

A study of the metallic silver dissolution with the MEA-NH₃-Cu system

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ABSTRACT

Leaching of silver from minerals has been studied for decades. Recently, research has been focused on the substitution of cyanide (because of its high toxicity) from hydrometallurgical operations. In this sense, the development of alternative-green leaching solutions for the recovery of metallic silver from minerals and urban mines is necessary. In this research, a thermodynamic-kinetic study of the alternative system “monoethanolamine (MEA)-ammonium sulfate-cupric sulfate” was performed for the dissolution of metallic silver, varying the pH and the cupric ion concentration at room temperature. Furthermore, this research aims to evaluate the silver dissolution behavior at a pH lower than 10.2, elucidating the rate determining step of the silver dissolution process at these conditions of pH and cupric ion concentration. Thermodynamic results confirm that the MEA and NH₃ can complex silver generating the species: Ag(MEA)₂⁺, AgMEA⁻, Ag(NH₃)₂⁺, AgNH₃⁺ respectively. It was evaluated the effect of varying the pH (8.8, 9.9 and 9) and the cupric sulfate concentration (0.1, 0.15 and, 0.2 M at pH 9) on the kinetics of silver dissolution. The results revealed, the possibility to leach a 39% of silver using a leaching solution containing: 0.15 M cupric sulfate, 0.05 M MEA and 0.4 M ammonium sulfate at pH 9. The kinetic analysis showed that the silver dissolution is controlled by the diffusion of fluid species through a porous layer composed of copper oxides, which was ratified by SEM and EDS analysis. Finally the present paper, open the possibility to optimize the molar ratio MEA:NH₃ to maximize the silver dissolution kinetics.

Keywords: Leaching, metallic silver, MEA, ammonium.

1. INTRODUCTION

Cyanidation is the most employed process to carry out the dissolution of precious metals such as: silver. However, it is extremely known, that the scientific community is investigating the development of alternative processes that are less toxic to the environment. In this sense, during several decades, the research has been focused in the silver leaching with thiourea and thiosulfate, respectively. It has been proposed the thiosulfate systems as the most promising leaching systems for silver and gold. [1-20]. The ammoniacal thiosulfate leaching system has been evaluated for the recovery of silver and gold, the researches have revealed that it presents an interesting advantage over the cyanidation in terms of the leaching kinetics; the gold and silver dissolution rates are 18-20 times higher than the cyanidation, due to the formation of a catalytic oxidant, the so-called “cupric tetraamine”. Furthermore, the re-adsorption of the silver-thiosulfate and gold-thiosulfate complexes in carbonaceous phases (Preg-Robbing) is considerably decreased. With respect to the process economy, the thiosulfate systems can be cheaper than the cyanide systems [21]. However, it is known that the thiosulfate systems present a very complex chemistry, due to the chemical and electrochemical interactions of the different species present in the system, which has become one of the main impediments to scale-up the thiosulfate systems to an industrial level [22].

On the other hand, according to AYLMOORE and MUIR [4], the instability of the ammoniacal thiosulfate solutions is related to the presence of cupric ions, which promote the irreversible thiosulfate degradation to tetrathionates or other thiosalts and consequently affects the silver dissolution kinetics and the process profitability.

Therefore, alternative processes have been proposed to carry out the precious metals dissolution, such as the ammoniacal systems without thiosulfate. The ammoniacal systems have been identified as an alternative process to cyanidation to leach silver and gold [23-26]. Actually, ammonia is less toxic than cyanide, and it can be easily regenerated by evaporation-absorption processes [27].

On the other hand, the ammonia, is used to complex the precious metals. However, an oxidizing agent such

as cupric ions is necessary to increase the oxidizing ability of the leaching system. It has been reported that cupric tetraamine can be formed in ammoniacal solutions containing cupric ions [27]; despite of this, copper oxides are formed, which decreases continuously the oxidizing ability of the leaching solution. Therefore, additional complexing agents for cupric ions are necessary which can retard the formation of copper oxides. In this sense monoethanolamine (MEA) has been used as a complexing agent-inhibitor of corrosion, which decreases the formation of copper oxides [28].

In the present work, it is presented the alternative-novel system “MEA-cupric sulfate-ammonium sulfate” for the leaching of metallic silver at room temperature and different pH values. The results are analyzed from a thermodynamic, kinetic and microstructural view-point.

2. MATERIALS AND METHODS

This section describes the materials, equipment, reagents, leaching solution composition and the experimental methodologies used in this research work.

Leaching solutions were prepared with analytical grade reagents and deionized water. The reagents were: metallic silver (99.999%, 1-3 μm , spherical, Alfa Aesar), monoethanolamine (MEA) (99,76 %, JT Baker), cupric sulfate pentahydrate (99%, Merck) and ammonium sulfate, crystals (29.2%, JT Baker).

The experimental work was divided in three main sections: Section 2.1 Thermodynamic study, Section 2.2 Leaching tests and Section 2.3 Chemical and morphological characterization of the solid residues.

2.1 Thermodynamic study

In order to elucidate the predominant species in the MEA-ammonia-copper-silver system, species distribution diagrams were constructed at room temperature using the Medusa Software and considering the equilibrium data contained in the Hydra database of the same software [29]. The thermodynamic data was complemented with equilibrium data for the Cu-MEA and Ag-MEA complexes. These diagrams were used to determine all the aqueous and solid species that can be formed in the leaching solutions at different pH and potential conditions.

2.2 Leaching tests

All silver leaching experiments were performed in an agitated batch reactor (250 mL glass beaker); the reactor was provided with a pH meter (pH 538 WTW), a pH electrode (SENSOREX), a redox potential electrode with Ag/AgCl reference (Cole-Parmer) and a magnetic stirring plate. The general procedure used for the leaching experiments was as follows: 200 mL of the leaching solution with MEA, cupric sulfate, ammonium sulfate (Table 1) and 0.1266 g of metallic silver were placed in the reactor at room temperature (25 °C).

