RECOVERY IMPROVEMENTS IN COPPER HEAP LEACHING BY USING EMEW® TECHNOLOGY

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ABSTRACT

Mining companies with hydrometallurgical processes have the intrinsic need to bleed a percentage of their rich electrolyte to keep the concentration of impurities at a certain level (such as chloride and ferric / ferrous ions). As this stream has a high concentration of copper, acid, and pollutants, the destination used for this solution is commonly the raffinate pond. It is well known by Fick's Law that this procedure impacts negatively on the leaching recovery as copper contribution to the raffinate increases the cationic load and therefore decreases the diffusional flux. In recent research, copper from electrowinning bleed was recovered using emew® technology before sending it to the raffinate. Two leaching columns – with raffinate fed with both emew®-treated and untreated bleed – were set to determine whether this copper depletion has an appreciable impact on the leaching recovery. The results showed a difference of 8.9% of copper recovery in favor of the emew® treated stream. The following publication details the procedure, results, and discussions of this interesting breakthrough.

INTRODUCTION

Ore leaching is not a selective process, and resulting pregnant leach solution (PLS) may often include different species besides the desired metal. In copper recovery, the solvent extraction process (SX) generates a clean and highly concentrated copper stream; however, it is inevitable for some pollutants to be dragged into the electrowinning process (EW). Due to the constant recirculation, some pollutants like Fe^{+2}, Fe^{+3} and Cl^{-} ions, increase their concentration inside the EW tank house causing current efficiency loss or poor deposit quality. To maintain an acceptable level of impurities, a determined volume of rich electrolyte is bled and replaced with process water. This purge or bleed stream is commonly sent to the raffinate pond, which is finally used for heap leaching. As the bleed stream has an important copper content – above 35 grams per liter – the impact of its discharge to raffinate compromises global recovery by an unwanted recirculating copper overload. Moreover, when the heap leaching cycle is over, the remaining moisture within it – typically 5% to 8% – is removed along with the ore, causing tons of copper to be lost every year.

The emew® technology can work under extreme operating conditions producing high-quality copper from highly contaminated solutions. Furthermore, it was not only the most appropriate tool to conduct the following experiment but the only available technology capable of doing so.

To begin with, a 40 gpl of synthetic copper sulfate solution was depleted with a lab scale emew® cell, obtaining a high-quality copper cathode and a 5 gpl of Cu and a +270 gpl of H_2SO_4 spent solution. Then, two leaching columns were mounted on a wooden rack to study the leaching behavior using different irrigation solutions:

- Synthetic raffinate mixed with a synthetic bleed solution
- Synthetic raffinate mixed with an emew®-treated synthetic bleed solution

EXPERIMENT

Two leaching columns were fed with copper oxide ore which mostly contained malachite and chrysocolla. The ore was classified by size: between -1’’+3/4’’ and -3/4’’+1/4’’ for the coarse material and a finer material corresponding to a -40 ASTM +60 ASTM particle size.

The ore grade was measured via atomic absorption spectrometry, giving 1.7% of Cu for the coarse mineral and 1.1% of Cu for the fine mineral. Each column was filled with 87% of coarse material and 13% of fine material.

Previous to leaching, both 11.5 kg mineral samples were submitted to curing and agglomerate. The procedure was conducted using 4% of water and a rate of 45 kg of H_2SO_4 per ton of mineral.

The raffinate solution was prepared using sulfuric acid at 98%, copper sulfate with 10% of water moisture, ferrous sulfate and sodium chloride. The concentration of each solution is shown in Tables 1, 2 and 3.

Table 1 – Raffinate Characterization

Element	gpl
Cu	1
Co	0.06
Fe^{+2}	3.30
Fe^{+3}	3.31
H_2SO_4	18.89

Table 2 – EW Bleed Characterization

Element	Cu	H_2SO_4	Fe^{+2}	Fe^{+3}	Cl^-
Unit	gpl	gpl	ppm	ppm	ppm
Minimum	34.72	133.32	2.00	778.00	20.00
Maximum	44.45	213.92	130.00	1586.00	52.33
Average	38.10	201.15	30.92	1111.48	34.36

Table 3 – Treated Bleed with emew® Technology

Element	gpl
Cu	5.40
H_2SO_4	279.72

As explained earlier, two solutions were synthetized for the leaching test. The first was made using raffinate solution mixed with emew® treated bleed and the second using raffinate mixed with untreated bleed (as it usually comes out of EW).

