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A Comparative Study of Cyanide and Thiosulfate for Silver Leaching from Tailings: A Kinetics Approach

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Abstract: The mining process has always generated residues that often still contain valuable metals. This work focuses on the re-processing of these residues by evaluating and comparing two reagents that can extract valuable silver from tailings. A preliminary kinetic study of silver leaching was conducted in both cyanide and thiosulfate media, and a comparative analysis was performed to determine the optimal leaching conditions. The mining residue was found to contain 83 g/ton of Ag and 0.28 g/ton of Au. This study, carried out for both cyanide and thiosulfate, involved determining the effects of the reagent concentration, temperature, and pH. For the reagent concentration, apparent reaction orders of n = 0.0531 and n = 0.41 were determined for cyanide and thiosulfate, respectively. The apparent activation energies were E_a = 21.7 kJ/mol for cyanide and E_a = 23.13 kJ/mol for thiosulfate, indicating mixed-control kinetics in both systems. Under the conditions studied, maximum silver recoveries of 92% and 93% were achieved using cyanide at 323 K and thiosulfate at 328 K, respectively. Notably, pH had no significant effect on the cyanide system, whereas for thiosulfate, the reaction order was n = 3.27. The results show similar behavior in both systems, but the thiosulfate system is more attractive due to its non-toxic nature and lower cost.

Keywords: tailing re-processing; thiosulfate; cyaniding; silver leaching; kinetics study

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1. Introduction

In Mexico, mining is one of the oldest economic activities, with a long tradition of processing minerals containing gold and silver. Over the years, various technologies have been employed, ranging from patio leaching and Pachuca tanks to grinding, flotation, and cyaniding circuits. More than 500 years of mining activity have resulted in significant environmental impacts, including acid mine drainage, waters transporting solids and

elements in the form of radicals, abandoned mineral deposits, and waste from processed minerals known as tailings. The latter are particularly abundant in the state of Hidalgo, Mexico, with an estimated volume of approximately 110 million tons [1]. These tailings contain significant amounts of silver (25–120 g/ton) and gold (0.3–1.5 g of Au/ton) [1–5], which remain trapped in pyritic and quartziferous minerals, hindering their adequate extraction. The presence of species that consume reactants, such as cyanide, and the encapsulation of precious metals have also limited the efficiency of the conventional extraction processes [5–9].

Several research studies have focused on leaching silver from tailings, with cyanide-based systems receiving the most attention and thiosulfate-based systems being less explored: an O_2–thiosemicarbazide system has also shown promising results [10]. Cyaniding has been the dominant method for extracting silver for over a century, primarily due to ability of CN^- ions to form stable complexes with silver in the presence of oxygen. However, this system has significant drawbacks, including its harmful environmental impact and limited effectiveness in leaching refractory minerals [11]. Furthermore, cyanide's toxicity poses serious health risks, and its use is becoming increasingly restricted globally [12]. Exploring alternatives to cyanide is motivated by the need to improve the extraction of precious metals from refractory minerals, where cyanide exhibits poor selectivity and results in low metal recovery. In contrast, thiosulfate-based leaching systems are considered a non-toxic alternative to traditional processing [13–16] and a method for dissolving refractory minerals [17,18]. Thiosulfate has an advantage over cyanide in terms of its selectivity for extracting silver from refractory phases, although its instability is a significant drawback. Researchers continue to explore alternative complexing reagents to cyanide, such as a thiosulfate–potassium ferricyanide system [19] and copper–tartrate–thiosulfate solutions [20]. This study compares the leaching kinetics of silver from tailings using both cyanide and thiosulfate systems.

The development of a thiosulfate-based leaching system for extracting silver from refractory ores represents a significant innovation in hydrometallurgy [21,22]. This technology has the potential to provide a more sustainable and environmentally friendly alternative to traditional cyaniding methods, which are often associated with environmental and health risks. Notably, the selective properties of thiosulfate enable the efficient extraction of silver from complex ores, reducing the need for energy-intensive processing methods and minimizing the waste generation.

Although thiosulfate has disadvantages such as a high reagent consumption, difficulties in gold and silver recovery, and limited industrial adoption, it offers interesting advantages, including lower toxicity and reduced health and environmental risks. Additionally, thiosulfate can leach gold and silver faster than cyanide in certain cases, with less interference from impurities in refractory minerals, and its cost is approximately 50% cheaper than cyanide, which offsets its high consumption. Furthermore, gold and silver recovery is feasible using sodium dithionite, achieving high recoveries [17].