Samples of the leaching solution were withdrawn at different times, for the silver analysis by atomic absorption spectrophotometry (Varian SpectrAA 220FS). All samples were kept in dark vessels to prevent the silver precipitation caused by light. The pH and redox potential were measured before the silver addition and during the leaching experiments (every 30 min). Once the experiments were concluded, the residues were filtered, rinsed with deionized water and left to air dry.

Table 1: Leaching solutions.

CONCENTRATION (M)			
CUPRIC SULFATE	MEA	AMMONIUM SULFATE	PH
EFFECT OF THE SOLUTION PH ON THE SILVER LEACHING			
0.2	0.05	0.4	8.8
0.2	0.05	0.4	9
0.2	0.05	0.4	9.5
EFFECT OF THE CUPRIC ION CONCENTRATION ON THE SILVER LEACHING			
0.1	0.05	0.4	9
0.15	0.05	0.4	9
0.2	0.05	0.4	9

2.2 Chemical and morphological characterization of the solid residues

The solid residues formed in all the leaching experiments were microstructurally characterized (superficially) to elucidate their morphology and local chemical composition by scanning electron microscopy (SEM) (Philips, XL30ESEM) and Energy-dispersive X-ray spectroscopy (EDS) (EDAX, Genesis).

3. RESULTS AND DISCUSSION

3.1 Thermodynamic study

A powerful tool for designing new leaching systems is the thermodynamics. It can be useful to elucidate all possible chemical and electrochemical events that can occur in a leaching system. Figure 1A illustrates the species distribution diagram for the Ag-MEA-NH₃-H₂O system using 0.05 M MEA, 0.4 M ammonium sulfate, 0.0058 M silver at 0.42 V_{SHE} and 25°C. It is possible to observe in this diagram, that MEA can form complexes with silver at pH ≥ 7; for example, if the leaching system is operated at pH 9, the formation of the silver monoMEA and diMEA (AgMEA⁺ and Ag(MEA)₂⁺) complexes takes place. It is also possible to produce silver-ammonia complexes such as: silver mono and diamine complexes (AgNH₃⁺, Ag(NH₃)₂⁺). On the other hand, as regards to the free MEA and NH₃ species, it is possible to observe in Figure 1A that MEA can also produce protonated complexes such as the hydrogen MEA species (HMEA⁺). In the case of the ammonium ions (NH₄⁺), it is evident (Figure 1A) that ammonia (NH₃) production predominates when the pH is increased above 9.2, approximately. It is worth mentioning that NH₃ is responsible to complex the dissolved silver.

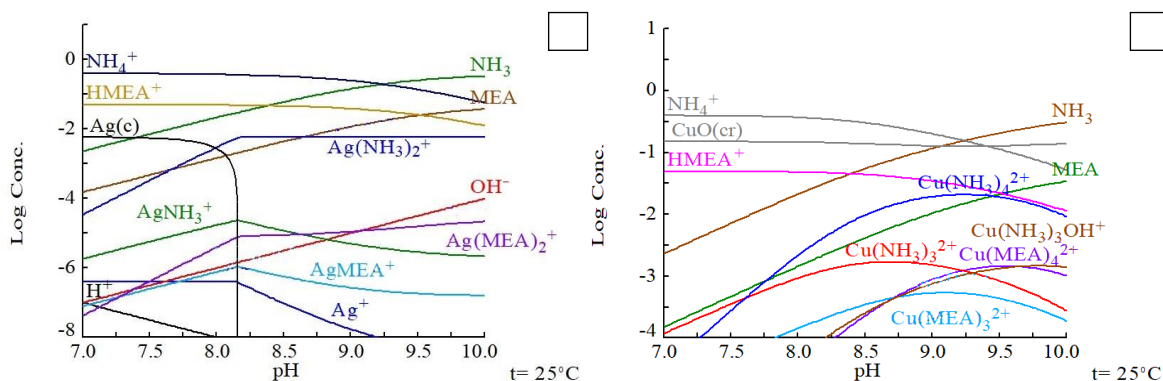


Figure 1: Species distribution diagram for the system: A) Ag-NH₃-MEA-H₂O with 0.05M MEA, 0.4 (NH₄)₂SO₄ 0.0058M Ag at 0.42V_{SHE}, 25°C and B) Cu-NH₃-MEA-H₂O with 0.05M MEA, 0.4 (NH₄)₂SO₄ 0.15M Cu at 0.42V_{SHE}, 25°C.

Figure 1A revealed that it is possible to dissolve metallic silver in ammoniacal-MEA solutions which have a redox a potential of 0.42 V_{SHE} approximately. The last result suggests that an oxidizing agent is neces-

sary to facilitate the silver oxidation. In this sense, the cupric ions can promote the silver oxidation. Figure 1B displays a species distribution diagram for the Cu-NH₃-MEA-H₂O system, where the formation of copper-MEA and copper-ammonia complexes are observed. The Cupric tetraMEA and triMEA complexes (Cu(MEA)₄²⁺ and Cu(MEA)₃²⁺, respectively) are formed in a pH range from 7 to 10 approximately, in addition, the cupric tetraamine and cupric triamine (Cu(NH₃)₄²⁺ and Cu(NH₃)₃²⁺, respectively) complexes are also formed in this pH window. These copper-MEA and copper-ammonia complexes can work as oxidizing agents for the metallic silver. It is worth mentioning, that all these copper-MEA complexes correspond to the partial stabilization of the cupric ions. Furthermore, another portion of the cupric ions is precipitated as the most stable phase, reported in these thermodynamic diagrams, i.e., copper oxides species.

