

## Hydrolysis of metallic ions in mineral processing circuits and its effect on flotation

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### ABSTRACT

Hydrolysis of metallic ions depends on pH and the products of hydrolysis either activate flotation, can lead to inadvertent activation of gangue particles, but can also depress flotation of valuable components. One of the most recently studied topics is the use of seawater in flotation. Seawater is a concentrated NaCl solution (about 0,6 mole/L) that also contains considerable amount of  $Mg^{2+}$  and  $Ca^{2+}$  ions. The hydrolysis products of  $Mg^{2+}$  strongly depress flotation of molybdenite over the pH ranges over which they form in the process water. This effect can be eliminated by removal of hydrolysing ions from the process water or by carrying out the flotation at the pH over which such a hydrolysis can be avoided. The former can be exemplified by prior precipitation of the harmful hydrolysing ions as, for example, in the University of Concepcion Patent. The latter can be exemplified by the use of metabisulfite to depress pyrite in the flotation of Cu-Mo sulfide ores in seawater, the process that is carried out at much lower pH which avoids formation of  $Mg^{2+}$  hydrolysis products.

### Keywords

Activation, Adsorption, Depression, Flotation, Ion hydrolysis, Metallic ions, Seawater

## 1. Introduction

Metallic ions, depending on pH, hydrolyze in aqueous environment. In general, unhydrolyzed species,  $\text{Me}^{2+}$ , predominate in acidic solutions, while  $\text{MeOH}^+$ ,  $\text{Me(OH)}_2$  and  $\text{Me(OH)}_3^-$  appear when pH is made more alkaline.

Metallic ions can appear in flotation pulps not only when added as flotation activators (e.g.  $\text{Cu}^{2+}$  in the flotation of sphalerite or as pyrrhotite's activator in the flotation of platinum group minerals in South Africa), they may also be present as a result of the processes in which different mineral particles suspended in water participate. The solubility of sulfides is so low that these minerals might be assumed inert. However, all the sulfides are reactive with oxygen, with the oxidation products being appreciably soluble in water. Therefore, metallic ions commonly appear in the pulps containing sulfide minerals. Perhaps the most studied have been copper sulfides, and it is well established that copper ions appear in the pulps resulting from grinding copper ores (Lascelles & Finch, 2002).

For our understanding of the hydrolysis phenomena and the effect of ion hydrolysis on adsorption of these ions onto mineral particles the most important have been publications coming from two teams: Professor Tom Healy's and Professor Maurice Fuerstenau's.

Experimental adsorption isotherm for  $\text{Co}^{2+}$  ions on silica is shown in Figure 1 (James & Healy, 1972a). The figure also shows hydrolysis products of  $\text{Co}^{2+}$  as a function of pH for  $\text{Co}^{2+}$  concentration of  $1.2 \times 10^{-4}$  M. As it is seen, over the acidic pH range over which  $\text{Co}^{2+}$  ions predominate in solution the adsorption is negligible. However, once the pH of  $\text{CoOH}^+$  formation is exceeded the adsorption of Co onto silica dramatically increases.

