KINETIC CONTROL STUDY OF GOLD LEACHING WITH CYANIDE FROM A FLOTATION CONCENTRATE IN A DRAFT-TUBE REACTOR

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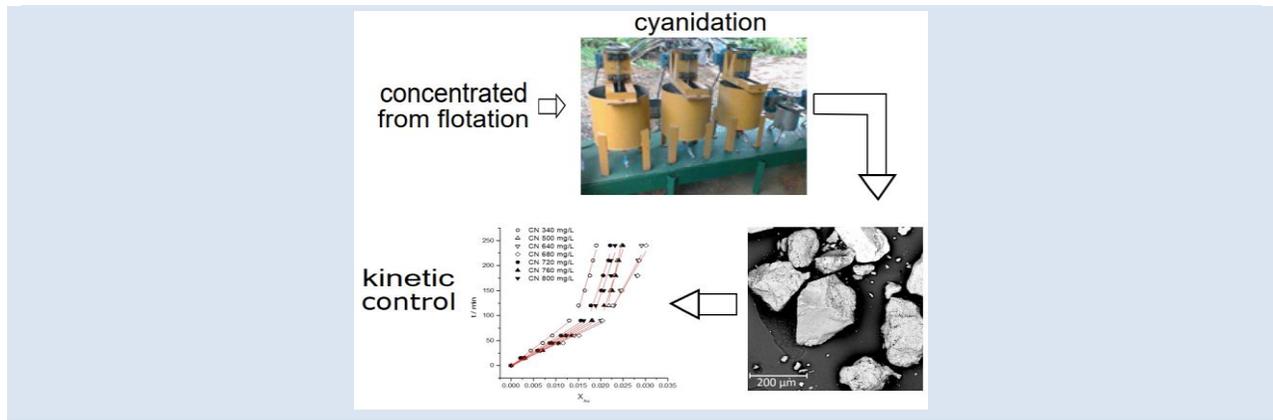
ABSTRACT

The knowledge of the kinetic control mechanisms of gold leaching in real process conditions is crucial for the correct process design and plant operation. This research evaluated the kinetic control mechanism on the gold leaching with cyanide in alkaline media from a previously floated ore. Before the leaching, a pre-treatment with sodium hypochlorite was carried out to eliminate remaining reagents from the flotation process. After the pre-treatment several leaching experiments were conducted keeping constant the pH, temperature and aeration rate, meanwhile the agitation velocity and cyanide dosage were varied. The analysis of leaching kinetic profiles indicated that the control of the reaction corresponds to the mass transfer in the ash produced by the reaction with two resistances to the leaching process. Furthermore, the analysis was complemented with scanning electron microscopy and x-ray dispersive energy (SEM-EDX) measurements confirming that the leached ore surface do not contain detectable levels of gold.

Keywords: gold, cyanide, kinetic, draft-tube reactor.

ESTUDIO DEL CONTROL CINÉTICO DE LIXIVIACIÓN CON CIANURO DE ORO A PARTIR DE UN MINERAL PRE-CONCENTRADO POR FLOTACIÓN

RESUMEN

El conocimiento de los fenómenos que gobiernan la cinética de lixiviación de oro en sistemas reales es crucial para el correcto diseño y operación de los procesos. El presente trabajo evaluó la cinética y tipo de control gobernante de las reacciones durante la lixiviación de oro con cianuro en medio alcalino en un mineral previamente concentrado por flotación. Previa a la experimentación, se realizó un pretratamiento del concentrado de flotación con hipoclorito de sodio en medio alcalino a pH 12 en un tanque agitado durante 3 horas. Luego del pretratamiento, se realizó una serie de experimentos de lixiviación con cianuro manteniendo constante el pH, la temperatura y la velocidad de aireación. Los parámetros controlados fueron la velocidad de agitación y la dosificación de cianuro. Luego de la aplicación de modelos matemáticos, los perfiles de lixiviación indicaron que el control cinético de la reacción corresponde a la transferencia de masa en ceniza producida por la reacción, con dos resistencias al proceso de lixiviación. Del mismo modo, este análisis se complementó con mediciones de microscopía electrónica de barrido con análisis dispersivo de rayos x (SEM-EDX) que confirman que la superficie expuesta en la solución no contiene niveles detectables de oro.

