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GOLD ELECTROLEACHING IN A POROUS BED REACTOR[a]

ELECTROLIXIVIACIÓN DE ORO EN UN REACTOR DE LECHO POROSO

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Artículo Investigación

ABSTRACT: The application of an electric potential difference on the leaching of an auriferous mineral typical of Colombian mining was analyzed in an electroleaching reactor. Electric potentials of 5, 30, and 60 volts were evaluated during 4, 6, and 20 hours. In each of the conditions evaluated, samples of the liquors were taken near the cathode and anode and were analyzed by atomic absorption spectrophotometry. It was observed that there is a direct relation between the applied electric potential and the migrational flow of the gold species to the anode. After the electroleaching process, the used electrodes were analyzed by SEM-EDX, where the presence of gold deposits was detected on the surface of the electrode under all the potential difference conditions applied. Based on the results obtained, a mechanism is proposed to explain the influence on the kinetics of gold cyanidation of the application of an electric potential difference on a column leaching process.

KEYWORDS: Electroleaching; cyanidation; dissolution kinetics; gold extraction.

RESUMEN: : En un reactor de electrolixiviación de lecho poroso se analizó la aplicación de la diferencia de potencial eléctrico sobre la lixiviación de un mineral aurífero típico en la minería colombiana. Se evaluaron potenciales eléctricos de 5, 30 y 60 voltios durante 4, 6 y 20 horas, en cada una de las condiciones evaluadas se tomaron muestras de los licores en las inmediaciones del cátodo y del ánodo y se analizaron por espectrofotometría de absorción atómica Se observa que existe una relación directa entre el potencial eléctrico aplicado y el flujo migracional de las especies de oro hacia el ánodo. Luego del proceso de electrolixiviación los electrodos utilizados fueron analizados por SEM-EDX, donde se detectó la presencia de depósitos de oro en la superficie del electrodo bajo todas las condiciones de diferencia de potencial aplicado. Con base en los resultados obtenidos, se propone un mecanismo para explicar la influencia en la cinética de cianuración de oro al aplicar una diferencia de potencial eléctrico a un proceso de lixiviación en columna.

PALABRAS CLAVES: electrolixiviación; cianuración; cinética de disolución; extracción de oro.

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1. INTRODUCTION

Gold complexes in an aqueous solution may exist in two oxidation states, aurous (Au^{+}) and auric (Au^{3+}). Thermodynamically speaking, these cations are stable in an aqueous solution. In order to stabilize these ions, it is necessary to introduce a complexing agent such as cyanide, thiosulfate, or thiourea, among others (Oraby *et al.*, 2015), and employ an adequate oxidizing agent, as no reaction will take place unless both are present in the solution (Nicol *et al.*, 1992). Complex formation due to the association of two or more simple species may give way to the formation of cationic, anionic, or neutral charge species. Depending on the number of charges in the components, the shape of the gold complex with cyanide is the anion $\mathrm{Au(CN_2^-)}$. Chemical reactions in the formation of this complex due to a cyanidation process have the following fundamental stages: absorption of oxygen in the solution, transport of cyanide and dissolved oxygen to the solid-liquid interface, absorption of reactants ($\mathrm{CN^-}$ and $\mathrm{O_2}$) and the solid surface, electrochemical reactions, desorption of soluble gold-cyanide complexes and other reaction products from the solid phase, and transport of desorbed products to the bottom of the solution (Marsden & House, 2006). The chemical reaction stage is rarely determining in most of the processes of gold complex formation. Therefore, mass transport is usually the stage that limits the reaction (Marsden & House, 2006).

The process of ionic species transport in a solution through a mineral porous bed appears under the application of a electric potential difference, and this is achieved by mass flow due to diffusion, migration, and electroosmosis. The contribution of each type of flow in the total mass flow is affected by factors such as the mineral's mineralogic composition, the solution's composition and conductivity, and the electrochemical properties of the species present in the fluid (Acar *et al.*, 1993). When an electric potential difference is applied on a mineral bed submerged in an electrolyte, the electric current is transported by the ions present in the solution. Electromigration is the term that describes the movement of individual ions in a solution induced by an applied electric current. Direction of ionic eletromigration occurs toward the electrode with the opposite charge. Anions will move toward the anode and cations will move toward the cathode. The degree of migration will depend on the mobility of the ionic species (Reddy & Cameselle, 2009).

