of particles produced for both copper and zinc sulphide precipitation can be attributed to dominant nucleation. The $\overline{L}_{1.0}$ results, shown in Figure 1(B), show that the number based mean size for the copper sulphide precipitate obtained under different metal to sulphide ratios was always lower than the number based mean size obtained for zinc sulphide. In addition, the number based mean size of copper sulphide particles produced under the conditions of excess sulphide was significantly smaller than that obtained using higher metal to sulphide ratio. These results are consistent with the *m0* data presented in Figure 1(A) and show that the large number of particles obtained for the lowest metal to sulphide ratio is due to the small nature of the copper sulphide particles produced under these conditions.

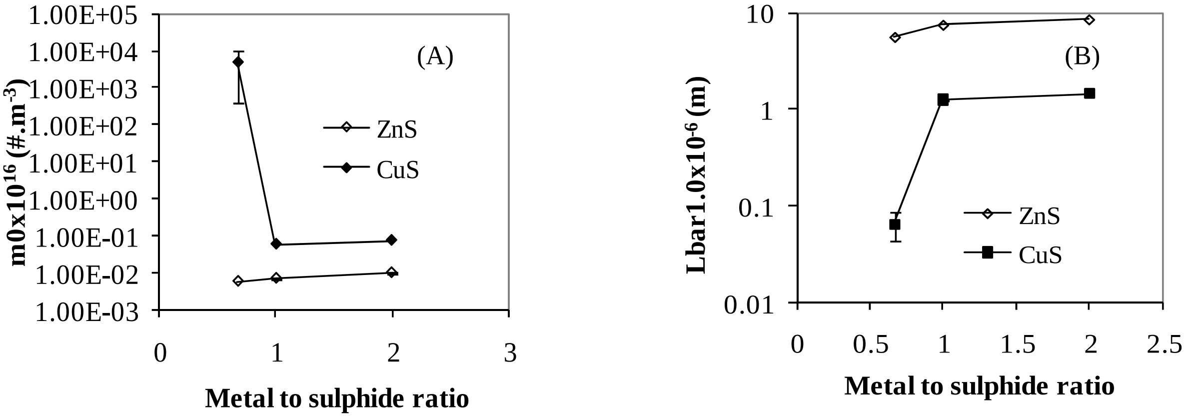

Figure 1. Change in *m0* (A) and $\bar{L}_{1.0}$ (B) for metal precipitates produced using different metal to sulphide ratios at pH6

Figure 2 shows the effect of the very small copper sulphide particles, produced in the presence of excess sulphide, on the settling characteristics of the precipitate obtained. According to Figure 2(A), the copper sulphide particles produced under the conditions of higher metal to sulphide ratio have relatively good settling characteristics. However, the very small copper sulphide particles produced using excess sulphide have very poor settling characteristics, with the precipitate taking much longer to settle out of solution. In contrast, the zinc sulphide precipitate has relatively good settling characteristics, irrespective of the metal to sulphide ratio used (Figure 2(B)). Furthermore, the final settling volume for the zinc sulphide precipitates, in all cases, was higher than the final settling volume of the copper sulphide precipitates obtained for 1:0.5 and 1:1.0 ratios. This indicates that the copper sulphide precipitates obtained using 1:0.5 and 1:1.0 ratios are more compact and therefore has better dewatering characteristics than the zinc sulphide precipitates.