Palabras Claves: oro, cianuro, lixiviación, cinética

1. INTRODUCTION

The leaching of gold ores with cyanide by carbon in leach (CIL) or carbon in pulp (CIP) are the most common methods for processing gold ores. However, cyanide has demonstrated limitations with refractory ores, so that the mineral normally is subjected to high-cost pre-treatments [1–4]. Moreover, cyanide reagent presents problems related to safety, high toxicity to human health and environmental impacts on ecological receptors [5].

Despite this, cyanide is still used by most mills due to its low costs, low technology needed for processing, and its relatively simple handling of wastes generated during industrial operations. With this method, the control of the operational parameters is essential for proper process performance. The dosage of cyanide, pH control, stirring system and oxygen levels are parameters that can produce acceptable or poor recoveries. Moreover, leaching kinetics are extremely sensitive to these operating parameters [6]. A common mistake frequently found in this kind of operation is the overuse of cyanide; considering that in the process of gold leaching, the amount of dissolved oxygen depends on the atmospheric pressure. Thus, to carry out the redox attack of gold and cyanide, the oxygen as oxidizing and reducing agents must be controlled to maintain the proper dosage of cyanide and alkalis for acceptable gold recovery performance [7].

The solid-liquid reaction has different possibilities for the control of the reaction rate. Some control possibilities can be evaluated depending on the particles sizes, which can be constant or size decreasing [8,9]. In the case of constant particle size, the reactions could be governed by external diffusion in the hydrodynamic boundary layer, diffusion through a layer of ash generated in the reaction, the chemical reaction on the active surface or a combination of the precede phenomena. Similarly, particles with decreasing size may be driven by the same controls, except for diffusion into the particle.

The knowledge of these controls is critical to set leaching kinetic models. In the literature, many models are mentioned, but there is no universal model, as each particular mineral interacts depending on their mineralogical structure, which will establish the way of controlling the kinetics [10–15]. Table 1 shows four models mainly used to the evaluation of the kind of reaction rate control.

Table 1. Model equations to control the rate of reaction between solid-fluid phases

Control type	Equation		τ
Eq.1. External diffusion with constant size	$\dfrac{t}{\tau} = 1 - \left(\dfrac{r_c}{R}\right)^3 = X_B$	(1)	$\dfrac{\rho_B \cdot R}{3b \cdot k_P \cdot C_L}$
Eq. 2, Diffusion in ash	$\dfrac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$	(2)	$\dfrac{\rho_B R^2}{6b D_e C_{L\_Sol}}$
Eq.3 Chemical Reaction	$\dfrac{t}{\tau} = 1 - \dfrac{r_C}{R} = 1 - (1 - X_B)^{1/3}$	(3)	$\dfrac{\rho_B}{b \cdot k \cdot C_{L\_Sol}{}^n}$
		(4)	
Eq.4. External diffusion to particles of decreasing size	$\dfrac{t}{\tau} = 1 - \left(\dfrac{R}{R_0}\right)^2 = 1 - (1 - X_B)^{2/3}$		$\dfrac{\rho_B \cdot y_{fA} \cdot R_0{}^2}{2 \cdot b \cdot C_{L\_Sol} \cdot D_e}$

The central role of process modeling design and operation in mining plants is now widely recognized and accepted [16–20]. Although most early models have been "steady state", more recently, "dynamic" models have been developed for processes with variables and/or unstable behavior over time. Indeed, there is an increasing tendency towards models of "high fidelity", which can predict the paths of key variables that affect the process performance, safety and economy [18]. The demand for more accurate models can often be attributed to the need for generating high returns in the minimum processing time, which have already been subjected to gradual improvements along several decades. In other cases, this trend is generated from strict environmental restrictions, safety and product specifications under which many mining processes commonly operate.

Under this, the modeling of leaching of gold, represents an extremely challenge from a scientific-technology point of view, since this type of process has an enormous inertia and significant number of physical-chemical phenomena, transport mass, energy, amount of momentum and at least three phases coexisting and reacting, which gives considerable complexity to the management and control. In this way, possible changes or fluctuations in the system parameters such as changes in ore grades, mineral type, type and amount of leaching reagents, impurity concentration, agglomeration of the ore, environmental effects and ionic strength could be better controlled.

On the other hand, gold production in Ecuador is one of the most important mining activities; however, it presents environmental problems associated with the use of cyanide in the production chain. Although several researchers about modeling the kinetics of gold leaching had been carried out, the knowledge of the particular conditions for a particular ore is needed. This research evaluates the kinetic control of gold leaching, towards the determination of the operational parameters and the right amount of cyanide to be used during the leaching process in a gold leaching plant from the south of Ecuador.

