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The effect of water quality change on copper flotation

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Abstract: Given the significant consumption and future demand for water resources, this paper intends to find the conditions for using a flotation process with different water quality. One of the alternatives is using water under secondary treatment with industrial water mixtures to partly recycle domestic wastewater and maximize metallurgical benefits. Results show that using wastewater (only with secondary treatment) in flotation is detrimental to copper recovery. However, molybdenum recovery is significantly improved. For mixtures with 50 [%] wastewater, 50 [ppm] frother, 20 [ppm] collector, and pH 10, copper recovery decrease amounts to 0.4 [%], while molybdenum shows a 2.4 [%] recovery increase. In addition, copper concentrate grade decreases by 1.4 [%], while molybdenum grade remains. Therefore, using wastewater is viable, particularly in the case of molybdenum. So, this study proposes using of water mixtures in the copper depression stage to improve molybdenum recovery.

Keywords: flotation, copper, molybdenum, water quality, wastewater

1. Introduction

About 94 [%] of domestic wastewater in the Chilean northern zone is not treated (secondary treatment), being directly released into the sea. This is counterproductive due to the scarcity of water resources in the northern zone and the continuous demand from industries. One of the processes most influencing water consumption is the flotation process mostly utilized in metallic mining, which constantly requirąes new methods and studies to optimize water use efficiency (Acuña, 2007; Finch, 1995, Fuertestenau et al, 2007; Gorain et al, 1998; Humire, 2012).

Flotation is a separation process based on hydrophobic differences in mineral surfaces. Separation is conducted through of air bubbles formed by the dispersion of air injected into a reactor. Flotation can be considered as a physicochemical-chemical process producing particle-bubble adhesion and later transport to the frother zone. This can be represented as a chemical reaction by collection kinetics (Finch and Dobby, 1990).

Flotation kinetics is related to hydrophobic particle collection velocity in a reactor. On the one hand, given the heterogeneous nature of minerals (particle size distribution, mineralization, liberation grade, surface reagent reaction) and, on the other hand, bubbles injected using a distribution of different sizes and shapes make process modelling complex.

Since flotation is conducted by surface charge differences, interaction with solutions is high and, therefore, pH or ORP conditions change the surface charge (Z potential) and, thus, process selectivity/separation efficiency (Rao, 2003). Additionally, the presence of colloidal material or <10 [µm] particles electrically charged can produce negative effects when interacting with the species of interest through coating (Rao and Finch, 1989). Given these interactions and the complexity of analyzing mineral surfaces interacting with solutions, it is necessary to experimentally assess the impact of water or

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mixture quality on metallurgical indicators (grade and recovery) and the process kinetics. Preliminary studies on synthetic mineral mixtures (chalcopyrite and molybdenite) may indicate that wastewater could be used in flotation without detrimental effects on metallurgical indicators (Zhang and Zhang, 2012).

Since this study deals with urban wastewater containing colloidal material and suspensions, it aims to assess the effect of water quality on flotation kinetics by determining frother and collector synergy to maximize metallurgical benefits. So, the following specific objectives are set.

- Characterize industrial and domestic wastewater mixtures physically and chemically to assess the effect of mixtures on flotation kinetics.
- Assess the effect of water mixtures on batch flotation kinetics in 5 [L] cells on standard frother and collector conditions experimentally.
- Assess the frother and collector synergy of an industrial wastewater mixture selected on copper, molybdenum, and gangue kinetics.

Water recycling can reduce water use in mineral processing. Donoso et al. (2012) suggest optimizing the flotation process and using more efficient equipment. Water and energy use can be reduced by implementing these measures. Water recycling has proven effective and successful in creating a new and reliable water supply without compromising public health. Water reuse is a widely accepted practice that will continue to grow. In addition, Northey et al. (2019) suggest that water footprint accounting can be helpful to mining companies by quantifying their water resource appropriation and identifying ways to reduce consumption.

2. Materials and method

Batch flotation tests were conducted at the lab to assess the use of secondary quality water in the flotation process using the following methodology.
First, a physicochemical water characterization was carried out. An experimental assessment of water mixtures with batch flotation tests was carried out. It was experimentally analyzed for frother and collector synergy. Adjusted grade and metallurgical data reconciliation, using Ichy Yen for a node.