The successful implementation of this technology could have far-reaching implications for the mining industry, enabling the efficient and responsible extraction of precious metals from refractory ores, as has occurred in other areas of study [23,24]. Future applications of this technology could include developing mobile processing units for remote mining operations or integrating thiosulfate-based leaching systems into existing mining infrastructure. As the demand for sustainable and environmentally responsible mining practices continues to grow, this innovation has the potential to play a critical role in shaping the industry's future.

Similarly, studies have evaluated the effectiveness of both cyanide and thiosulfate in leaching silver from residues generated by the mining and metallurgical industry, as

well as small-scale mining [25–27], with favorable results obtained in both systems. However, the use of non-toxic reagents prevails and is preferable due to environmental and health concerns.

2. Materials and Methods

2.1. The Experimental Materials

The materials used in this study were tailings from the Velasco tailing dam, located in the state of Hidalgo, Mexico. The samples were taken from the tailing dam, brought to the laboratory, and subjected to quartering and homogenization to obtain a representative sample.

2.2. The Experimental Equipment

The equipment used in this study included the following:

- An X-ray diffractometer (XRD PHILIPS X'PERT, Eindhoven, The Netherland) for mineralogical characterization of the samples; and the indexing for the obtained diffractograms was carried out with the MATCH version 1.1 software (developed by Crystal Impact, Bonn, Germany).
- An atomic absorption spectrometer (AAS- Perkin Elmer Model 2100, Waltham, MA, USA) for elemental quantification of the samples;
- A 1000 mL glass reactor with a flat bottom, mounted onto a heating plate with magnetic stirring;
- A thermometer to control the system temperature;
- An analytical digital balance (OHAUS Analytical Plus AP10S, Parsippany, NJ, USA) with a precision of 0.001 g (1 mg) for weighing the samples and reagents.

2.3. The Experimental Methods

Sample preparation: The sample was prepared to a particle size of −200 to +270 mesh (53–74 μm) before analysis.

Sample characterization: Characterization of the sample was performed using XRD and AAS.

Leaching experiments: Leaching experiments were conducted with cyanide and thiosulfate. The experimental conditions were as follows:

Cyanide leaching: Cyanide concentration: 5×10^{-2} to 5.1×10^{-3} M; temperatures between 288 and 333 K; a sample weight of 40 g/L; sodium hydroxide [NaOH] concentrations ranging from 5×10^{-2} to 1.1×10^{-3} M; a reaction volume of 500 mL; and a stirring speed of 750 rpm.

Thiosulfate leaching: Sodium thiosulfate [$Na_2S_2O_3$] concentrations from 0.2 to 2.4 M; temperatures between 288 and 333 K; a sample weight of 40 g/L; pH values between 8 and 11; and a reaction volume of 500 mL.

The experimental reaction rate constants (k_{exp}) were determined from the silver leaching curves, which represented the fraction of silver leached as a function of time. The calculation of the k_{exp} values was based on the progressive reaction period, excluding the induction time and the final stabilization period of the reaction. By analyzing the curves obtained for both cyanide and thiosulfate media (the concentration of the reagent, temperature, NaOH concentration, and pH), the k_{exp} values were calculated, providing insights into the kinetics of the silver leaching process.

2.4. Monitoring and Analysis

During the leaching experiments, the solubility of Ag in the system was monitored, and the samples were analyzed using atomic absorption spectroscopy. The pH was maintained

constant by adding 0.2 M NaOH. The results obtained were treated according to the fraction of Ag extracted in both systems.

3. Results and Discussion

3.1. Characterization of the Material

The average chemical composition of the study material is presented in Table 1. The dominant elements identified are silica, aluminum, calcium, iron, and potassium, accompanied by minor concentrations of manganese, magnesium, sodium, silver, and gold. Additionally, sulfur, titanium, phosphorous, zinc, lead, and copper are present as trace elements. This composition is consistent with previous studies on tailings from the same processing but different mineral veins, although variations in the Ag content are observed, with higher contents found in these residues [1,2,26].

Table 1. Average chemical composition of the Velasco waste tailings.

Element	wt. %	Element	wt. %
Si	29.32	Ag	83 [1]
Al	3.41	Au	0.28 [1]
Ca	2.69	S	0.38
Fe	2.41	Ti	0.16
K	2.40	P	0.031
Mn	1.21	Zn	0.036
Mg	0.70	Pb	0.031
Na	0.76	Cu	0.012

[1] These are in g/ton.