Up to now, it is possible to mention that the cupric-MEA complexes as well as the cupric-ammonia complexes can work as the oxidizing species to facilitate the oxidation of the metallic silver. Once the silver is oxidized, the silver ions are stabilized in the leaching solution through its complexation with the free MEA and ammonia available in the leaching system. As shown in Figure 1A, silver can predominantly form the Ag(MEA)₂⁺ and Ag(NH₃)₂⁺ complexes.

3.2 Leaching tests

Based on the theoretical results, it is possible to leach silver with this alternative system. Therefore, in the present section, it is presented experimental evidence of the silver leaching with the MEA-NH₃-Cu-H₂O system at different pH values and three cupric ions concentrations. The results are discussed from a kinetic point of view, in order to understand the phenomena that affect the silver leaching kinetic under the present conditions of pH and cupric ions concentration.

3.2.1 Effect of the solution pH on the silver leaching

Figure 2, shows the silver extraction vs time curves for the leachings carried out with 0.2 M Cu²⁺, 0.05 M MEA, 0.4 M (NH₄)₂SO₄, 0.125 g Ag, at different pH (8.8, 9 and 9.5) adjusted with sodium hydroxide and room temperature. It is worth mentioning, that these leaching tests were performed to evaluate the effect of the pH on the silver leaching kinetics and extraction. It is observed in Figure 2 (Curve B), that in the case of the pH of 9, the silver extraction and kinetics was the highest of the all tested pH values, i.e., a silver extraction of 34% is obtained at 360 min. In the case of the system operated at pH of 9.5 (see Figure 2, curve C), the silver leaching kinetics was the slowest, affecting the silver recovery, e.g., it is possible to leach a 18% at 360 min. Finally, when the leaching system is operated at pH of 8.8 (see Figure 2, curve A), the silver leaching kinetics is similar to that found with the case of pH 9 during the first 30 min, when the leaching experiment proceeds it is possible to obtain a 25% of silver extraction at 360 min. These results clearly reveal the existence of an operation window, which can increase the silver leaching kinetics and % of extraction.

In order to understand the phenomena that take place in the previous leaching experiments, a complementary thermodynamic analysis was carried out. Figure 3 (A, B and C) illustrates the species distribution diagrams for the Ag-NH₃-MEA-H₂O system at 0.42, 0.38 and 0.41 V vs SHE which correspond to the measured redox potential for the leaching experiment done at pH 8.8, 9 and 9.5, respectively. It is evident that under these pH values, the formation of the silver complexes Ag-MEA and Ag-NH₃ is not affected, i.e., from a thermodynamic view-point, the silver dissolution is favored in the three experimental scenarios. The Ag_(c) can be oxidized to Ag⁺, and this species can be complexed by the ammonia and MEA present in the solution, producing the same complexes described in Figure 1A.

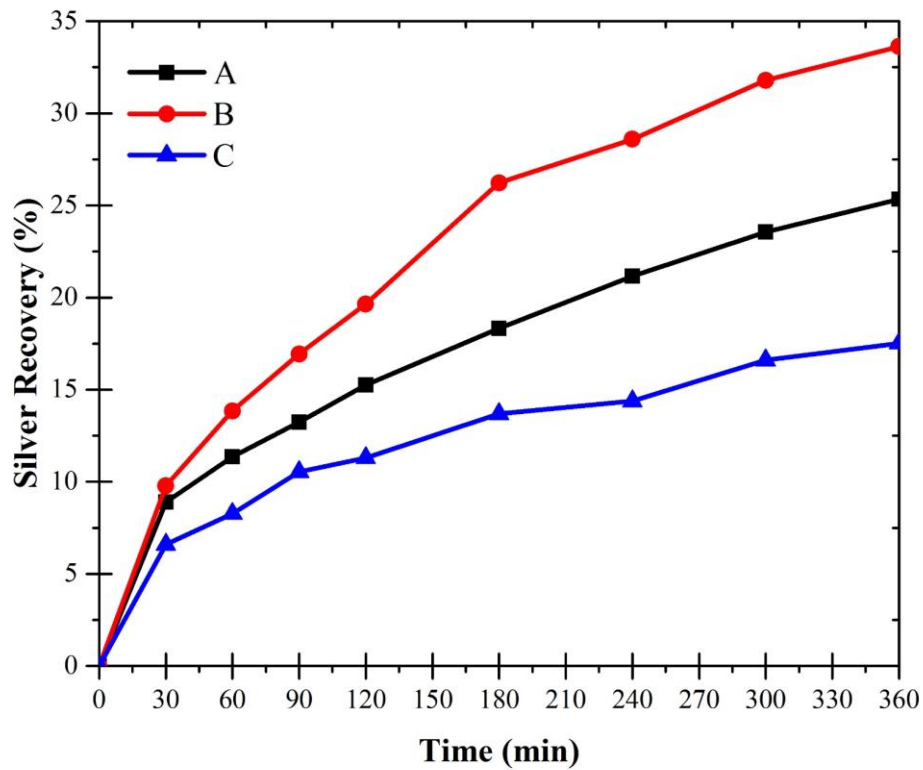


Figure 2: Effect of the pH on the silver leaching kinetics employing a leaching solution with 0.2 M Cu^{2+} , 0.05 M MEA, 0.4 M $(\text{NH}_4)_2\text{SO}_4$, 0.125 g Ag at room temperature and pH (adjusted with sodium hydroxide) of: A) 8.8, B) 9 and C) 9.5.

