Physico-chemical factors in flotation of Cu-Mo-Fe ores with seawater: a critical review

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Abstract: This paper aims to provide a comprehensive review on the physico-chemical factors governing the flotation of Cu-Mo-Fe sulfide ores in seawater, which is different from NaCl or KCl solutions because it contains hydrolysable ions such as Mg^{2+}, Ca^{2+}, HCO_3^-, CO_3^{2-}, etc., which can precipitate with lime as hydroxides, Ca, and Mg insoluble salts. Under pH 9.0 Mg^{2+} ions do not depress molybdenite. However, over the critical pH of precipitation of $Mg(OH)_2$ (pH>10.0), molybdenite is strongly depressed in seawater. This detrimental effect on molybdenite discards the use of lime to depress pyrite in Cu-Mo-Fe ores floated in seawater. In plant practice, the use of sodium metabisulfite (MBS) has replaced lime as a pyrite depressant. It works at pH 6.5-7.0 where the natural floatability of molybdenite is enhanced. Consequently, pH control in rougher and cleaning circuits, and the use of MBS to depress pyrite, have allowed the successful use of non-desalinated seawater in flotation of Cu-Mo-Fe sulfide ores at industrial scale.

Keywords: seawater flotation, chalcopyrite, molybdenite, pyrite, metabisulfite

1. Introduction

Sustainable use of water in mining industry is currently a serious challenge in dry regions. Seawater could be used in mineral processing; however, it has been usually considered a water of low quality for the flotation of Cu-Mo ores (low Cu and Mo recovery, high lime consumption, etc.). Its high salinity and low flotation recovery of some valuable species (chalcocite, covellite, molybdenite, etc.), have hindered the application of saline water in the flotation process (Rey and Raffinot, 1966; Lekki and Laskowski, 1972; Haig-Smillie, 1973; Alvarez and Castro, 1976).

However, seawater also exhibits some advantages and it has been used in Chile to float copper ores for decades (Burn 1930; Morales, 1975). Initially, the use of seawater was restricted to small flotation plants close to the coast. Subsequently, *Carolina de Michilla*, and *Las Luces (Minera Las Cenizas)*, have been using seawater in medium copper scale mining for many years (Monardes, 2009; Moreno et al., 2011). The latter one is still operating with seawater around 20 years. The first large-scale mining (>100,000 metric tons/day) located around 150 km from the coast and 2,600 m.a.s.l., assuming the costs of catchment and pumping, was the *Esperanza* plant in 2011 (now *Centinela*-Antofagasta Minerals) (Parraguez et al., 2010), and later on *Sierra Gorda* plant (KGHM) in 2014, located at similar altitude and distance from the coast. Large-scale flotation plants demand high performance (metals recovery, concentrate grade, depression of impurities, etc.), and a more elaborate process is required.

Currently, the technology applied in Chile to float chalcopyrite ores in non-desalinated seawater consist in a rougher circuit operated at natural pH (8.0-8.5), with the subsequent addition of sodium metabisulfite ($Na_2S_2O_5$) (MBS) at regrinding and cleaning stages to depress pyrite at pH around 6.5 -7.0. Hence, rougher circuit operating without or small amount of lime, and depression of pyrite in cleaning stages at low pH, are the key factors for the Cu-Mo-Fe flotation technology in seawater. This scheme is completely different from the traditional one in fresh water, which applies in the rougher circuit a pH 10.0-10.5 adjusted with lime; and then regrinding and cleaning stages for depressing pyrite at pH 11.0-

12.0. It must be noted that, the depression of pyrite by MBS in fresh water is inefficient and in seawater only works properly with pyrite content lower than 3% (sulfide base). Therefore, in plant practice, this limits the use of MBS in seawater with high pyrite Cu-Mo-Fe sulfide ores. This behavior is not yet understood.

The use of seawater in mineral flotation has traditionally focused only on its salinity without considering its diverse ionic composition. Electrolyte solutions such as NaCl and KCl do not hydrolyse, and their effect is attributed to high ionic strength. However, seawater contains hydrolysable ions such as magnesium, calcium, carbonate, etc., which can precipitate when pH increases. Additionally, in the case of seawater, the minor or secondary ions such as Mg^{2+}, CO_3^{2+}, SO_4^{2-}, etc. may play a significant role on surface phenomena, including bubble coalescence and froth layer thickness growth (Laskowski and Castro, 2008; 2012).

Hence, the objective of this paper is twofold:
-   Review the chemistry of seawater in terms of their chemical composition and changes that occur with pH changes.
-   Review how the changes in seawater ions speciation induced by pH can affect molybdenite flotation and pyrite depression from Cu-Mo-Fe ores in seawater.

2. Precipitation of seawater at high pH

Salinity of seawater is typically around 35‰ but varies slightly among different places. Sodium and chloride ions contribute approximately 86% to total salinity of seawater. Some of the main secondary ions are sulfate (2.7 g/Kg), magnesium (1.29 g/Kg), calcium (0.41 g/Kg), bicarbonate (0.145 g/Kg), borate (0.027 g/Kg) ions, etc. Seawater is always made up of the same types of salts and they are always in the same proportion to each other (even if the salinity is different than average).

Seawater has a natural pH of around 7.8-8.2, which basically depends on the concentration of the ion-pairs bicarbonate/carbonic acid, and boric acid/borate ($B(OH)_3$/$B(OH)_4^-$). These equilibriums are responsible for the alkaline pH of seawater and for its buffering capacity, i.e., seawater can resist drastic pH changes even after the addition of bases and acids (Pytkowicz and Atlas, 1975). The buffer capacity is mainly given by the chemistry of carbonic acid. Carbon dioxide (CO_2) reacts with water to form carbonic acid (H_2CO_3), which in turn rapidly dissociates to form a bicarbonate ion (HCO_3^-) and a hydrogen ion (H^+) (pKa1=6.35). Subsequently, in a second step the HCO_3^- ion dissociates to form carbonate ions (CO_3^{2-}) and a hydrogen ion (H^+) (pKa2=10.33). Therefore, when more CO_2 dissolves in seawater, it becomes more acidic. In the alkaline pH range, carbonate ion concentrations increase with increasing pH. Seawater is approximately 2.8 times more enriched with bicarbonate than fresh water, based on molarity. The concentration of ions HCO_3^- and CO_3^{2-} are equivalent at pH 10.33 in fresh water.

Table 1. Typical chemical composition of seawater for a salinity of 35‰ (Castro and Huber, 2005).

Chemical ion	Concentration in ‰, (g/Kg)	Total salinity, %
Chloride	19.345	55.03
Sodium	10.752	30.59
Sulfate	2.701	7.68
Magnesium	1.295	3.68
Calcium	0.416	1.18
Potassium	0.390	1.11
Bicarbonate	0.145	0.41
Bromide	0.066	0.19
Borate	0.027	0.08
Strontium	0.013	0.04
Fluoride	0.001	0.003
Other	Less than 0.001	Less than 0.001

Nevertheless, the most important chemical aspect to be considered in flotation systems is the precipitation of seawater at alkaline pH. By addition of NaOH, magnesium hydroxide ($Mg(OH)_2$) is

formed in seawater at pH>10, while lime addition forms Mg(OH)$_2$, calcium carbonate (CaCO$_3$), and other insoluble Ca salts.