When an electric field is established throughout a capillary, excess counterions across the region of the electric double layer adjacent to the particles of the medium move toward the electrode with the opposite charge. The movement of these species generates a net tension that is transferred to the molecules of the surrounding fluid through viscous forces, producing a flow in the insterstitial fluid known as the electroosmotic flow (Acar *et al.*, 1995; Valenzuela *et al.*, 2016). Under an electric potential difference, the electroosmotic flow depends mainly on the porousness and z-potential, and is independent from the size of the mineral bed pores. Therefore, the transport of species by electroosmosis is a phenomenon that may be significant in a leaching process (Acar *et al.*, 1995).

There are a large number of studies on the use of electro processing in the extraction of metals in solutions, however, the reactions when transferring metals in solutions of different chemical composition by electric current-electrochemical leaching occupy a special place in the studies of electrochemical processes (Kenzhaliyev *et al.*, 2015). This work investigates the influence of an electric potential difference on gold leaching in an auriferous mineral by applying electric potentials of 5, 30, and 60 volts in 4, 6, and 20 hours.

2. EXPERIMENTAL

In order to meet the goal of this study, an electroleaching reactor was built using polyvinyl chloride (PVC), 6 cm in diameter and 30 cm high, following a 5:1 height-diameter ratio (Lin & Luong, 2004; Loong, 2007). The working mineral comes from the northeastern region of the Antioquia department in Colombia (see Figure 1). It has an Au tenor of 41 ppm, composed mainly by Quartz, pyrite, Sphalerite, Zeolite and Argentite and a particle size distribution that guarantees the flow of the leaching solution through the mineral bed without clogging, 80 % of the ore has a particle size between 2000 and 2800 microns and the remaining 20 % is between 150 and 2000 microns.

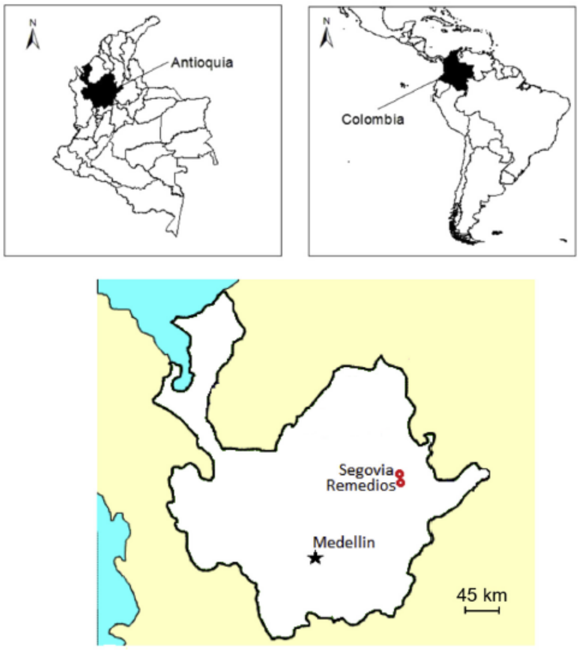

Figure 1: Area of procedure of the working mineral. Fuente: Own elaboration.

In order to determine the effect of the voltage and the time of treatment on gold extraction, a complete general factorial design was built with three completely randomized levels (Montgomery, 1991)as is shown in Table **??**. The response variable was the concentration of gold in the leaching liquor. Based on preliminary tests it was determined that the voltages to be evaluated are 0, 5, 30 and 60 Volts and the times of 2, 4, 6 and 20 hours, The current was adjusted to 4 amperes.

Tabla 1: Experimental design matrix.

Natural variables		
Test	Voltage	Time
1	5	4
2	5	2
3	60	4
4	5	6
5	60	2
6	30	4
7	5	20
8	30	20
9	60	20
10	30	6
11	30	2
12	60	6

The electroleaching reactors were loaded with approximately 1450 g of mineral and were filled with a sodium cyanide solution of 0.04 M. The sodium cyanide used was Merck brand analytic grade. Voltage was applied within the reactor through a feeding source, reference BK PRECISION BK1740A. The distribution of electrodes was established so that the electrode in the lower part of the reactor worked as an anode and the upper electrode worked as a cathode. The leaching liquors were analyzed in an atomic absorption spectrophotometer, reference Thermo Scientific iCE 3000 series. The electrodes were analyzed by SEM-EDX, in a scanning tunneling microscope, reference Phenom XL.

A scheme of the electroleaching reactor is shown in Figure 2. The density, pore volume, and working mineral porousness were respectively determined at 3.14 g/cm^3, 386 cm^3, and 0.46. The porosity and pore volume of the working ore in the reactor were determined by the ratios shown in equations 1, 2, 3, 4, the average particle density was determined following the method described by ASTM D854-14 (D854-14, 2014).

