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ARTICLE INFO

ABSTRACT

The declining grades of copper ore associated with the additional processing of clay-based minerals and the use of seawater are problems that copper mining companies are currently facing, where froth flotation and tailing management operations become challenging for operators. In both cases, the detrimental effect is intensified by the presence of calcium and magnesium ions in seawater and their precipitation under alkaline conditions. This research proposes a partial seawater desalination treatment to improve the flotation and thickening performance in clay-containing ore. The proposed seawater treatment promotes the removal of calcium and magnesium ions using carbon dioxide gas and a sodium hydroxide solution. Flotation tests were conducted in a batch cell using synthetic minerals composed of mixtures of chalcopyrite, kaolin, and quartz. Meanwhile, tailings settling assays were performed in a PTFE 30 mm turbine type stirrer with an in-situ characterization of aggregates (using a focused beam reflectance measurement (FBRM) probe). The results showed an improvement in flotation and flocculation performance when tests were carried out with treated seawater at pH > 10.5, where the copper recovery increased from 82% to 95%, compared to seawater without salt removal; meanwhile, the settling rate of flocculated tailing increased from 5.0 m/h to 11.5 m/h. As expected, the sedimentation outcomes showed a clear relationship with the aggregate size. In this context, the partial seawater desalination treatment could be a promising alternative to face the challenges generated by clays and seawater for copper mining companies.

1. Introduction

Copper ore processing plays an important role in the transition to sustainable energy, transportation, and industrial systems (Elshkaki et al., 2016). In 2016, annual world production was 20.1 million metric tons (USGS, 2018); however, the copper demand is expected to increase by around 70 million metric tons by 2050, approximately 300% more than in 2010 (Elshkaki et al., 2016). Most of the large copper deposits are located in arid or semi-arid regions, including northern Chile, southern Peru, and Australia (Northey et al., 2017). In particular, seawater has acquired an interesting position to ensure copper production in Chile, which is the largest producer worldwide, as water scarcity is a problem in northern regions of the country.

Currently, there are several copper mining companies using seawater, either by submitting it to a reverse osmosis plant (RO) or using it directly without disturbing its salinity (Wang and Peng, 2014; Cis-

ternas and Gálvez, 2018; Herrera-León et al., 2018). In this context, the consumption of desalinated and non-desalinated seawater has increased considerably from 2010 to 2017, representing an average annual growth rate of approximately 52% (Cochilco, 2018). The use of desalinated seawater offers the advantage of ensuring current and future copper production, as the water quality is suitable in the copper mining operations. However, an RO plant requires a high investment for its construction (Herrera-León et al., 2019), and it is an energy-intensive process that increases carbon dioxide (CO_2 (g)) emissions as, in Chile, the main source of energy is based on fossil fuels (Molinos-Senante and González, 2019). Additionally, brine discharge from an RO plant can produce negative impacts in the surrounding marine ecosystems, as the discharge contains chemical reagents used in the process (such as antiscalants and biocides, among others), and a higher temperature and inorganic salts concentration compared to seawater (Jones et al., 2018). Otherwise, the direct use of seawater offers the

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advantages of avoiding the construction of desalination plants, with their associated operational costs and environmental impacts (Lattemann and Höpner, 2008). However, seawater in the copper mining companies generates operational challenges as some processes and operations would need to adapt to the new water quality (Cisternas and Gálvez, 2018; Jeldres et al., 2016; Castro, 2012).

Chilean copper mining companies also face serious problems with declining copper ore grades and, consequently, with the additional processing of gangue (waste) associated with the presence of complex minerals like clays (Norgate and Jahanshahi, 2010; Chen and Peng, 2018; Jeldres et al., 2019). As copper ore grades decrease, more ores with high-clay content need to be extracted and processed to produce the same amount of concentrate. In freshwater, the processing of copper sulphide ores that contain clay has become a significant problem in the flotation process and tailing thickening operation. In the first case, clays prevent the adsorption of the collector on valuable minerals, increase pulp viscosity and generate high entrainment of gangue, increase reagent consumption due to the high surface area, poorer selectivity, and impede flotation (Chen et al., 2018: Liu and Peng, 2014; Ndlovu et al., 2013). Additionally, some swelling clays can change the rheology and froth stability, leading to a reduction in flotation grade and recovery (Farrokhpay et al., 2016). While in the second case, clays are slow-settling particles that lead to deficient water recovery (Jeldres et al., 2017a). These operational concerns become more difficult when seawater is used, as it contains different dissolved ions. A recent study by Uribe et al. (2017) reported that calcium and magnesium ions significantly affect chalcopyrite flotation if kaolin is present in the ore. This is because calcium and magnesium ions are hydrolyzed and hydrated in the form of $CaOH^+$, $MgOH^+$, and $Mg(OH)_2(s)$ species when the flotation process operates under alkaline conditions, in order to depress non-valuable minerals, such as pyrite (FeS_2). In this context, the researchers of the previous study mentioned that these species would deposit onto the chalcopyrite and kaolinite surfaces, generating heterocoagulation that reduces the copper recovery. Calcium and magnesium ions also have a detrimental effect on copper-molybdenum sulphide ores, reducing the recovery molybdenite considerably and reducing slightly the copper recovery when the process is carried out in alkaline conditions (pH > 9.5) (Castro, 2018). This situation can be explained by the fact that, at high pH values, colloidal precipitates of calcium and magnesium are deposited on the edges and micro-edges of molybdenite, reducing its floatability. In the same line, Laskowski et al. (2014) demonstrated that the Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions have an inhibiting effect on the froth layer thickness due to the adsorption of $CaOH^+$ and $MgOH^+$ species on bubbles, leading to loss the frothability and, therefore, to the reduction of the froth stabilization.