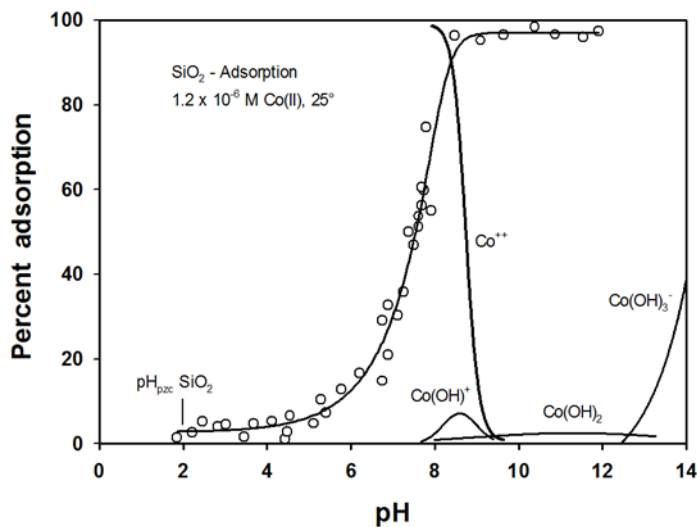


Figure 1. Experimental adsorption isotherm for  $\text{Co}^{2+}$  at  $1.2 \times 10^{-4}$  M on silica at 25 °C. Hydrolysis products of  $\text{Co}^{2+}$  are also shown as the percentage of each aquo complex as a function of pH (from James & Healy, 1972a; with permission of Elsevier).

The importance of these findings for understanding of flotation phenomena was clearly demonstrated by M.C. Fuerstenau and Palmer (1976). Figure 2 shows that quartz (the mineral that is negatively charged in almost whole pH range) as expected does not float with anionic collector. This mineral can, however, be activated by metallic ions. It is activated over the pH range over which the tested metallic ions hydrolyse, form hydroxy-complexes and adsorb onto minerals. The adsorbing hydrolyzed species depending on the flotation process can either activate or depress this process. What is important here is the adsorption of metallic ion hydrolysis products and the fact that this adsorption takes place over the pH range over which such hydrolysis products appear in solution. Since the ion hydrolysis phenomena are well known it is possible to manipulate the flotation process in such a way that it either leads to activation or depression.

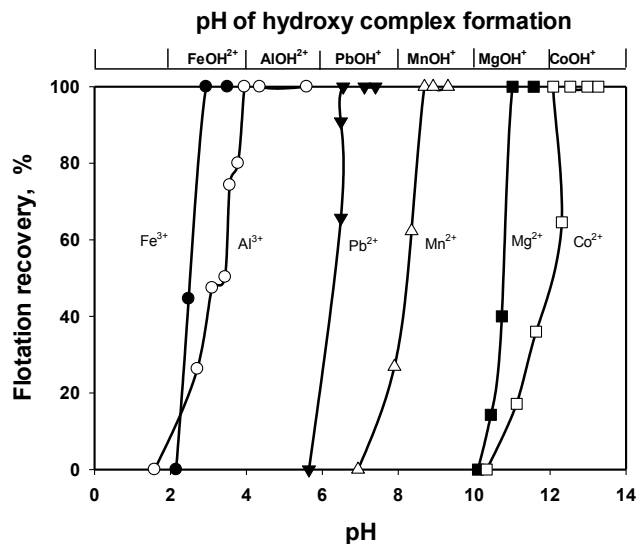


Figure 2. The pH ranges of quartz flotation with sodium alkyl sulfonate ( $10^{-4}$  M) in the presence of different metallic ions (10-4M) (from Fuerstenau & Palmer, 1976; with permission of the Society for Mining, Metallurgy and Exploration).

The process water recycled in plant closed water circuits constitutes a very concentrated electrolyte solution. Perhaps the best example is Mt. Keith plant in Western Australia. To mimic this plant process water the synthetic process water prepared with the use of: 48.2 g/L of NaCl, 24.4 g/L of  $MgSO_4 \cdot 7H_2O$ , 2.1 g/L of KCl, 1.25 g/L of NaCl and 0.29 g/L of  $NaHCO_3$  is often used (Merve-Genc et al., 2012). Limited resources of fresh water in many parts of the world (as, for example, in the Atacama desert in Chile) make the use of seawater the only sustainable solution. Sea water is a concentrated solution of NaCl (about 0.6 M) with high content of  $Mg^{2+}$  (1.3 g/L) of  $Ca^{2+}$  (0.4 g/L) and also sulfate ions (2.7 g/L). The ions present in such process waters – as it will be shown - may heavily affect the flotation processes. To complicate it further, in some flotation processes, metallic ions are added to the pulp to activate flotation of some particular minerals.

