Improvements in Copper heap leaching by use of wetting agents

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Abstract

In times of economical down turn and therefore a period of lower copper prices, it is increasingly important to improve current copper extraction processes with respect to efficiency. So far approx. 20 % of the world copper production is gained by hydrometallurgical leaching processes, mainly by leaching of oxide copper ores with sulphuric acid and subsequent SX/EW-treatment.

Several trials on the use of wetting agents in heap leaching of Chilean oxide copper ores have been successfully conducted at IME, Institute of Process Metallurgy & Metal Recycling at the RWTH Aachen University in cooperation with BASF SE, Ludwigshafen. The trials have been realized in an 8-column setup each with a diameter of 300 mm and a height of 2 m, simulating industrial heaps. The individual surfactant has been added to barren solution of each column and fed continuously over 5 weeks on top of each "heap". Daily outflow was investigated with respect to volume and Cu-content. The copper extraction rates of the columns treated with surfactants are compared to the results of two reference columns which are equally treated only without adding a surfactant to the barren solution. The trials with different ore-sources show for specific designed surfactants a positive effect on the copper extraction rate in heap leaching independently from the pre-treatment of the ores. This confirms the hypothesis that an increased productivity of a hydrometallurgical copper-plant can be achieved by using tailor made wetting agents.

Introduction

Generally copper ores are classified into sulfidic and oxidic copper ores, whereas oxidic ores are a naturally oxidation product of sulfidic ores. Therefore usually oxidic and sulfidic copper ores are in adjoining sites. [1] Whereas sulfidic copper ores are mainly treated by pyrometallurgical processes and oxidic ores by hydrometallurgical processes. Approx. 20 % of worlds copper production are gained by hydrometallurgical leaching processes, mainly by heap leaching with sulfuric acid and subsequent solvent extraction (SX) and electro winning (EW) treatment.

Typical ore heaps in heap leaching are 4 - 12 m high and have a base area of several thousand square meters and are made up of 100,000 - 500,000 t of ore. [1], [2], [3] Depending on the type of

ore leaching of these heaps require several month. During this time, approx. 70 % - 75 % of the leachable copper compounds are dissolved and extracted from the ore. An improvement of the leaching conditions must aim on shorter leaching times as well as on a higher copper extraction rate, thus to an increase in copper productivity and lower costs per ton of copper.

Because leaching processes include interactions between solid (ore) and liquid (sulfuric acid) phases such improvements may be achieved by the use of wetting agents.

This has already been proofed in the field of alkaline gold leaching. BASF SE developed so far a tailor-made wetting agent for gold leaching. This wetting agent improves the gold recovery by 5-10 % [4], [5], [6]. Motivated by these positive results, the idea of this work is to investigate the influence of wetting agents on copper ore heap leaching regarding the kinetic of leaching and the copper recovery rate.

Fundamentals

Heap leaching

Heap leaching belongs to the group of percolation leaching processes and operates over ground. The procedure is illustrated in Figure 1.The oxide copper ore is piled up on leach pads, which have a slight slope of approx. 3° and a rubber lining, which seals the ground under the heap. These heaps are 4 to 12 meters high and can exceed 100 meter in length with a base area of several thousand square meter, covering 100,000 to 500,000 tones of ore.
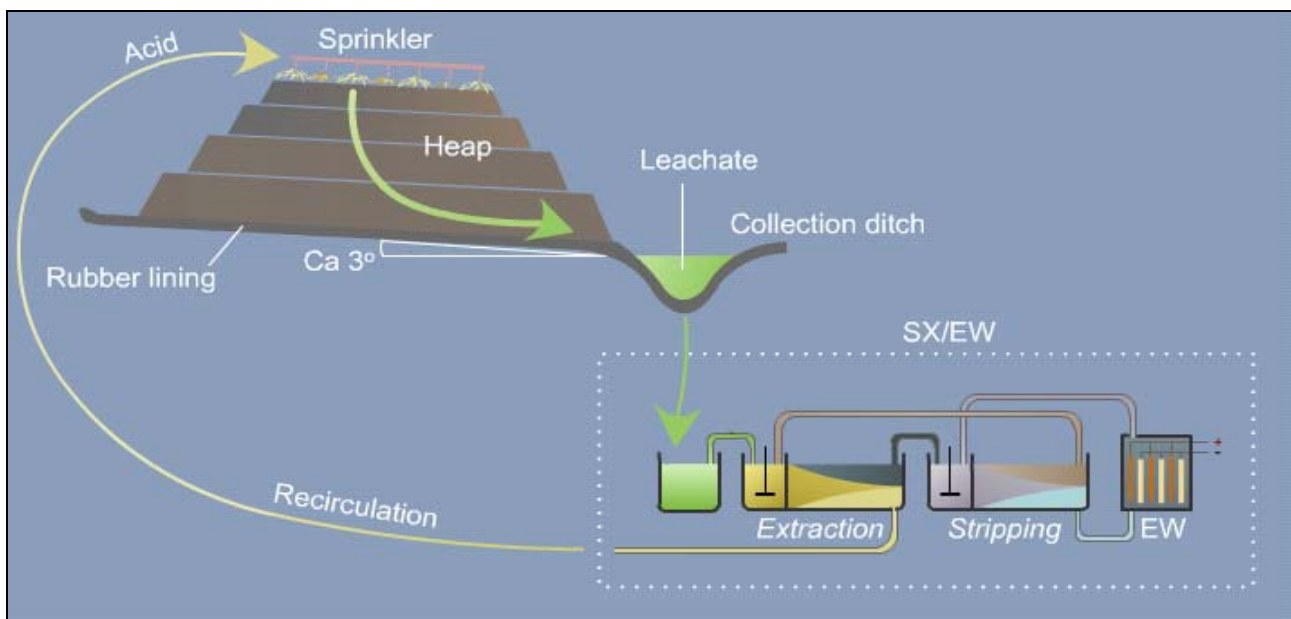