As the synthetic bleed solution was being processed inside the emew® cell, it was noted that the presence of ferric and ferrous ions did not have a direct impact on either the current efficiency or the deposit quality. Although this was not the case, any possible negative effect can easily be diminished by a slight variation in the inflow and/or the applied current density in the emew® cell.

Even though the presence of chloride ions does not affect current efficiency, it can negatively impact on deposit quality, as shown by Aragón and Camus [1], where it is concluded that concentrations above 50 ppm of chloride ions in conventional EW tank houses produce an observable increase in the deposit grain size, and even can cause depth cavities when chloride ions go above 100 ppm. On the contrary – inside the emew®

cell – the high chloride bleed solution used for the test (133 ppm) was easily electrowon resulting in good quality and smooth copper cathodes – even smoother than cathodes obtained with the chloride-free bleed solution (just cupric ions and sulfuric acid).

Returning to the leaching experiences, the mixture between raffinate and emew®–treated and untreated bleed solutions resulted in two different outputs. Characterization is detailed in Table 4.

Table 4 – Output Characterization

Solution	Raffinate plus treated bleed (gpl)	Raffinate plus untreated bleed (gpl)
Cu	1.02	1.22
H_2SO_4	20.35	19.96
Fe^{+2}	3.28	3.28

Proportions and flow data of raffinate and bleed solution were kindly provided by Codelco División Chuquicamata within the framework of emew® preliminary studies to recover copper from bleed streams.

Once the agglomerate and curing procedure was finished, the columns were loaded. Both columns containing 11.5 kg of mineral were irrigated at the same rate and under the same conditions for a period of 29 days. As a control test, the first one was leached using raffinate mixed with untreated bleed solution – typical of any current mining circuit – and the second one, using a mixture of raffinate and emew® depleted bleed purge. A PLS sample was taken once a day from each column and the irrigation solution was replaced as necessary to the extent that tanks were running out of it. The outcoming PLS samples were stored in drums for the final copper mass balance. The copper recovery results are shown in Figure 1.

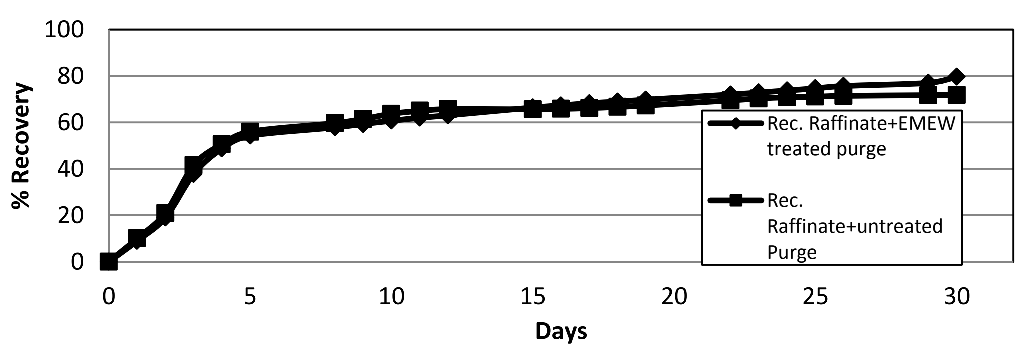

Figure 1 – Copper recovery curves in leaching tests

DISCUSSION

Figure 1 shows an equal recovery trend in both tests for the first five days, reaching 55% of the copper removed. From day 5 to 13, a slight difference in favor of raffinate with untreated purge can be seen and from the fourteenth day on, the curves began to constantly diverge until the end of the experiment reaching an 8.9% in favor of leaching using raffinate mixed with emew®–treated bleed solution. Results show a substantial improvement when the ore is irrigated with a lower concentrated copper solution.

One explanation to this phenomenon is the renowned first Fick's Law. It relates the diffusive flux to the concentration field, the diffusion coefficient and the particle radio. It says that the flux goes from regions of high concentration to regions of low concentration with a magnitude proportional to the concentration gradient.

$$Q_A = D_{eff} \frac{dC_A}{dr}$$

In connection with this experiment, lower copper concentration in the aqueous media will produce a dC_A difference, accelerating the leaching process. Based on this, the divergence seen in the curves is explained due to the difference in concentrations of the irrigation solutions. As shown in Table 4, raffinate mixed with treated purge has a lower copper concentration which results in a larger dC_A gradient. Diffusional flux is favored by this phenomenon and therefore the copper recovery from the ore is increased to the aforementioned percentage.