2.1. Physicochemical water characterization

Wastewater and industrial water used in the flotation process were characterized. Secondary treatment wastewater was obtained from a treatment plant in northern Chile. Industrial water was obtained from Chuquicamata process plant. Characterization involved the following analyses: the Orion 4 Star equipment was used to determine electrical conductivity and pH effluent, while COD was determined using the closed reflux method. Dissolved and suspended solids were determined by drying at 103-105 °C and incinerated at 550 °C. Chloride was determined using the argentometric method, and sulfate was determined using a Hanna HI 83225 photometer. (Donoso et al., 2012)

2.2. Experimental assessment of water mixtures in batch flotation tests

A protocol was established for batch flotation tests. The equipment (described in a later section) was prepared for tests, making changes if necessary. For batch flotation tests, six different water mixtures were prepared, the composition being the following: distilled water, 100 [%]; industrial water: 100 [%]; wastewater: 100 [%]; residual-industrial water: 80 [%] – 20 [%], respectively; residual-industrial water: 50 [%] – 50 [%], respectively; residual-industrial water: 20 [%] – 80 [%], respectively. Experimental tests were conducted on the mixtures prepared according to the protocol above. Each test was repeated three times. The samples obtained were filtered and dried to obtain Cu, Mo, and Fe. The metal assays were obtained by X-ray fluorescence (Siemens 303).

2.3. Grade fit and metallurgical data reconciliation, using Ichy Yen for a node

The final concentrate grade of copper (Cu), molybdenum (Mo), and iron (Fe) was assessed by X-ray fluorescence at intervals of 1, 2, 4, 8, and 16 minutes, and the sampled mass was obtained for each species. The feed grade, final concentrate, and tailings grade were used to calculate mass yield ($Y = (f-t) / (c-t)$). The mass yield was reconciled using the Ichy Yen methodology for the three metals analyzed

(Cu, Fe, and Mo) to ensure consistency with mass balance. This methodology allows for accurate and reliable measurements of the final concentrate grade and mass yield, essential parameters in mineral processing.

2.4. Experimental analysis of frother and synergy

A mixture of wastewater and industrial water (50 [%] – 50 [%]) was prepared for a single test. This base sample was used for each frother and collector tested. Tests were conducted by changing the frother concentration but keeping the collector concentration. Tests were made by changing the collector concentration but keeping the frother concentration. After this process, samples were collected, filtered, and dried to make chemical analyses and determine Cu, Mo, and Fe content.

2.5. Lab equipment (flotation cell)

A D-12 experiments was used for 250 [g] – 2,000 [g] cells. This cell includes a special diffuser and impeller and 250 [g] – 1,000 [g] tanks appropriate for this kind of test.

The equipment consists of a cast iron base, an aluminum column and holding bracket, a closed suspended mechanism, including an anti-friction bearing for the axis and a stainless steel vertical tube with an air-control valve, a diffuser, and impeller, (both of them specially designed), a transmission guard; a rubber base; a 0.4 [Hp], 1,800 [rpm], three-phase, 60 [Hz], and 220 [V]; and a V strap for speed transmission, regulated by an electrical speed variator (frequency meter) with a 220 [V] single phase input. The suspended mechanism is balanced by a spring, being easy to raise and lower with a hand crank on one side of the equipment. The mechanism can be secured in any vertical position with the safety pin activated by a string on the opposite side of the hand crank. This pin must be removed when the hand crank is operated. When the desired position is reached, the pin is released, thus securing the mechanism.

2.6. Changes in make-up water and reagents used.

The water quality used aimed to keep the frother level (pulp height) since the types of frothers interacting with the types of waters may differ in the amount of water transported to the concentrate. The standard procedure of using a fixed amount of water was changed to avoid mistakes.

2.7. Reagents

Aero® MX-7017 promoter was used as collector, a sulphide ore collector, the dosage used was: 10 [ppm], 20 [ppm], and 30 [ppm]. OrePrep® F-533 Frother (CYTEC) was used as an alcohol, heavy aldehydes, esters, and glycols mixture. The dosage used was 25 [ppm], 50 [ppm], and 75 [ppm]. Limestone was used for tests as a pH modifier. Usually, 1.2 [g] is used for adjusting pH to 10.