## 2. $Cu^{2+}$ ions as activators in flotation

As it is known sphalerite does not float without activation and copper sulfate is commonly applied to activate it. In our studies on activation of sphalerite by  $Cu^{2+}$  we used the electrokinetic measurements (Laskowski et al., 1997) following the interpretation introduced by James and Healy (1972b). Figure 4 shows schematically the general zeta potential – pH curve in the presence and absence of hydrolysable ions. The curve reveals three charge point reversals (CR.1, CR.2 and CR.3). The position of CR.1 coincides with the i.e.p. of  $SiO_2$  (solid particles used in the experiment). The high pH charge reversal point (CR.3) results from coating of  $SiO_2$  surface by metal hydroxide; CR.3 is the i.e.p. of this metal hydroxide. The CR.2 point is at the pH of surface precipitation of metal hydroxyl-complexes induced by pH.

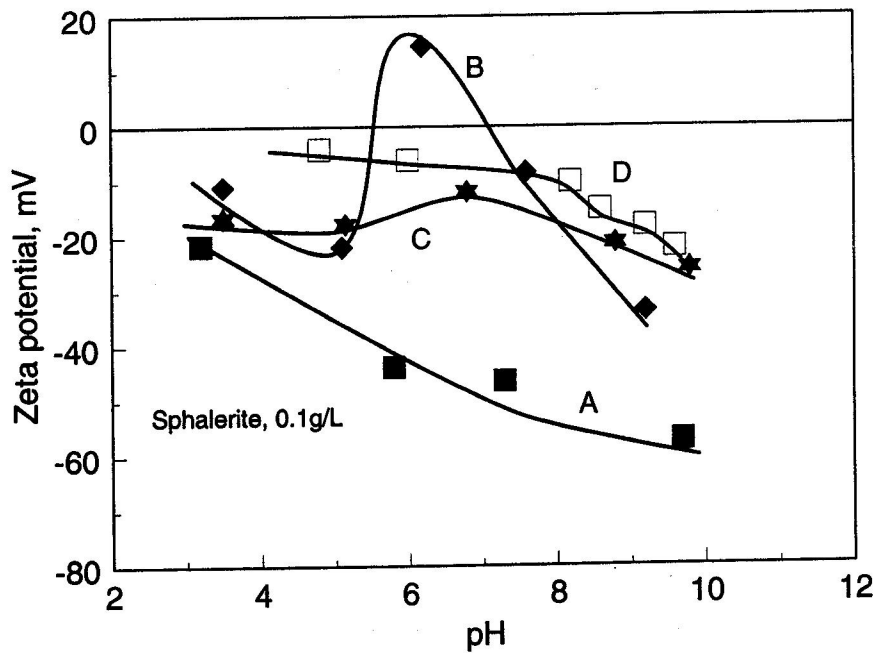


Figure 3. Effect of pH and conditioning time on the zeta potential of sphalerite in the presence of copper ions. A, in H<sub>2</sub>O; B, in 10<sup>-3</sup> M CuSO<sub>4</sub>, 5 min; C, in 10<sup>-3</sup> M CuSO<sub>4</sub>, 15 hrs; D, zeta potential of chalcocite (from Laskowski et al., 1997; with permission of Elsevier).