In agreement with the chemical behavior described above, the lime consumption by pulps prepared with Cu ores in seawater is high (over 8 times, to reach pH 10) (Fig. 1). The high demand of lime is explained by two factors: (i) the buffer capacity of the bicarbonate/carbonic acid, and (ii) the precipitation reactions of Mg hydroxide and Ca carbonate (Parraguez et al., 2009; Castro et al., 2010; Castro et al., 2012c; Veki, 2013; Hirajima et al., 2016; Jeldres et al., 2016; Qiu et al., 2016; Li et al., 2017).
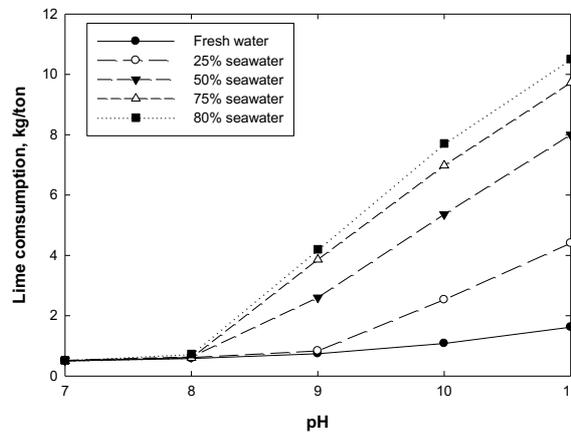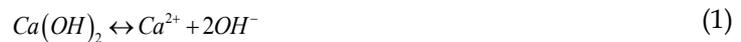

Fig. 1. Effect of seawater dilution on consumption of lime needed to adjust pH in the flotation of a copper sulfide ore (Castro et al., 2010)

Precipitates formed in seawater at pH>10 are detrimental to the flotation process, particularly the colloids of magnesium hydroxide, and, to a less degree, calcium carbonate (Parraguez et al., 2009; Castro 2012a; Castro 2012c; Hirajima et al., 2016; Qiu et al., 2016; Suyantara et al., 2018). The precipitation reactions are described by the following equations:

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \qquad (1)$$

$$Mg^{2+} + Ca(OH)_2 \leftrightarrow Mg(OH)_2 + Ca^{2+} \qquad (2)$$

$$CO_3^{2-} + Ca(OH)_2 \leftrightarrow CaCO_3 + 2OH^- \qquad (3)$$

3. Bubble coalescence in seawater

In order to collect and transport particles of valuable minerals in the flotation process, small bubbles (0.5-2.5 mm) are usually required. Fine bubbles formed in the cell tend to increase its size by coalescence. Organic frothers play the role of preventing coalescence keeping bubbles stable as fine sizes (< 2 mm) in the conventional flotation process with freshwater. It is well known that bubble coalescence can be completely prevented at frother concentrations exceeding the critical coalescence concentration (CCC). This is an important parameter introduced by Laskowski et al. during studies on frother characterization (Cho and Laskowski, 2002; Laskowski et al., 2003; Grau et al., 2005; Grau and Laskowski, 2006).

Inorganic electrolytes also prevent bubble coalescence (Lessard and Zieminski, 1971, Craig et al., 1993; Weissenborn and Pugh, 1995; Firouzi et al., 2015), increasing gas holdup in flotation systems (Quinn et al., 2007; Kracht and Finch, 2010). The same phenomenon controls the bubble size in seawater, and even in the absence of frother fine bubbles are formed (Castro et al., 2010; Manono et al., 2013, Wang and Peng, 2013).

A more complex surface chemistry phenomenon occurs when bubbles are generated in electrolyte solutions (seawater contains around 0.6 mol/dm^3 NaCl) in blend with a frother agent, such as, methyl isobutyl carbinol (MIBC) or a polyglycol type frother (10-20g/Mg) (Quinn et al., 2007; Bournival et al., 2012). Although the mechanisms of preventing bubble coalescence by frothers and electrolytes are completely different, studies by Castro et al. (Castro et al., 2012b; Ramos et al., 2013; Castro et al., 2013) indicate that a synergistic effect exists, i.e., the size of the bubble is reduced by dissolved electrolytes,

but an additional decreasing occurs if a frother agent is added to the same system (Fig. 2). Flotation in seawater usually requires lower frother consumption (<15 g/Mg). Furthermore, in some cases electrolyte solutions do not require any frother addition, because small bubbles are stabilized only by dissolved electrolytes (Quinn et al., 2007, Castro and Laskowski 2011).
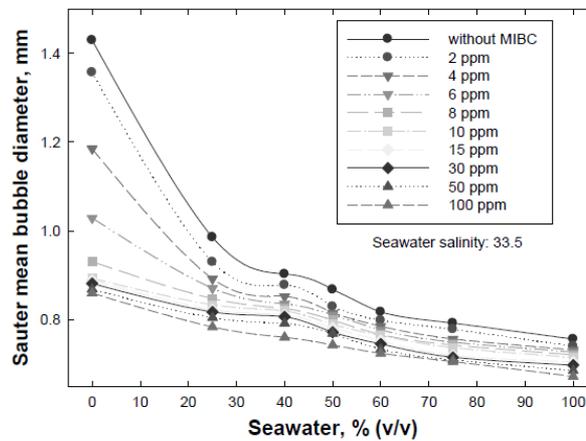

Fig. 2. Sauter bubble size as a function of dilution of seawater (%), at different MIBC concentrations (Castro et al., 2010; Laskowski et al., 2014)

On the other hand, frothability (i.e., the ability to form stable froth when air is injected in the flotation cell) and particularly the froth layer thickness, is lower in seawater. Some dissolved ions in seawater such as Ca^{2+}, Mg^{2+}, and SO_4^{2-} are able to inhibit the froth layer growth (Laskowski, et al., 2014).

In addition, the frothability of Cu ores under typical flotation conditions, in fresh water, is strongly dependent on pH, showing a maximum froth layer thickness at pH 10.5 (see Fig. 3). This pH 10.5 matches with the pH usually employed in rougher circuits with fresh water, pointing out that a high froth layer thickness is preferred in plant practice. However, the froth layer thickness in seawater is not only thinner but also less dependent on pH. For this reason, when floating copper ores at pH 8.0-8.5 in seawater, froth is not abundant, and the layer thickness does not vary with pH. This behavior is due to the ions dissolved in seawater. Under the conditions of Fig. 3, Ca^{2+}, Mg^{2+} and SO_4^{2-} ions, at similar concentration that in seawater but dissolved in distilled water, showed an inhibiting effect on the froth layer thickness growth, being the effect of Ca^{2+} ions the greatest (Laskowski et al., 2013; 2014). Therefore, the deleterious effect of seawater on frothing may be produced by its different constituent's ions.
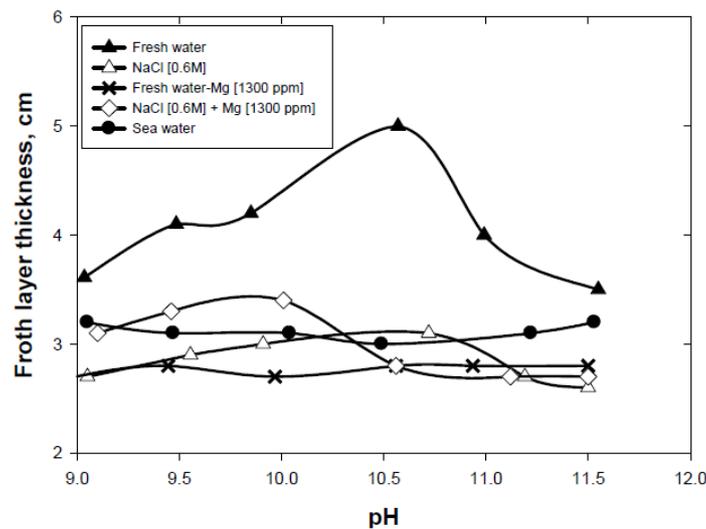