In relation to the behavior of clay-based tailings with seawater in the thickening operation, little information is available about the impact of seawater under alkaline conditions. However, it is known that saline water exerts different effects on particle flocculation (Goñi et al., 2015; Quezada et al., 2017; Romero et al., 2018). For instance, there are cases where the electrolytes improve the particle aggregation, while in other situations seawater harms the aggregate growth (Witham et al., 2012; Lee et al., 2012; Ji et al., 2013; Costine et al., 2018; Liu et al., 2018). Regarding the last point, Peng and Di (1994) indicated that calcium and aluminum ions could significantly affect the performance of polyacrylamide (PAM) flocculant in the flocculation of kaolinite suspension. The researchers demonstrated that Ca^{2+} and $CaOH^+$ cations can be adsorbed by the PAM carboxyl group, forming complexes, such as $(COO)_2Ca$ or $COOCa(OH)$. The consequence was the reduction in the available PAM functional groups leading to low particle aggregation performance. Mpofu et al. (2003) studied the effect of calcium ions on the zeta potential of kaolinite particles. The researchers demonstrated that at pH > 9 and a calcium ion concentration of 10^{-1} M, the zeta potential turned from negative to positive. This was explained in relation to the adsorption of hydrolyzed calcium species (e.g., $Ca(OH)^+$) or even the precipitation of $Ca(OH)_2$ onto the mineral surface. In this context, it is expected that flocculation of the particles in clay-based tailings using seawater under alkaline conditions will be affected by calcium and magnesium precipitates, which could cause poor performance in thickening operations.

Based on the aforementioned antecedents, it is clear that calcium and magnesium ions in seawater generate complex precipitates under alkaline conditions, which are detrimental to the flotation process when clays are present in the ore, and this could be harmful for the thickening operations of clay-based tailings. To address this problem, a partial seawater desalination treatment for reducing the concentration of calcium and magnesium ions is considered as a potential solution instead of using seawater or desalinated water in the operations of copper mining companies (Jeldres et al., 2019; Cisternas and Gálvez, 2018; Arias et al. 2017; 2018). This strategy has been proposed by Castro (2010) and Jeldres et al. (2017b) using a mixture of lime (CaO) and sodium carbonate ($NaCO_3$) to improve the recovery of copper and molybdenum minerals in the flotation of copper-molybdenum sulphide ores. However, this type of treated seawater or other seawater treatments to process copper sulphide ores with clay content have not yet been evaluated. This research aims to propose a partial seawater desalination treatment by reducing the calcium and magnesium ions to improve the flotation efficiency of chalcopyrite with clay content and the flocculation performance of clay-based tailings under alkaline conditions. The proposed treatment uses CO_2 (g) as precipitator and sodium hydroxide (NaOH) as an alkali source to promote the removal of calcium and magnesium ions from seawater.

2. Materials and methods

2.1. Partial seawater desalination treatment: Calcium and magnesium removal

2.1.1. Materials

Seawater samples from the San Jorge Bay in Antofagasta (Chile) were used to perform the tests and the composition is shown in Table 1. The main reagents used to conduct the partial seawater desalination treatment were pure CO_2 (g) as a source of CO_2 (g), and NaOH solution as an alkaline reagent. Additionally, deionized water was used to wash all the experimental equipment.

The experimental equipment used in the treatment of seawater included: a three flask reactor with a capacity of 2 L equipped with a thermometer and a magnetic stirrer; a CO_2 (g) steel cylinder that was connected to a decompressor and an automatic rotameter (Alicat Scientific, 1–100 ml/min) to control the flow rate of CO_2 (g) in the reactor; and an automatic potentiometric tritimeter (Shott Tritoline 700) that was connected to a pH electrode to precisely control the injection of NaOH solution and to measure the pH of seawater in the reactor.

