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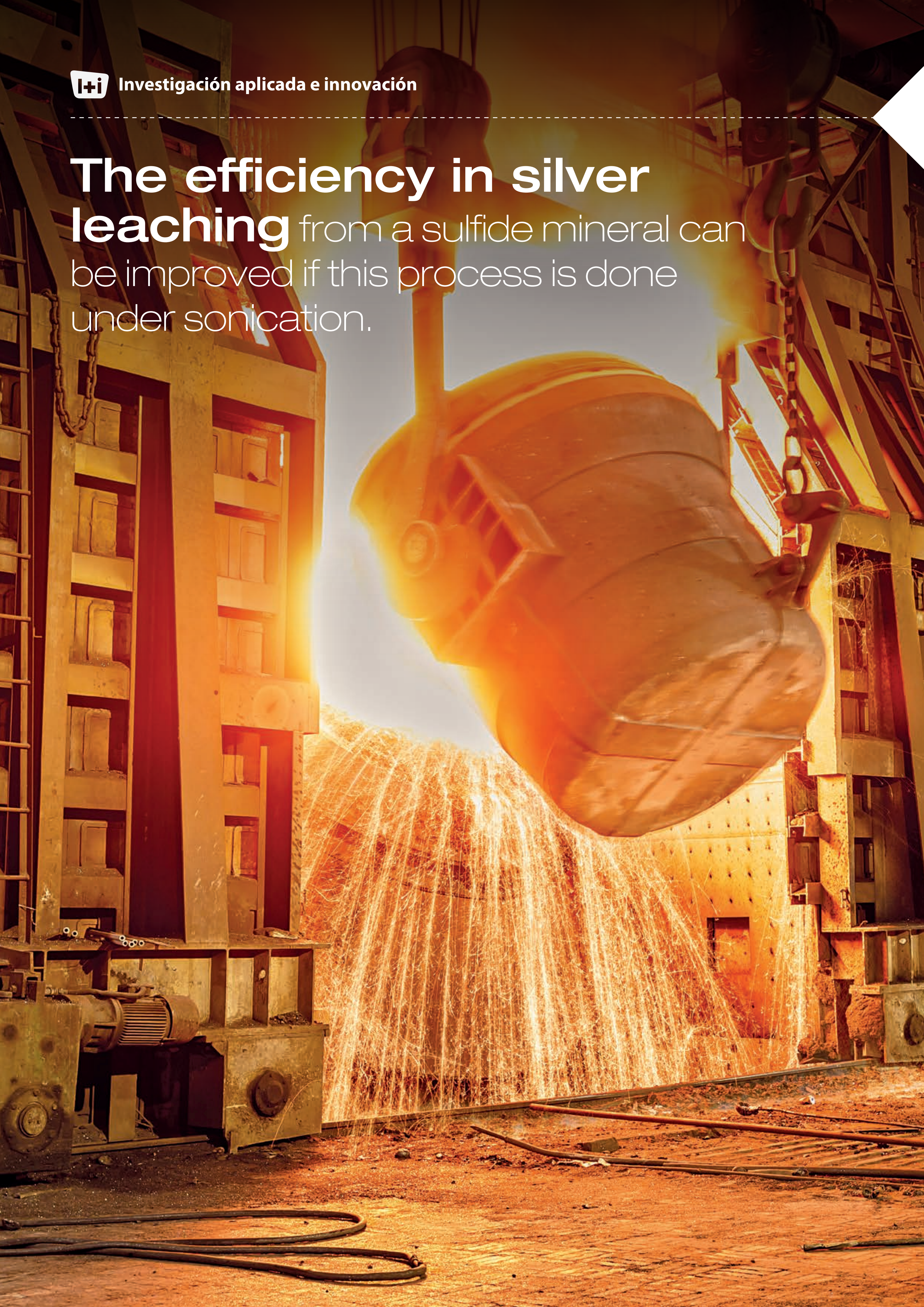