Furthermore, the X-ray diffraction analysis revealed the primary mineral phases comprising the material, including quartz, albite, berlinite, potassium jarosite, and natrojarosite, as shown in Figure 1.

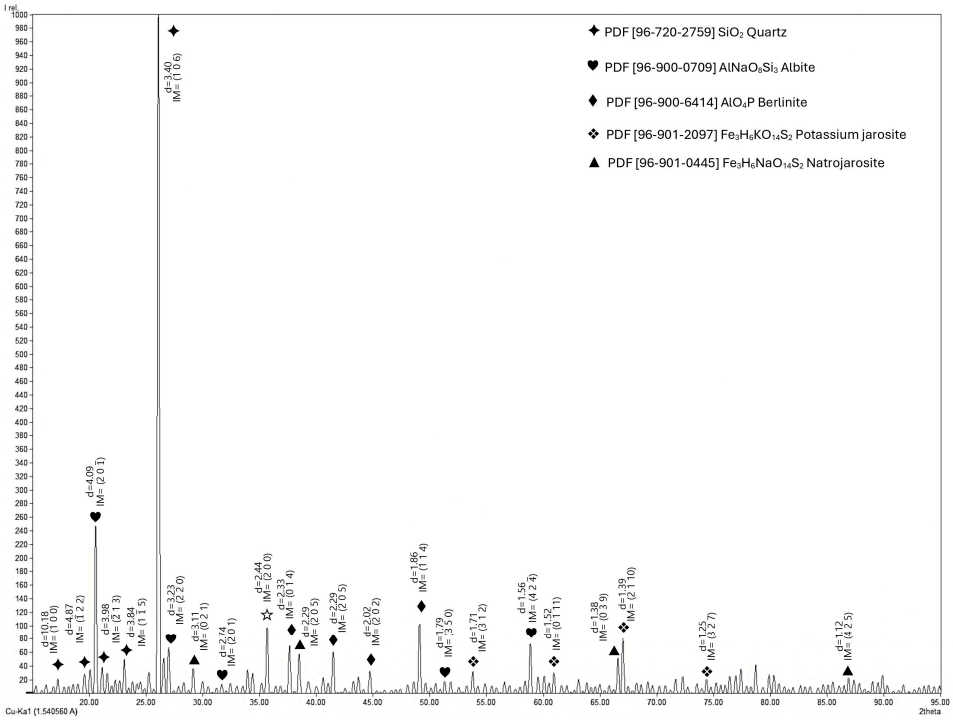

Figure 1. XRD spectra form samples of tailings from Velasco dam.

3.2. Kinetic Studies of Cyanidation in an Alkaline Medium

To elucidate the kinetic parameters governing the leaching of Ag from the tailings into cyanide media, a comprehensive experimental program was carried out. The effects of the cyanide concentration, temperature, and the NaOH concentration on the leaching process were systematically evaluated, allowing the reaction order and activation energy of the system to be determined.

Due to the complexity of the residual mineralization of the tailings, the basic stoichiometry of the cyaniding of the silver contained in them can be formulated considering that silver may be present in native form, as sulfide, and contained in jarositic compounds. For this, the chemical reactions occurring with cyanide are represented below:

Native silver:

$$4Ag_{(s)} + 8CN^- + O_2 + H_2O \rightarrow 4Ag(CN)_2^- + 4OH^- \quad (1)$$

Silver sulfide is governed by the following sequence of reactions in (2)–(4):

$$Ag_2S \rightarrow 2Ag^+ + S^{2-} \quad (2)$$

$$Ag_2S + 4CN^- \rightarrow 2Ag(CN)_2^- + S^{2-} \quad (3)$$

$$2S^{2-} + 2H_2O + O_2 \rightarrow 4OH^- + 2S \downarrow \quad (4)$$

Silver in jarosite compounds:

$$(K, Ag)Fe(SO_4)_2(OH)_{6(s)} + 3OH^-_{(aq)} \rightarrow 3Fe(OH)_{3(s)} + 2Ag\left(OH\right)_{(s)} + 2SO^{2-}_{4(aq)} + K^+_{(aq)} \text{Slow} \quad (5)$$

$$Ag(OH)_{(s)} + 2CN^-_{(aq)} \rightarrow Ag(CN)^{2-}_{(aq)} + OH^-_{(aq)} \text{Fast} \quad (6)$$

3.2.1. The Effect of Cyanide Concentration

The effect of cyanide concentration on the leaching process was studied by varying [NaCN] (5×10^{-2}, 3.06×10^{-2}, 2.04×10^{-2}, and 5.1×10^{-3} M) while maintaining constant conditions: [NaOH] at 1×10^{-2} M, a temperature of 298 K, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Samples were taken at predetermined times to monitor the dissolution of Ag, which was analyzed through atomic absorption spectrometry.