Figure 1:   Scheme of the heap leaching process with subsequent SX/EW-treatment [8]

A sprinkler system is installed on top of each heap allowing the diluted sulfuric acid to be fed uniformly over the ore. While the solution percolates through the heap, copper is leached out of the ore. The pregnant leaching solution is collected by a drainage system below the heap and is led through a collection ditch into a pond. By the following solvent extraction (SX) the PLS is cleaned and concentrated. The copper rich solution is transferred to electro winning whilst the copper poor solution is refreshed with sulfuric acid and fed as barren solution again to the heap.

Modelling copper heap leaching

Leaching implies a reaction between solid particles and a liquid phase. The "shrinking core" model describes the leaching process of an idealized oxide copper ore particle [1]. This particle reacts from the surface inwards. During the continuous reaction a leached rim is formed, composed mainly of gangue. The rim encloses a shrinking unleached core, so that reagents and dissolved reaction products must diffuse through the leached rim. The conversion is limited by the mass transport of both through the growing rim. Figure 2 illustrates this reaction model in the case for copper and Figure 3 shows a copper particle from own experiments before and after 4 weeks leaching in a solution of 2% H_2SO_4 showing a white leached rim.
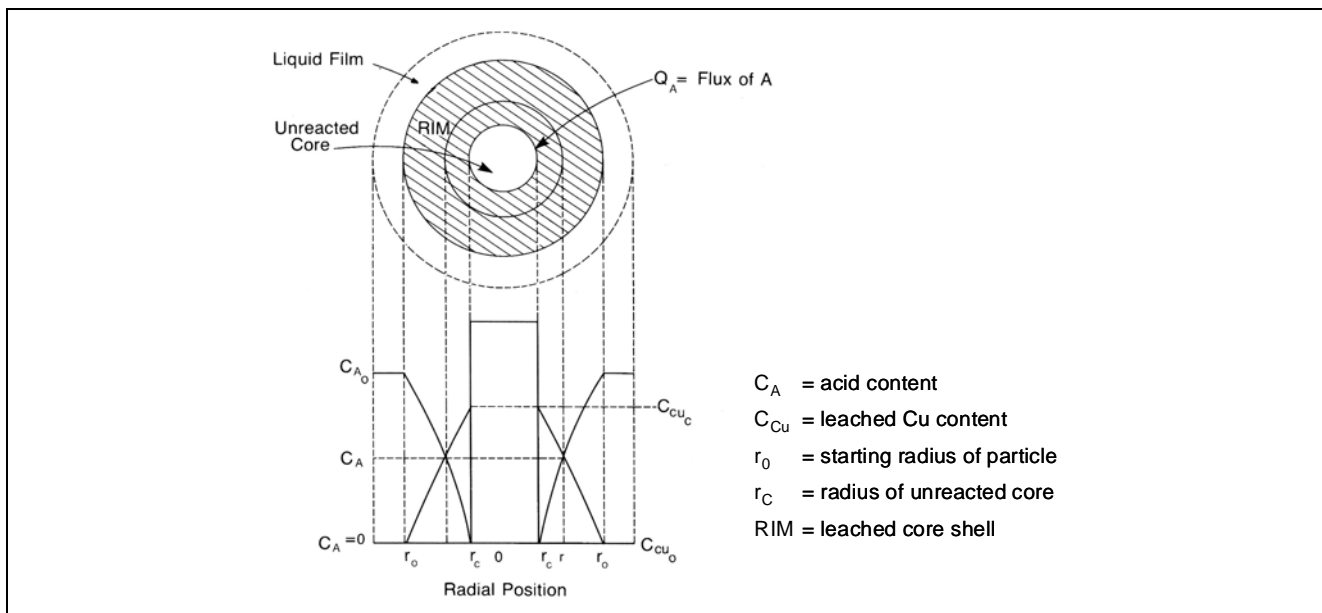