Fig. 3. Froth layer thickness as a function of pH, for a Cu ore floated with MX-7017 (thionocarbamate, 26 g/Mg); MX-945Promoter (21 g/Mg); MIBC (21g/Mg), in different type of waters (Laskowski et al., 2014)

4. Depression of molybdenite by magnesium ions in seawater

Salinity by itself is not detrimental to froth flotation. Hydrophobic minerals (bituminous coal, graphite, sulfur, etc.) show high floatability in NaCl solutions (Klassen and Mokrousov, 1963; Pugh et al., 1997; Fuestenau et al., 1983; Kurniawan et al., 2011; Chang et al., 2018). The floatability of molybdenite also increases in NaCl solutions, in good agreement with its natural hydrophobicity (Lucay et al., 2015). However, due to its anisotropic properties (hydrophobic face sites and hydrophilic edge sites), the natural hydrophobicity of molybdenite decreases with particle size (Castro and Correa, 1995; Lopez-Valdivieso et al., 2012; Castro et al., 2016). Hence, fine particles exhibit a low faces/edges ratio, i.e., they are less hydrophobic than coarse particles what does not necessarily improve its floatability in saline solutions.

Laskowski and Iskra (1970) and Laskowski et al., (1991) working with methylated quartz (as a model of hydrophobic mineral), demonstrated that an increase of NaCl concentration from 0 to 0.5 mol/dm^3 compressed the electrical double layer, resulting in a reduction of the repulsive electrical forces, a shorter induction time; and an improved flotation response. Pan and Yoon (2018) confirmed that the wetting films formed on weakly hydrophobic surfaces becomes metastable in pure water, due to the strong double-layer repulsion. In the presence of KCl, the films can become unstable and rupture due to double-layer compression, which in turn allows the hydrophobic forces to become dominant and hence cause the film to rupture. Li et al. (2017) claim that chalcopyrite improved its floatability with the concentration of NaCl and KCl solutions, possibly due to lower energy barrier and stability of hydration layer on chalcopyrite surface through compressing the electrostatic double-layer force.

One of the main limitations of seawater for the flotation of the by-product molybdenite is its strong depression at pH> 9.5 (Fig. 4). The molybdenite depression takes place when the critical pH of precipitation of Mg(OH)$_2$ is reached. It is also believed that hetero-coagulation of Mg(OH)$_2$ occurs on the surface of molybdenite by slime coating mechanisms (Castro and Laskowski 2011; Castro, 2012a; Castro et al., 2012c; Ramos and Castro, 2013; Veki, 2013; Nagaraj and Farinato, 2014; Castro et al., 2014; Laskowski and Castro, 2015; Hirajima et al., 2016; Qiu et al., 2016; Nagaraj et al., 2016; Laskowski and Castro, 2017; Suyantara et al., 2018). However, taking into account the specificity of the depressing action of Mg hydroxide on molybdenite, a chemisorption on the molybdenite surface (edge sites) must be considered, e.g., eventual formation of Mg molybdate (MgMoO$_4$) (Ricci et al., 1951).

Magnesium hydroxide begins to precipitate at bulk solution around pH 9.5-10.0 in seawater, but at pH below 9.0 does not precipitates, and does not depress molybdenite. Therefore, pH is one of the most important factors of controlling the flotation/depression of molybdenite in Cu-Mo ores flotation in seawater. This concept also extends to saline and hyper-saline waters containing Mg. In addition, losses of Mo may occur largely in cleaning circuits at pH 11-12, when pyrite is depressed with lime (Fig. 5).
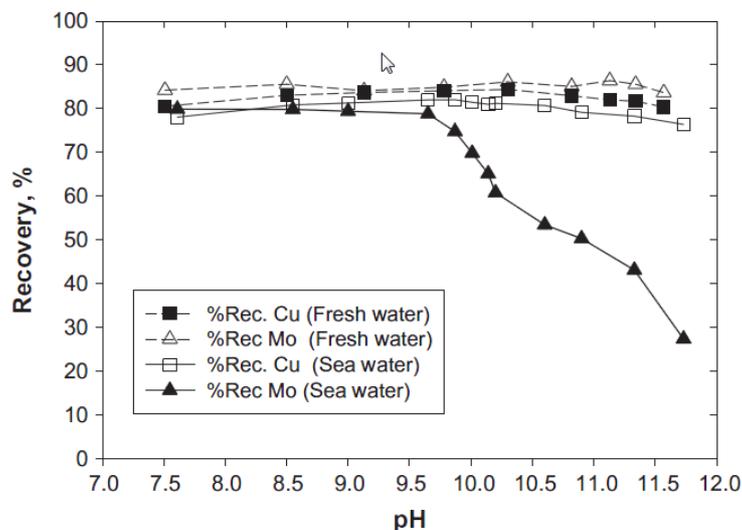

Fig. 4. Cu and Mo rougher flotation recovery at laboratory scale (with typical collectors and frother agents) in fresh water and seawater, as a function of pH adjusted by lime (flotation at 35% solids) (Ramos et al., 2013; Laskowski et al., 2014)
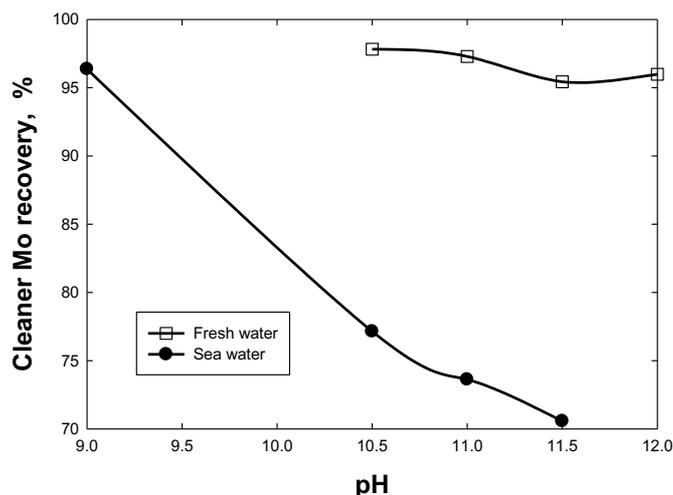
Fig. 5. Mo recovery in cleaner flotation (first cleaner) at laboratory scale, as a function of pH adjusted by lime, for a copper ore floated in fresh water and seawater (rougher: pH 9 in seawater; and pH 10.5 in fresh water) (Castro, 2012a)

The mechanism of molybdenite depression by interactions with $Mg(OH)_2$ suggest the formation of a hydrophilic coating of this colloidal precipitate on molybdenite particles. Different experimental techniques (SEM-AES, XPS, and ToF-SIMS) claim that colloidal $Mg(OH)_2$ adsorb onto the micro-edges on faces and edges of molybdenite particles at pH>10, where depression takes place (Komiyama et al., 2004; Qiu et al, 2016).