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Ultrasound-Assisted Leaching as a Greener Method in Mineral Processing: Improved Silver Extraction from a Sulfide-Based Mineral Concentrate Without Increasing Cyanide Consumption

Lixiviación asistida con ultrasonido como método de mayor ecoeficiencia en el procesamiento de minerales: extracción mejorada de plata de un concentrado basado en sulfuros sin consumir más cianuro

RESUMEN

Uno de los objetivos en el desarrollo de nuevos métodos hidrometalúrgicos es mejorar la eficiencia en la extracción de metales nobles sin intensificar el uso del agente lixiviante. Esto es particularmente importante cuando compuestos peligrosos (como el cianuro) participan en el procesamiento de minerales. El presente artículo muestra que la lixiviación de plata bajo ultrasonido permite un aumento de hasta 300% en la cantidad de plata lixiviada, sin incrementar el consumo de cianuro, lo cual sugiere que la sonicación remueve subproductos sólidos que interfieren con el proceso de lixiviación. Apoyando esta hipótesis, se observa que en ausencia de ultrasonido el consumo de cianuro se incrementa a lo largo del experimento, aún cuando ya la extracción máxima de plata fue alcanzada. La mayor eficiencia en la extracción de plata con disminución del consumo de cianuro indica que la lixiviación asistida por ultrasonido puede constituirse como un método más ecoeficiente en el procesamiento de minerales.

ABSTRACT

Improving the efficiency of noble metal extraction without increasing the consumption of the leaching agent is one of the goals in the development of novel hydrometallurgical routes. This is particularly important when dangerous compounds (such as cyanide) are involved in mineral processing. Ultrasound-assisted leaching is presented here as an advantageous process able to increase the amount of silver leached from a polymetallic sulfide-based mineral by ~300%, without increasing cyanide consumption. Our results suggest that sonication removes solid by-products that hinder the leaching process. While in the absence of sonication cyanide consumption rises steadily even though silver leaching has reached a maximum, under sonication both cyanide consumption and silver extraction follow similar trends, indicating that side reactions are decreased. The enhanced efficiency in both silver extraction and cyanide consumption indicate that ultrasound-assisted leaching can be introduced as a greener method in mineral processing.

Palabras Clave
Lixiviación, ultrasonido, sonicación, plata, cianuro.

Key words
Leaching, ultrasound, sonication, silver, cyanide.

INTRODUCTION

One of the challenges the mining industry faces in this century is the development of more efficient strategies for mineral processing. From an economic point of view, these strategies are needed because ores around the world are increasing their complexity and reducing their levels of metals of interest.[1], [2] However, from the point of view of sustainability, more environmentally-friendly methods are also needed in order to comply with tighter government regulations and social demands.[3] Thus, an efficient strategy needs to be focused not only on increasing productivity, but also respecting the ecosystems and reducing the impact on environment and society.

Cyanides are one of the most dangerous chemicals used during mineral processing. Even though there is a robust set of procedures for handling, storing and decomposing cyanide, this ion rises concerns as it is lethal for living organisms (it interferes with key biological processes due to its affinity for metals of biological relevance, such as iron and cobalt).[4] The affinity of cyanide for other type of metals, such as gold and silver (coinage metals), turns this ion into one of the most efficient for leaching coinage metals from ores and mineral concentrates.[2], [5]–[7] While several strategies are focused on replacing cyanide with less toxic compounds, such as thiosulfates and thiourea,[1], [8]–[11] sometimes these agents do not perform as efficiently as cyanide. In these cases, strategies are focused on reducing the amount of cyanide consumed during leaching. This latter set of strategies is particularly important in the processing of complex minerals, where cyanide is predominantly consumed in side reactions (e.g. decomposition or complexation with other metals).[12] Side reactions can also lead to the formation of solid by-products, which interfere with the efficiency of the processing.