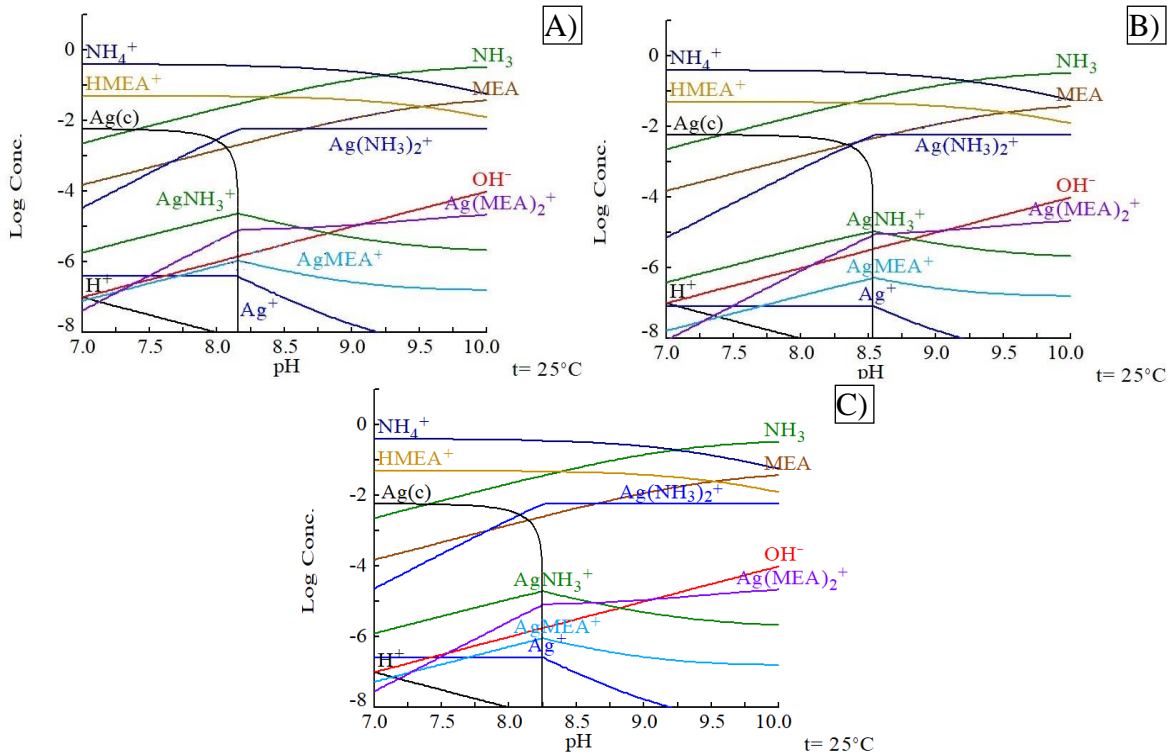


Figure 3: Species distribution diagrams for the Ag-NH₃-MEA-H₂O system with 0.0058 M Ag, 0.4 M $(\text{NH}_4)_2\text{SO}_4$, 0.05 M MEA and room temperature at A) $0.42 V_{\text{SHE}}$, B) $0.38 V_{\text{SHE}}$ and C) $0.41 V_{\text{SHE}}$.

Figure 4 displays the species distribution diagram for the Cu-MEA-NH₃-H₂O system in the form of molar fraction vs pH. It is possible to observe the predominant formation of stable copper oxides followed by cupric tetraamine (Cu(NH₃)₄²⁺). Another important characteristic of these diagrams, is that both copper species are formed in different proportions at the three studied pH. It is worth mentioning, that in several works related to ammoniacal thiosulfate systems [4], it has been mentioned that cupric tetraamine species are a catalytic oxidant which can accelerate the silver and gold dissolution. In this sense, in the present alternative system, the thermodynamics reveal that cupric tetraamine can be also formed in different concentrations which is a direct function of the pH. Therefore, this suggests that the different concentration of cupric tetraamine present in each leaching experiment promotes a change in the silver leaching kinetics. Actually, Figure 2, showed that the highest silver extraction and kinetics was obtained when the pH of the solution was 9; this behavior can be explained by the observation of Figure 4B, in this figure it is evident that the cupric tetraamine concentration was the highest under this condition, which promotes an increase in the silver leaching kinetics and extraction.

On the other hand, in the case of the leaching experiments performed at pH 8.8 and 9.5, the silver dissolution rate and extraction was decreased (Figure 2). The last can be related to a decrease in the cupric tetraamine concentration (Figure 4A and 4B, respectively), which affects the silver leaching kinetics.