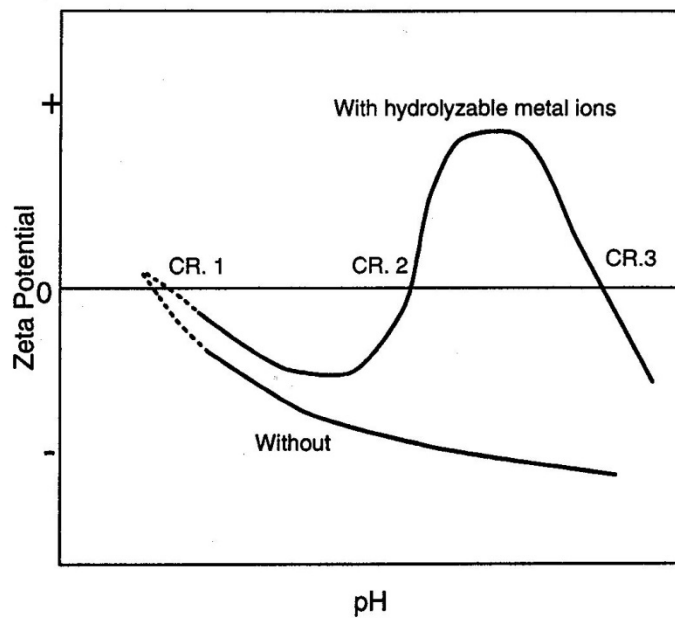


Figure 4. Schematic illustration of the general electrophoretic mobility behavior of colloidal systems in the presence and absence of hydrolysable ions (from James & Healy, 1972b; with permission of Elsevier).

Following the James and Healy's interpretation, Figure 3 shows that copper hydroxy-complexes accumulate on the sphalerite surface over the pH range over which Cu<sup>2+</sup> ions hydrolyze. These tests also show that since copper hydroxide is not stable on the ZnS surface it is converted into copper sulfide

(activation) with time.

Exceptional activity of  $\text{Cu}^{2+}$  hydroxy-complexes confirms Figure 5 (Iskra & Laskowski, 1969). It shows the effect of pH on the flotation of quartz made hydrophobic by methylation (by reaction with trimethylchlorosilane) when frother is the only reagent used. As this Figure demonstrates, at low copper ion concentration the flotation is depressed over a narrow pH range from 6.5 to 7.5. The agreement of these flotation tests with the distribution diagram for  $\text{Cu}^{2+}$  ions (Fig. 6) is excellent. The pH range over which the flotation of hydrophobic methylated quartz is depressed coincides perfectly with the pH range over which  $\text{Cu}^{2+}$  hydroxy-complexes predominate in solution.

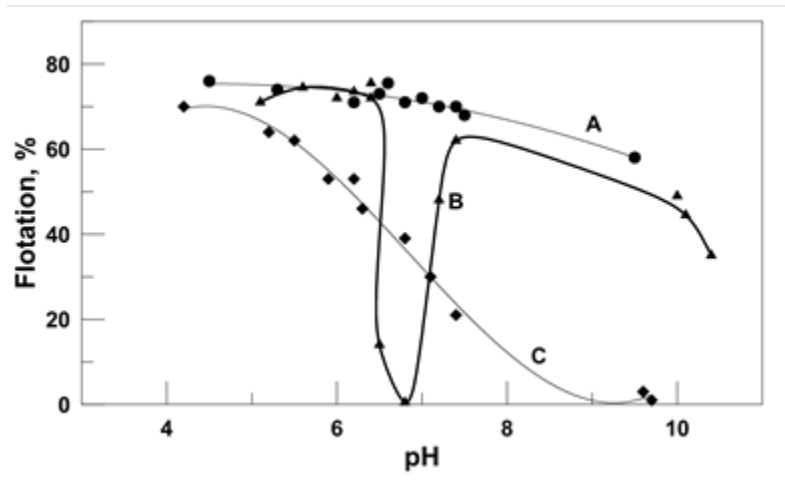


Figure 5. Flotation of methylated quartz at 20 mg/L concentration of  $\alpha$ -terpineol without  $\text{Cu}^{2+}$  (curve A), at  $1.5 \times 10^{-4}$  M  $\text{Cu}^{2+}$  (curve B), and at  $1.5 \times 10^{-3}$  M  $\text{Cu}^{2+}$  (curve C) (from Iskra & Laskowski, 1969; with permission of Taylor and Francis).