Figure 2: Concentration profile of acid and leached copper through the cross section of an idealized particle [1]
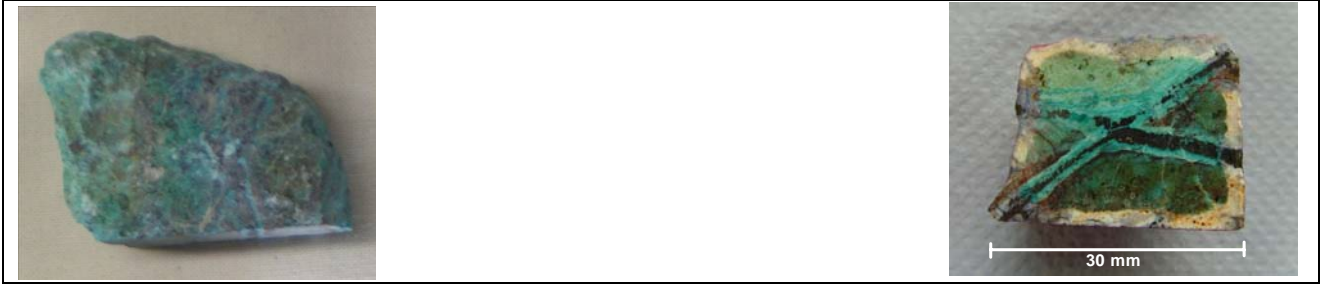
Figure 3:   Copper ore particle before (left) and cross section of the particle after 4 weeks leaching in 2% H_2SO_4 showing a white leached rim (right). [9]

This model implies that the reaction occurs so quickly that only diffusion of the reaction partners through the surface layer is the controlling factor for the reaction rate (1. Fick's law). By assumption that the ore particle is a sphere with a starting radius of r_0, it contains the following amount (mol) of copper:

$$[n_{Cu}] = \frac{\frac{4}{3} \cdot \pi \cdot r_0^3}{V_{m,Cu}} mol \tag{1}$$

r_0: starting radius, $V_{m,Cu}$: molar volume of Cu in the ore particle defined as
$V_{m,Cu} = M_{Cu} / (\rho_{ore} \cdot X_{Cu,ore})$

The leaching reaction rate at any (time depending) core radius r_c of this particle can be described using Fick's law as follows:

$$\frac{dn_{Cu}}{dt} = \left(4 \cdot \pi \cdot r_c^2\right) \cdot D_{eff} \cdot \frac{dc_{Cu}}{dr} \tag{2}$$

Here c_{Cu} stands for the copper concentration of the liquid phase at the reaction front (Figure 3) and D_{eff} for the effective diffusion coefficient. By appropriate transformation and integration the following equation results:

$$\frac{dn_{Cu}}{dt} = -\left(4 \cdot \pi \cdot D_{eff}\right)\left(C_{Cu,c} - C_{Cu,0}\right)\frac{r_C r_0}{(r_0 - r_C)} \tag{3}$$

$C_{Cu,0}, C_{Cu,c}$: copper concentration of the liquid phase at the starting radius r_0 and core radius r_C respectively

A corresponding term can be developed for the acid consumption n_A:

$$B \cdot \frac{dn_{Cu}}{dt} = \frac{dn_A}{dt} \tag{4}$$

$$\frac{dn_{Cu}}{dt} = \left(\frac{1}{B}\right)\left(-4 \cdot \pi \cdot D_{eff}\right)\left(C_{A,c} - C_{A,0}\right)\frac{r_C r_0}{(r_0 - r_C)} \tag{5}$$

B: constant; n_A: amount of acid consumed; $C_{A,0}, C_{A,c}$ acid concentration of the liquid phase at at the starting radius r_0 and the core radius r_C respectively

The constant B can theoretically be derived from the stoichiometrical ratio of the leaching reaction, but typically this constant is determined experimentally. By introduction of "F" as leached fraction (extraction yield):

$$F = \frac{V_0 - V_c}{V_0} = 1 - \frac{r_c^3}{r_0^3}$$

(6)