There is a variety of manners in which cyanide leaching can be enhanced. The most straightforward is the increase in cyanide concentration, since according to the principles of chemical equilibrium the reaction is pushed forward as higher amounts of reactants are used. It is also possible to increase temperature and pressure to force the reaction to take place,[13]–[15] but these methods are often energy-intensive and/or require expensive designs of reactors. There is another family of methods in which leaching is favored by applying energy from different sources, such as microwaves and ultrasound.[16]–[19] The incorporation of these methods in a leaching process (assisted leaching) allows for the transfer of energy in relatively simpler, less demanding setups.

Ultrasound waves are mechanical (not electromagnetic) waves which, when propagated in a liquid medium, generate cavities ("bubbles") as the result of cycles of expansion and compression.[20] These cavities collapse implosively, completing the process known as cavitation. The scale of the parameters involved in cavitation are extreme: the generation-implosion cycle of a cavity lasting usually 400 μs (microseconds), forms a cavity in the sub-microscopic range, while the implosion generates local pressures of 1000 atm and temperatures of thousands of degrees Celsius.[21] Due to the small size of cavities, these changes cannot be seen at a macroscopic level, but strongly affects the medium and its content. In particular, in the presence of solids, cavitation generates a powerful jet of solution which impacts the solid at very high speeds, temperatures and pressures, damaging the surface and exposing new zones of the solid.[20], [21] Thus, in the case of mineral leaching, ultrasound can be an effective way to facilitate the exposure of zones which can be impermeable to the leaching agent, as demonstrated in previous publications.[17], [18], [22]

In the present research article, we study the effect of ultrasound in a leaching process. We find that the ultrasound-assisted leaching increases the recovery of silver by 300% and at the same time it maintains the same consumption of cyanide. Since the efficiency in cyanide usage is enhanced, ultrasound-assisted leaching constitutes a greener method in hydrometallurgy.

FUNDAMENTALS

Cyanide leaching for silver (or gold) follows equations (1) or (2), for pure metal and sulfide, respectively:

$$4M_{(s)} + 8CN^-_{(ac)} + O_{2(g)} + 2H_2O_{(l)} = 4M(CN)_2^-{}_{(ac)} + 4OH^-_{(ac)} \quad (1)$$

$$M_2S_{(s)} + 4CN^-_{(ac)} + H_2O_{(l)} = 2M(CN)_2^-{}_{(ac)} + OH^-_{(ac)} + HS^-_{(ac)} \quad (2)$$ [6], [9], [23]

Of course, these are only two of the large number of possible reactions which can take place on the surface. Senanayake has reviewed both desired and undesired reactions occuring during cyanidation.[6]

Sonication (the application of ultrasound to chemical reactions) begins with application of an alternating electrical field producing a mechanical vibration in a transducer, which then generates a vibration in a container (sonication bath) or in a rod (sonication probe).[21] This vibration leads to molecular vibration and generates an acoustic pressure (P_a), following the displacement of molecules originated from ultrasound waves. It can be defined (as a function of time) as:

$$P_a = P_A.\mathrm{Sin}(2\Pi.f.t) \qquad (3)$$

Where P_A is the amplitude of pressure wave, f is the frequency of the sound wave and t is the time. The pressure amplitude is related to the intensity I of the sound wave, the density of the medium ρ and the speed of the acoustic wave c by:

$$P_A = (2.I.\rho.c)^{½} \qquad (4)$$

For a frequency of 20 kHz, an intensity of 1 $W.cm^{-2}$ in water, the pressure amplitude is 1.7 x 10^5 $N.m^{-2}$.[20]

METHODS

CAUTION: Cyanides are very dangerous and should be used with extreme care in the laboratory. This reagent should be handled using appropriate PPE (personal protection equipment) such as apron, gloves and protection glasses. All experiments should be done in a hood and the pH of solutions needs to be above 10 at all stages to avoid the formation of cyanide fumes. All materials in contact with cyanide need to be sunk in a solution containing an oxidizing agent such as sodium hypochlorite (bleach) or hydrogen peroxide to decompose cyanide before disposing of residues.