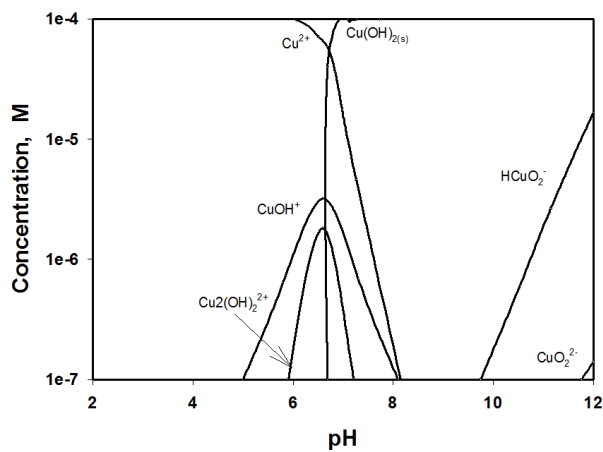


Figure 6. Logarithmic concentration diagram for  $1 \times 10^{-4}$   $\text{Cu}^{2+}$  (from Fuerstenau & Palmer, 1976; with permission of the Society for Mining, Metallurgy and Exploration).

The hydroxy-complexes may be responsible for either depression (Figure 5) or activation (Figures 2 and 7). As Figure 7 shows the methylated hydrophobic quartz, which was depressed by  $\text{Cu}^{2+}$  ion hydrolysis products, over exactly the same pH range may be activated. The activation takes place when the adsorbed hydrolysis products

become adsorption centers for the added collector. This happens when to the depressed methylated quartz sodium oleate collector is added. Fuerstenau et al (1988) used talc to show how adsorption of hydrophilic hydroxy-complexes depress flotation of hydrophobic by nature talc.

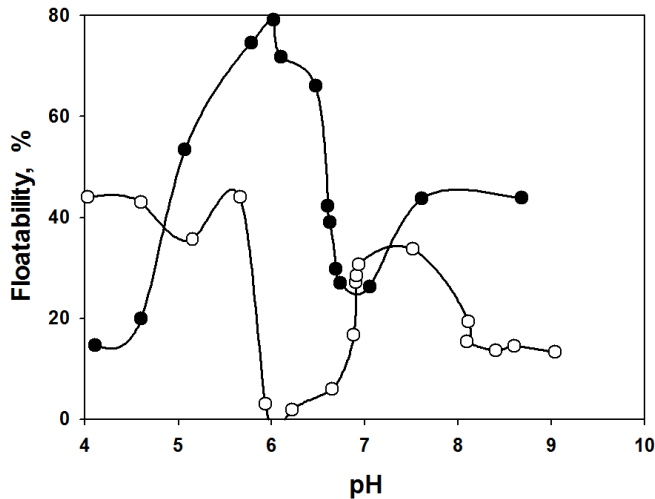


Figure 7. Flotation of methylated quartz as a function of pH in  $1.5 \times 10^{-5}$  M solution of  $\text{Cu}^{2+}$  at  $\alpha$ -terpienol concentration of 20 mg/L (curve o), and at sodium oleate concentration of  $1.5 \times 10^{-5}$  (curve ●)

In South Africa in the flotation of sulfide ores containing platinum group elements copper ions are utilized to activate and enhance recovery of pyrrhotite. This can, however, cause inadvertent activation of gangue. Figure 8