2.1.2. Method

The partial seawater desalination treatment removes Ca^{2+} and Mg^{2+} ions from the seawater using a NaOH solution in an atmosphere rich in CO_2 (g). The removal rates of these ions were evaluated using

Table 1
The seawater composition at San Jorge Bay.

Ions	Value (mg/L)	Ions	Value (mg/L)
Magnesium	1413	Bicarbonate	137
Calcium	400	Phosphate	< 0.20
Sodium	11,100	Sulphate	2795
Potassium	389	Nitrate	1.90
Chloride	19,888	Fluoride	0.888

different pH values (pH 10, pH 10.5, and pH 11) and CO_2 (g) doses (0 ml, 70 ml, and 210 ml of CO_2 (g)). The tests were performed by placing 2 L of seawater in the reactor at room temperature and stirring continuously. First, the NaOH solution was introduced sequentially into the reactor using the automatic potentiometric tritimeter until a constant pH value was reached. CO_2 (g) was then injected for a specific period of time through the immersion tube into the reactor using the automatic rotameter, along with NaOH solution to keep the pH of the solution constant, which was constantly monitored throughout the experimentation process. Finally, the solution into the reactor was filtered using a vacuum filtration system (membrane filter 0.22 μm, Merck Millipore) to separate the calcium and magnesium precipitates. Atomic Absorption Spectrometry (AAS) analyzed the concentration of Ca^{2+} and Mg^{2+} ions in the filtered solution. All the tests were carried out three times in order to guarantee valid results.

2.2. Flotation tests of chalcopyrite with clay content

2.2.1. Materials

The synthetic ore samples were prepared with KGA-1b kaolin particles acquired from Acros Organics S.A, chalcopyrite provided by Ward's Science S.A., and quartz provided by Don Capó. The synthetic ore sample contains 2.9% chalcopyrite, 24.3% kaolin, and 72.7% quartz, and a quantitative X-ray powder diffraction (XRD) analysis indicates that kaolin contains 84% kaolinite and 16% halloysite. In addition, kaolin had a density of 2.6 g/cm^3 and an average size of 12 μm, while the average size of the chalcopyrite and quartz was 1680 μm. The synthetic minerals were floated using a laboratory scale Denver flotation machine with a 2 L flotation cell, and the pH of the pulp was adjusted using NaOH solution. The reagents used were TC-123 as a primary collector (12 g/t) and Matfroth-355 as a frother (13 g/t).

2.2.2. Method

The recovery and copper grade of synthetic ore samples (chalcopyrite, kaolin, and quartz) were evaluated using different water qualities: i) seawater at pH 8.3 (natural), ii) seawater at pH 11, and iii) treated seawater at pH 11. It is worth mentioning that seawater at the natural pH is the base case to contrast the other experimental tests, as it is the current situation that several copper mines are using to address the water scarcity problem, as mentioned above.

First, a synthetic ore sample of 950 g was ground using a stainless steel laboratory ball with 0.5 L and a frother for 18 min. The particle size distribution obtained was p80 < 170 μm. The pulp was then transferred to the flotation cell and water was added to made up a volume of 2 L for each test. A collector was added to the pulp and NaOH solution to adjust the pH at 11. The flotation pulp was stirred at 800 rpm to mix the reagents at a constant rate for 1 min. After this time period, the air was introduced into the cell as a flotation gas, at a flow rate of 5 L /min, and the froth was scraped every 10 s for a time period of 12 min (flotation time). In addition, the AAS technique was used to determine the composition of the flotation concentrates. Duplicate tests were performed to ensure good reproducibility of results.

2.3. Flocculation tests of clay-based tailings

2.3.1. Materials

Pulps of 250 g and 13% wt. with a solid ratio of 92.30% quartz and 7.70% kaolin were used for settling tests and for measuring of floc chord length distribution. Each pulp contained different liquid phases: i) seawater at pH 8.3 (natural), ii) seawater at pH 10.5, iii) saline water with 0.01 M $CaCl_2$ at pH 10.5; iv) saline water with $MgCl_2 \cdot 6H_2O$ 0.05 M at pH 10.5, and v) treated seawater with CO_2 (g) at pH 10.5.

2.3.2. Settling tests of tailing with clay content

The settling tests were conducted using a PTFE 30 mm turbine type stirrer, placed in the axial position, in a vessel of 1 L capacity and diameter of 100 mm. All tests were performed by placing the stirrer 20 mm above the vessel bottom. The pulp was preconditioned by mixing the saltwater solid suspension at 450 rpm for 20 min. After this time period, in the same vessel, the mixing rate was changed to 125 rpm and diluted flocculant was added to the suspension. The suspension was flocculated for 60 s.