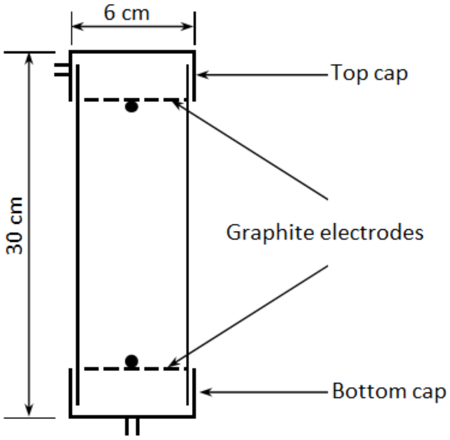

Figure 2: Column electroleaching reactor. Fuente: Own elaboration.

$$Volume = \frac{\Pi * Diameter^2}{4} * Height \tag{1}$$

$$Apparent\ Density = \frac{Mass}{Volume} \tag{2}$$

$$Porosity = 1 - \frac{Apparent\ density}{Particle\ density} \tag{3}$$

$$Poro\ space\ volume = Porosity - Volume \tag{4}$$

3. RESULTS

Samples were taken for each of the evaluated conditions of the liquid found near the anode and the cathode of the reactor. All tests were conducted at room temperature (25 ^{o}C). When graphing the variation in gold concentration in accordance to the leaching time in the anode liquor at different voltages, it can be observed that the increase in gold concentration is directly proportional to the increase in the voltage applied (see Figure 3). This implies that the higher the electric potential difference applied, the larger the migrational flow of the $Au(CN_2^-)$ species will be to the anode. Taking into account that the biggest contribution in matter transport under the application of an electric potential difference in a mineral bed is transport by electromigration (Acar *et al.*, 1995), equation 5 can be proposed for $Au(CN_2^-)$ species transport by migration to the anode.

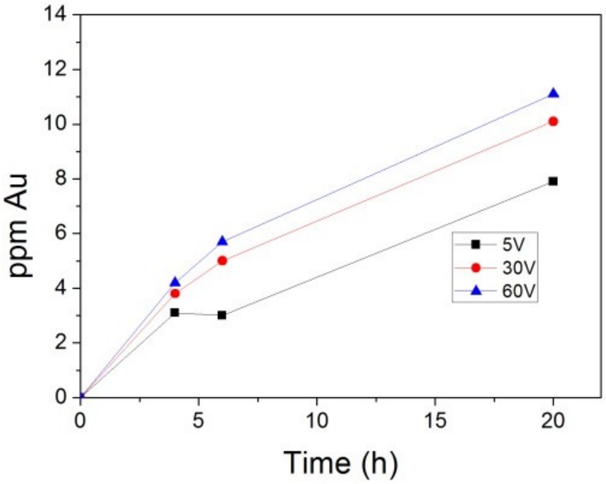

Figure 3: Variation in gold concentration in the anodic liquor at different voltages. Fuente: Own elaboration.

$$J^{m}_{Au(CN_2^-)} = C_{Au(CN_2^-)}(U^{*}_{Au(CN_2^-)} + K_e)\frac{\eth E}{\eth x} \tag{5}$$

When graphing the variation in gold concentration in accordance to time in the cathode liquor at different voltages, it can be observed that species concentration decreases as voltage increases. Taking into account the charge of the Au(CN_2^-) gold-cyanide complexes, it is presumed that these ions will be directed toward the anode when applying an electric potential difference; therefore, the gold species near the cathode will tend to travel toward the electrode with the opposite charge, and therefore, its concentration will decrease. The migrational flow of these species will be larger as the potential difference increases, as can be observed in Figure 4. Taking this into account, it is possible to propose equation 6 for Au(CN_2^-) species transport by migration near the cathode.

$$J^{m}_{Au(CN_2^-)} = -C_{Au(CN_2^-)}(U^{*}_{Au(CN_2^-)} + K_e)\frac{\eth E}{\eth x} \tag{6}$$

When analyzing the cathodes by SEM-EDX, the presence of gold deposits was detected on the surface of the electrode under all the potential difference conditions applied. Figure 5 shows one of these deposits. According to this, it can be proposed that Au(CN_2^-) gold complexes that are found in proximity to the electric double layer of the cathode lose electromotive force in the electrode's electric field; therefore, the distribution of charges around the cathode is distorted, a diffusion of ionic complexes toward the Helmholtz layer appears, and complexes are divided, liberating the metal in the shape of positively charged metallic cations. These are deposited on the cathode's surface. This mechanism is illustrated in Figure 6. The aforementioned affirmation is supported by Wilkinson's observations (Wilkinson, 1986).