Figure 2A illustrates the relationship between the leaching time and the fraction of dissolved silver. From the slopes of the curves, the experimental kinetic constants were determined, and they were similar, suggesting that changes in the cyanide concentration had no significant impact on the overall leaching process.

On the other hand, Figure 2B shows, in a logarithmic form, the treatment of the data obtained from Figure 2A. Clearly, an apparent reaction order of $n = 0.0531$ can be seen for the range of CN^- concentrations studied. This confirms that CN^- has virtually no effect on the overall rate of the cyaniding process. This suggests that the reaction is controlled by factors such as the contact surface between CN^- and Ag, temperature, or the presence of reactants (maybe NaOH) [11,12]. Therefore, silver cyaniding is a zero-order reaction, meaning that the reaction rate does not depend on the cyanide concentration. Thus, the reaction may be controlled through cyanide's diffusion to the silver surface rather than the cyanide concentration itself to this effect.

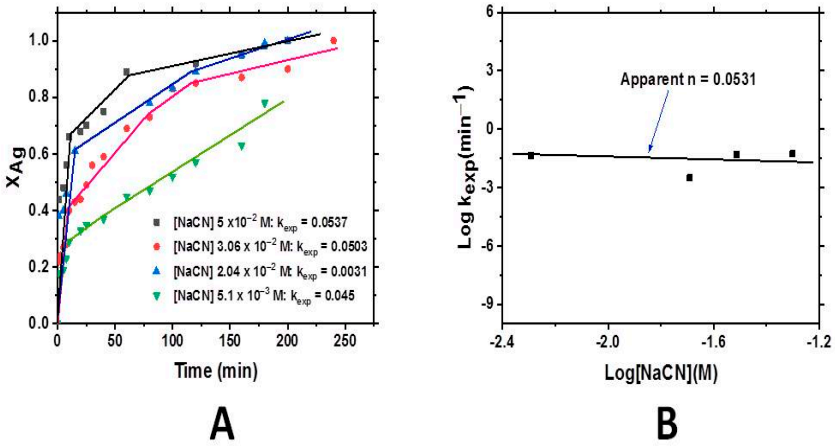

Figure 2. Silver leaching with cyanide; effect of [NaCN] concentration: (**A**) k_{exp} and (**B**) reaction order n = 0.0531.

3.2.2. The Effect of Temperature on Cynide Leaching

The effect of temperature on the leaching process was studied by varying the temperature (288, 298, 308, 323, and 33 K) while keeping the other parameters constant: [NaCN] at 2.4 × 10^{-2} M, [NaOH] at 1 × 10^{-2} M, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Figure 3A shows the values of the cyanided silver fraction as a function of time for each temperature tested. From the observed data, the corresponding k_{exp} values were determined and are shown.

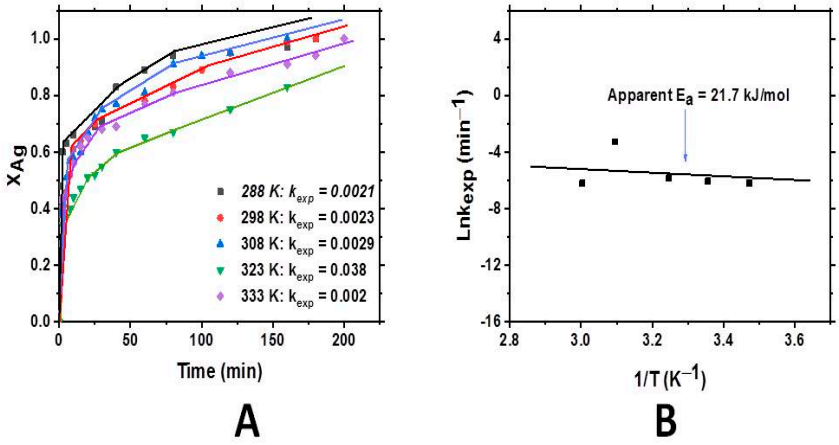

Figure 3. Kinetic study of silver cyaniding; temperature effect: (**A**) k_{exp} and (**B**) E_a = 21.7 kJ/mol.