The batch settling tests were conducted after the aforementioned flocculation process, using a closed cylinder of 300 cm^3 (35 mm internal diameter) by gently pouring the slurry into the vessel after mixing time (60 s), and then slowly inverting the cylinder two times by hand. The change of the mud line was registered and defined as the vertical position of the suspension-supernatant interface. All of the tests were carried out three times in order to guarantee valid results.

2.3.3. Floc size measurement

The Particle Track G400 with focused beam reflectance measurement (FBRM) technology was used to measure the floc size. This is a probe-based instrument that was inserted in the beakers containing the pulps to track the changing particle size and count in real-time at full process concentrations. To measure the sizes of the flocs, a laser beam was launched down the probe tube through a set of optics, which was focused to a tight beam spot at the sapphire window. The optics rotated at a fixed speed (typically 2 m/s) resulting in the beam spot rapidly scanning across particles as they flowed past the window. As the focused beam scanned across the particle system, individual particles or particle structures will backscatter the laser light to the detector. These distinct pulses of backscattered light were detected, counted, and the duration of each pulse was multiplied by the scan speed to calculate the distance across each particle. This distance was defined as the chord length, a fundamental measurement of the particle related to the particle size. Typically, thousands of particles were counted and measured per second, allowing a precise and highly sensitive chord length distribution to be reported in real-time. The chord length distribution tracks how the particle size and count change from the beginning until the end of a process. Statistics from each chord length distribution, such as counts in fine and coarse size classes, can be trended over time.

3. Results and discussion

3.1. Partial seawater desalination treatment

Partial seawater desalination treatment aims to the reduce calcium and magnesium ions concentrations. The removal of calcium and magnesium species was evaluated at different pH values (10, 10.5, and 11) and CO_2 (g) doses (0 ml, 70 ml, and 210 ml). The results are shown in Figs. 1 and 2 for the removal rates of calcium and magnesium, respectively.

In Fig. 1, it is observed that the calcium removal rate increases considerably as the CO_2 (g) doses and pH increase. At pH 11 and in an atmosphere rich in CO_2 (g) (210 ml) the removal rate of calcium reached 60.5%. Meanwhile, at the same pH with 70 ml of CO_2 (g) and without CO_2 (g), the calcium removal rate decreases from 30.8% to 23.8%. Instead, at pH 10.5 with 210 ml of CO_2 (g), the calcium removal rate decreases by almost half (33.3%), compared to the treated seawater at pH 11 and the same dose of CO_2 (g). The behavior of calcium removal rate is different at pH 10 with and without CO_2 (g) due to the low performance of precipitation that was reached. This indicates that at pH 10, without CO_2 (g), the calcium removal rate was 1.5%, while with 70 and then 210 ml of CO_2 (g) the calcium removal rates were 1.75% and 8.25%, respectively.
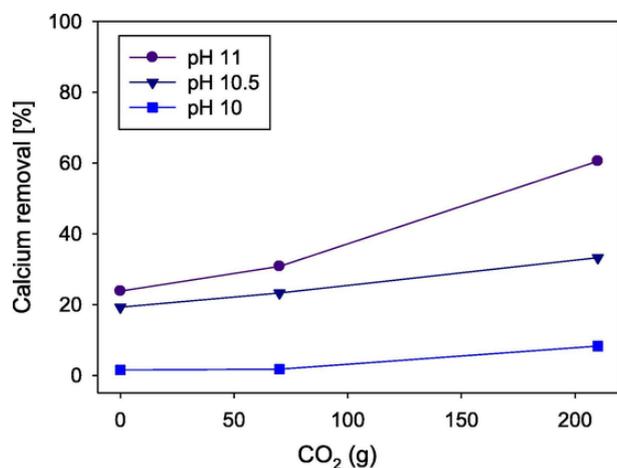
Fig. 1. Calcium removal rate from seawater at different pH and doses of CO_2 (g).
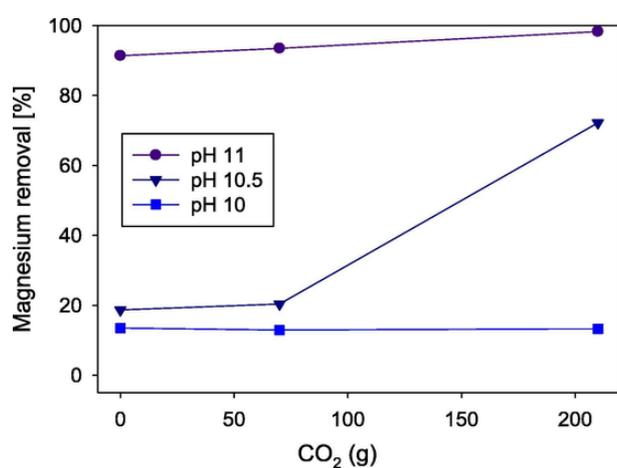

Fig. 2. Magnesium removal rate from seawater at different pH and doses of CO_2 (g).