3. Results and discussion

3.1. Physicochemical water characterization

Table 1 shows that secondary wastewater conductivity is significantly higher the industrial water conductivity, being consistent with the values of dissolved solids. Using wastewater in flotation produces better kinetics since bubble sizes are smaller (Hofmeier et al, 1995). Nevertheless, the presence of ions such as magnesium and calcium may have a negative effect (hydroxide formation) at basic pH. Since hardness shows similar values and the difference in dissolved solids lies in chloride, a positive kinetic effect is assumed. In addition, the difference in surface tension, with higher wastewater values, can cause a negative effect. However, the surface tension value is not significant for coalescence control; however, the surface tension gradient is quite significant (Dukhin et al, 1998).

Comparing the suspended solids of industrial water versus wastewater, a value 20 times higher is observed in the former. This is due to the fine material (under 400 mesh) remaining in the water processed, deteriorating the operation owing to coating mechanisms, particularly if solids are colloidal and electrically charged (Rao and Finch, 1989).

Finally, iron concentration is significantly high in industrial water because of the degradation of grinding elements (iron produced by a reduction environment during comminution) and, in some cases, activating pyrite, causing an impact on selectivity because the collector is adsorbed by activated pyrite (Peng et al, 2012). Since the recycled water goes through flotation and aeration, it has enough oxygen to change Fe^{+2} and Fe^{+3}. In addition, in an oxidizing environment (wastewater), a 634 [mV] redox potential is measured on-site.

Table 1. Physical characterization of industrial and secondary water

Parameter	Units	Chuquicamata industrial water	Bayesa secondary water
pH		8.6	8.1
Conductivity	[mS/cm]	1.53	4.61
Dissolved solids	[mg/L]	1.02	2.66
Suspended solids	[mg/L]	10.0	0.5
COD	[mg/L]	0.8	2.8
Iron	[g/L]	341.8	0.05
Cloride	[mg/L]	210.6	1343.0
ORP	[mV]	220.2	396.5
Sulfates	[mg/L]	184.4	352.7
Surface tension	[mN/m]	47.3	66.6
Hardness	[g/L]	433.7	633.9

3.2. Comparing recovery with water mixtures (Cu and Mo)

Figs. 1 (a) and (b) show a Cu and Mo recovery decrease when incorporating wastewater, except for 80% of wastewater in Mo. This may be due to the interaction between suspended solids and urban wastewater, which can have a depressing effect on molybdenum, or it can limit the adsorption of collector. Tests were conducted with 50 [ppm] frother and 10 [ppm] collector concentrations. Results below show Mo recovery improvement when varying reagent dosage. The high concentration of frother (above critical coalescence) allows the block of the effect of high salinity (1343 [ppm] of chlorine in wastewater) or the remaining surfactant from industrial water; both conditions induce smaller bubble sizes. However, the difference in ORP could have a strong influence on the surface oxidation of Cu or Mo.

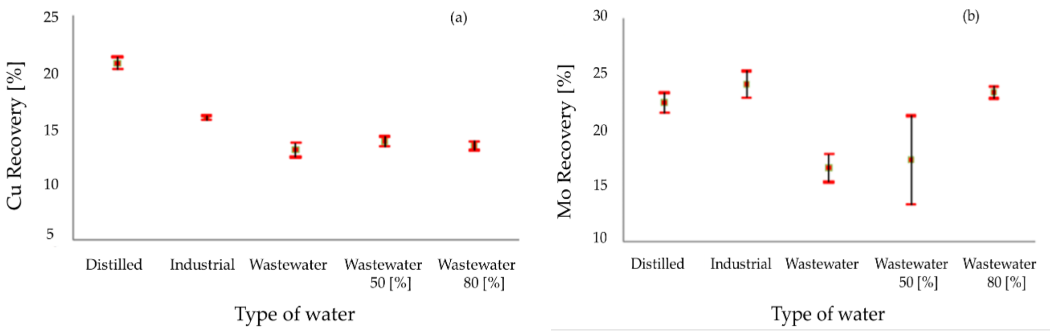

Fig. 1. (a) Cu recovery with different types of water; (b) Mo recovery with different types of water

3.3. Comparing grades and water mixtures (Cu and Mo)

In comparing Figs. 2 (a) and (b), a copper grade detriment is also observed. However, in the case of molybdenum, the impact is more minor. So, a more significant domestic wastewater redox potential improves selectivity in the case of molybdenum.

3.4. Operational curve comparison with types of water for Cu and Mo

The Cu grade and recovery curve for different water qualities (Fig. 3) indicates a significant detriment, particularly when compared with the case of distilled water. In these conditions of frother and collector, adding wastewater has a negative effect in all cases, mainly dissolved gangue and fine colloidal material (Vasudevan et al., 2012). This result requires further analysis of the mineral surface of tailings to determine if the negative effect of water can be compensated with a dispersant agent.