2. EXPERIMENTAL PART

A mineral previously concentrated by flotation, with a concentration ratio of one ton of ore concentrated from 20 tons of ore milled was used for this research. The law of floated material, determined by fire assay was 106.48 g/ton. To perform the corresponding analysis, a sample of 500 g of the mineral was taken and processed to obtain a concentrated sample of 10 g of mineral, which was used to determine the ore grade.

The particle size distribution analysis was conducted under ASTM standards. A representative sample of 1000 g of concentrated was sieved through 50, 60, 100, 140 and 200 mesh for a period of 15 minutes in an electric sieve. After this, each sample was removed from the screens and was weighed to make the respective calculations to obtain the particle size distribution of the material.

Comparative tests of gold recovery by leaching the ore concentrate treated and untreated were conducted. This analysis allowed to know the percentage of gold recovery, using a pre-treatment which consisted of the addition of calcium hypochlorite for 2 hours, in order to remove the remaining reagents from the flotation process. The ore was subjected to agitation in batch reactors at an alkaline pH of 12 and 70% (v/v) of calcium hypochlorite. Subsequently, the pulp was drained with water for the experiments.

2.1 Cyanide leaching

The cyanidation test in a stirred tank is a standard test that seeks to determine specific consumption of reagents for a particular mineral and kinetic curves of evolution in time for gold leaching. The operational parameters are shown in Table 2.

Besides, SEM observations and EDX elemental composition of samples were performed in mineral samples before and after leaching experiments with SEM Phenom ProX microscope. Prior to the observations, the samples were dried in a stove at 38°C for 24 hours, then the samples were fixed in holders with conductive tape and sputter with carbon. The SEM conditions were 15kV and 10-5 torr in a sample holder provided with charge reductor.

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Table 2. Operational parameters

Parameter	Value
Solids percent	15%
NaCN concentration	300-800 mg/L
Reaction time	4 hours
Effective reactor capacity	27.1 L
Reactor capacity	34.61 L
Reactor design	Draft type " suction tube "
Fluid movement	mechanical stirring by paddle type impeller
Stirring speed	490, 560 and 700 rpm.
Operating temperature	Ambient temperature
Oxygen injection rate	Auto sucked in " suction tube " by mechanical agitation
pH	10.5

3. RESULTS AND DISCUSSIONS

3.1 Gold and silver concentration.

To determine the law of Au and Ag, analyses by fire assay were performed, whose values were 106.4 and 58.84 g/ton for Au and Ag respectively. Regarding sieve analysis of floated ore, the particle size distribution was expressed as percentage retained versus cumulative particle diameter in micron fraction. The experimental data was adjusted by the application of Weibull equation, which describes the size distribution of solids in comminution processes, as shown in equation 5.

$$f(x, P_{80}, m) = \left(1 - \exp\left(\ln(0.2) \cdot \left[\frac{x}{P_{80}}\right]^m\right)\right) \cdot 100 \quad (5)$$

Where f (x, m, P_{80}) corresponds to a particle size distribution spread, the 80th percentile of the distribution of particle size and particle size distribution is the percentage. With the equation 5 and its model parameters, it is possible to estimate the $\overline{d_{50}}$, solving numerically the equation to a value

equal to 50%. In this case, the calculated value for the average size is equal to 86.1 microns.

3.2 SEM-EDX analysis.

Figure 1 shows the mineral image and its elemental analysis. Table 2 summarizes the elemental concentration found after this characterization.
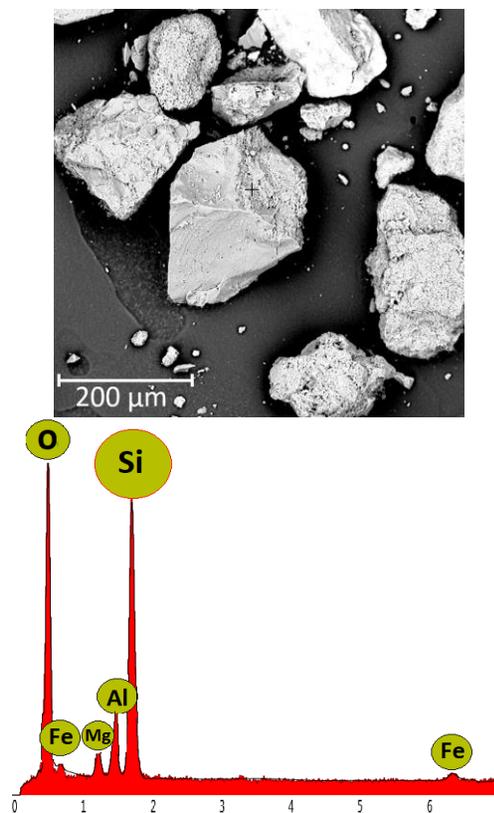

Figure 1. SEM-EDX analysis of the grain floated mineral.