With respect to magnesium (see Fig. 2), it is clear to observe that at pH 11 with CO_2 (g) doses and without CO_2 (g), the removal remained above 90.0%. However, at the same pH value with 210 ml of CO_2 (g), it was possible to remove most of the magnesium salts in seawater (98.3%). Instead, at pH 10.5 whit 210 ml of CO_2 (g), the magnesium removal rate was 72.2%, a lower value than in the previous case. Moreover, at pH 10.5, the magnesium removal rate remained similar to 70 ml of CO_2 (g) and without CO_2, which are 20.4% and 18.6% respectively. At pH 10, a low magnesium removal performance is observed in an atmosphere rich in CO_2 (g) and without CO_2 (g), as about 13% of the removal rate was reached.

Table 2 shows the final concentration of calcium and magnesium ions in the treated seawater, according to the different pH values and CO_2 (g) doses that are related to the calcium and magnesium removal rates in Fig. 1 and Fig. 2, respectively. In Table 2, the precipitation of calcium and magnesium species occurs due to the dissolution of CO_2 (g) in seawater in an alkaline environment. However, the precipitation of calcium and magnesium species at pH 10 in an atmosphere rich in CO_2 (g) and without CO_2 (g) is slightly reduced due to the solubility of calcium, which starts to decrease at a pH higher than 9.5, while the solubility of magnesium starts to decrease at a pH higher than 10.5 (Ayoub et al., 2014; El-Manharawy and Hafez, 2003).

In this context, for the treated seawater at pH 10.5 without CO_2 (g), the calcium precipitation was higher than magnesium (see Fig. 1), where its concentration was reduced from 400 mg/L to 323 mg/L, as its solubility was affected. For the same treated seawater with 210 ml of CO_2 (g), the concentration of calcium and magnesium was strongly

Table 2
Calcium and magnesium ions concentration before and after partial seawater desalination treatment.

pH	CO_2 (g) (ml)	Calcium (mg/L)	Magnesium (mg/L)
8.3 (seawater at natural pH)			
	–	400	1413
10	0	394	1222
	70	393	1230
	210	367	1225
10.5	0	323	1149
	70	307	1125
	210	267	393
11	0	305	121
	70	277	92
	210	158	24

reduced from 400 mg/L and 1413 mg/L to 267 mg/L and 393 mg/L, respectively (see Table 2). This situation occurs due to the dissolution of CO_2 (g) in seawater, which is explained by the carbonate system. It is a weak acid-base system and considers the species, such as CO_2 (g), aqueous carbon dioxide (CO_2 (ac)), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). The continuous injection of CO_2 (g) into seawater leads to the oversaturation of the carbonate species, which interact with the calcium and magnesium ions of the seawater.

This situation promotes the formation of different species, including calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) (Al-Anezi and Hilal, 2006). In this context, for the treated seawater at pH 11 with 210 ml of CO_2 (g), the maximum removal rate of calcium (60.5%) and magnesium (98.3%) was reached, where the concentration of the treated seawater was reduced from 400 mg/L and 1413 mg/L to 305 mg/L and 121 mg/L, respectively (see Table 2). Another factor that also promoted the precipitation of these species was their high pH value, as the pH of seawater increases, the dissolution performance of CO_2 (g) also increases (Zhao et al., 2013), leading to a higher rate of calcium and magnesium precipitates in seawater.

3.2. Flotation of chalcopyrite with clay content

The copper recovery and copper grade were evaluated by chalcopyrite flotation with and without clay content using different water qualities (seawater at natural pH, seawater at pH 11, and treated seawater that removed 60.5% of calcium and 98.3% of magnesium). Fig. 3 shows that chalcopyrite flotation in a clay-free system using seawater at pH 11 reached 98% copper recovery, the highest recovery obtained in comparison with the same system at pH 8.3 (90% copper recovery) and systems with clay content. This situation can also be appreciated in the kinetic parameters (see Table 3), where the chalcopyrite flotation in a clay-free system using seawater at pH 11 showed the fastest flotation rate (1.95 min^{-1}), reaching a copper recovery of 96%.