It is well known that leaching has two controlling processes. At the beginning the leach rate is very fast due to the presence of copper on the particle surface, where the leaching solution instantly dissolves the copper. As time passes and the amount of copper on the surface decreases, the leaching solution must diffuse into the particle to contact more copper. Since this is a more complex process than the initial chemical reaction, the leaching rate slows down.

Chemical reaction in copper leaching happens rapidly – almost instantaneously – leaving diffusion as the prime cause of the downfall. This can be better illustrated by analyzing the slopes of each curve in Figure 2, where each of them represents the leach rate.

It is also important to mention the free acid generation (via electrowinning). Even though pH difference between solutions is relatively small and at those low values the leaching efficiency does not have substantial variations, it is well known that a higher concentration of acid allows better diffusion into the particle. What is also noteworthy is the money savings due to the constant acidulation through this exercise. Raffinate pond must be constantly fed with free acid in order to keep pH down to a level where leaching is efficient, and in this context, emew® allows an important saving by a continuous acid mass discharge equivalent to 1.54 times the mass of plated copper.

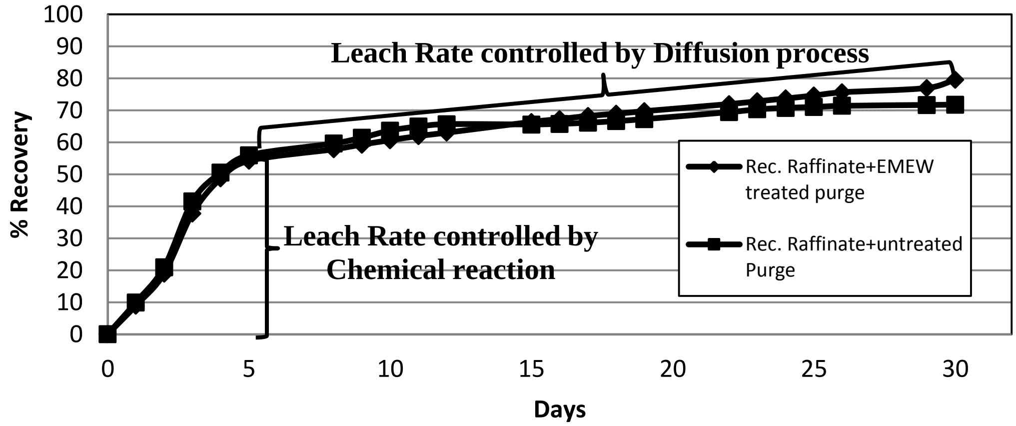

Figure 2 – Global recovery and leach rate control

It is noted in Figure 2 that chemical reactions occur at an equal rate for both experiences, but once accomplished, the recovery suffers a violent deceleration indicating a change in the leaching control. The curves intersect each other at day 14 and finally separate by the end of the test.

Considering just the diffusion-controlled leach rate and then calculating the slope of this curve, the difference between them is as follows:

$$m_{\text{Raffinate+treated purge}} = 0.9476 \text{ [\%Rec/day]}$$
$$m_{\text{Raffinate+untreated purge}} = 0.5613 \text{ [\%Rec/day]}$$

Some authors have investigated the influence of the ionic charge of the leaching solution in global recovery. Aguad, Jordan and Vargas [2] discovered that high concentration of ions in the leaching solution impacts negatively on recovery. Their experiment was focused on the SO_4^{-2} ion, and the results showed that its high concentration hinders diffusion, leading to a non-efficient recovery.

CONCLUSIONS

The experience shows the impact of copper concentration in the leaching process. Experimental outcomes clearly demonstrated the benefits of low copper concentration solutions over those with high copper concentrations. The final leaching curves diverged at the end, resulting in a better copper recovery when adding an emew® depleted bleed stream to the raffinate solution. This 8.9% difference established that leaching in the metallurgical processes can be improved by removing copper from bleed streams previous to its discharge into the raffinate ponds.

The emew® cell is the only technology capable of processing highly-contaminated solutions to produce high-quality copper.

REFERENCES

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