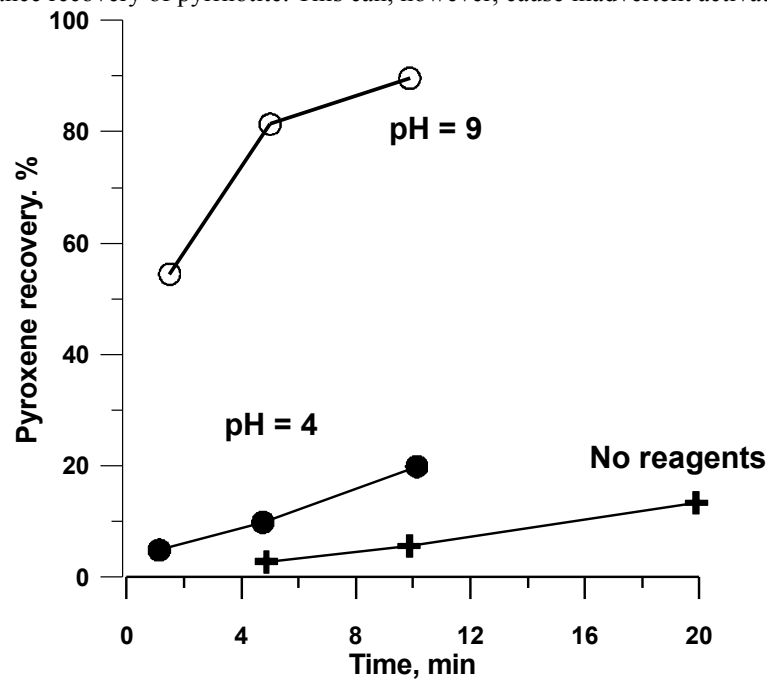


Figure 8. Effect of pH on flotation of pyroxene with SIBX at  $5 \times 10^{-5}$  M  $\text{Cu}^{2+}$  (from Mailula et al., 2003; with permission of CIM).

shows the effect of pH on flotation of pyroxene with iso-butyl xanthate at  $5 \times 10^{-5} \text{M Cu}^{2+}$  (Mailula et al., 2003). As this figure indicates while at pH 4 the activation is negligible, it is very substantial at pH of 9. This effect can be reduced when addition of copper salts follows addition of xanthate.

### 3. Flotation in seawater

In our recent paper (Laskowski & Castro, 2015) the high electrolyte process water systems were classified into:

- A, High electrolyte concentration systems which do not require adjustment of pH (A1) and which require pH changes (A2);
- B, The system in which collector precipitates with ions present in the pulp;
- C, Saturated NaCl-KCl brines as in the flotation of potash ores.

Salt flotation process (Klassen & Mokrousov, 1963), the process in which inherently hydrophobic minerals are floated in electrolyte solutions without any other reagents, is the best example of A1. The flotation of Cu-Mo sulfide ore in seawater, the process in which pH is raised using lime to depress pyrite, exemplifies A2. The flotation of phosphate ores in seawater with the use fatty acid collector exemplifies case B. In this case  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions must be complexed and removed from the system to avoid precipitation of the collector (Yousef et al., 2003; Nanthakumar et al., 2009). 6-7 molar NaCl-KCl saturated brines constitute a special case and require a separate discussion (Laskowski, 2013).

The main problems in flotation of most sulfide ores result from the presence of pyrite. Common way to depress its flotation is by the use of lime and highly alkaline pH. In the case of Cu-Mo ores these problems result from the fact that this widely used flotation technology was developed to control flotation of pyrite and not to optimise flotation of molybdenite. Lime and high pH depresses not only pyrite but it is also responsible for poor recovery of molybdenite (Castro, 2012; Castro et al . 2014).

The main thesis of this paper is that the depressing effect of the hydrolysis products of metallic ions can be avoided either by removing these ions or the products of their hydrolysis from the flotation system, or by carrying out the process at the pH range over which these metallic ions do not hydrolyze. The research needed to develop the technology of flotation in which seawater is used instead of fresh water can be broadly split into two streams: water desalination projects aimed at reduction of seawater salinity, and physico-chemical studies aimed at better understanding of what really causes molybdenite depression. While water desalination by reverse osmosis is now seriously considered by many companies, the University of Concepcion Patent (Castro, 2010) shows that removal of all ions from seawater is not necessary since only some of them cause depression of molybdenite. This latter technology will be discussed further in this paper.