Regarding the copper concentrate grade of clay-free systems, the chalcopyrite flotation at pH 8.3 had the best quality of concentrate (10.3% grade of copper) compared to the chalcopyrite flotation at pH 11, which reached a copper concentrate grade of 5.5% being almost the half of the previous case. It is worth mentioning that the mineralogy of copper sulphide ores is a relevant factor in the seawater copper flotation (Castro, 2012; Castro, 2018). For porphyry copper ores with a high presence of chalcopyrite, the copper recovery is slightly reduced using seawater, compared to freshwater (Castro, 2012). This is be-
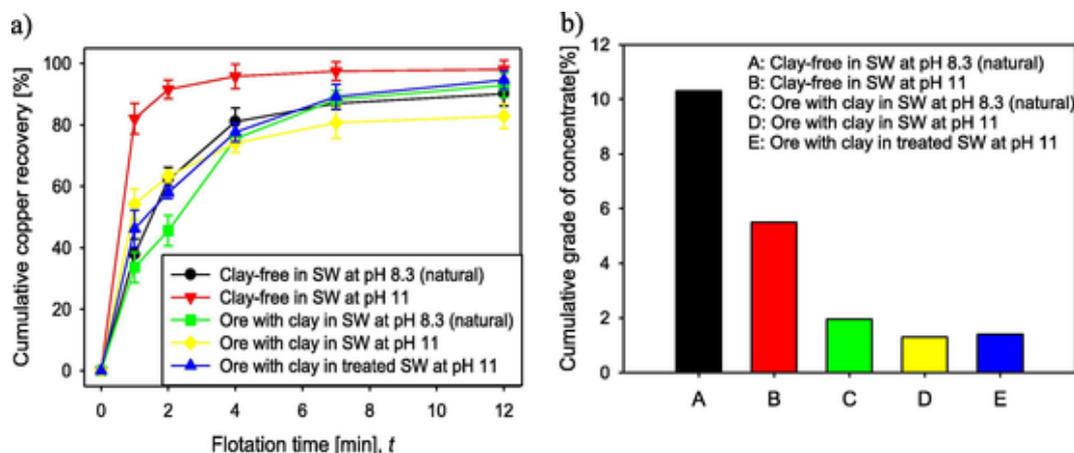
Fig. 3. Effect of different water qualities on: a) copper recovery, and b) grade of copper concentrate.

Table 3

The kinetic parameters for rougher tests of chalcopyrite with and without clay, using different water qualities. SW: seawater.

Experimental conditions	K_c (min^{-1})	R_∞ (%)
Clay-free in SW at pH 8.3	0.57	89
Clay-free in SW at pH 11	1.95	96
Ore with clay in SW at pH 8.3	0.37	94
Ore with clay in SW at pH 11	0.70	81
Ore with clay in treated SW at pH 11	0.55	91

cause the adhesion of hydrolyzed and hydrated calcium and magnesium species ($CaOH^+$, $MgOH^+$, and $Mg(OH)_2$) is weak on the chalcopyrite surface, producing only electrostatic mechanisms in the interaction with the mineral and not the adsorption of the species on its surface (Castro, 2018). The situation is different when copper sulphide ores have a predominance of chalcocite (CuS_2), bornite (Cu_5FeS_4), or energite (Cu_3AsS_4) where seawater is detrimental for the recovery of copper because these minerals are sensitive to pH as was stated by Alvarez and Castro (1976), Smith and Heyes (2012), and Yepsen et al. (2019).

Regarding the systems with clay content, chalcopyrite flotation using seawater at pH 11 was strongly affected compared to seawater at a natural pH, as copper recovery decreased from 93% to 82%, and the copper grade fell down from 2.0% to 1.3% (see Fig. 3). The low flotation performance at pH 11 was due to the calcium and magnesium ions generating complex precipitates under alkaline conditions, causing the heterocoagulation between the kaolin and chalcopyrite. The heterocoagulation phenomenon caused a hydrophilic coating formed by the clay, which adhered onto the surface of valuable minerals preventing their interaction with bubbles and/or collector (Jeldres et al., 2019). Therefore, this phenomenon and the mechanical entrainment that reduces the quality of concentrate could be the primary feature responsible for kaolin behavior on the copper recovery and quality of concentrate in the flotation process using seawater under alkaline conditions. It is worth mentioning that the results presented in this study are consistent with the study reported by Uribe et al. (2017). When analyzing kinetic parameters (see Table 3), we found that kaolin has a negative impact on chalcopyrite flotation, since, at both conditions (pH 8.3 and pH 11), the value of the kinetic constant decreases markedly. This demonstrates that clay delays the flotation rate of copper ore.