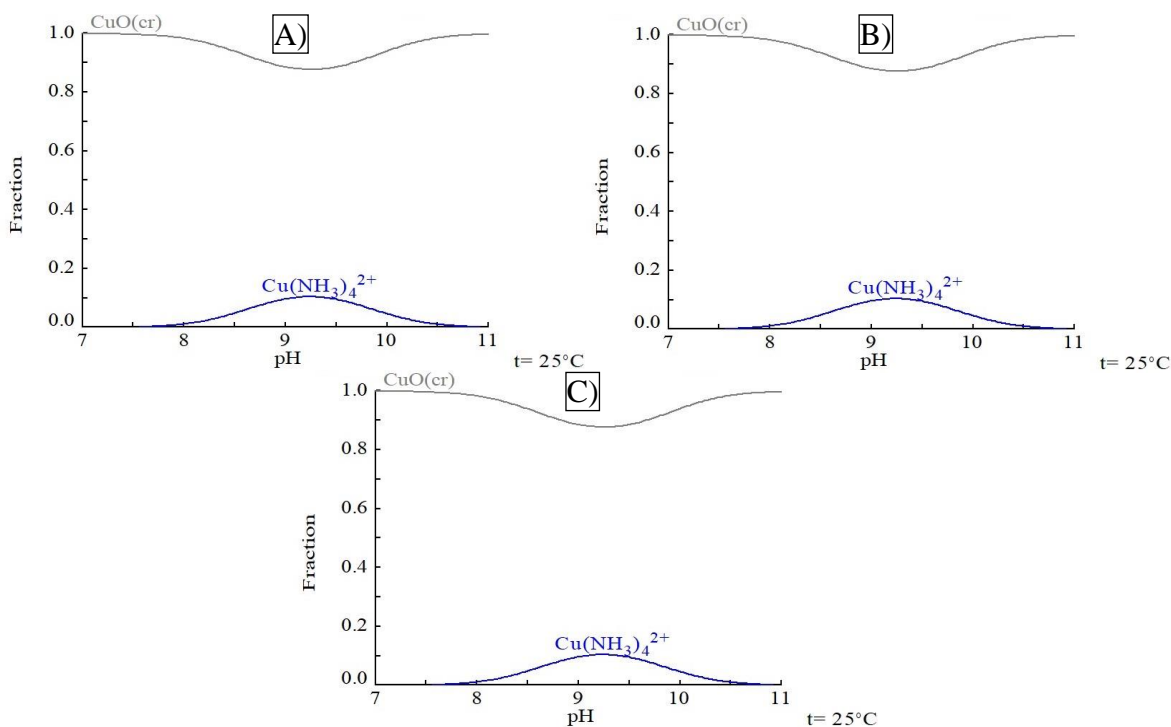


Figure 4: Species distribution diagrams for the Cu-NH₃-MEA-H₂O system, with 0.2 M Cu²⁺, 0.05 M MEA, 0.4 M (NH₄)₂SO₄ and room temperature at A) 0.42 V_{SHE}, B) 0.38 V_{SHE} and C) 0.41 V_{SHE}.

It is important to mention, that copper oxides are formed in the three pH scenarios (Figure 4), probably this copper oxides species can decrease the silver dissolution kinetics, due to the formation of a physical barrier between the fluid reactants and the unreacted silver.

With the aim to determine the rate determining step of the silver leaching process with this alternative solution, the shrinking core kinetic model (SCM) for spherical particles was used. Equation 1 is characteristic for a process which kinetics is controlled by the diffusion of the fluid species (reactants or products) through a porous ash layer [24]:

$$t(6bDeC_A/R_p^2\rho B) = 1-3(1-X)^{2/3} + 2(1-X) \tag{1}$$

where, X = silver fraction reacted in a certain time t(s), b = stoichiometric factor for the surface reaction A(s) + bB(aq) = products, D_e = effective diffusion coefficient for the fluid species through a porous layer

(m^2/s), C_A = concentration of the fluid reactant (mol/m^3), R_p = particle radius, (m), ρ = molar density of silver (mol/m^3).

The leaching data reported in Figure 2, was fitted to the SCM (Eq 1). The results are shown in Figure 5 and it reveals that the silver leaching kinetics in these experiments is controlled by the diffusion of the fluid species through a porous layer. According to the thermodynamic diagrams shown in Figure 4, the porous layer can be composed of copper oxides.

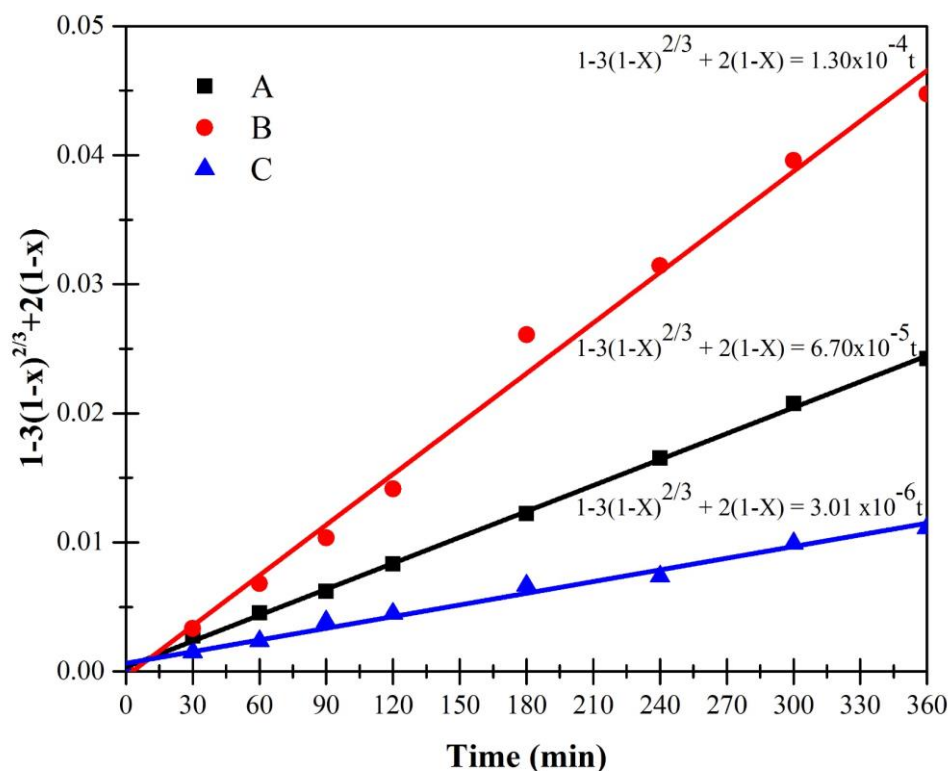


Figure 5: Silver leaching data fitted to Diffusion Control Model, Shrinking Core in Spherical Particles. Silver dissolution with 0.2 M Cu^{2+} , 0.05 M MEA, 0.4 M $(NH_4)_2SO_4$, 0.125 g Ag at room temperature and different pH: A) 8.8, B) 9 and C) 9.5.