In the case of molybdenum, the grade and recovery curve (Fig. 4) shows that the different water mixtures reach grades and recover similarly to the ideal case (distilled water), mainly the 80 [%] wastewater mixture. Nonetheless, since Mo grade measurements can indicate a more significant experimental error, the experiment must be repeated.

Fig. 5 (a) shows the results of copper grade and recovery by changing the frother dosage and keeping

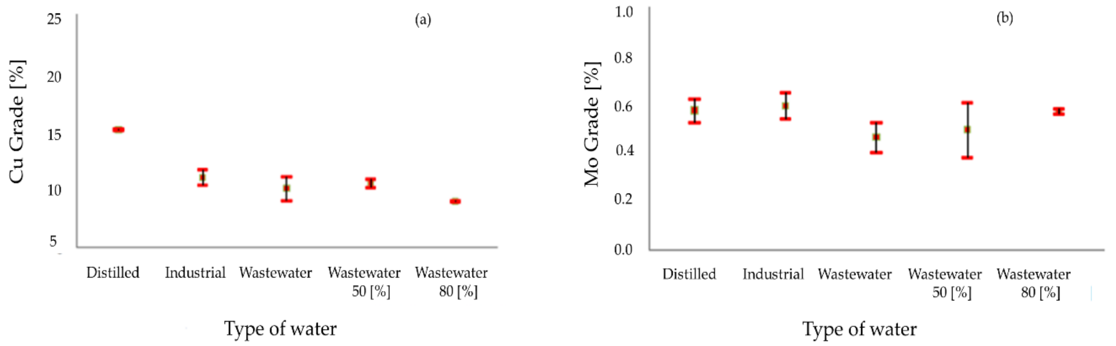

Fig. 2. (a) Cu grades with different types of water; (b) Mo grades with different types of water

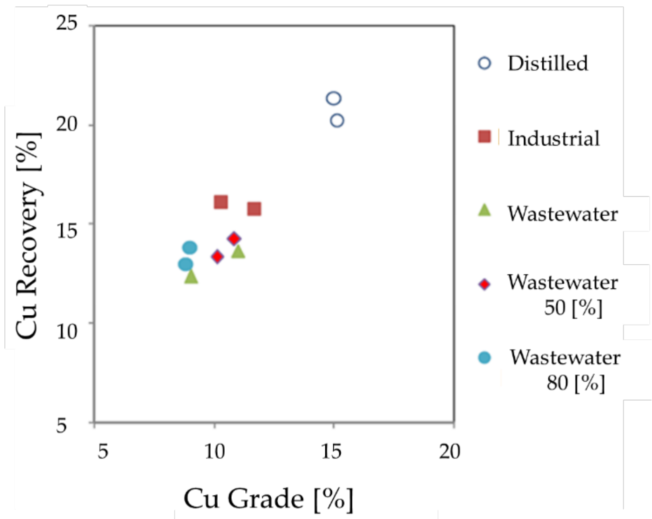

Fig. 3. Cu grade in de final concentrate, recovery curves and duplicated water mixtures

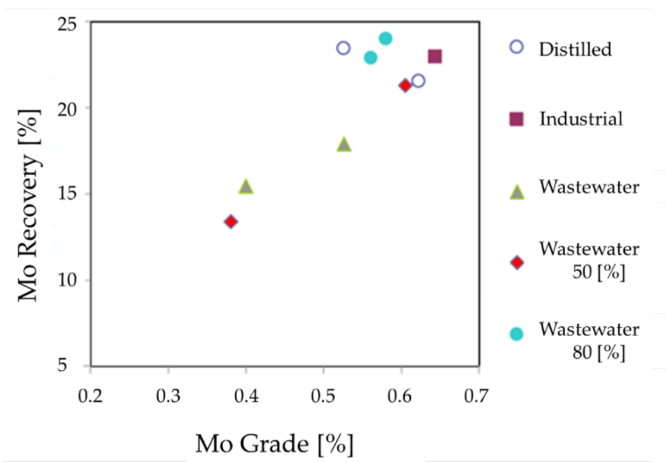

Fig. 4. Mo grade in the final concentrate, recovery curve and duplicated water mixtures

the collector dosage at 10 [ppm], using a mixture with equal amounts of industrial water and wastewater. Fig. 5 (b) shows the results of copper grade and recovery by changing the collector dosage with a 50 [ppm] frother, using a mixture with equal amounts of industrial water and wastewater. However, there needs to be a to be clear tendency.