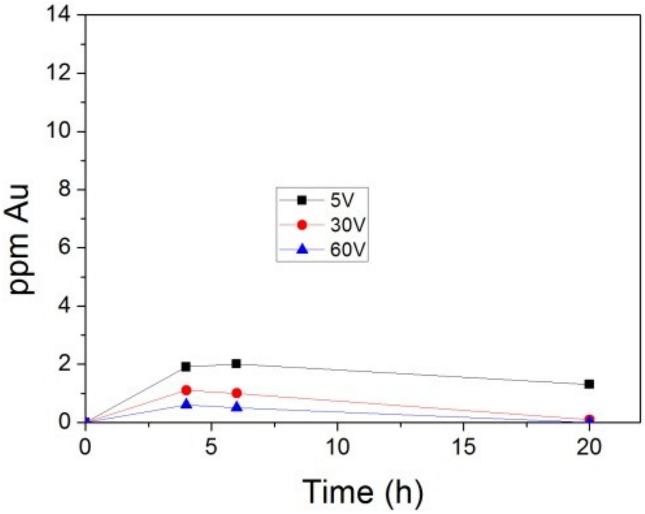

Figure 4: Variation in gold concentration in the cathodic liquor at different voltages. Fuente: Own elaboration.

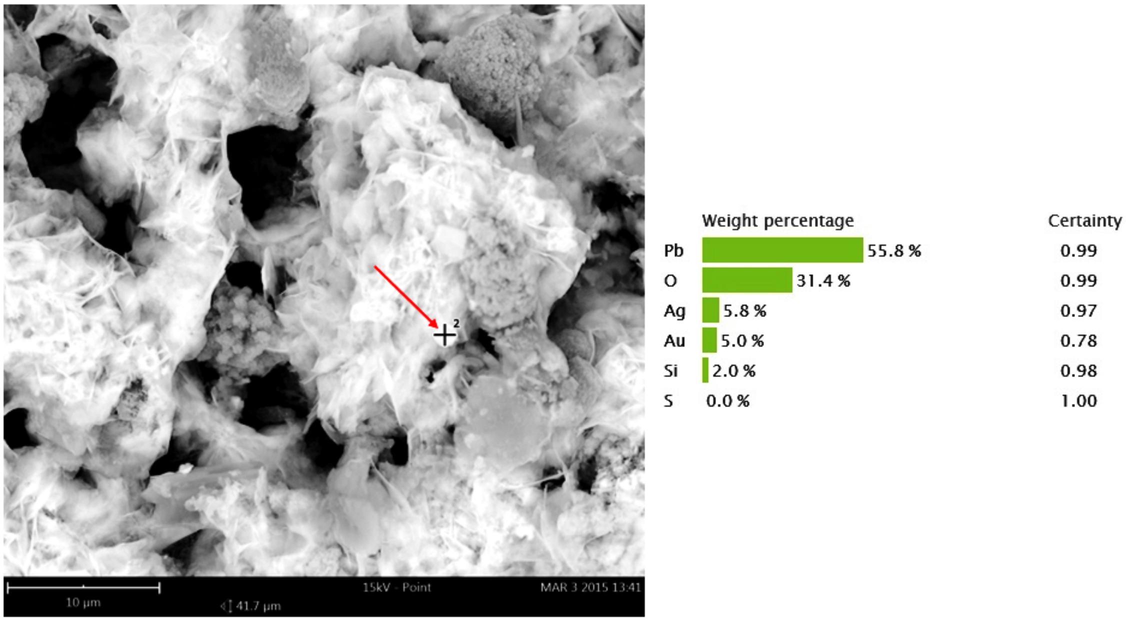

Figure 5: Gold and silver deposit on the cathode's surface. Fuente: Own elaboration.

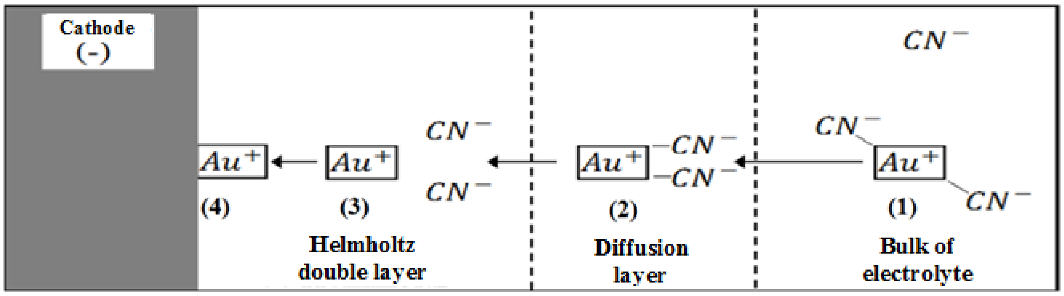

Figure 6: Proposed mechanism for gold deposition in the cathode. Fuente: Own elaboration.