Castro et al. (2014) reported that the induction time of molybdenite increased with pH under conditions where Mg hydroxide precipitated at bulk solution and molybdenite was depressed. This suggests that the adsorption of $Mg(OH)^+$ ions and interactions of the molybdenite surface with colloidal $Mg(OH)_2$ reduces its hydrophobicity. These findings are in agreement with those reported by Suyantara et al. (2018) using contact angle measurements and atomic force microscopy to examine the surface of the molybdenite coated by $Mg(OH)_2$. This is also supported by Rebolledo et al. (2017) findings that demonstrated that sodium hexametaphosphate (a dispersing agent), restored the floatability of molybdenite depressed by $Mg(OH)_2$. However, another explanation is also likely because sodium hexametaphosphate react with Mg ions forming soluble complexes and this effect may inhibit the precipitation of $Mg(OH)_2$, as it was suggested for chalcopyrite (Li et al., 2018). Small amounts of $CaCO_3$ has also been identified during precipitation of $Mg(OH)_2$. However, the precipitated $CaCO_3$ seems to have little effect on the floatability of molybdenite (Qiu et al, 2016).

Further evidences on the effect of $Mg(OH)_2$ were obtained when the magnesium hydroxide precipitated at pH>10.0 was removed from seawater by solid/liquid separation. The floatability of molybdenite was restored when Mg-free seawater was employed (Castro 2010b; Jeldres et al., 2017). Magnesium ions seem to have other effects that can also contribute to explain the results reported in this paper. The adsorption of Mg species on air bubbles may contribute to the depression of molybdenite. An experimental technique was developed to study the electrokinetic behaviour of gas bubbles in aqueous electrolyte solutions. It was found that bubbles were negatively charged in NaCl solutions whereas, under certain conditions, they become positively charged in $MgCl_2$ solutions (Li and Somasundaran, 1991; 1992). The observed charge reversal in the pH range of 9 to 11 was attributed to the precipitation of $Mg(OH)_2$ at the gas-liquid interface, while the reduction in the magnitude of the zeta potential of the bubble observed in the acidic pH range was considered to be due to the specific adsorption of Mg^{2+} ions (Li and Somasundaran, 1991). Later on, Han et al., (2004) confirmed a very high affinity of $Mg(OH)^+$ ions and the colloid $Mg(OH)_2$ to the bubble surface.

5. Flotation of copper sulfides in seawater

Mineralogy of Cu sulfide ores is also a key factor in seawater flotation. Pioneering contributions were made by Lekki and Laskowski (1972) and Alvarez and Castro (1976), when working with pure samples

of copper and iron sulfides in NaCl solutions and seawater. They found that chalcopyrite, a mineral without natural floatability – in the presence of flotation reagents – kept its floatability in seawater in a wide range of pH. Instead, the flotation of chalcocite was strongly dependent on pH, exhibiting a peak at pH 9.0-9.5, as shown in Fig. 6 (Alvarez and Castro, 1976).

Micro-flotation tests carried out with pure chalcopyrite in a Partridge-Smith cell showed a high floatability in seawater up to pH 10. However, floatability decreased at pH values over 10, when either lime or NaOH was added. These results are in agreement with findings of Hirajima et al. (2016); and Li et al., (2017). However, flotation tests at laboratory scale with a real Cu-Mo ore in seawater, showed that chalcopyrite flotation was unaffected at pH>10 (Ramos et al., 2013; Laskowski et al., 2014). These results suggest that $Mg(OH)_2$ was not able to depress chalcopyrite under the hydrodynamic conditions predominating in a flotation cell. This finding suggests that the adhesion of colloidal $Mg(OH)_2$ to the chalcopyrite surface is weak. It seems that only electrostatic mechanisms take place in the interaction with chalcopyrite, while a stronger adsorption of $Mg(OH)^+$ and $Mg(OH)_2$ on the molybdenite surface (eventually chemisorption) may be responsible of its permanent depression.

The floatability of chalcocite is more sensitive to seawater, and is strongly decreased when salinity of the solution increased by gradual addition of seawater at pH 8.3-8.5 (Fig. 7).
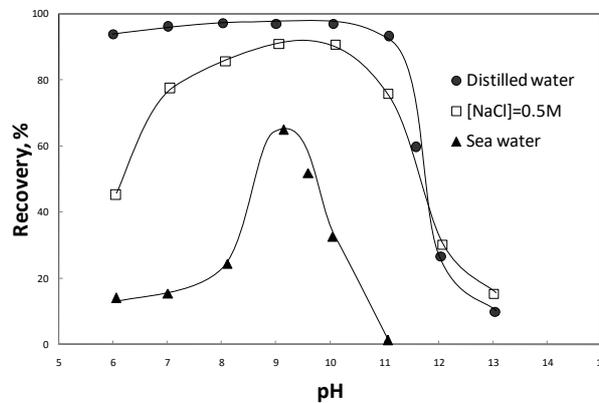

Fig. 6. Effect of pH (adjusted by NaOH/HCl) on the flotation of chalcocite in a Hallimond tube (15 mg/dm^3 IsopX and 10 mg/dm^3 amyl alcohol) (Alvarez and Castro, 1976)
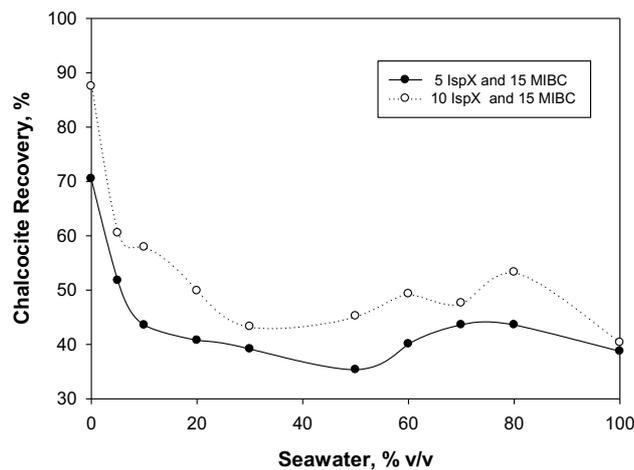

Fig. 7. Effect of salinity on chalcocite flotation in a Partridge-Smith micro-flotation cell as a function of seawater/distilled water mixtures (%), at pH 8.3 in the presence of IsopX (5 and 10 ppm) and MIBC (15 ppm)

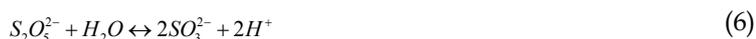## 6. Role of metabisulfite on pyrite depression in seawater

As stated before, the use of lime at pH>9.5 in seawater is not compatible with obtaining high Mo flotation. This finding is one of the single most significant advances in Cu-Mo seawater flotation, which lead to the replacement of lime by MBS.