V_0: starting volume of the ore particle, V_c: Volume of the shrinking core

Upon substitution of equation 5 the following function for F results after integration as a function of the leaching time. [8]

$$1 - \frac{2}{3} \cdot F(t, r_0) - (1 - F(t, r_0))^{2/3} = \left(\frac{2 V_{m,Cu} \cdot D_{eff} \cdot C_{A,0}}{B \cdot r_0^2} \right) \cdot t$$

(7)

The complete leaching time of a particle (F = 1) can be now calculated easily using following equation 7:

$$t(F = 1) = \frac{B \cdot r_0^2}{6 V_{m,Cu} \cdot D_{eff} \cdot C_{A,0}}$$

(8)

B, $V_{m,Cu}$, and r_0 are constant properties of the ore, which can not be influenced by process parameters like the use of wetting agents. The bulk concentration of the sulfuric acid outside a particle is a constant as well if short time periods are considered. The effective diffusion coefficient implies the effective porosity ε_{eff} and the labyrinth factor τ.

$$D_{eff} = D \cdot \frac{\varepsilon_{eff}}{\tau}$$

(9)

D: diffusion coefficient; ε_{eff}: void fraction or micro-porosity (accessible volume fraction in ore reached for the solution), τ: labyrinth-factor

The labyrinth factor for a given ore can be treated as a constant. The effective porosity composes of the wettable pore volume and the total volume of the ore particle. By assumption that the capillaries in the particle have a circular cross section of a constant radius r_K the effective porosity is:

$$\varepsilon_{eff} = \frac{n_K \quad \pi \quad r_K^2 \quad l_p}{V_{ges}}$$

(10)

n_K: number of capillaries, r_K: capillary radius, l_p: penetration length

In Equation 10 only the penetration length l_p can be influenced by wetting agents and is described by the following Washburn equation. [7], [10], [11].

$$l_p = \sqrt{\frac{r_K \quad \gamma_L \quad \cos\theta \quad t_p}{2\eta}}$$

(11)

t_p: time needed for complete penetration, η: dynamic viscosity, γ_L: surface tension; θ: contact angle

Through adequate use of wetting agents it is possible to change the values of the surface tension γ_L and the contact angle θ so that the term $\gamma_L \cdot \cos θ$ rises. This means wetting agents can increase the penetration length of a fluid.

Substitution leads to Equation 12, which illustrates a direct correlation between total leaching time, surface tension and contact angle.

$$t(F=1) = \frac{2B}{9D} \frac{r_0^5}{C_{A,0}} \frac{\tau}{n_K} \frac{1}{r_K^2} \sqrt{\frac{2\eta}{r_K \quad t_p \quad \gamma_L \quad \cos θ}} \tag{12}$$

As explained before with the right use of wetting agents it is possible to increase the term $\gamma_L \cdot \cos θ$. That means wetting agents cause a deeper penetration of the ore particles and may lead to shorter total leaching times and a higher recovery.

Requirements of wetting agents

By analysis of the previous attempts to introduce wetting agents to leaching processes in the last decades, the following performance profile of requirements for wetting agents was developed.

- good wetting performance at temperatures up to 60°C
- improved capillary penetration of ores
- no negative impact on further processing steps (SX, EW)
- low dosage concentration (due to technical and economical requirements)
- stable in acid solution
- low foaming
- biodegradable / no eco-toxicity

Based on these requirements, BASF SE chemists have been designing, developing and screening nonionic surfactants for leaching applications [3], [4]. Those nonionic surfactant which passed the screening, are tested in various column trials on different ore batch.

Column Trials - Experimental Procedure

In earlier column trials the nonionic surfactant EVD61549 achieved so far the most promising results [9], [12].The following leaching trial was designed to find the best application method for this surfactant.

Experimental set-up

For simulation of a heap leaching processes eight columns were set up at the IME. Each leaching column system consists of a pump to transport a constant flow rate of leaching solution to the column, a sprinkler system to irrigate the leaching solution uniformly over the column diameter, a column filled with ore where the leaching takes place and a collecting device to store the pregnant solution which leaves the column.

The picture on the left side of Figure 6 shows the pumps and in the background, the storage drums for the leaching solution. The picture in the middle shows a detailed view of the sprinkler system that disperses the solution uniformly on the top of the column. For constant dosage of solution, each sprinkler has a magnetic valve under the storage vessel connected to a unit controlling the feeding of the barren solution. The white layer below the sprinkler system is made of polyethylene(PE)-granules, which shall lead to an even more uniform distribution of solution on the ore's surface. The picture on the right shows the eight columns of the IME, each with a diameter of 300 mm and a height of 2 m. Every column is mounted onto a perforated stainless steel base and fixed in a frame. Under each column is a 30 l-barrel positioned for collecting the pregnant solution.