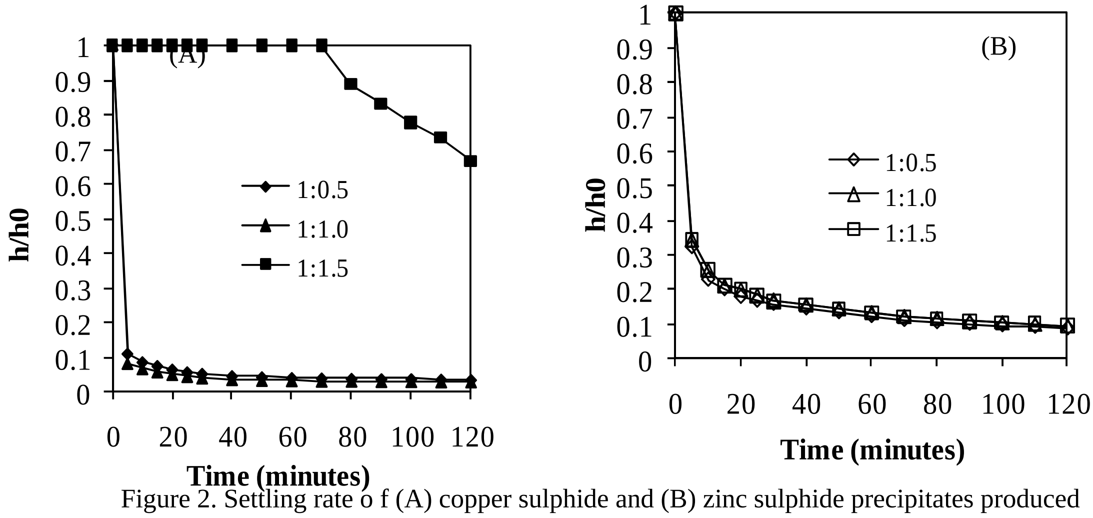

Figure 2. Settling rate o f (A) copper sulphide and (B) zinc sulphide precipitates produced under different metal to sulphide ratios at pH6

According to DLVO theory (i.e. quantitave theory of colloid stability), the stability of the particles in aqueous suspensions is determined by the balance between the van der Waals forces of attraction and the electrical repulsions due to the electrical charge on the surface of the particles (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). The electrical charge on the surface of the particles may be caused by chemical reactions at the surface, lattice imperfections and surface adsorption. Kolthoff and Moltzau (1935) observed that metal sulphides strongly adsorbed H_2S, HS^- and S^{2-}. Thus, the particles produced in the presence of excess sulphide are more likely to carry a significant surface charge and therefore become stabilised in suspension due to electrical repulsions. This phenomenon, in addition to the very small particle size, was identified as the possible reason for the poor settling characteristics of the copper sulphide precipitate produced at low metal to sulphide ratio in this study. To evaluate this, the surface characteristics of the particles which did not readily settle were investigated, using zeta potential measurements, to quantify the surface charge of the particles produced under different metal to sulphide ratios.

The change in surface charge of particles produced under different metal to sulphide ratios is shown in Figure 3. The zeta potential decreases with an increase in the metal to sulphide ratio for both copper and zinc sulphide particles. However, the magnitude of the zeta potential for the copper sulphide particles is larger than the zeta potential of the zinc sulphide particles produced under similar conditions.

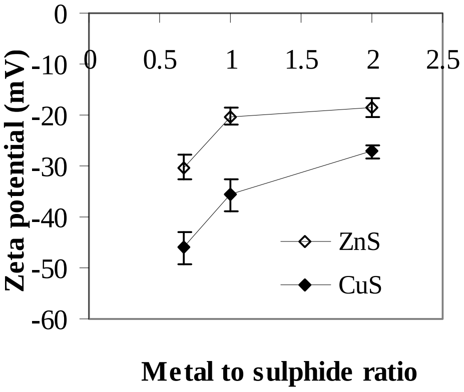

Figure 3. Change in zeta potential of the metal sulphide particles produced using different metal to sulphide ratios at pH 6.

For the copper sulphide particles produced in the presence of excess sulphide (i.e. lowest metal to sulphide ratio) the zeta potential obtained was significantly more negative than that of the particles produced under the conditions of higher metal to sulphide ratio (as seen in Figure 3). Since all the other precipitate had better settling characteristics, the poor settling characteristics obtained for the copper sulphide particles produced in the presence of excess sulphide could be attributed to the small mean particle size and the electrical repulsions due to significantly higher surface charge carried by the particles produced under these conditions.