The use of MBS in the seawater flotation technology is a key factor, because is able to depress pyrite around pH 6.5-7.0 compared with pH 11-12 adjusted by lime in fresh water. Depression of pyrite at low pH is highly beneficial for molybdenite, because its intrinsic floatability at pH 6.5-7.0 is significantly improved, as stated previously (Castro, 2012a,c; Castro et al., 2014; Nagaraj et al., 2016; Qiu, et al., 2016). The mechanisms of pyrite depression by MBS in seawater are not yet well understood. According to Mu et al., (2016), the depression of pyrite and Cu-activated pyrite by sulfoxy depressants (sulfite, bisulfite, metabisulfite, $SO_{2(g)}$) is complex, and a number of mechanisms have been proposed, such as:

(i)   Oxidation of xanthate and dixanthogen to perxanthate (Grano et al., 1997; Yamamoto, 1980; Khmeleva et al., 2002);

(ii) Desorption of dixanthogen from the pyrite surface (Miller, 1970; Khmeleva et al., 2002, 2003);

(iii) Formation of iron/copper hydroxides on copper-activated pyrite, rendering the surface hydrophilic (Shen et al., 2001; Khmeleva et al., 2002); and

(iv) Dissolution of the hydrophobic elemental sulfur (S^0) on the pyrite surface, forming thiosulfate ion ($S_2O_3^{2-}$) (Li et al., 1995; Khmeleva et al., 2005, 2006; Dávila-Pulido et al., 2011).

The depressing effect of MBS on pyrite is strongly associated to its reducing and acidifying properties (Uribe et al., 2017). When MBS is dissolved in water, SO_2 is released, which subsequently reacts with water giving sulfite ions and H^+ ions, lowering the solution pH (see eqs. (4), (5) and (6)). Hence, pH 6.5-7.0 usually applied to depress pyrite in seawater, is the natural result of the acidifying effect, by addition of 150-200 g/Mg of MBS (no acid is added).

At the same time, as MBS is a reducing agent, the redox potential decreases as the MBS concentration increases (Fig. 8). The dissolution of MBS in water occurs through the following reactions:

$$S_2O_5^{2-} \leftrightarrow SO_2 + SO_3^{2-} \tag{4}$$

$$SO_2 + H_2O \leftrightarrow SO_3^{2-} + 2H^+ \tag{5}$$

$$S_2O_5^{2-} + H_2O \leftrightarrow 2SO_3^{2-} + 2H^+ \tag{6}$$

Equation (6) is the global reaction, showing that the sulfite ion is the final product after MBS dissolution. On the other hand, it seems that pyrite is more susceptible to be depressed at pH slightly acid. The flotation of pyrite with ethyl xanthate, as a function of pH showed a minimum around pH 6.0-6.5 (Fuerstenau et al., 2007). In agreement with these findings, it has also been claimed that MBS is a stronger pyrite depressant at pH 6.5-7.0 compared with pH 10-12 (Bulut et al., 2011).

Explanation of these results has been hypothesised as being due to the formation of ferric hydroxide on the surface of pyrite (Lopez Valdivieso et al., 2005; Cushing et al., 2017). By oxidation of pyrite ferrous ions may be released to the solution, which oxidizes to ferric ions, and then precipitate as ferric hydroxide forming a hydrophilic coating on the pyrite surface.

The largest information on pyrite depression with MBS comes from the flotation of poly-metallic ores and Cu-activated pyrite (Grano et al., 1997; Shen et al., 2001). The improved floatability of Cu-activated pyrite is attributed to an ion exchange reaction between ferrous ions and cupric ions (Moslemi and Gharabaghi, 2017). As a result, a surface layer of CuS and hydrophobic sulphur (S^0) is formed on pyrite, according to the next reaction:

$$FeS_2 + Cu^{2+} \leftrightarrow CuS + Fe^{2+} + S^0 \tag{7}$$

However, evidence shows that Cu_2S is formed on the pyrite surface and probably polysulfides instead of elemental sulphur (Ejtemaei and Nguyen, 2017). Additionally, the activation of pyrite needs a reducing redox potential (Peng et al., 2012).

Depression of Cu-activated pyrite by MBS has been explained, e.g., by oxidation of the elemental sulfur layer (or polysulfide) on the pyrite surface (Davila-Pulido et al., 2011). Alternatively, according to Grano et al. (1991), MBS dissolves as sulfite ions, which are able to dissolve elemental sulfur (S°) on pyrite, according to the following reaction:

$$SO_3^{2-} + S^0 \leftrightarrow S_2O_3^{2-} \tag{8}$$

Therefore, sulfite ions seem to play a protagonist role in the mechanisms of pyrite depression by MBS (Chander, 1988; Davila-Pulido et al., 2011; Mu et al., 2016). For instance, the decomposition ethyl xanthate by sulfite ions result in formation of ethyl perxanthate (Grano et al., 1997). The effect of sodium sulfite on the flotation of sphalerite and pyrite, in the presence of copper ions, shows that it promotes the formation of copper hydroxide on the surface of pyrite leading depression (Shen et al., 2001).

The Cu^{2+} ions responsible for the activation of pyrite may have the following origins: (i) Cu^{2+} ions dissolved from Cu oxide minerals; (ii) Cu^{2+} ions present in the process water; and (iii) Cu^{2+} ions produced by galvanic effects between sulfide minerals. It has also been hypothesised that Cu ions would also play a role in the depression of Cu-activated pyrite by MBS, both in fresh and in seawater. In the INCO's process the mixture between MBS and air is used to oxidize cyanide, being low concentrations of Cu^{2+} ions a catalyst. A similar oxidizing role may play Cu^{2+} ions on the pyrite surface in the presence of MBS (Uribe et al., 2017).

On the other hand, evidences showing that an aeration stage is highly necessary to pyrite depression have been reported. Khmeleva et al. (2002) investigated the effect of sulfite ions on the flotation of Cu-activated pyrite with xanthate, and claimed that depression was stronger with air purging. Similar results were reported with sphalerite and MBS (Davila-Pulido et al., 2011). In the same line, conditioning pyrite with O_2 improves its depression (Shen et al, 2001).

Barrick Gold Corporation developed the aeration-metabisulphite process (Air-MBS) to depress pyrite in seawater (Gorain, 2009; Gorain, 2012). This process consists of applying a preliminary aeration stage and then adding MBS to depress pyrite in seawater.

Sulfite ions are a stronger reducing agent compared with metabisuphite ions ($S_2O_5^{2-}$). However, it is not an acidifying agent, but conversely is an alkalizing agent (see eq. (9) and Fig. 9). This can also be a factor that must be taken into account.

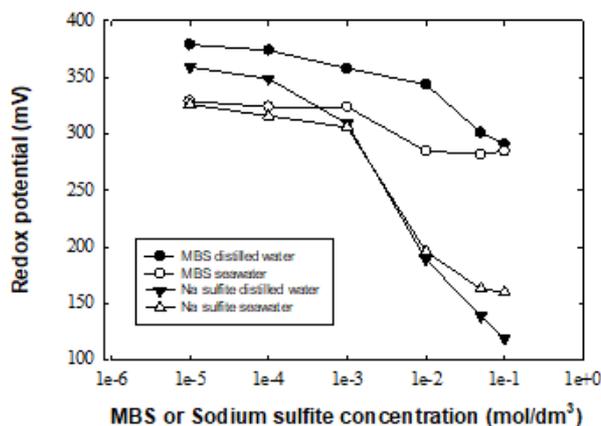$$SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + OH^- \tag{9}$$

Fig. 8. Redox potential (Eh) measurements of sodium metabisulfite (MBS) and sodium sulfite solutions prepared in distilled water and seawater (SHE: standard hydrogen electrode) (Uribe et al., 2017)
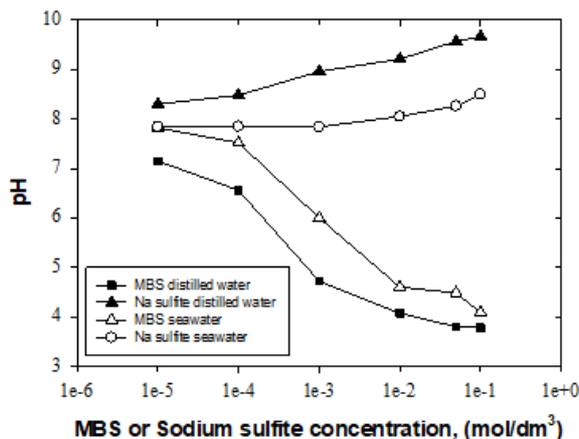

Fig. 9. Effect of concentration on the pH of sodium metabisulfite (MBS) and sodium sulfite solutions prepared in distilled water and seawater (Uribe et al., 2017)

7. Conclusions

The major conclusions from the present work are:

1. Lime consumption in seawater pulps at pH 10.0-10.5, is several times higher than in fresh water, because OH^- ions dissolved from lime react with some hydrolysable ions such as Mg^{2+} and CO_3^{2-} ions precipitating as $Mg(OH)_2$ and $CaCO_3$; and to a less extent, they are consumed by the natural bicarbonate/carbonate buffer.