Traditional leaching using cyanide: 50 grams of a mineral concentrate containing mostly pyrite and silver (silver content: 1300 g/ton, as determined by atomic absorption spectroscopy) were mixed with 200 mL of a solution NaCN 8 g/L in a 500 mL beaker. Cyanide concentration in the range 1 – 15 g/L were tested but the optimal concentration was found to be 8 g/L. A pH of 11 and a temperature of 20 °C were maintained throughout the experiments. Agitation was done through a mechanical overhead stirrer, which was set to 100 rpm in all cases. The amount of cyanide was kept constant during the leaching process by replenishing the quantity of sodium cyanide consumed, which was measured by titrating the solution with silver nitrate, using rhodamine B as indicator. The amount of silver leached was determined by atomic absorption spectroscopy, using a Perkin Elmer AAnalyst 1000 instrument.

Ultrasound-assisted leaching: The setup described in the previous section was also employed here, only differing in that the beaker containing the solid/liquid mixture was placed inside a Branson sonicator bath (Bransonics 220). The temperature of the leaching system increases to a maximum of 60 °C. Losses of volume due to evaporation were calculated to be below 5%, which does not affect the results shown below.

Pretreatment of mineral samples with ultrasound: In order to understand the manner in which ultrasound operates, mineral samples were exposed to sonication under distilled water (100 g of mineral in 500 mL of water) for four hours. After rinsing with distilled water the mineral concentrate was dried and leached.

RESULTS

Figure 1 compares the amount of silver leached with and without the use of ultrasound, showing an increase in almost 300% when ultrasound is used. Since sonication produced a rise in the temperature of the solution, it is possible that the enhanced leaching of silver is partially due to a thermal effect. However, previous reports on high-temperature leaching do not show more than a 40% increase in efficiency in silver leaching, which indicates that the effect observed here is due to sonication.

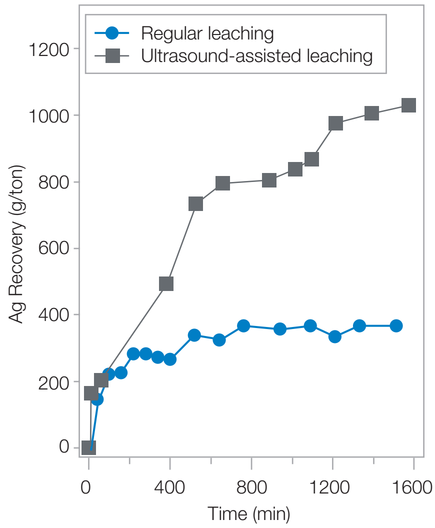

Figure 1: Silver leaching over time with and without ultrasound assistance. A deviation of ± 10% applies in all cases. Source: Own data.

As mentioned in the introduction, sonication operates by facilitating the removal of passivated surfaces in the mineral concentrate. These passivated surfaces may be present even before the leaching process (as result of previous treatment of the mineral) or may be formed as the reaction proceeds. The trends in silver leaching (Figure 1) are very similar in the first stages of the reaction (time frame = 0-100 minutes) and they start to be markedly different at times above 400 minutes, suggesting that sonication enhances silver leaching by removing passivating layers produced during the reaction, not before. To confirm this, a pre-treatment was done by sonicating the mineral concentrate in distilled water prior to leaching. Figure 2 shows that ultrasound pre-treatment does not result in a significant increase in silver leaching, further supporting the fact that sonication removes surface by-products of the leaching reaction. Table I summarizes the efficiency in silver extraction for each treatment.

Table I. Amount of Ag leached (g/ton) using diverse sonication treatments. In all cases the amount leached at time = 400 minutes was considered. The same conditions of leaching are used in all cases. Source: Own data.