3.2.2 Effect of the cupric ion concentration on the silver leaching

Another important variable in the silver dissolution kinetics is the concentration of the oxidizing agent, i.e., cupric ions. Figure 6 shows the effect of three cupric ions concentration (0.1, 0.15 and 0.2 M) on the silver leaching kinetics with 0.05 M MEA, 0.4 M $(NH_4)_2SO_4$, 0.125 g Ag at room temperature and pH of 9 adjusted with sodium hydroxide. The results of Figure 6 reveal that the silver leaching kinetics is very similar for the systems containing 0.1M and 0.15M of cupric ions. On the other hand, when the cupric ion concentration is increased at 0.2 M, the silver leaching kinetics is decreased, i.e., is slower than the systems with 0.1 or 0.15 M Cu^{2+} . For example; for the systems containing 0.15 M and 0.2 M Cu^{2+} it is possible to leach a 39% and 32%, respectively (see Figure 6, curve B and C, correspondingly).

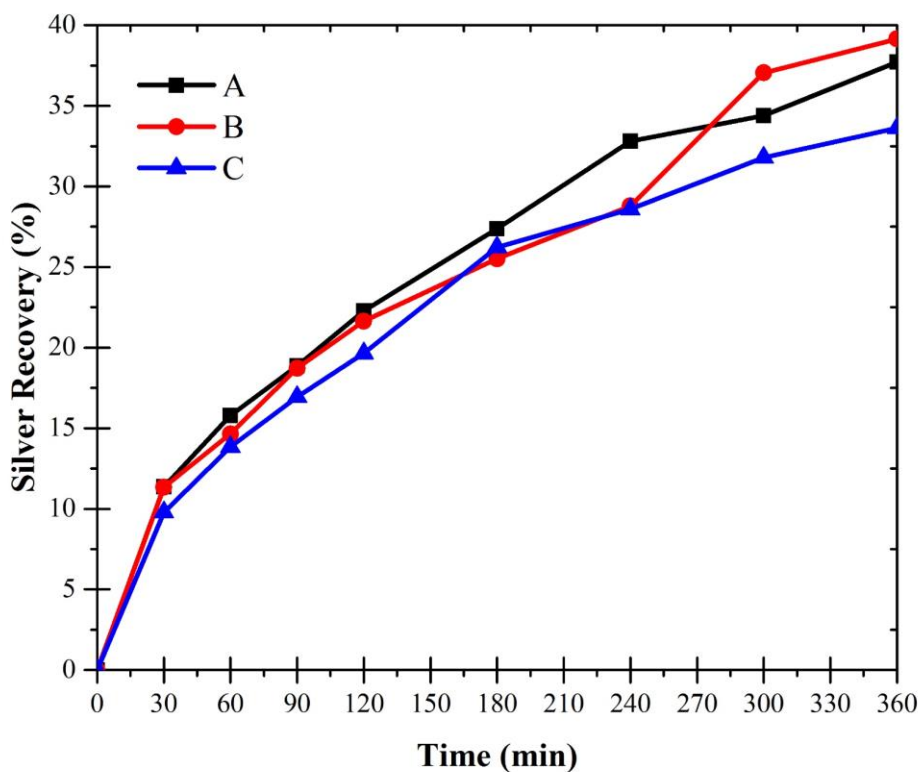


Figure 6: Effect of the cupric ion concentration on the silver leaching kinetics with 0.05 M MEA, 0.4 M (NH₄)₂SO₄, 0.125 g Ag at room temperature, pH 9 and A) 0.1 M Cu²⁺, B) 0.15 M Cu²⁺ and C) 0.2 M Cu²⁺.