Figure 6:   Experimental set-up: pumps with control system and storage drums (left), sprinkler system (middle) and the IME-8-column set-up (right)

Ore preparation before leaching

The chemical composition and therefore the leaching behaviour of every ore batch varies, even if the batch belongs to the same mining site. According to this effect, it is important to be able to compare the leaching results of each column amongst the other columns. That means all columns treated with surfactant have to be compared to reference columns of the same ore batch which are treated equally but without the use of surfactant. Therefore the ore preparation has to ensure an optimum of similarity in ore quality respectively leaching behaviour in all columns. That means every ore filling in the columns has to be equal to each other in chemical composition and in size distribution. Especially the size distribution is an important factor, because the time needed to leach an ore particle completely is proportional to the square of the particle radius (Equation 8).

The whole procedure of the ore preparation to achieve similar ore fillings is shown in Figure 4. The complete ore batch from the mine Escondida, Chile was separated by size into the fractions 0 - 1 mm, 1 - 10 mm, 10 - 20 mm and 20 - 30 mm.. The fraction bigger than 30 mm was crushed and led back to the sieving. The fraction minor 1 mm was distorted to ensure that no interfering effects of the fines take place during leaching e.g. channelling , which are known to be triggered by a high concentration of fines.
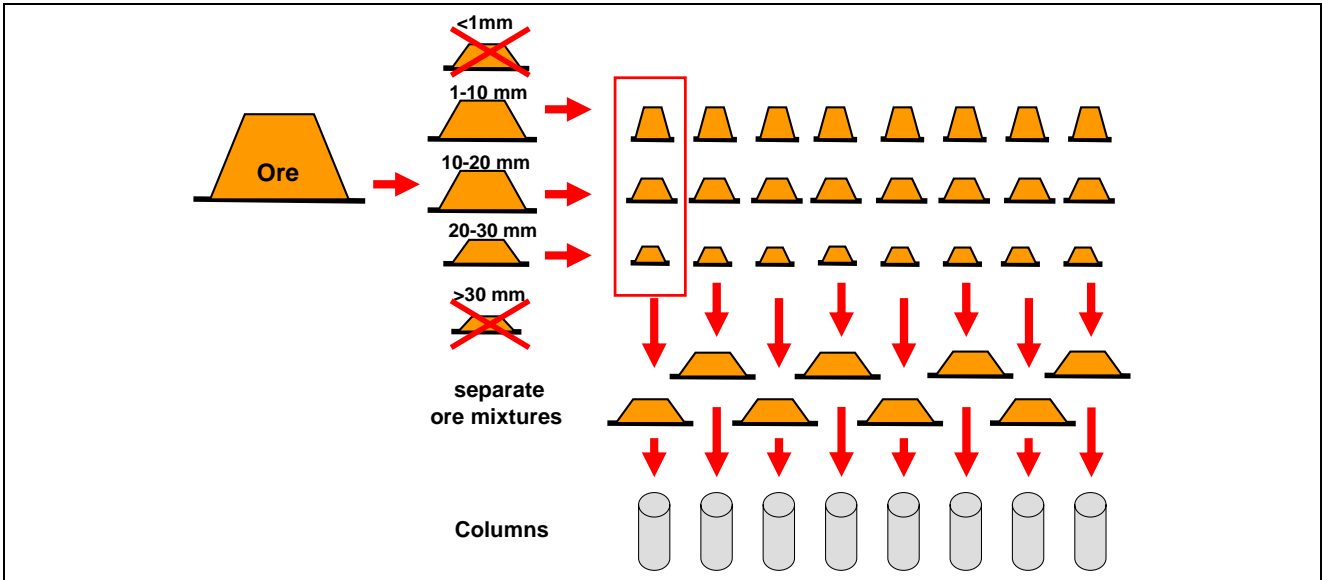

Figure 4:   Preparation of the ore batch to achieve 8 similar ore mixtures (fillings).