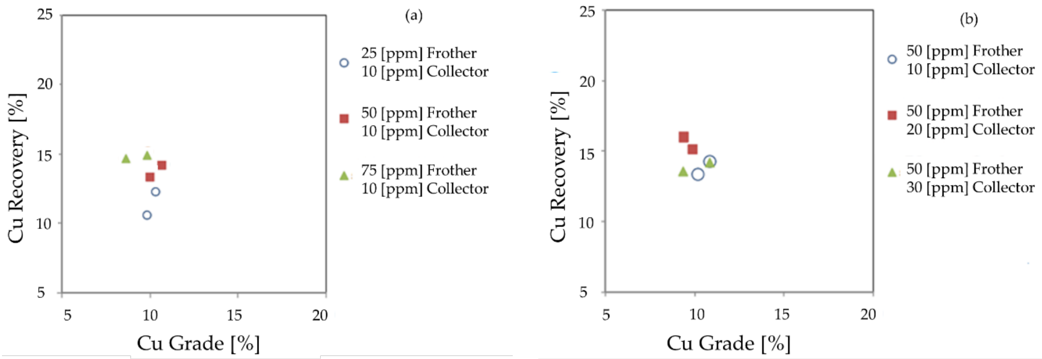

Fig. 5. (a) and (b) Cu grade, recovery curve and frother dosage

In general, there is a tendency for greater recovery if the frother dosage is increased. This is due to an effect on the bubble size (or coalescence reduction). However, concentrations over 10 [ppm] (polyglycols) should be over critical coalescence (Azgomi et al, 2006) and, therefore, recovery should not be affected. However, entrainment could explain recovery with the frother dosage and the concentrate grade decrease (Kratch et al,2012).

Fig. 5 (b) shows the frother and collector synergy with a 20 ppm grade increase. However, the greater the frother concentration, the lower the frother grade owing to the activation of pyrite floated by concentrate soiling.

3.5. Collector, frother, grade, and recovery analysis

Figs. 6 and 7 show the effect of dosage and frother on copper recovery with 1:1 domestic and urban wastewater mixtures. The collector shows its maximum since pyrite competes with chalcopyrite. The frother shows an increase despite the dosage being over critical coalescence.

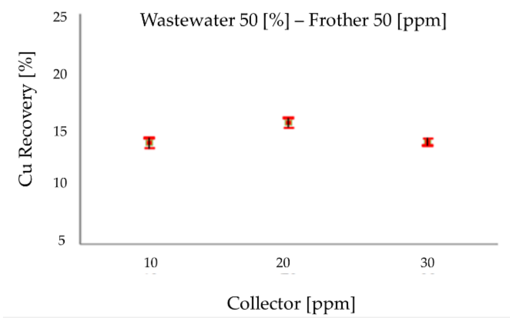

Fig. 6. Cu recovery and collector synergy

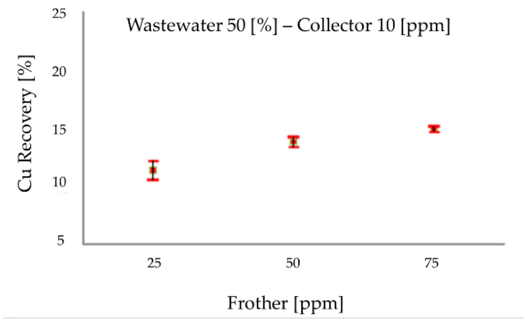

Fig. 7. Cu recovery and frother synergy

Figs. 8 (a) and (b) show the effect of reagents on copper grades. No significant copper grade differences are observed due to the extent of data uncertainty.

Unlike copper, Fig. 9 shows significant Mo recovery compared to Cu; However, the frother and collector dosage could be optimized. This could be explained by an ORP change when adding wastewater, which would facilitate the collector adsorption by molybdenite (Zhang and Zhang, 2012).

Figs. 10 and 11 show more favorable frother and collector conditions, obtaining higher grades than the base case. As to the frother, lower concentrations result in better grades, i.e., a more selective process. This is consistent with recent studies on frothers and water transport.