2. Molybdenite is strongly depressed in seawater by colloidal $Mg(OH)_2$, which precipitates and remains strongly attached on edges and micro-edges on the molybdenite surface at pH> 9.5.

3. Seawater is able to inhibit bubble coalescence giving rise to fine bubbles, similar to what frothers do.

4. Height of the froth layer formed on the flotation cell is lower in seawater than in fresh water. In fresh water the froth layer is pH dependent showing a peak around pH 10.5, while in seawater it is virtually pH independent.

5. Sodium metabisulphite successfully depresses pyrite at pH 6.5-7.0, replacing the detrimental use of lime in seawater. In addition, it has the advantage that it works in the pH range where the natural floatability of molybdenite is improved.

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References

ALVAREZ, J and Castro, S., 1976. Chalcocite and Chalcopyrite flotation in seawater and highly saline media. Proceedings IV Encontro Nacional de Tratamento de Minerios. São José dos Campos, Brazil, Vol.1, pp. 39-44.

BOURNIVAL, G., Pugh, R.J. and Ata, S., 2012. Examination of NaCl and MIBC as bubble coalescence inhibitor in relation to froth flotation. Minerals Engineering, 25, 47-53.

BULUT, G., Ceylan, A., Soylu, B. and Goktepe, F., 2011. Role of starch and metabisuphite on pure pyrite and pyritic copper ore flotation. Physicochem. Probl. Miner. Process. 48(1), 39–48.

BURN, A.K., 1930. The flotation of chalcopyrite in seawater. Bulletin Institution of Mining and Metallurgy, N° 314.

CASTRO, P. and Huber, M.E., 2005. Marine Biology (5th Edition) Ed. McGraw Hill.

CASTRO, S., Correa, A., 1995. The effect of particle size on the surface energy and wettability of molybdenite. Vancouver: 1st UBC-McGill International Symposium on Processing of Hydrophobic Minerals and Fine Coal. CIM MET SOC, pp. 43–57.

CASTRO, S., Venegas, I., Landero, A. and Laskowski, J.S., 2010. Frothing in seawater flotation systems. Proc. 25th Int. Mineral Processing Congress, Brisbane, pp. 4039-4047.

CASTRO, S., 2010b. Proceso para pre-tratar agua de mar y otras aguas salinas para su utilización en procesos industriales. Patente de Invención Provisional, Universidad de Concepción, n°00475/INAPI (12 de mayo 2010) (Spanish text).

CASTRO, S. and Laskowski, J.S., 2011. Froth flotation in saline water. KONA Powder and Particle Journal No.29, 4-15.

CASTRO, S., 2012a. Challeges in flotation of Cu-Mo sulfide ores in seawater. In: Water in Mineral Processing – Proc. 1st Int. Symposium (J. Drelich, ed.), SME, pp. 29-40.

CASTRO, S., Toledo, P. and Laskowski, J.S., 2012b. Foaming properties of flotation frothers at high electrolyte concentrations. In: Water in Mineral Processing – Proc. of the First International Symposium, SME, (J. Drelich, Ed.), pp. 51-60.

CASTRO, S., Rioseco, P. and Laskowski., J.S., 2012c. Depression of molybdenite in sea water. In: Proc. XXVI International Mineral Processing Congress, New Delhi-India.

CASTRO S., Miranda, C., Toledo P. and Laskowski, J.S., 2013. Effect of frothers on bubble coalescence and foaming in electrolyte solutions and seawater. Int. J. Miner. Process., 124, 8-14.

CASTRO, S., Uribe, L. and Laskowski, J.S., 2014. Depression of inherently hydrophobic minerals by hydrolyzable metal cations: molybdenite depression in seawater. 27th Int. Mineral Processing Congress (IMPC 2014), Santiago, Chapter 3, pp. 207-216.

CASTRO, S., Lopez-Valdivieso, A., Laskowski, J.S., 2016. Review of the flotation of molybdenite. Part I: Surface properties and floatability. International Journal of Mineral Processing 148, 48–58.

CRAIG, S.J.V., Ninham, B.W. and Pashley, R.M. 1993. The effect of electrolytes on bubble coalescence in water. J. Phys. Chem., Vol. 97, 10192-10197.

CHANDER, S., 1988. Inorganic depressants for sulphide minerals, in: (Somasundaran, P. and Moudgil, B. M.) Reagents in mineral processing. New York, Marcel Dekker: 429-469.

CHANG, Z., Chen, X. and Peng, Y., 2018. The effect of saline water on the critical degree of coal surface oxidation for coal flotation. Minerals Engineering. 119, 222-227.

CHO, Y.S. and Laskowski, J.S., 2002. Effect of flotation frothers on bubble size and foam stability. Int. J. Mineral Processing, 64, 69-80.

CUSHING, M. L., Ghahreman, A., Kelebek, S., 2017. Electrochemical characteristics of iron sulfide minerals in the presence of SMBS and TETA and the case for their joint action. COM, Annual Conference of Metallurgists Organized by MetSoc of CIM, 1-10.

DÁVILA-PULIDO, G.I., Uribe-Salas, A., and Espinosa-Gómez, R., 2011. Comparison of the depressant action of sulfite and metabisulfite for Cu-activated sphalerite. International Journal of Mineral Processing 101, 71–74.

EJTEMAEI, M. and Nguyen, A.V., 2017. Characterisation of sphalerite and pyrite surfaces activated by copper sulphate. Minerals Engineering. Vol. 100, 223-232.

FIROUZI, M., Howes, T. and Nguyen, A.V., 2015. A quantitative review of the transition salt concentration for inhibiting bubble coalescence. Advances in Colloid and Interface Science.222, 305-318.

FUERSTENAU, D.W., Rosenbaum, J.M., Laskowski, J., 1983. Effect of surface functional groups on the flotation of coal. Colloids Surf. 8, 153–173.

FUERSTENAU, M.C., Jameson, G.J., Yoon, R.H., 2007. Froth Flotation: A Century of Innovation. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado.

GORAIN, B., 2009. Separation of copper minerals from pyrite in buffered water solutions using air-metabisulfite treatment. U.S. Provisional Patent n°61/266,770.

GORAIN, B. K., 2012. Developing solutions to complex flotation problems. Proc. International Mineral Processing Congress (IMPC 2012), New Delhi-India.