Furthermore, the apparent activation energy of the system was determined by plotting ln k_{exp} vs. 1/T × 10^3 (Figure 3B). The obtained value was E_a = 21.7 kJ/mol, indicating a mixed-control process where both chemical and diffusion processes influenced the reaction rate. This value supports the conclusion that the process is controlled by both the diffusion of cyanide towards the Ag surface and the chemical reaction of complexation.

3.2.3. The Effect of OH^- Concentration

The effect of OH^- concentration on the leaching process was studied by varying [NaOH] (5 × 10^{-2}, 3 × 10^{-2}, 1 × 10^{-2}, 3.3 × 10^{-3}, and 1.1 × 10^{-3} M) while keeping the other parameters constant: CN^- at 2.4 × 10^{-2} M, a temperature of 298 K, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Figure 4A shows the fraction of dissolved silver as a function of the reaction time.

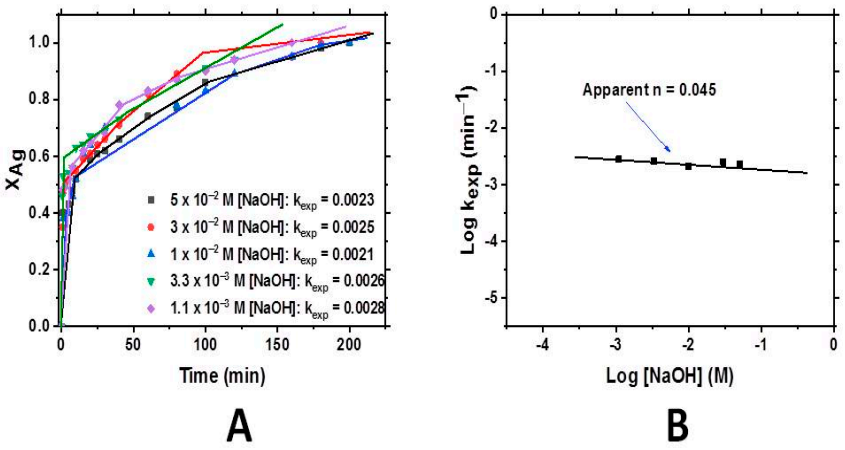

Figure 4. Kinetic study of silver cyaniding; [NaOH] concentration effect: (**A**) k_{exp} and (**B**) reaction order, n = 0.045.

Consistent with the previous analysis, the data from Figure 4B were treated to graph the relationship between log k_{exp} and log OH^-, thereby assessing the impact of this variable on the reaction rate. The results yielded a reaction order of n = 0.045 within the studied range of OH^- concentrations. These findings indicate that the OH^- concentration has no influence on the overall process rate. Apparently, this variable has no significant impact on the leaching rate of silver. This could suggest the rapid decomposition of silver-containing species, followed by the rapid complexation of silver by cyanide ions. Then, the retarding effect is the diffusion of cyanide and/or OH^- towards the Ag surface once it is exposed [11].

3.3. Kinetic Studies of Alkaline Leaching in a Thiosulfate Medium

A series of experiments was undertaken to determine the rate of dissolution of the silver present in the tailings utilizing thiosulfate [$S_2O_3^{2-}$] and evaluating the effects of varying the thiosulfate concentrations, temperature, and pH.

As in the case of cyaniding, the stoichiometry of silver leaching into the thiosulfate medium can be described considering native silver, silver sulfide, and silver contained in jarositic compounds. The reactions that represent the leaching process in these cases are as follows:

Native silver:

$$2Ag^+_{(s)} + O_2 + Na_2S_2O_{3(aq)} + NaOH_{(aq)} \rightarrow NaAg[S_2O_3] + 2Na^+ + 2OH^- \quad (7)$$