One significant observation is that for the case of anodes, gold deposits were not detected for the evaluated conditions. This possibly implies that the gold complexes present in the liquor close to the anode remain in the solution and are not reduced in the electrode.

Once the electroleaching stages finished, the concentration of gold was determined in the working mineral by fire assay, aiming to establish the percentage of gold recovery under the evaluated conditions. A direct relation can be seen between the applied voltage and the percentage of recovery (see Figure 7).

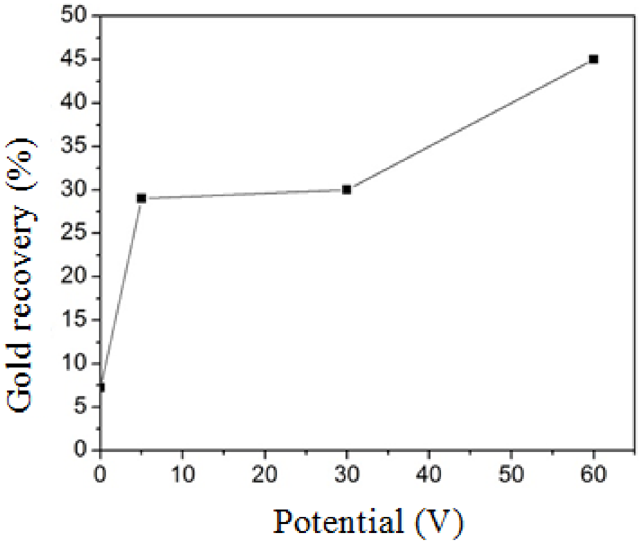

Figure 7: Percentage of gold recovery in accordance to voltage during 20 hours of treatment. Fuente: Own elaboration.

The increase in gold recovery with the applied electric potential could be associated to the fact that once the $\mathrm{Au(CN_2^-)}$ complex formation is achieved, the electric potential difference will be affecting the electromotive speed of the gold-cyanide complex through the diffuse layer. The higher the electric potential difference, the stronger the electromotive force acquired by the molecule, and therefore, molecules will travel faster toward the bottom of the solution. This phenomenon, along with the electromigration transport of the $\mathrm{Au(CN_2^-)}$ complex in the mineral bed will promote an increase in gold leaching kinetics.

The low recovery rate, may be associated with an inefficient release of the gold particles, taking into account the results obtained, it is proposed that once the $\mathrm{Au(CN_2^-)}$ ions found inside the electric double layer surrounding the gold particles are affected by the electric potential difference, they are forced to leave the double layer into the bosom of the solution by the electroosmosis phenomenon. At the same time, the $\mathrm{Au(CN_2^-)}$ ions found at the bottom of the solution are affected by the electric potential difference, which confers them electromotive force and transports them toward the electrode with the opposite charge (the anode, in this case) due to the electromigration phenomenon.

4. CONCLUSIONS

There is a direct relation between the electric potential applied to the leaching bed and the electromotive speed acquired by the $\mathrm{Au(CN_2^-)}$ species found at the bottom of the solution; therefore, the migrational flow of species to the anode will be larger. This implies that the concentration of species increases in the anodic region, and decreases in the cathodic region.

The molecules of $\mathrm{Au(CN_2^-)}$ found inside the electric double layer surrounding the gold particles are affected by the electric potential difference and forced to leave the double layer into the bottom of the solution by the electroosmosis phenomenon.

Taking into the account the fact that the largest contribution in matter transport in a mineral bed under the application of a electric potential difference is transport by electromigration, equations for the transport of $\mathrm{Au(CN_2^-)}$ species to the anodic region and from the cathodic region are proposed.

The $\mathrm{Au(CN_2^-)}$ gold complexes that are found in proximity to the electric double layer of the cathode lose electromotive force in the electrode's electric field; therefore, the distribution of charges around the cathode is distorted, a diffusion of ionic complexes to the Helmholtz layer appears, and complexes are divided, liberating the metal in the shape of positively charged metallic cations. These are deposited on the cathode's surface.

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