In Fig. 3 it is interesting to note that the partial desalination treatment of seawater in the chalcopyrite flotation with clay content increased the recovery by up 95% compared to the clay system using seawater at pH 11 (82% copper recovery), but the flotation rate be-

came slower because the kinetic constant was reduced from 0.70 to 0.55 min^{-1}. The high performance of treated seawater was because the concentration of divalent ions decreased, which led to reduced heterocoagulation between chalcopyrite and kaolin. However, the concentrate grades reached using treated and untreated seawater at pH 11 were similar, 1.4% and 1.3%, respectively. We consider that the low concentrate grade obtained was due to the entrainment produced of fine clay particles, and that calcium and magnesium precipitates were not responsible for this situation. Therefore, it is necessary to seek alternatives complementing the partial seawater desalination treatment in the flotation process in order to improve the copper concentrate grade.

3.3. Flocculation of clay-based tailings

The flocculation performance of clay-based tailings was evaluated using different pulps containing different liquid phases (natural seawater; seawater at pH 10.5; saline water with 0.01 M $CaCl_2$ at pH 10.5; saline water with $MgCl_2 \cdot 6H_2O$ 0.05 M at pH 10.5, and treated seawater with CO_2 (g) at pH 10.5. It is worth mentioning that the flocculation tests were performed after flotation tests. This situation led to the pH of seawater, saline water, and treated seawater decreasing from 11 to 10.5 due to the influence of the atmospheric CO_2 (g), which acidified the liquid phases in a short time (El-Manharawy and Hafez, 2003). The sedimentations of clay-based tailings using seawater at natural pH were efficient (see Fig. 4) due to the settling rate increased monotonically with the reagent dose (in the range 1–89 g/ton). However, when
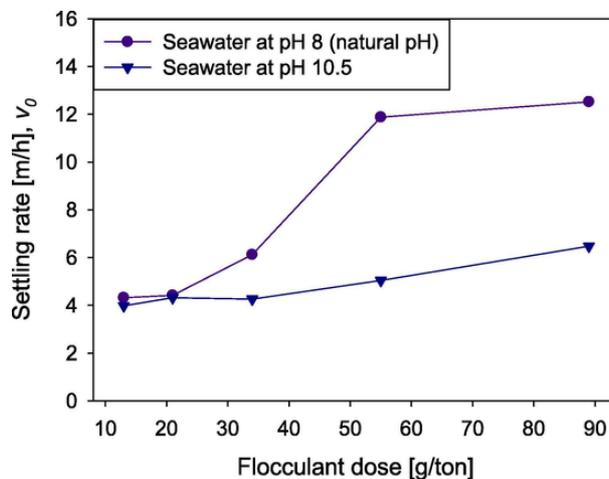
Fig. 4. The effect of the flocculant dose and pH on the settling rate of kaolin suspensions in seawater.

the pulp was brought at pH 10.5, the sedimentations were noticeably slower.

For instance, at a flocculant dosage of 55 g/ton, the settling rate in seawater at a natural pH was 11.9 m/h, while at pH 10.5 it was 5.0 m/h. This behavior is explained by the reduction of the size of the floc when flocculation was carried out under alkaline conditions. As shown in Fig. 5, after 60 s, once flocculation began, the mean chord length at natural pH was 160 μm, while at pH 10.5 it was 120 μm.

In analyzing the effect of the main divalent ions present in seawater, magnesium was the principal aspect responsible for the low sedimentation performance when working at pH 10.5 (see Fig. 6). At a flocculant dosage of 55 g/ton, the settling rate obtained in the presence of magnesium chloride was 3.2 m/h, while for calcium chloride, it was 6.5 m/h. This phenomenon also coincides with the floc size response (see Fig. 7). After 60 s, a mean chord length of 120 μm was reached in the presence of calcium chloride, while 100 μm was found in the presence of magnesium chloride.