Four measurements on the same sample were performed; it was observed that the surface exposed to chemical attack presented elements such as Si, O, Sb, Fe, C, Al, Mg and K.

The results draw the attention since there is not Au, Ag or S on the mineral surface. This indicates that both Au and Ag are within the mineral particle and reagents responsible for the leaching reaction must penetrate a siliceous structure in order to get places where the chemical reactions occur. Therefore, it is quite plausible to assume that the limiting step of the reaction rate must be controlled by a mechanism of penetration of reagents to the centers where are

located the Au and Ag.

Table 2. Grain composition

Element Name	Weight Concentration
Silicon	26.3
Oxygen	60.2
Aluminium	5.9
Magnesium	3.4
Iron	4.2

3.3 Kinetic control analysis of floated ore with sodium cyanide in alkaline medium

To carry out the leaching tests, it was first necessary to perform a pre-treatment in the floated mineral, in order to remove chemical species that allow concentrating the ore.

3.3.1 Pre-treatment of floated ore.

To perform the oxidative pre-treatment on the surface of the concentrate, we proceeded to contact an amount of solid sample with an oxidizing solution of 70% calcium hypochlorite, in order to adjust at alkaline pH of 12. The pre-treatment took a total time of three hours. Similarly, exploratory leaching tests were performed without pretreatment for comparison of the two possible operating scenarios, as shown in Figure 2.

Figure 2 shows the gold concentration after the leaching of both ores, with treatment and without treatment. The untreated leaching process produces a low gold recovery because the floated mineral is covered with reagents, which block or passivate the gold surface, avoiding redox process needed to leaching of Au from the metal surface. Therefore, the use of calcium hypochlorite 70% for removal or disposal of the products used in the flotation process is relevant.
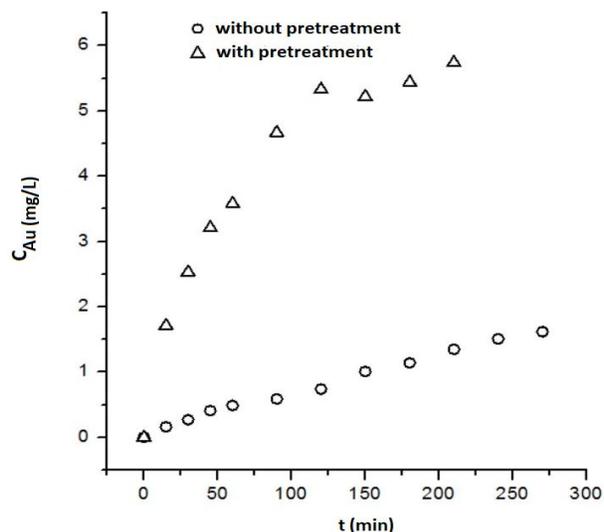

Figure 2. Effect of pre-treatment in the leaching dynamics of a concentrated ore.

3.1.2 Effect of the cyanide concentration on reaction rate.

The effect of the sodium cyanide concentration in the leaching reaction velocity of the floated concentrate pre-treated is showed in Figure 3. The y axis represents the gold conversion fraction and the x axis the time in where the reaction was produced.
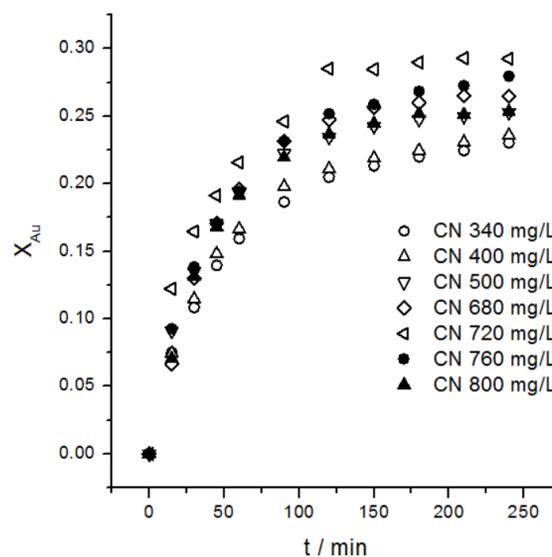