Previous publications showed that magnesium hydroxy-complexes and magnesium hydroxide accumulating on the surface of molybdenite particles are responsible for molybdenite depression (Castro 2012, Castro et al., 2014; Nagaraj et al., 2016). Also, depressing effect of kaolinite on chalcopyrite flotation in seawater is

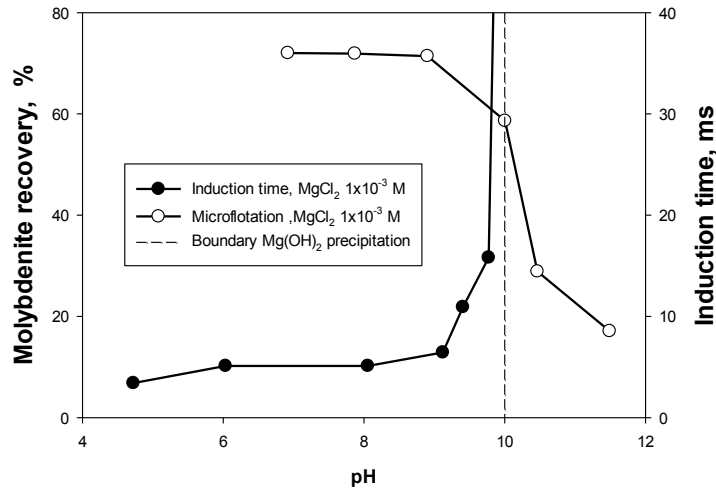


Figure 9. Induction time and molybdenite recovery as a function of pH in  $1 \times 10^{-3}$  M  $\text{MgCl}_2$  solutions (from Castro et al., 2014)

is the most severe in the pH range over which  $\text{Mg}^{2+}$  hydrolyze (Uribe et al., 2017a). In our more recent tests the induction time technique was used to study the effect of  $\text{Mg}^{2+}$  ions on wettability of molybdenite particles, and these tests, as shown in Figure 9, entirely confirms the previous conclusions (Castro et al., 2014). For simplicity only the results obtained in  $10^{-3}$  M  $\text{MgCl}_2$  solution are shown here, the results obtained in seawater and in the 0.6 M NaCl solution containing 1,300 ppm  $\text{Mg}^{2+}$  ions totally agree with what is shown in Figure 9. All this clearly demonstrate that the  $\text{Mg}^{2+}$  ions hydrolysis products are responsible for the observed phenomena.

If coating of the molybdenite surface by precipitating magnesium species is responsible for depression (as in the case of slime coating) then dispersion of these coagulating particles should be able to restore molybdenite

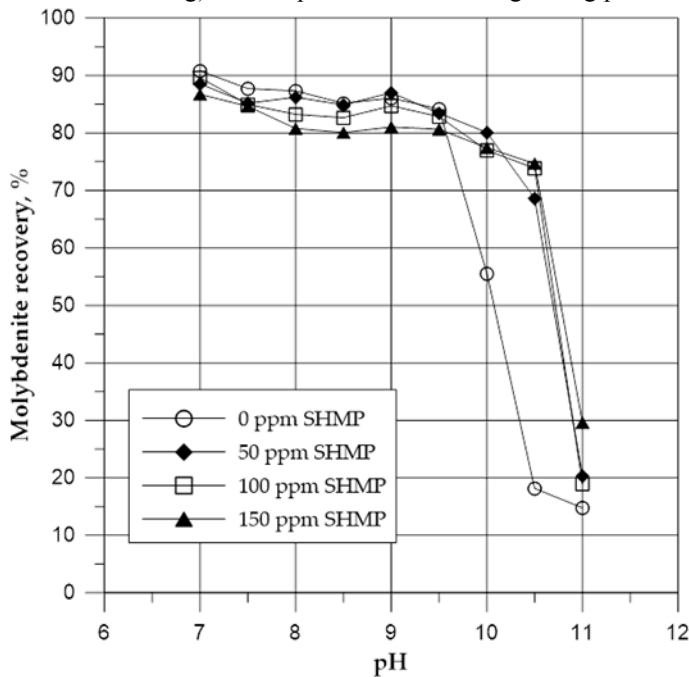


Figure 10. Recovery of molybdenite as a function of pH at various concentrations of SHMP (from Rebolledo et al., 2017).