Based on the antecedents, treated seawater was used since as it has a low concentration of calcium and magnesium ions. As shown in Fig. 6, seawater treated at pH 10.5 notably increased the settling rate com-
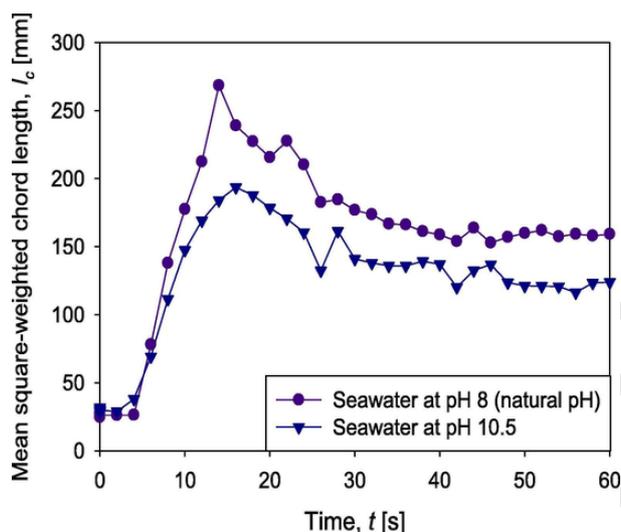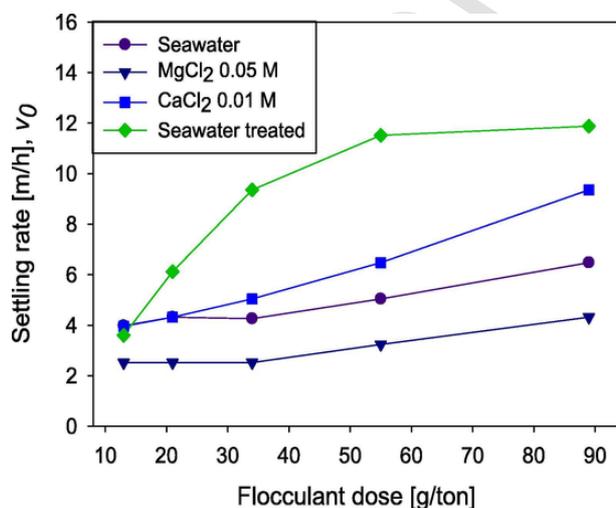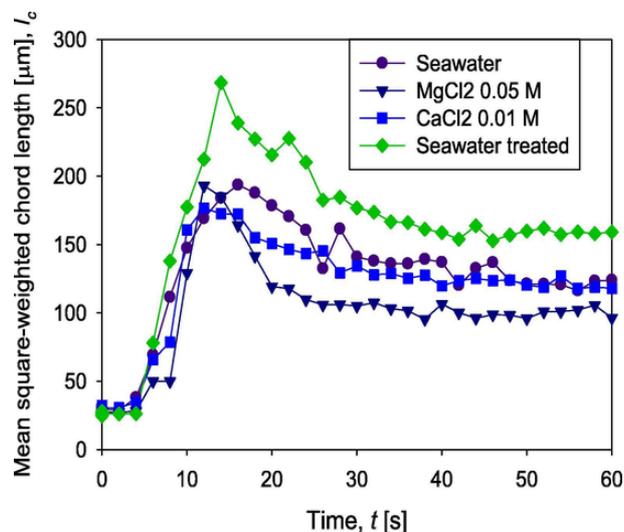
Fig. 7. The effect of the type of water on the mean chord length of flocculated kaolin suspensions at pH 10.5 and 55 g/ton.

pared to untreated seawater with the same pH value. For instance, at a flocculant dosage of 55 g/ton, the settling rate was 5.0 m/h in untreated seawater. While using treated seawater, the settling rate increased up to 11.5 m/h. Again, it can be seen that the sedimentation results were directly related to the flocculation kinetics, where the size of the floc after 60 s was 120 μm in seawater, while it reached 160 μm in treated seawater (see Fig. 7). Therefore, treated seawater improves the flocculation performance of clay-based tailings compared to seawater at pH 10.5, which is the current situation in some copper mining operations. In this context, treated seawater could significantly increase water recirculation, so that it can be used in upstream operations, resulting in considerable water savings for copper mining companies.

4. Conclusions

A partial seawater desalination treatment, reducing calcium and magnesium ions was proposed to improve the flotation of chalcopyrite with clay content and the flocculation performance of clay-based tailings in the thickening operations. Under an alkaline conditions, treated seawater significantly improved the copper recovery from 82% to 95%, compared to untreated seawater. A similar situation occurred with the flocculation of clay-based tailings, where the settling rate increased markedly, from 5.0 m/h to 11.5 m/h. This is because the treated seawater prevents the formation of complex precipitates of calcium and magnesium, which are detrimental to the flotation process and thickening operation. In this context, the partial seawater desalination treatment could be a promising alternative to face the challenges generated by clays and seawater in copper mining companies.

CRediT authorship contribution statement

Constanza Cruz: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. **Jahir Ramos:** Investigation. **Pedro Robles:** Investigation. **Williams H. Leiva:** Writing - original draft, Investigation. **Ricardo I. Jeldres:** Conceptualization, Methodology, Writing - original draft. **Luis A. Cisternas:** Conceptualization, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 5. The effect of the pH on the mean chord length of flocculated kaolin suspensions in seawater.

Fig. 6. The effect of the flocculant dose and type of water on settling rate of kaolin suspensions at pH 10.5.