Figure 3. Conversion of Au at different dosages of sodium cyanide (stirring speed: 700 RPM)

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To evaluate the kind of kinetic control in the leaching process in a systematic way, it was varied the dose of cyanide, keeping constant all of the other operational parameters. The experiments were conducted at 700 rpm of rotation speed, the results are shown in Figure 3. In this experiment, the cyanide concentration remained around the initial concentrations in each case. In this figure, it is clear that there is a dependence on the concentration of sodium cyanide. Likewise, we can verify that at high concentrations of cyanide there is a decreasing in the leaching rate. To verify what kind of speed control system governs the dissolution process, the classic kinetic models regarding the conversion of solids in aqueous media were used. Figure 4 represents the graphical modelization of kinetic control when the cyanide concentration is varied. The models applied were previously presented in the equations 1-4 in Table 1.
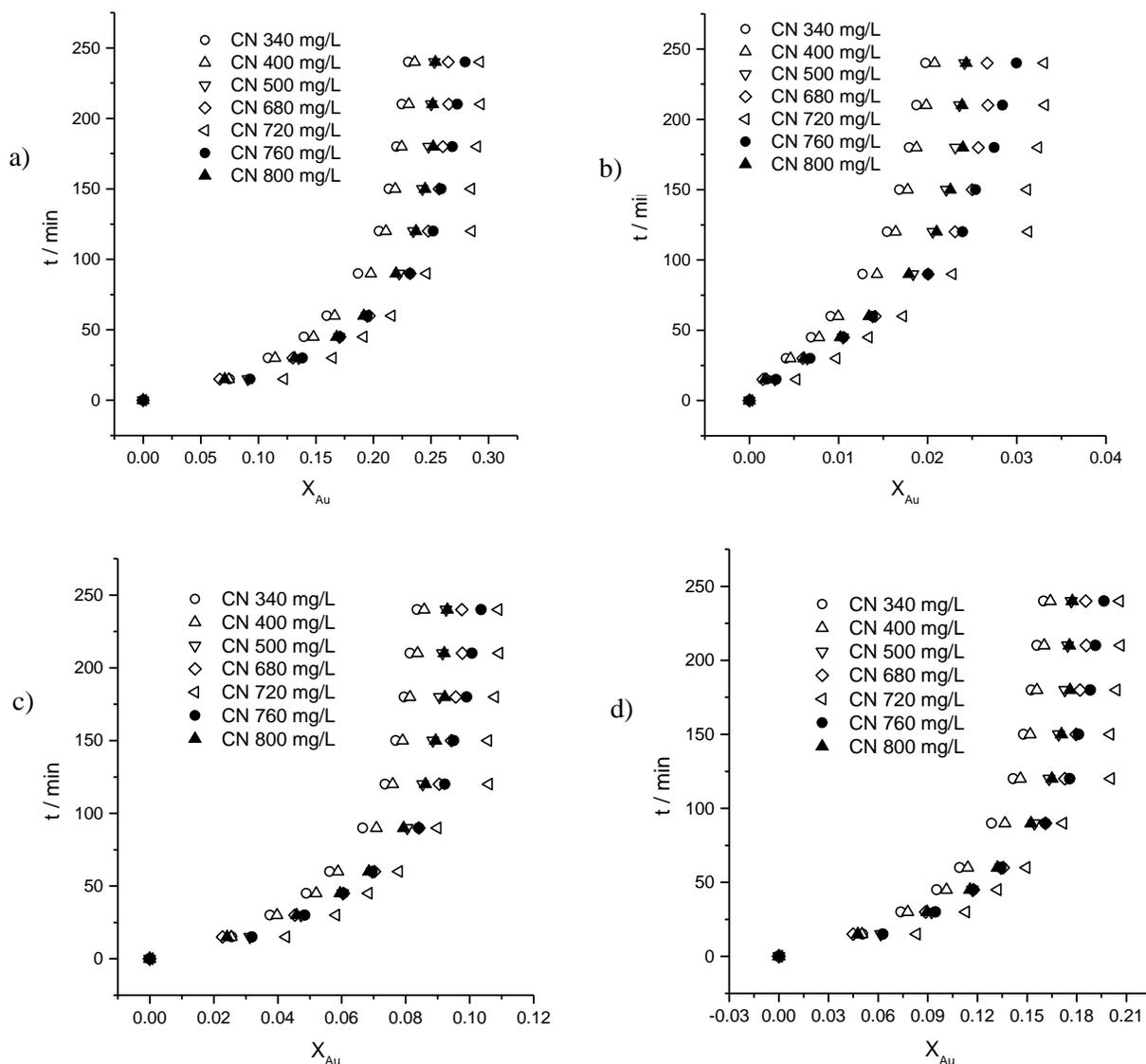