Silver sulfide is governed by the following sequence of reactions (8)–(10):

$$Ag_2S \rightarrow 2Ag^+ + S^{2-} \quad (8)$$

$$Ag_2S_{(s)} + O_2 + Na_2S_2O_{3(aq)} + NaOH_{(aq)} \rightarrow Ag_2[S_2O_3] + 2Na^+ + S^{2-}_{(aq)} \quad (9)$$

$$2S^{2-} + 2H_2O + O_2 \rightarrow 4OH^- + 2S \downarrow \quad (10)$$

Silver in jarositic compounds:

$$(K, Ag)Fe(SO_4)_2(OH)_{6(s)} + 4OH^-_{(aq)} \rightarrow KOH_{(aq)} + AgOH_{(s)} + Fe(OH)_{3(s)} + 2SO_4^{2-} \text{Slow} \quad (11)$$

$$2Ag(OH)_{(s)} + Na_2S_2O_{3(aq)} \rightarrow Ag_2S_2O_{3(aq)} + 2OH^-_{(aq)} + 2Na^+ \text{Fast} \quad (12)$$

3.3.1. The Effect of Thiosulfate Concentration

The effect of thiosulfate concentration on the leaching process was studied by varying [$Na_2S_2O_3^{2-}$] (0.2, 0.4, 1, 1.2, and 2.4 M) while maintaining the other variables as constant: a temperature of 298 K, a pH of 9, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Figure 5A illustrates the fraction of leached silver as a function of the reaction time. From the slopes of the lines, the experimental reaction rate constants (k_{exp}) were determined. However, no increase in the reaction rate is observed as the thiosulfate concentration increases. This could be due to the reaction becoming saturated with thiosulfate, meaning that further increases in its concentration do not lead to increased reaction rates, and in this part of study, the reaction is controlled by diffusion rather than chemical control.

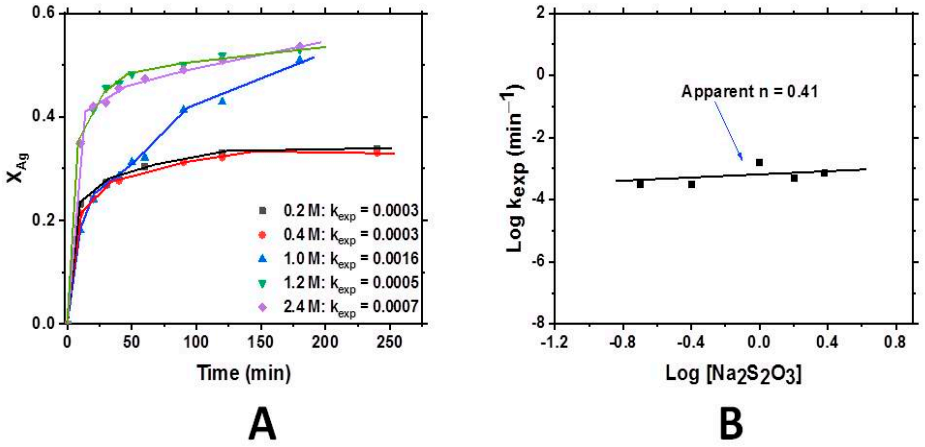

Figure 5. Kinetic study of silver leaching; effect of [$Na_2S_2O_3$] concentration: (**A**) k_{exp} and (**B**) reaction order n = 0.41.

In Figure 5B, dependence of log k_{exp} on log [$Na_2S_2O_3$] is observed. It can be seen that in a range of thiosulfate concentrations from 0.2 to 2.4 M, a reaction order of n = 0.41 is established. The reaction order obtained can be attributed to the fact that at low thiosulfate concentrations, the leaching rate of silver is primarily governed by the complexing reagent itself. Nevertheless, as is evident from the figure, beyond a thiosulfate concentration of 1 M, the leaching rate increases with respect to further increases in the reactant concentration and is influenced by the oxygen levels in the system. In contrast, in other studies [28] where thiosulfate was used during the leaching of a SEDEX-type ore, a reaction order of 5.03 was established for silver leaching, indicative of a strong dependence of the reaction rate on the reagent concentration. In this case, the effect of thiosulfate is small due to the silver being in metallic form, which promotes its rate of leaching.

3.3.2. The Effect of Temperature on Thiosulfate Leaching

The effect of temperature on the leaching process was studied by varying the temperature (288–333 K) while maintaining the other variables as constant: [$Na_2S_2O_3$] at 0.25 M, a pH of 9, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Figure 6A illustrates the fraction of leached silver as a function of the reaction time. An increase in the reaction rate of silver leaching is observed as the working temperature is increased.