The Effect of Operating PH on yhe Precipitation Behaviour

The results for the effect of operating pH on the precipitation efficiency are shown in Table 2. The results show that the amount of copper and zinc precipitated from solution (i.e. copper and zinc ions conversion) is dependent on the operating pH. As the operating pH increases, the amount of metals ions precipitated from solution is also increased. However, the amount of copper ions precipitated from solution was higher than the amount of zinc ions precipitated in all cases indicating that the solubility of the formed copper sulphide was lower than that of zinc sulphide.

Table 2. Percentage conversion for Cu^{2+} and Zn^{2+} ions for metal to sulphide ratio of 1:1.5 at different operating pH

pH	Cu^{2+} conversion (%)	Zn^{2+} conversion (%)
2	87.54 ± 1.63	-*
3	-	83.09 ± 1.53
4	88.19 ± 1.17	83.27 ± 0.45
6	97.94 ± 0.29	93.54 ± 0.95
8	-	99.95 ± 0.01

*ZnS is soluble at pH 2, hence there is no data.

The change in zeroth moment (*m0* – equivalent to number of particles) and number based mean size ($\bar{L}_{1.0}$) for copper and zinc sulphide precipitates produced using excess sulphide concentration at different operating pH values are shown in Figure 4. For copper sulphide, *m0* decreased significantly when the operating pH was decreased from 6 to 4 and increased slightly when the process was operated at pH 2 (Figure 4(A)). In the case of zinc sulphide, the change in *m0* was small relative to the change in *m0* observed for copper sulphide. However, there is an optimum pH value at which the lowest *m0* was obtained in both cases. For copper sulphide, the lowest *m0* was obtained at pH 4 and at pH 6 for zinc sulphide.

On the other hand, Figure 4(B) shows that as the operating pH for copper sulphide precipitation is decreased from 6 to 4, $\bar{L}_{1.0}$ is significantly increased and $\bar{L}_{1.0}$ at pH 2 is slightly smaller than that obtained at pH 4 but also significantly larger than $\bar{L}_{1.0}$ obtained at pH 6. For zinc sulphide particles, $\bar{L}_{1.0}$ decreases slightly as the pH is decreased below pH 6 and a slight decrease at pH 8 $\bar{L}_{1.0}$ is also observed. These trends are in agreement with the *m0* results and indicate that there is an optimal pH at which larger metal sulphide precipitates are obtained and the results also show that there is not much difference in the mean size of the copper and zinc sulphide particles produced below pH 4.

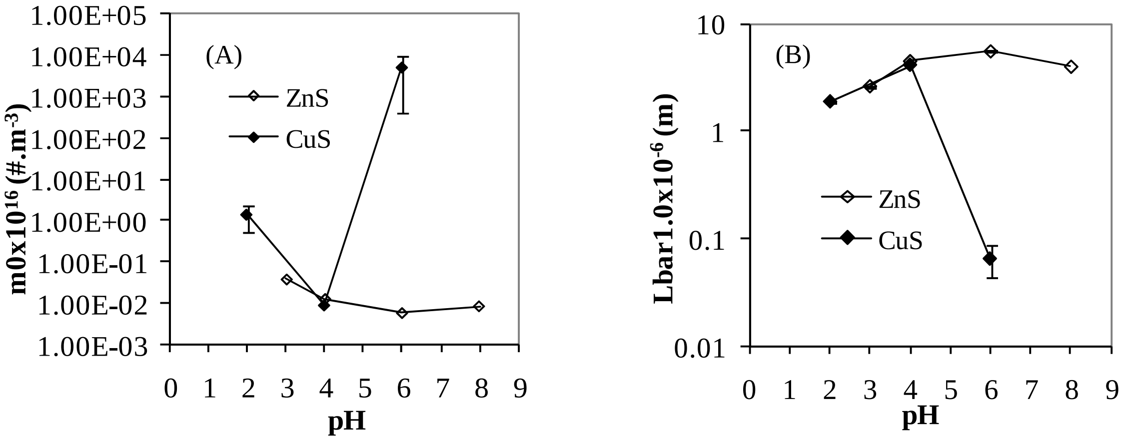

Figure 4. Change in *m0* (A) and $\overline{L}_{1.0}$ (B) for metal sulphide precipitates produced using metal to sulphide ratio of 1:1.5 at different operating pH