Figure 4. Representation of complex controls kinetic adjusted to different control models at 700 RPM: a) eq. 1, b) eq. 2, c) eq. 3, d) eq. 4. (according to Table 1)

The analysis of Figure 4 highlights the possibility that the concentrate can be treated with sodium cyanide as a complex agent of Au, and oxygen as an oxidizing agent, for the leaching process, whose speed reaction is governed by mass transfer within the particle, which was verified graphically. Similarly, it was verified that at one point, the dissolution process shows a change in its resistance, associated with a change in the slope at the model representation of diffusion through the ash layer. This can be explained because as more of the reaction is generated more refractory ash in the depths of the etched particle is generated, making it more difficult to penetrate the reagents which produce the complex and oxidation of Au.

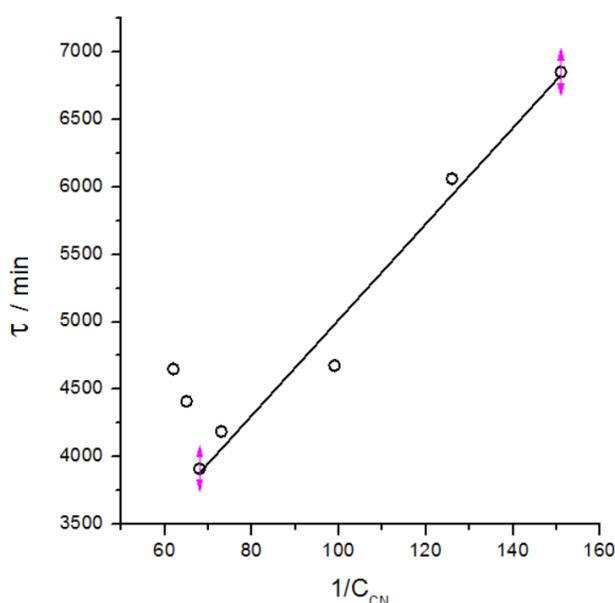Figure 5 shows the linearization of the model diffusion rate for ash.

Figure 5. Control characteristics of kinetic parameter of diffusion rate for ash at 700 RPM

From Figure 5, it is possible to calculate the slope of the graph which represents the diffusion in ashes. Thus, the representation of τ as an inverse function of the concentration of the bleaching agent is shown in Figure 6. One characteristic of this figure is the linearity of τ respect to the inverse of the concentration, as expressed explicitly the equation

derived from τ in Table 1, for kinetic diffusion control ashes. However, between the inverse values of the concentration of sodium cyanide around 60 mg/L and 70 mg/L, a disruption occurs in the values of τ, probably attributed to the formation of gold oxides on the active surface, due to the local effect of pH caused by the high concentration of cyanide ions in the vicinity of the gold surface. Therefore, despite the increase in the concentration of sodium cyanide for producing more gold recovery, it must be restricted to use the optimal dosages, since the excessive use of cyanide caused loss of efficiency in the dissolution process, with wasteful spending of cyanide and low gold recovery.

3.1.3 Effect of stirring speed on the reaction rate.

The effect of mechanical agitation in leaching reactors was studied, in order to observe if there is any dependency on this factor in the reaction rate. According to the analysis discussed in the previous section, it was verified that the kinetic control occurs by diffusion in ash, which is no dependent on the agitation. However, external diffusion theory explains that there is a strong dependence between the speed and the controlled reaction mechanism. Figure 6 shows the effect of the rotational speed on the kinetic control.