flotation. This was tested (Rebolledo et al., 2017). Sodium hexamethaphosphate (SHMP) was used as a dispersant since Lu et al. 2011) found that SHMP very actively interacts with  $Mg^{2+}$  ions. Figure 10 shows that the molybdenite flotation depressed over the pH range from 9.5 to 10.5 can be restored when SHMP is utilized.

In the same series of the tests also the effect of pH and added SHMP on pyrite flotation was studied. It was found that depression of pyrite started only when pH of 10 was exceeded, that is only when  $Ca^{2+}$  hydrolysis products started appearing in the solution.

The results which were selected to illustrate the main thesis of this paper all agree that the key factor in all these results is pH: the flotation results are not affected by pH when it is far away from those in which  $Mg^{2+}$  ions hydrolyze. When the process is carried out at the pH at which  $Mg^{2+}$  hydrolyze these hydrolysing ions must be removed from the system. In the University of Concepcion Patent (Castro, 2010) this is achieved by treating seawater with lime, precipitation of magnesium hydroxides and its separation from the treated process water by decantation/settling. When pyrite depressant that works in a slightly acidic environment, that is far from the dangerous pH range, is used the flotation of molybdenite is improved (Uribe et al., 2017b). Figure 11 shows pH ranges of hydrolysis for  $Mg^{2+}$  ions.

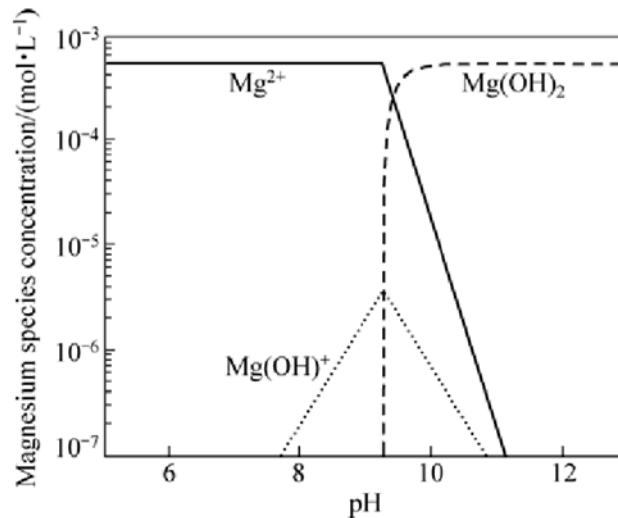


Figure 11. Logarithmic concentration diagram for  $5 \times 10^{-4}$  M  $Mg^{2+}$ .

#### 4. Conclusions

1. Metallic ions hydrolyze in water in a given pH range.
2. The hydrolysis products are exceptionally surface active and can either activate or depress floatability of given particles.
3. The  $Mg^{2+}$  hydrolysis products tend to accumulate on the surface of molybdenite particles and depress their flotation.
4. Seawater is a concentrated solution of NaCl (about 0.6 M) that also contains  $Mg^{2+}$  ions (1,300 mg/L) and  $Ca^{2+}$  ions (400 mg/L). The presence of  $Mg^{2+}$  ions in seawater is the main reason for depression of molybdenite flotation when pH is raised with lime to depress pyrite.

5. Depression of molybdenite in seawater can be reduced by either elimination of such hydrolyzing ions from the process water (desalination, prior precipitation of  $Mg^{2+}$  ions from seawater) or by carrying out the flotation at much lower pH using the pyrite depressant that works under acidic conditions.

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