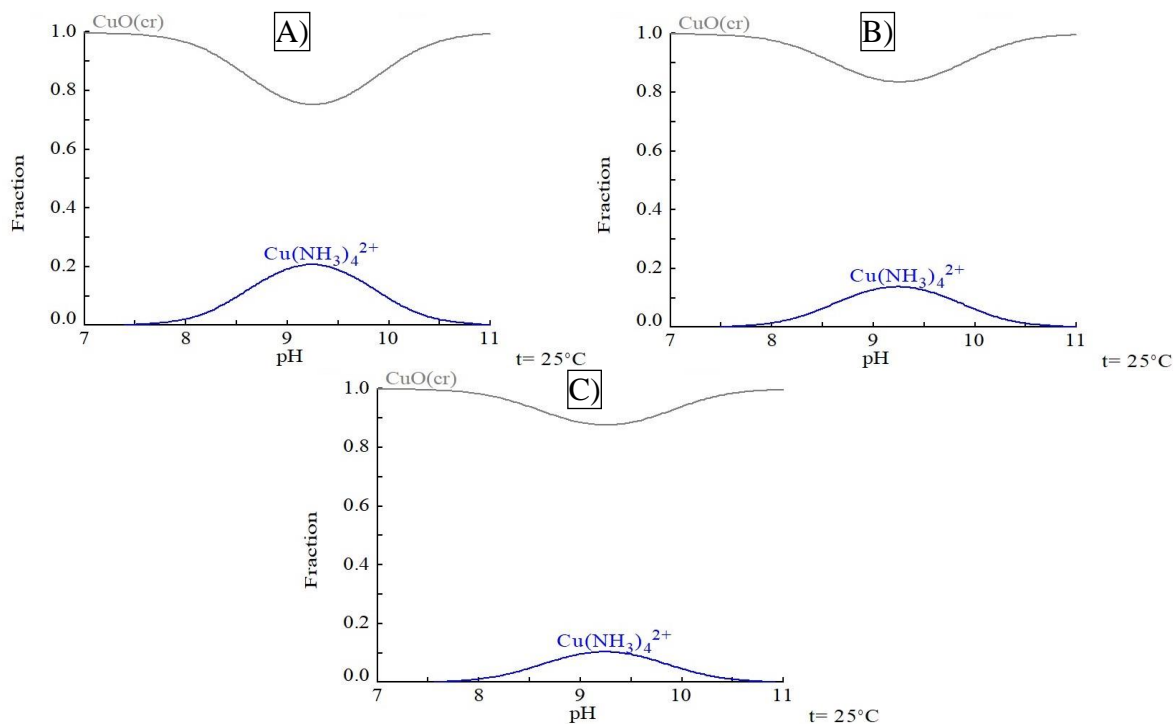


Figure 7: Species distribution diagrams for the Cu-NH₃-MEA-H₂O system with 0.05 M MEA, 0.4 M (NH₄)₂SO₄, room temperature and cupric ion concentration of A) 0.1 M, B) 0.15 M and C) 0.2 M.

A possible explanation of the previous behavior can be given from a thermodynamic view-point. Figure 7 illustrates the species distribution diagrams for the Cu-NH₃-MEA-H₂O system at different cupric ions concentrations. The results reveal that an increase in the cupric ion concentration from 0.1 to 0.2 M promotes the precipitation of copper oxides (see Figure 7, A and C). The copper oxides can precipitate on the silver particle surface, and these oxides can behave as a physical barrier which can decrease the silver leaching kinetics.

3.3 Characterization of the solid residues

The characterization of the solid residues obtained in the leaching experiments was carried out by SEM and EDS. This study was performed to complete the understanding of the phenomenon responsible to decrease the silver leaching kinetics. It is important to mention that, according to the species distribution diagrams shown in Figures 4 and 7, the formation of copper oxides layers on the silver particle is possible. Based on the kinetics results shown in Figure 5, it was proposed that the copper oxides can be porous, and can behave as a physical barrier which promotes a diffusion control of the process.

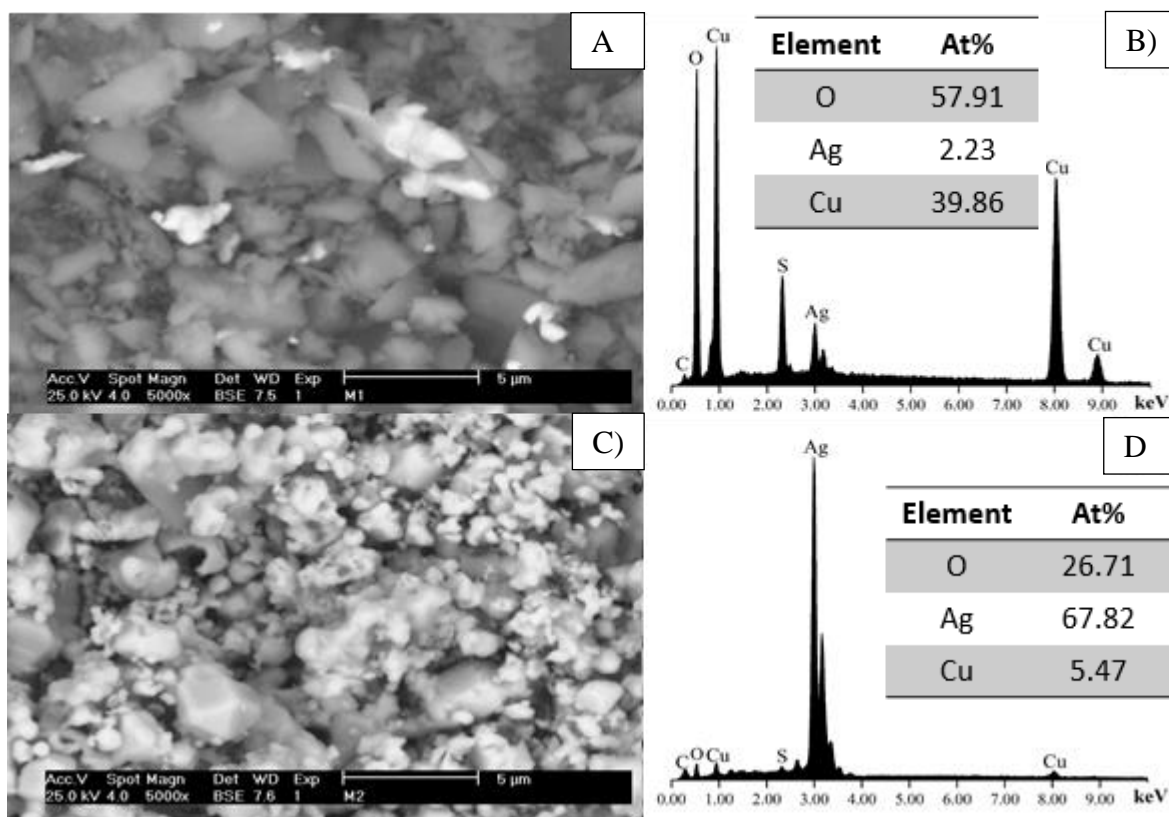


Figure 8: Characterization of the solid residues obtained at different pH. Experimental conditions: 0.2 M Cu²⁺, 0.05 M MEA and 0.4 M (NH₄)₂SO₄. A) Morphology at pH 8.8, b) Chemical composition at pH 8.8, c) Morphology at pH 9, d) Chemical composition at pH 9.