After homogenizing, each fraction was separated into eight portions with the same weight. At a time three portion (from every fraction one) were mixed and homogenized separately. That way eight similar ore mixtures were achieved, with four equal, known points in their size distribution (Figure 5).
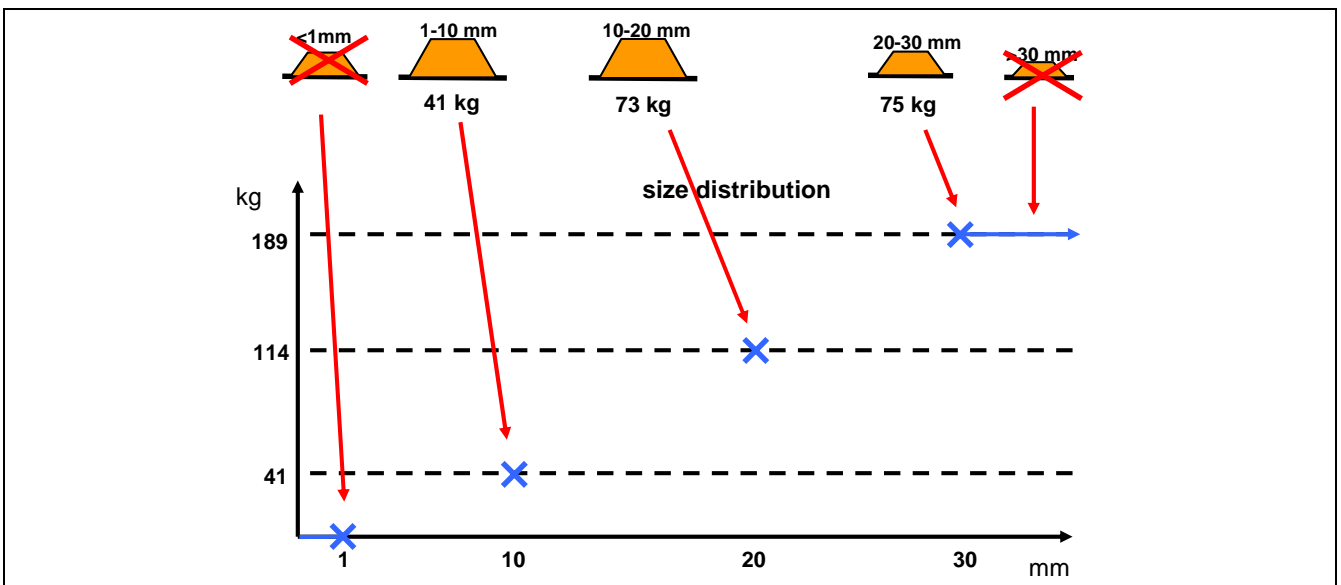

Figure 5:   Known size distribution of all eight ore mixtures.

Leaching procedure

In many industrial heap leaching plants the ore is agglomerated and treated with concentrated sulfuric acid before the ore is piled up to heaps for leaching. Therefore the following leaching procedure has been designed to be close to the industrial heap leaching conditions and to consider stability requirements of the wetting agent.

Since after agglomeration the ore is already wetted and improving wetting is an important ability of surfactants, it was interesting to evaluate, if the surfactant still contributes to an improved recovery by e.g. an enhanced penetration of the ore capillaries. The following operating chart (Table 1) was worked out to answer this question. The ore mixtures of the reference columns 1 and 2 were wetted with water prior to charging into the columns and were leached only with sulfuric acid. The ore mixture of column 4 was filled dry into the column. The ore mixture of column 3 was wetted with water and the ore mixtures of columns 5 and 6 were wetted with a 100 ppm surfactant solution before filling into the columns. The columns 3 to 6 were leached with sulfuric acid and 100 ppm surfactant.

Table 1:   operating chart

Column	ore mixture		leached with?
	wet?	**wetted with?**	
1	√	H_2O	2 % H_2SO_4
2			
3	√	H_2O	2 % H_2SO_4 + 100 ppm **EVD61549**
4	No	---	
5	√	H_2O + 100 ppm **EVD61549**	
6			

Wetting took place just before charging the column. Therefore the ore mixture was irrigated with an amount of water / surfactant solution corresponding to 5 % of the weight of the mixture. Afterwards the ore was mixed until it was homogeneously wetted and filled into the columns. At the next day the leaching was initiated by irrigating the leaching solution onto the columns. The flow rate for this trial was set to 0.5 l/h for each column, which correlates to 7 l/m²·h. The columns were continuously leached over 36 days. During this time approximately 400 l of leaching solution was irrigated over each column, which is about twice the weight of ore in each column.

The daily outflow of the pregnant solution was collected below each column and analyzed with respect to volume, copper content and the surface tension.

Results and Discussion

The analysis of the oxidic copper ore batch of the mine Escondida, Chile resulted in an average copper content of 0,916 % (Table 2). With an average amount of 175 kg of ore in a column the total copper content per column amounts to 1603 g.