In Figure 6, the kinetic analysis of the reaction controlled by diffusion through the ash layer is shown. The analysis of slopes at different regimes of agitation shows the coupled controls of reaction rate by external diffusion.
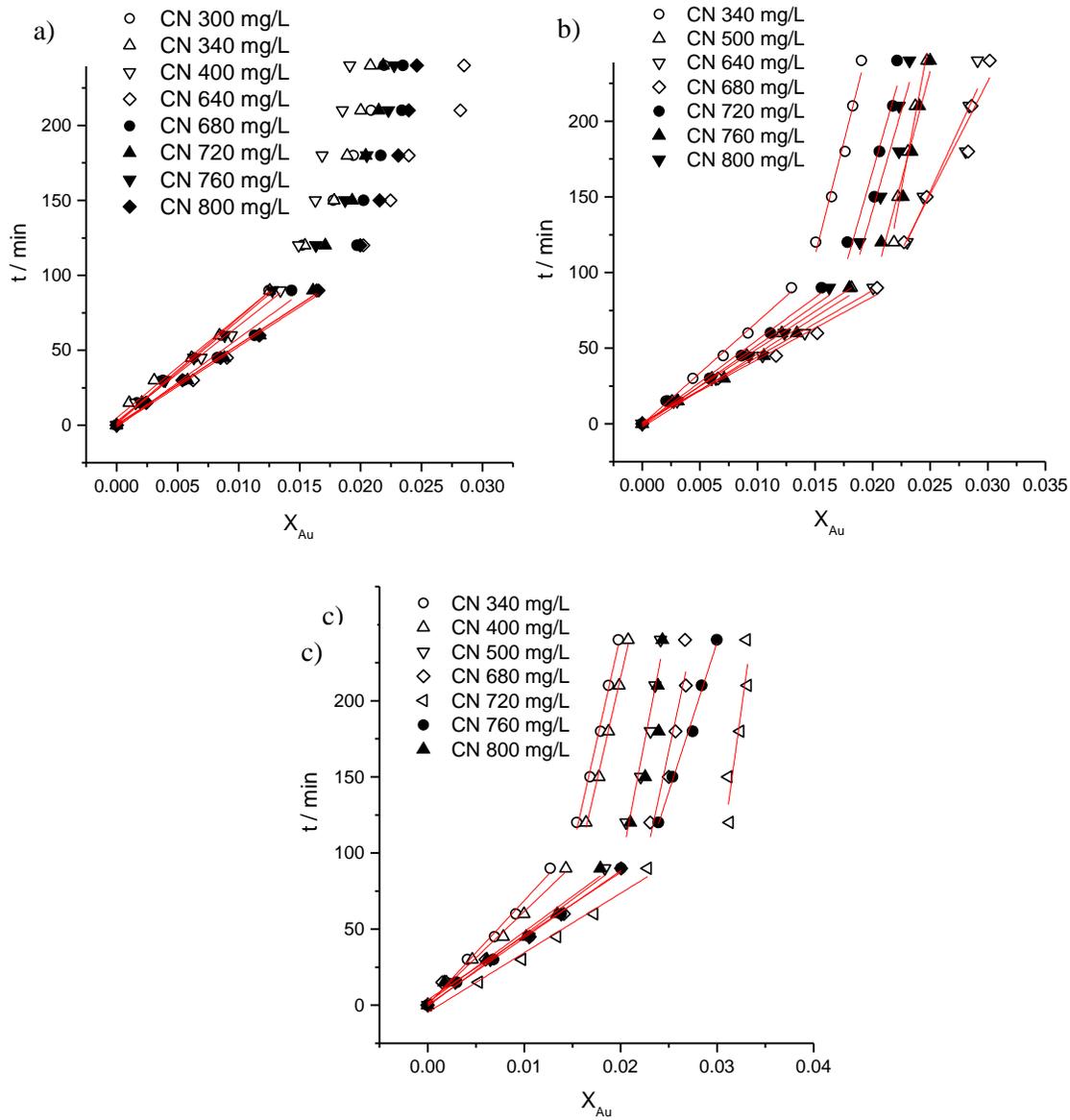
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Figure 6. Representation of control kinetic conversion from Au to Au-CN complex for different dosages of sodium cyanide at a stirring rate of: a) 490 RPM, b) 560 RPM, c) 700 RPM
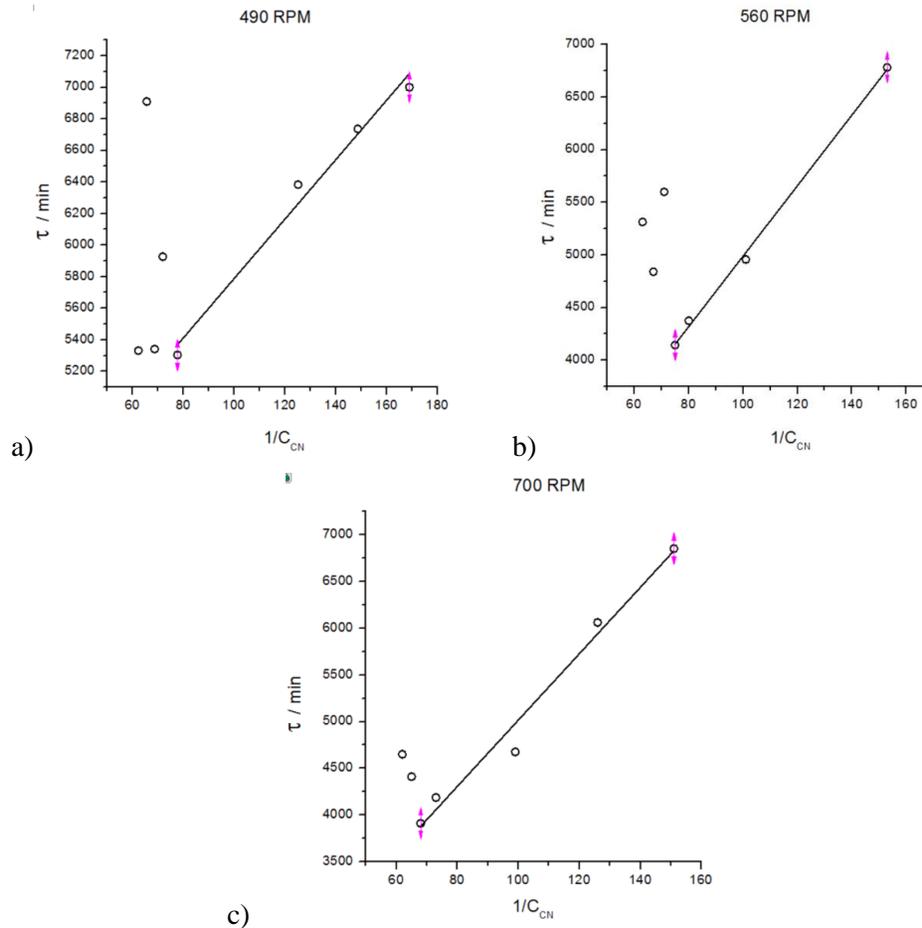
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Figure 7. Representation of characteristic kinetic parameter τ of control of velocity speed to diffusion of ash at different agitation speeds: a) 490 RPM, b) 560 RPM, c) 700 RPM