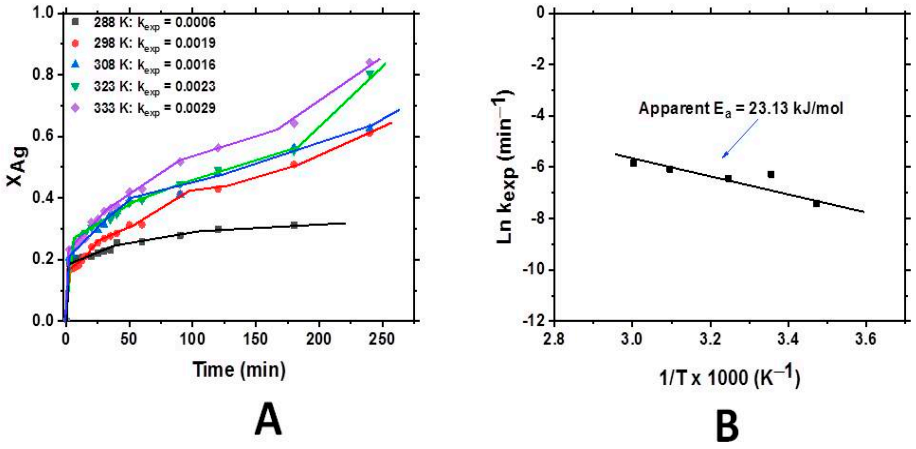

Figure 6. Kinetic study of silver leaching in [$Na_2S_2O_3$] media; temperature effect: (**A**) k_{exp} and (**B**) E_a = 23.13 KJ/mol.

The apparent activation energy of the silver leaching system using thiosulfate was determined by plotting the ln value of the experimental rate constants (k_{exp}) against the reciprocal of the working temperatures studied. The slope of the resulting line represents the activation energy. Figure 6B shows the treatment of these data, where E_a was determined to be 23.13 KJ/mol. This value is also indicative of a mixed-controlled process for the silver compound, facilitated by the thiosulfate ions, where both diffusion and chemical reactions play a roll. This value is slightly above the other values found [19,26,28,29], where silver leaching into a thiosulfate medium is controlled by the diffusion of the reagent towards the surface of the Ag and possibly by the desorption of the reaction products into the fluid. However, another study carried out in a thiosulfate–oxygen–copper system [25] found an activation energy of 43.5 KJ/mol during the leaching of the Ag contained in tailings from the same region, possibly due to the copper acting as a catalyst and forming complexes with thiosulfate, thereby increasing the rate of the chemical reaction as the temperature increased. In this case, of a mixed-control scenario, both chemical and diffusion processes influence the overall reaction rate. During chemical reaction, the thiosulfate ions react with silver to form a stable complex, which may be influenced by factors like the thiosulfate concentration, temperature, and pH. On the other side, the transport of the thiosulfate ions to the silver's surface or the removal of the reaction products may be limited by diffusion, which could be affected by factors like the stirring rate, particle size, and solution viscosity. So, in the overall reaction, both processes may occur simultaneously, with neither being entirely rate-limiting.

3.3.3. The Effect of pH

The effect of pH on the leaching process was studied by varying the pH (8, 9, 10, and 11) while maintaining the other variables constant: a temperature of 298 K, [$Na_2S_2O_3$] at 0.25 M, a stirring speed of 750 rpm, a solution volume of 500 mL, a sample weight of 40 g/L, and a total reaction time of 240 min. Figure 7A shows the fraction of leached silver versus the reaction time. Increasing slopes and k_{exp} values can be observed, indicating a significant effect of pH on the overall reaction process (n = 3.27), with a marked reaction rate at a pH of 10.

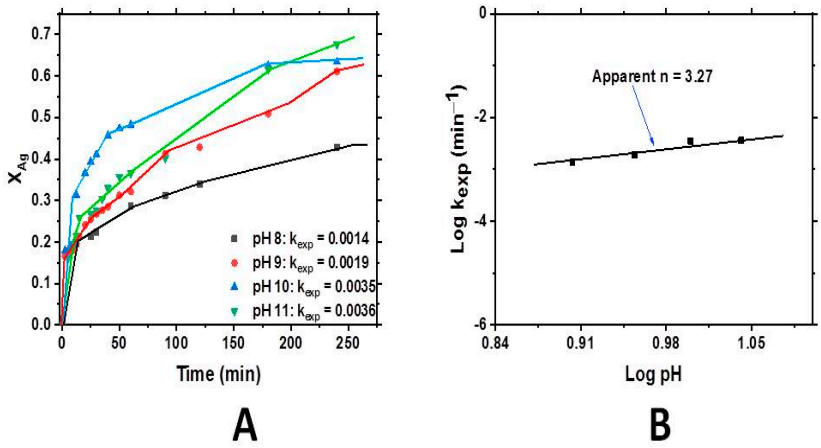

Figure 7. Kinetic study of silver leaching in [$Na_2S_2O_3$] media; pH effect: (**A**) k_{exp} and (**B**) reaction order, n = 3.27.