Figure 8 illustrates the morphology (Figure 8A and C) and the chemical composition (Figure 8B and D) of the solid residues obtained at pH 8.8 and 9. The EDS analysis reveals the presence of silver in the solid residues, which is consistent with the leaching results of Figure 2, i.e., the silver extraction does not correspond to the 100%. Furthermore, the EDS analysis shows the presence of Cu and O in the solid residue, which can be probably related to the presence of copper oxides, this result is consistent with the thermodynamic analysis shown before.

On the other hand, with respect to the morphology of the solid residue, it is possible to observe in the Figure 8A and C, that the copper oxides (dark particles) are deposited on the unreacted silver (bright particles). Actually, the copper oxides are formed in a higher amount in the case of pH 8.8 than in the case of pH

9 (See Figure 8A and C, respectively), this result is also consistent with the thermodynamic analysis shown in the Figure 4, where it was observed that the copper oxides precipitation is more favored at pH 8.8 than at pH 9. The copper oxides layers behave as a physical barrier for the direct contact between the fluid reactants and the metallic silver, which decreases the silver leaching kinetics.

Finally, in the case of the solid residues obtained at different cupric ions concentrations. It is possible to observe in Figure 9 A and C the morphology of the solid residue obtained with 0.1 and 0.15 M Cu^{2+} , respectively. The formation of copper oxides is favored when the cupric ion concentration is increased. This result is in good agreement with thermodynamic analysis shown in Figure 7.

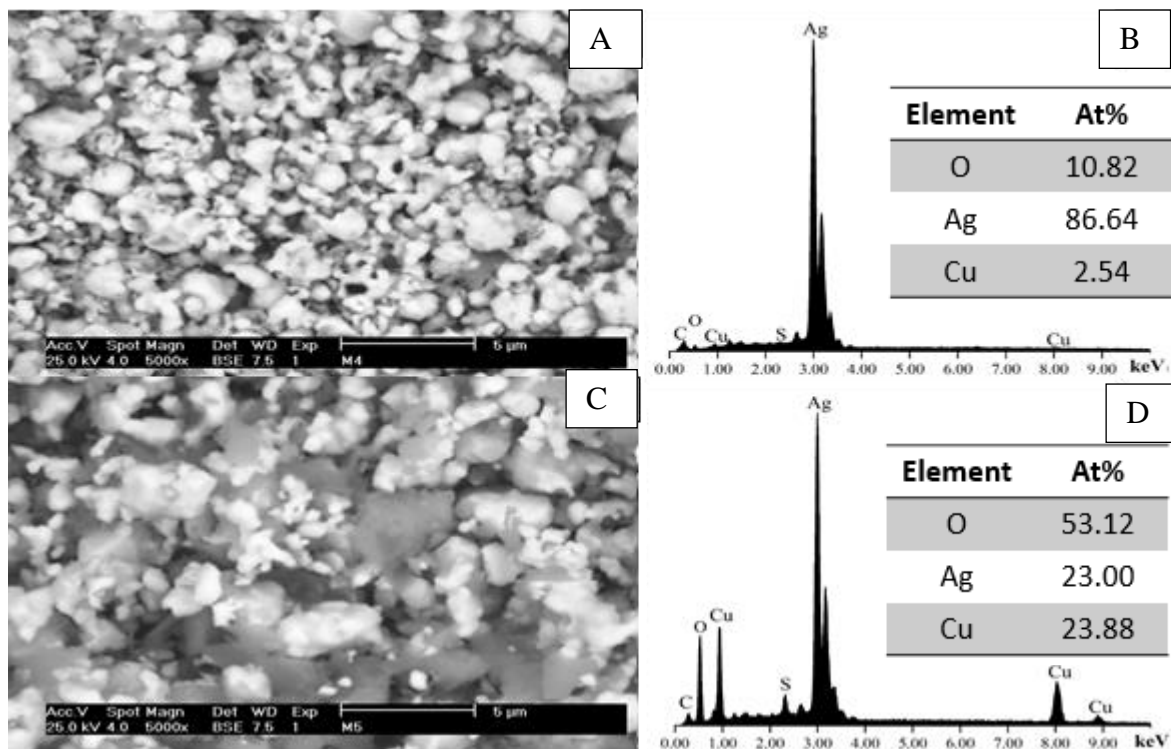


Figure 9: Characterization of the solid residues obtained at different cupric ions concentrations. Experimental conditions: 0.05 M MEA, 0.4 M $(\text{NH}_4)_2\text{SO}_4$, and pH 9. a) Morphology for 0.1 M Cu^{2+} , b) Chemical composition for 0.1 M Cu^{2+} , c) Morphology for 0.15 M Cu^{2+} , d) Chemical composition for 0.15 M Cu^{2+} .

4. CONCLUSIONS

The results of the thermodynamic-kinetic study revealed that the alternative system “MEA-ammonia-copper” is able to leach metallic silver in a pH range from 8.8 to 9.5. The best leaching solution studied can leach a 39% of silver in 6 h employing 0.15M Cu^{2+} -0.05M MEA-0.4M $(\text{NH}_4)_2\text{SO}_4$, pH 9 at room temperature. The thermodynamic analysis revealed that MEA can complex the cupric ions. These complexes can also oxidize the metallic silver.

The silver leaching kinetics is affected by the pH of the leaching solution. Copper oxides precipitation on the unreacted silver particles is higher at pH of 8.8 and 9.5 than at pH 9. The copper oxides layers are porous and promote a diffusion control of the process kinetics.

The precipitation of copper oxides layers on the silver particles is favored when the cupric ion concentration is increased from 0.1 to 0.2 M. This phenomenon could inhibit the silver dissolution.

These results open a rich opportunity to continue doing research with this alternative leaching system, from a mechanistic and optimization view-point, in order to increase the silver leaching kinetics and extraction.

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