According to Kolthoff and Moltzau (1935), sulphide precipitation involves the reaction of bisulphide ions (HS^-) to initially form the metal hydroxysulphide, which by the secondary loss of hydrogen results in the formation of the metal sulphide. Lewis and van Hille (2006) and Karbanee et al. (2008) have also suggested that the principle sulphide species participating in the sulphide precipitation reaction was the bisulphide ion. Thus, the results shown in Figure 4 can be explained according to the pH-dependent speciation of aqueous hydrogen sulphide ($H_2S(aq)$) as shown in Equation (1) and (2).

$$H_2S(aq) \leftrightarrow HS^- + H^+ \qquad pK_1 = 6.99 \qquad (1)$$

$$HS^- \leftrightarrow S^{2-} + H^+ \qquad pK_2 = 17.4 \qquad (2)$$

There is good agreement of values for the pK_1 in literature but the values for pK_2 vary considerably between 12 and 18 (Garrels and Naeser, 1958; Wagan et al, 1968; Stephens and Cobble, 1971; Giggenbach, 1971; Meyer et al, 1983; Licht et al, 1990). The pK_2 value used in this study, as shown in Equation (2), is the value most recently determined by surface sulphidation of crystalline sulphur (Migdisov et al, 2001) and it is in good agreement with other non-calorimetrically determined pK_2 values (Giggenbach, 1971; Meyer et al, 1983; Licht et al, 1990).

As the operating pH of the precipitating system is decreased, the relative proportion of $H_2S(aq)$ increases and the concentration of the HS^- ions available for the metal precipitation is decreased. This reduces the supersaturation, which may lead to a reduction in primary nucleation and result in a smaller number of larger particles. The data presented in Figure 4 suggests this is the case for copper sulphide precipitation. As the low concentration of HS^- ions is consumed they are replenished by the system striving to maintain equilibrium, which accounts for the still significant copper precipitation at pH 2. At pH 6, the initial HS^- concentration is significantly higher, resulting in higher supersaturation and greater primary nucleation, hence the greater number of significantly smaller particles.

Figure 5 shows the results obtained for zeta potential measurements of the particles remaining in suspension at different operating pH values. In all cases, the zeta potential of the particles becomes less negative with a decrease in operational pH. These results can be explained based on the observations made by Kolthoff and Moltzau (1935) concerning the strong adsorption of sulphide species ($H_2S(aq)$, HS^- and S^{2-}) to metal sulphide surfaces. The observed decrease in the zeta potential of the particles is associated with a decrease in the relative concentration of the negatively charged HS^- and S^{2-} species in solution at low pH.

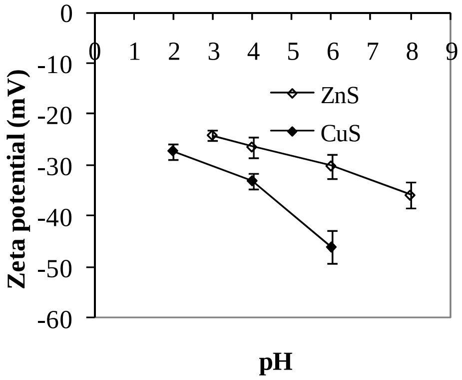

Figure 5. Change in zeta potential of metal sulphide precipitates produced using metal to sulphide ratio of 1:1.5 at different operating pH

The change in the settling rate of the particles produced at different operational pH values is shown in Figure 6. In most cases, a decrease in the operating pH was shown to have a positive effect on the settling characteristics of the particles. The poor settling characteristics obtained for copper sulphide at pH 6 was significantly improved at low operating pH and the precipitate with the best settling and dewatering characteristics was obtained at pH 2. Although the settling characteristics of zinc sulphide precipitates were relatively good for all operational pH, the more compact precipitates with improved dewatering characteristics were obtained at pH 2 and 4.