GRANO S.R., Johnson N.W., Ralston J., 1997, Control of the solution interaction of metabisulphite and ethyl xanthate in the flotation of the Hilton ore of Mount Isa Mines Limited, Australia, Minerals Engineering, 10, No.1, 17-45.

GRANO, S.R., Lauder, D.W., Johnson, N.W., Smart, R.St.C. and Ralston, J., 1991. Comparison of ethyl xanthate and diisobutyldithiophosphinate collectors for the lead roughing of the Hilton ore of Mount Isa Mines Ltd. Fifth Extractive Metallurgy Conference. Australasian Institute of Mining and Metallurgy Publisher, Parkville, pp. 203–210.

GRAU, R.A. and Laskowski, J.S., 2006. Role of frothers in bubble generation and coalescence in a mechanical flotation cell. The Canadian Journal of Chemical Engineering., 84(2):170-182.

GRAU, R.A., Laskowski, J.S., Heiskanen, K., 2005. Effect of frothers on bubble size. International Journal of Mineral Processing 76, 225–233.

HAIG-SMILLIE, L. D., 1973. Sea Water Flotation. Texade Mines, Ltd. GILLES BAY, B. C., November 29.

HAN, M.Y., Ahn, H.J., Shin, M.S., Kim, S.R., 2004. The effect of divalent metal ions on the zeta potential of bubbles. Water Science and Technology. 50(8) 49-56.

HIRAJIMA, T.; Suyantara, G.P.W.; Ichikawa, O.; Elmahdy, A.M.; Miki, H.; Sasaki, K., 2016. Effect of Mg^{2+} and Ca^{2+} as divalent seawater cations on the floatability of molybdenite and chalcopyrite. Miner. Eng., 96–97, 83–93.

JELDRES, R.I., Arancibia-Bravo, M.P., Reyes, A., Aguirre, C.E., Cortes, L., Cisternas, L.A., 2017. The impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores. Miner. Eng. 109, 10–13.

JELDRES, R.I., Forbes, L., Cisternas, L.A., 2016. Effect of Seawater on Sulfide Ore Flotation: a Review. Miner. Process. Extr. Metall. Rev. 37, 369–384.

KHMELEVA, T.N., Skinner, W., Beattie, D.A., Georgiev, T.V., 2002. The effect of sulphite on the xanthate-induced flotation of copper-activated pyrite. Physicochem. Probl. Miner. Process. 36, 185–195.

KHMELEVA, T.N., Beattie, D.A., Georgiev, T.V., Skinner, W.M., 2003. Surface study of the effect of sulfite ions on copper-activated pyrite pre-treated with xanthate. Miner. Eng. 16, 601–608.

KHMELEVA, T.N., Skinner, W., Beattie, D.A., 2005. Depressing mechanisms of sodium bisulphite in the collectorless flotation of copper-activated sphalerite. Int. J. Miner. Process. 76 (1–2), 43–53.

KHMELEVA, T.N., Chapelet, J.K., Skinner, W.M., Beattie, D.A., 2006. Depression mechanisms of sodium bisulphite in the xanthate-induced flotation of copper activated sphalerite. Int. J. Miner. Process. 79 (1), 61–75.

KLASSEN, V.I. and Mokrousov, V.A., 1963. An Introduction to the Theory of Flotation, Butterworths, London.

KOMIYAMA, M., Kiyohara, K., Li, Y., Fujikawa, T., Ebihara, T., Kubota, T., and Okamoto, Y., 2004, "Crater structures on a molybdenite basal plane observed by ultra-high vacuum scanning tunneling microscopy and its implication to hydrotreating." Journal of Molecular Catalysis A: Chemical, 215(1–2). pp. 143–147.

KRACHT, W., Finch, J.A., 2010. Effect of frother on initial bubble shape and velocity. International Journal of Mineral Processing 94 (3-4), 115-120.

KURNIAWAN, A., Ozdemir, O., Nguyen, A., Ofori, P., Firth, B., 2011. Flotation of coal particles in $MgCl_2$, NaCl, and $NaClO_3$ solutions in the absence and presence of Dowfroth 250. Int. J. Miner. Process. 98, 137–144.

LASKOWSKI, J.S., Iskra, J., 1970. Role of capillary effects in bubble-particle collision in flotation. Trans. IMM, Section C., 79, C6-C10.

LASKOWSKI, J.S., Xu, Z., Yoon, R.H., 1991. Energy barrier in particle-bubble attachment and its effect on flotation kinetics. Proc. 17th Int. Mineral Processing Congress, Dresden, Vol., 2, pp. 237-249.

LASKOWSKI, J.S., Cho, Y.S. and Ding, K., 2003. Effect of frothers on bubble size and foam stability in potash ore flotation systems, Canadian J. Chem. Eng., 81, 63-69.

LASKOWSKI, J.S. and Castro, S., 2008. Flotation in concentrated aqueous electrolyte solutions. Proc. 11th International Mineral Processing Symposium, Belek-Antalya, Turkey, pp. 281-290.

LASKOWSKI, J.S. and Castro, S., 2012. Hydrolyzing ions in flotation circuits: sea water flotation. Proc. XIII International Mineral Processing Symposium, Bodrum-Turkey, pp. 219-227.

LASKOWSKI, J.S., Castro, S. and Ramos, O., 2013. Effect of seawater main components on frothability in the flotation of Cu-Mo sulfide ore. Physicochem. Probl. Miner. Process. 50(1), 17−29.

LASKOWSKI, J. and Castro, S., 2014. Flotation in highly concentrated electrolyte solutions. Proc. IMPC 2014 (Keynote), Santiago, Chile.

LASKOWSKI, J. and Castro, S., 2015. Flotation in concentrated electrolyte solutions. International Journal of Mineral Processing 144, 50–55.

LASKOWSKI, J. S. and Castro, S., 2017. Hydrolysis of metallic ions in mineral processing circuits and its effect on flotation. COM 2017 Conference of Metallurgists, Vancouver, August 27-30.

LEKKI, J. and Laskowski, J.S., 1972. Influence of NaCl on the flotation of copper sulphide ores. Minerales, Vol. 27, (118), 3-7. (Spanish text).

LESSARD R.R., and Zieminski, S.A., 1971. Bubble Coalescence and Gas Transfer in Aqueous Electrolyte Solutions. Industrial & Engineering Chemistry Fundamentals, 10(2), 260-269.

LI, C. and Somasundaran, P., 1991. Reversal of bubble charge in multivalent inorganic salt solutions – effect of magnesium. J. Coll. Interf. Sci., 146, 215-218.

LI, C. and Somasundaran, P., 1992. Reversal of bubble charge in multivalent inorganic salt solutions – effect of aluminium. J. Coll. Interf. Sci., 148, N°2, 587-591.

LI, Y., Li, W., Xiao, Q., He, N., Ren, Z., Lartey, C. and Gerson, A. R., 2017. The Influence of Common Monovalent and Divalent Chlorides on Chalcopyrite Flotation. Minerals 2017, 7, 111.

LI, J., Miller, J.D., Wang, R.Y., Le Vier, M., 1995. The ammoniacal thiosulfate system for precious metal recovery. Proceedings XIX Int. Mineral Processing Congress, SME, Littleton, Colorado, USA, vol. 4, pp. 37–42.