Figure 7 shows the representation of τ respect inverse of the concentration of sodium cyanide for three different regimes stirring. In this figure, it is possible to note that there is independence from the variation of τ with agitation, although at the lower test speed there is a slight effect, probably because at lower speeds the mineral tends to settle in the bed reactor causing an imperfect mixing. However, in general terms, it is noted that the stirring speed in the operating limits tested not showing relevant effects on the overall performance of the leaching reaction. On the other hand, the velocity rate is not constant as it depends on the agitation, particle ratio and the concentration of the reagents. Furthermore, SEM-EDX analysis confirms that the controlling step of the reaction rate occurs by diffusion through ash.

4. CONCLUSIONS

The kinetic control of the cyanide leaching over a pre-floated mineral was studied. The experimental conversion of Au was about 30% of soluble Au. The process required an oxidative pretreatment with calcium hypochlorite at alkaline pH in a stirred tank for at least 3 hours to remove the remaining flotation reagents. Indeed, preliminary tests showed that the untreated mineral leached substantially less than the mineral pre-treated, indicating the passivation effect of these agents on the active surface of the mineral. Moreover, the kinetic control on the rate of leaching was verified by the application of solid-liquid models. The kinetic control mechanism corresponds to control the mass transfer of leaching through a layer of ash generated during the reaction. Similarly, it was verified that no other controls influence the leaching rate. This evidence is supported by SEM-EDX analysis, which showed the absence of Au and Ag in the surface of the particles arranged to be attacked by the leaching reagents, indicating that these reagents must necessarily cross the mineral

structure in which the metal is immersed. Further kinetic experiments showed a change in the resistance to mass transfer around 100 minutes after the start of the reaction. After this time, kinetic control is verified by mass transfer, with greater resistance, since it is more refractory to oxidative attack on the mineral core of mineral species. From the chemical point of view, it was found that there is an operating limit on the use of cyanide corresponding to approximately 650 mg/L of sodium cyanide. Values above this dosage indicated that the leaching rate and recovery decrease dramatically.

5. ACKNOWLEDGMENTS

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