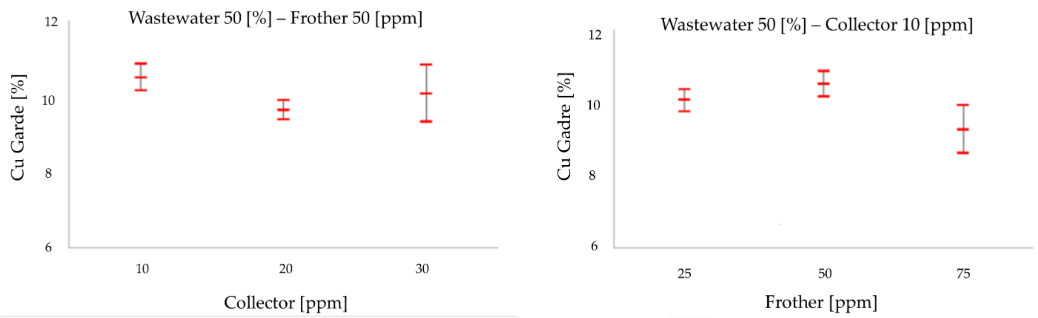

Fig. 8. (a) Cu grades for collector and (b) frother synergy

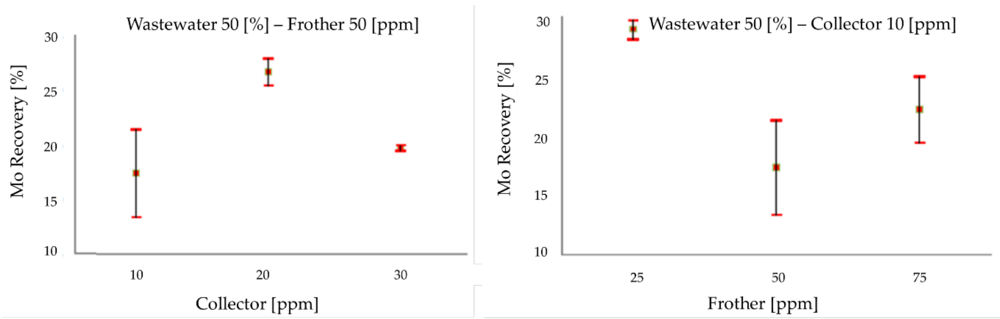

Fig. 9. Mo recovery and frother synergy

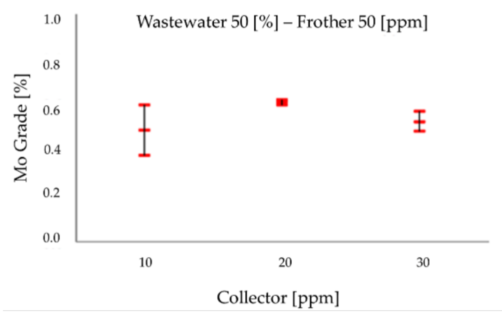

Fig. 10. Mo grades and collector synergy

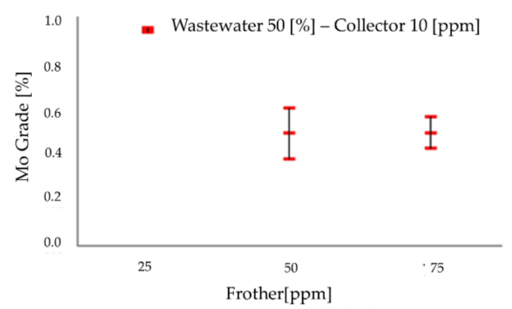

Fig. 11. Mo grades and frother synergy

4. Conclusions

The use of secondary quality water mixed with industrial water is experimentally assessed, showing that they can be used in flotation. This is particularly more efficient for molybdenum concentration, while it has a negative impact on copper.

The results with balanced grades show that the use of wastewater (only with secondary treatment) in flotation causes a detriment to copper recovery. However, molybdenum recovery is significantly improved (2.4 [%]). The copper concentrate grade is reduced by 1.4 [%]. For molybdenum, the concentrate grade remains. In the case of a higher pH, an improvement is observed in Mo recovery (4.8 [%]), with grades increasing by 0.4 [%].

Therefore, the use of wastewater is viable, particularly for molybdenum. It is therefore proposed to use water mixtures in the copper depression stage to improve Mo recovery, which is complex to achieve in most concentration plants.

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