Method	Ag leached (g/ton)
Traditional leaching of as-received mineral	251
Traditional leaching of pre-sonicated mineral	314
Ultrasound-assisted leaching of as-received mineral	780
Ultrasound-assisted leaching of pre-sonicated mineral	1020

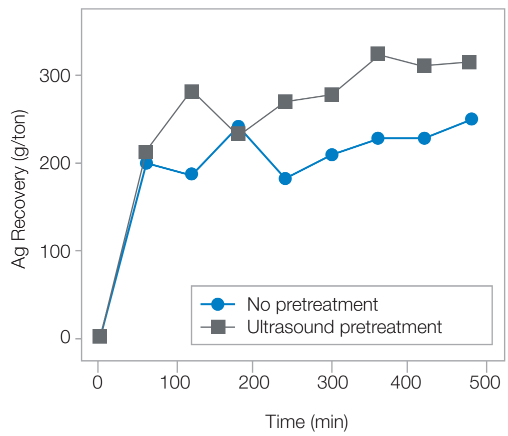

Figure 2: Comparison of silver extraction during traditional leaching with and without sonication as pre-treatment. Both pl both with traditional leaching. All points have a deviation of ±10%. Source: Own data.

The results in Table I indicate that ultrasound-assisted leaching is able to enhance significantly the efficiency in silver extraction. It is interesting to note that the ultrasound-assisted leaching of the pre-treated sample with sonication increases even further the extraction of silver, rising up to around 400% with respect to the traditional leaching. Even though the sonication pretreatment does not seem to increase the efficiency of traditional leaching, it is clear that the pretreated sample is sufficiently activated to respond better to ultrasound-assisted leaching, reaching an extraction of 1020 g/ton in the first 400 minutes (Table I). This demonstrates that ultrasound assistance also improves the kinetics of a leaching process.

From an environmental point, it is also important to determine if this increase in silver extraction is accompanied by an increase in cyanide consumption. Figure 3 shows that cyanide consumption after 1600 minutes of leaching is similar for traditional and ultrasound-assisted leaching. Since the results in Table I show that ultrasound-assisted leaching increases by 300% the amount of silver leached with respect to the traditional leaching, and knowing that cyanide consumption is the same in both cases, it is clear that the efficiency in cyanide consumption also triplicates under sonication. Worth noticing is the fact that even though silver extraction in traditional leaching reaches a maximum at ~500 minutes (Figure 1), the consumption of cyanide continues growing steadily, clearly indicating that this is the result of side reactions. Cyanide consumption during ultrasound-assisted leaching follows the trend observed in Figure 1 for silver extraction, implying that in this case the occurrence of side reactions consuming cyanide is decreased. More importantly, it indicates that the mechanism of reaction between the mineral and the cyanide solution is similar throughout the reaction. This fact confirms that ultrasound-assisted leaching also promotes a more efficient use of cyanide during mineral processing.

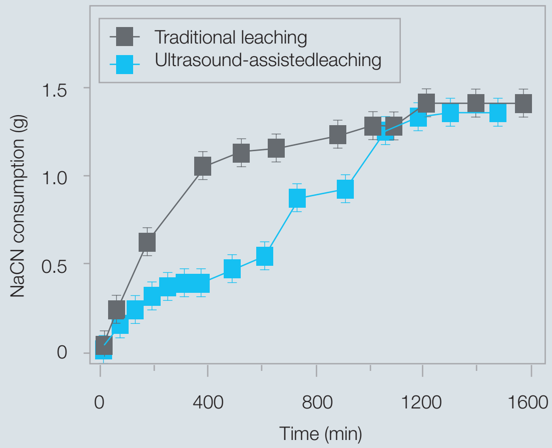

Figure 3: Cyanide consumption during leaching with and without sonication. The amount of cyanide was determined by titrating the free cyanide at indicated times. Source: Own data.

CONCLUSIONS

The efficiency in silver leaching from a sulfide mineral can be improved if this process is done under sonication. The results suggest that ultrasound removes the surface layers of by-products formed during the first stages of the reaction; surface characterization studies are needed to understand the nature of such by-products. Despite of the increase in silver extraction, sonication does not increase cyanide consumption, indicating that the removal of surface layers facilitates the continuous exposure of silver on the surface. Further research is needed to assess the effect of ultrasound-mediated heating and the impact of cavitation in cyanide stability.

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