Figure 7B shows the dependence of k_{exp} on the pH values, confirming that pH has influence on the overall rate of the silver leaching reaction due to the reaction order of 3.27 obtained.

Finally, the optimal conditions for both cyaniding and silver leaching using thiosulfate systems were determined. Under these conditions, a maximum silver recovery of 92% was achieved through cyaniding at 323 K, and 93% leached silver was obtained when using thiosulfate at 298 K (Figure 8). Similar results have been reported in the treatment of Ag_2S, where a recovery of 90.5% was achieved [21]. However, despite both systems yielding comparable silver recovery rates, the use of cyanide is less desirable due to its toxicity and hazardous nature, as well as the higher working temperature required.

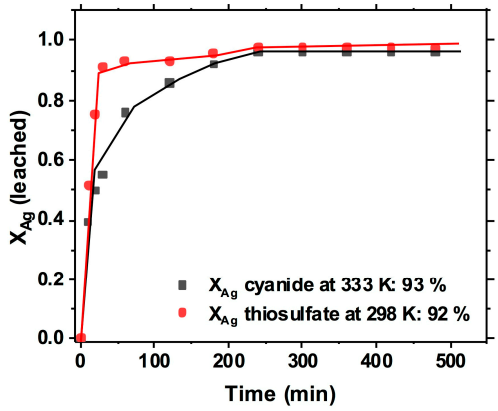

Figure 8. Comparison of cyaniding and thiosulfate leaching for silver recovery.

These silver recovery values are excellent and surpass those obtained through other methods such as high-energy milling, which achieved only 53% silver recovery [29], or chlorinated roasting with cyanide residues, which resulted in 54.7% recovery [30]. Other systems reported silver recoveries of up to 77.34% [31] and 70.38% in a copper–tartrate–thiosulfate system [20].

Several studies have highlighted the metallurgical challenges associated with recovering gold and silver from refractory mining waste. The primary limitation is the encapsulation of 60–65% of these metals within quartz and pyritic matrices, which hinders their dissolution through conventional leaching methods [32]. Furthermore, the presence of cyanide-consuming minerals such as pyrite and the association of silver with jarosite-type phases further complicate the metal recovery due to their low solubility and reactivity [6,32].

Cyanide remains the most effective lixiviant for silver extraction, particularly at concentrations above 0.004 mol/L and high temperatures, achieving up to 100% recovery [18]. Thiosulfate systems have a comparable performance at higher reagent concentrations [18]. However, the low selectivity of lixiviants in the presence of refractory minerals often results in the dissolution of unwanted species, thereby reducing the recovery efficiency [11].

Roasting refractory ores can lead to the formation of Fe-silicates that encapsulate silver oxide, limiting their recovery. However, the addition of Na_2SO_3 has been shown to mitigate this effect and enhance silver extraction [33]. Alkaline pretreatments (with Na_2S, NaOH, and $Ca(OH)_2$) have improved the gold and silver recovery, particularly at temperatures between 80 and 90 °C, by decomposing jarosites and liberating the encapsulated metals. This process has achieved recoveries of up to 80% for silver and 55% for gold [32,34]. Nevertheless, these processes may also release toxic elements, such as arsenic and lead, from the mineral structure, posing environmental risks [35].

4. Conclusions

Maximum silver recoveries of 93% and 92% were achieved at 298 K for the thiosulfate leaching system and at 323 K for the cyanide leaching system. At all of the temperatures tested, the process is mixed-controlled, influenced by both diffusion and chemical reaction systems. The activation energy (E_a) for the thiosulfate system was 23.13 kJ/mol, while for the cyanide system, it was 21.7 kJ/mol, being fairly similar in both cases. Both chemical and diffusion processes influence the overall reaction, where lixiviant ions react with the surface of metallic silver slowly and the transport of reactant ions to the silver's surface or the removal of reaction products is fast until the diffusion is slowed and a chemical reaction occurs rapidly, and then the aforementioned process occurs again and again. Based on the obtained data, it can be concluded that the thiosulfate system is the most suitable option due to its non-toxic nature and lower environmental impact compared to cyanide.

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