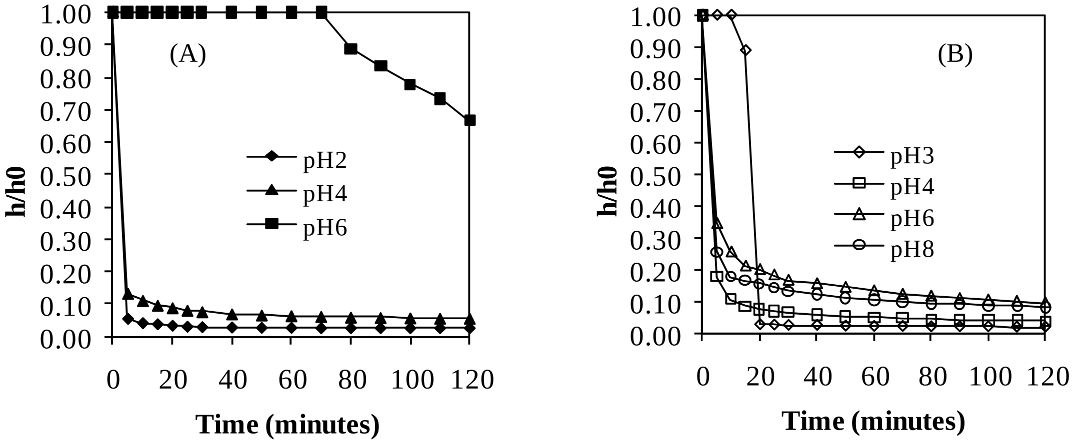

Figure 6. Settling rate of (A) copper sulphide and (B) zinc sulphide precipitates produced under different metal to sulphide ratio at pH6

Furthermore, the good settling characteristics observed for copper at low pH can be directly linked to the mean particle size and zeta potential results shown in Figure 4 and Figure 5, respectively. At low operational pH, the magnitude of the negative zeta potential for the copper sulphide particles was lower and the mean particle size was significantly increased. Thus, the electrical forces of repulsion amongst particles were reduced and particle coagulation due to gravitational force was improved as the particles size improved.

4. CONCLUSIONS

Metal to sulphide ratio and operating pH have been shown to have a significant effect on the amount of copper and zinc ions precipitated from solution. An increase in the amount of sulphide present in solution for sulphide precipitation was found to have a positive effect on the amount of copper and zinc ions precipitated from solution when the process was operated at pH 6. However, the amount of copper and zinc ions precipitated from solution was decreased when the precipitation processes were conducted at operational pH below 6 even though an excess amount of sulphide was available in solution. The nature, surface and settling characteristics of the copper and zinc sulphide precipitates were found to be strongly influenced by the metal to sulphide ratio and operating pH. A large number of copper sulphide particles with small mean size, a significantly high surface charge and poor settling characteristics were obtained when copper sulphide precipitation process was conducted with excess amount of sulphide present in solution at pH6. When the process was conducted using operational pH below 6 with excess amount of sulphide present in solution, the mean size and zeta potential of the resulting copper sulphide particles were improved while the number of copper sulphide particles in suspension was decreased and the settling characteristics of the formed precipitates were improved. For zinc sulphide precipitation, a small change in the number of particles in suspension and the mean particle size was obtained for all the different metal to sulphide ratio and operating pH conditions. However, a decrease in the metal to sulphide ratio resulted in an increase in the zeta potential of the particles when the process was operated at pH 6. When the precipitation process was conducted using low metal to sulphide ratio at pH below 6, the zeta potential on the produced zinc sulphide particles was reduced and the settling and dewatering characteristics of the precipitates were improved. Consequently, the pH-dependent aqueous sulphide speciation was found to be the most important factor influencing the nature and solid-liquid separation characteristics of the copper and zinc sulphide precipitates produced during sulphide precipitation processes.

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