LI, W., Li, Y., Xiao, Q., Wei, Zh. and Song, S., 2018. The Influencing Mechanisms of Sodium Hexametaphosphate on Chalcopyrite Flotation in the Presence of $MgCl_2$ and $CaCl_2$. Minerals, 2018,8(4), 150.

LEKKI, J. and Laskowski, J.S., 1972. Influence of NaCl on the flotation of copper sulfide ores. Minerales, Vol. 27, (118), 3-7. (Spanish text).

LOPEZ-VALDIVIESO, A., Sanchez-Lopez, A.A. and Song, S., 2005. On the cathodic reaction coupled with the oxidation of xanthates at the pyrite/aqueous solution interface. International Journal of Mineral Processing, 77, 154.

LOPEZ-VALDIVIESO, A., Madrid-Ortega, I., Valdez-Pérez, D., Yang, B., Song, S., 2012. The heterogeneity of the basal plane of molybdenite: its effect on molybdenite floatability and calcium ion adsorption. Santiago: 9th International Mineral Processing Conference. PROCEMIN, pp. 21–23.

QUINN, J.J., Kracht, W., Gomez, C.O., Gagnon, C., Finch, J.A., 2007. Comparing the effect of salts and frother (MIBC) on gas dispersion and froth properties. Minerals Engineering, 20 (14), 1296–1302.

LUCAY, F., Cisternas, L. A., Gálvez, E. D., and López-Valdivieso, A., 2015, Study of the natural floatability of molybdenite fines in saline solutions. Effect of gypsum precipitation. Minerals & Metallurgical Processing Journal, 32, 203–208.

MANONO, M.S., Corin, K.C. and Wiese, J.G., 2013. The effect of ionic strength of plant water on foam stability: A 2-phase flotation study. Minerals Engineering, 40, 42-47.

MILLER J.D., 1970, Pyrite depression by reduction of solution oxidation potential. Report to EPA Water Quality Office, Grant No. 12010 DIM.

MONARDES, A., 2009. Use of seawater in grinding-flotation operations and tailing disposal, Proc. 11th Symp. Mineral Processing Moly Cop 2009 (Spanish text).

MORALES, J.E., 1975. Flotation of the Andacollo's ore in pilot plant by using seawater, Minerales, n°130, Vol. 30, 16-32 (Spanish text).

MORENO, P.A., Aral, H., Cuevas, J., Monardes, A., Adaro, M., Norgate, T., Bruckard, W., 2011. The use of seawater as process water at Las Luces copper–molybdenum beneficiation plant in Taltal (Chile). Miner. Eng. 24 (8), 852–858.

MOSLEMI, H. and Gharabaghi, M., 2017. A review on electrochemical behavior of pyrite in the froth flotation process. Journal of Industrial and Engineering Chemistry, 47, 1–18.

MU, Y., Peng, Y., and Lauten, R. A., 2016. The depression of pyrite in selective flotation by different reagent systems – A Literature review. Minerals Engineering, 96-97, 143–156.

NAGARAJ, D.R., Farinato, R., 2014. Chemical factor effects in saline and hypersaline waters in the flotation of Cu and Cu-Mo ores. Presented at the XXVII International Mineral Processing Congress, XXVII International Mineral Processing Congress, Santiago, Chile.

NAGARAJ, D. R., Farinato, R., and Tercero, N., 2016. Probing the interface and interphase region of molybdenite edge and face in ore flotation pulps: effect of Mg2+ ions and their hydrolysis products. Proc. 28th Int. Mineral Pocessing Congress, Quebec City, 2016.

PAN, L., and Yoon, R., 2018. Effects of electrolytes on the stability of wetting films: Implications on seawater flotation, 2018.

PARRAGUEZ, L., Bernal, L. and Cartagena, G., 2009. Chemical study for selectivity and recovery of metals sulphides by flotation using seawater. Proc. PROCEMIN 2009, pp.323-333.

PARRAGUEZ, L., Bernal, L. y Cartagena, G., 2010. Flotación con agua salina en proyecto Esperanza. Proc. WIM2010 (Water in Mining), 2° Congreso Internacional en Gestión del Agua en la Industria Minera, Gecamin, 9 de junio 2010, Santiago-Chile (Spanish text).

PENG, Y., Wang, B. and Gerson, A., 2012. The effect of electrochemical potential on the activation of pyrite by copper and lead ions during grinding. International Journal of Mineral Processing. Volumes 102–103, 141-149.

PUGH, R.J., Weissenborn, P. and Paulson, O., 1997. Flotation in inorganic electrolytes; the relationship between recover of hydrophobic particles, surface tension, bubble coalescence and gas solubility. International Journal of Mineral Processing, 51(1–4), 125-138.

PYTKOWICZ, R. M. and Atlas, E., 1975. Buffer intensity of seawater. Limnology and Oceanography. Vol. 20 (2), 222-229.

QIU, Z., Liu, G., Liu, Q., Zhong, H., 2016. Understanding the roles of high salinity in inhibiting the molybdenite flotation. Colloids Surf. Physicochem. Eng. Asp. 509, 123–129.

QUINN, J. J., Kracht, W., Gómez, C. O., Gagnon, C. and Finch, J. A., 2007. Comparing the Effect of salts and frother (MIBC) on gas dispersion and froth properties. Minerals Engineering, Vol. 20, 1296-1302.

RAMOS, O., Castro, S. and Laskowski, J.S., 2013. Copper-molybdenum ores flotation in sea water: Floatability and frothability. Minerals Eng., 53, 108-112.

REBOLLEDO, E., Laskowski, J. S., Gutierrez, L., and Castro, S., 2017. Use of dispersants in flotation of molybdenite in seawater. Minerals Engineering, 100, 71–74.

REY, M. and RAFFINOT, P., 1966. Flotation of ore in sea water: high frothing, soluble xanthate collecting. World Mining, June, 18.

RICCI, J. E. and Linke, W.F., 1951. The System Magnesium Molybdate-Water and the 25° Isotherm of the System MgMoO$_4$-MgCl$_2$-H$_2$O. J. Am. Chem. Soc.,73(8), 3603–3607.

SHEN, W.Z., Fornasiero, D., and Ralston, J., 2001.Flotation of sphalerite and pyrite in the presence of sodium sulfite. International Journal of Mineral Processing, 63, 17–28.

SUYANTARA, G.P.W.; Hirajima, T.; Miki, H.; Sasaki, K., 2018. Floatability of molybdenite and chalcopyrite in artificial seawater. Mineral Engineering, 115, 117–130.

URIBE, L., Gutierrez, L., Castro, S and Laskowski, J.S., 2017. Effect of redox conditions and copper ions on pyrite depression by sodium metabisulfite and sodium sulfite in seawater. CIM Journal, Vol. 8, N°4, 215-222.

VEKI, L., 2013. The use of seawater as process water in concentration plant and the effects on the flotation performance of Cu-Mo ore. Master's thesis, University of Oulu Faculty of Technology.

WANG, B. and PENG, Y., 2013. The behaviour of mineral matter in fine coal flotation using saline water. Fuel, 109, 309–315.

WEISSENBORN, P.K., Pugh, R.J., 1995. Surface tension and bubble coalescence phenomena of aqueous solutions of electrolytes. Langmuir 11 (5), 1422–1426.

YAMAMOTO, T., 1980. Mechanism of depression of pyrite and sphalerite by sulfite. In: Jones, M.J. (Ed.), Complex Sulfide Ores. Inst. Miner. Metall., London, pp. 71–78.