Table 2:   Analytical results of six different samples of the ore specimen of the mine Escondida

Sample	A	B	C	D	E	F	Average
Cu content in %	0,97	0,94	0,85	1,02	0,97	0,85	**0,916**

The concentration of the surfactant in the pregnant solution was analyzed indirectly by measuring the surface tension. An increase of the surfactant in a solution results in a decrease of surface tension. The surface tension was determined using a bubble tensiometer (SITA t 60). A decrease in surface tension was only detectable in the pregnant solution of the column 4 (started with dry ore mixture) (Figure 6). This slight decrease in surface tension corresponds to a surfactant concentration of 1 to 2 ppm. In previous trials similar results were achieved and it stresses again the strong adsorption behaviour of the surfactant EVD61549 on the copper ore.
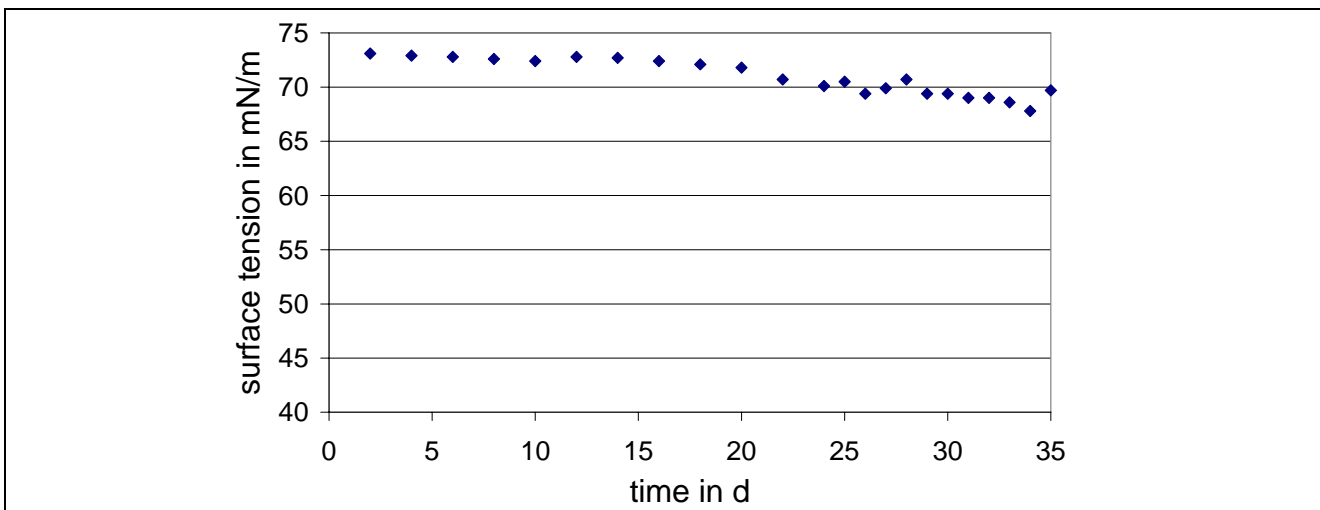

Figure 6:   Surface tension of the pregnant solution of the column 4 over 35 days of leaching. All surface tension were measured at a bubble lifetime of 35.000 ms.

The evaluation of the copper content of the pregnant solutions is illustrated in Figure 7. The extraction rate is the accumulated amount of copper in the pregnant solution divided by the total copper content in the column. Leaching is more dependant on the amount of used leaching solution (acid input) than on the leaching time. A relation of the extraction rate to the accumulated volume of leaching solution therefore is more expressive than a relation to leaching time. Since the losses of solution in a column is very small, it is acceptable to correlate the extraction rate to the known volume of the pregnant solution instead of the leaching solution.
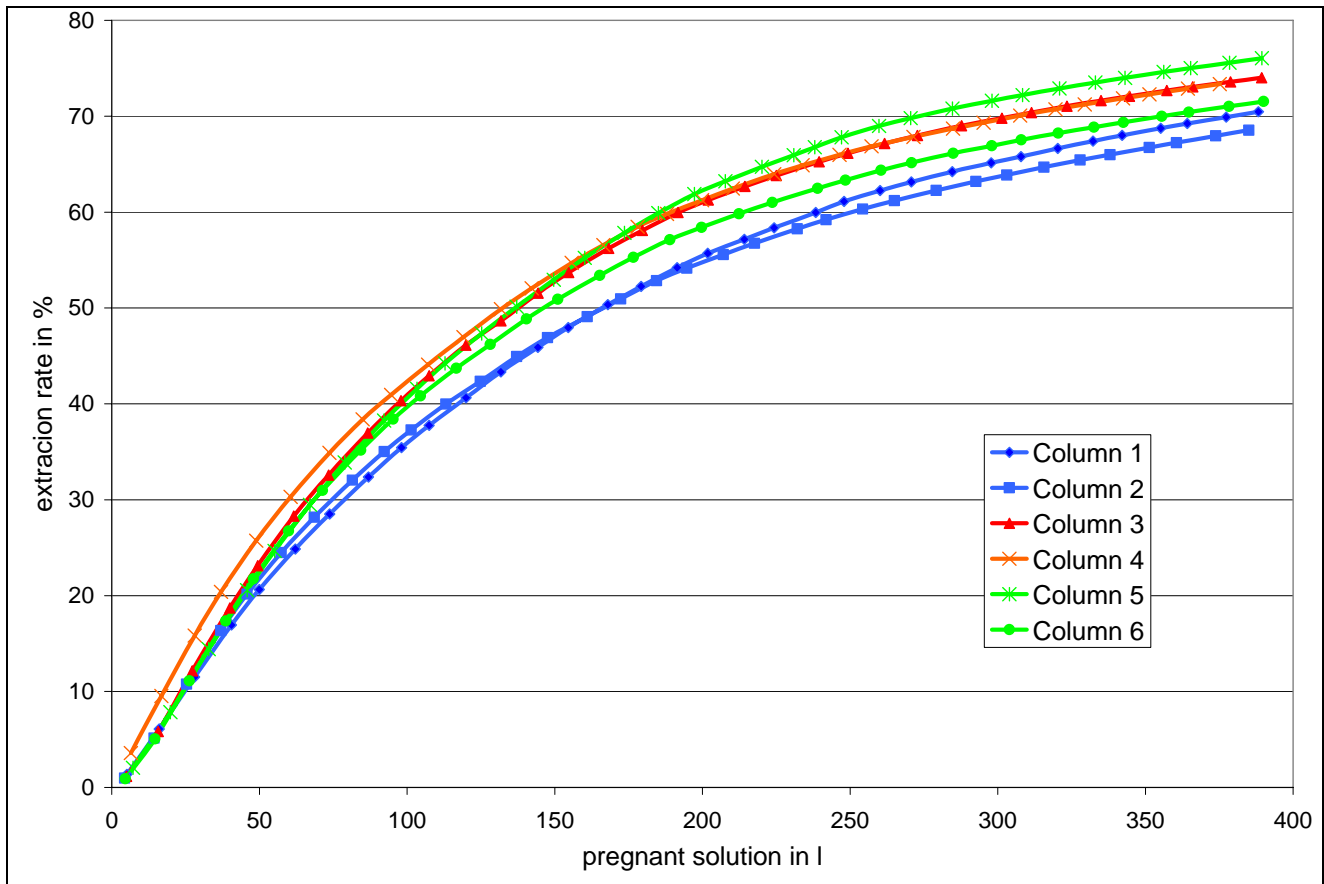
Figure 7:   Illustrated is the copper extraction rate for every column over the accumulated volume of pregnant solution.

The reference column 1 and 2 reached over 36 days and a total application of ca. 380 l of diluted sulfuric acid an extraction rate of 69,91 % and 67,95 %. The column 3, wetted with water, and the column 4, which started with a dry ore mixture, reached after being treated with 380 l of diluted sulfuric acid with 100 ppm of nonionic surfactant EVD61549 with 73,59 % and 73,35 % almost the same extraction rates. The equally treated columns 5 and 6, ore mixtures wetted with a 100 ppm surfactant solution and leached with diluted sulfuric acid with 100 ppm surfactant, reached a extraction rate of 75,58 % and 71,03 %. The average extraction rate of columns 5 and 6 is at 73,30 % which is very close to the extraction rates of the columns 3 and 4.

According to the average result of the columns 3 to 6, the improvement of the extraction rate to the reference columns 1 and 2 is between 3,5 % and 5,4 %. Even with varying starting conditions, the surfactant EVD61549 reaches a comparable improvement of the leaching process.

Conclusion

The outcome of this trial supports the good performance of the nonionic surfactant EVD61549 in previous trials. The realized average improvement of the copper extraction with this surfactant to the reference column reached 3,5 % to 5,4 %. Additionally it has been proven, that the surfactant EVD61549 reaches comparable improvements even with varying process conditions. Further evaluations considering even more closely currently performed process conditions are on their way.

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