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Kinetic Aspects and Thermo chemical Analysis of Silver Cementation from Residual X Ray Fixer by Cementation on Zinc

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Abstract: Silver cementation with zinc from residual X ray fixers was studied. The chemical analysis of XRF showed 5.16 g L^{-1} (Ag), 0.56 g L^{-1} (Al), 5.24 g L^{-1} (K), 7.02 g L^{-1} (Na) and 172.56 g L^{-1} (S). The process was thermodynamically simulated using Fact Sage software by constructing the potential-pH diagram at 298.15 K (25°C). This diagram showed *that the process leads to metallic silver together with residual unreacted zinc. The parameters experimentally evaluated were: pH (ranged from 3.0 to 7.0), temperature (ranged from 298.15 K (25°C) to 318.15 K (45°C)) and the Ag:Zn weight ratio (1:1, 1:2, 1:3, 1:4 and 1:5). The maxim silver cementation (99.99 % Ag) was obtained at 90 s of reaction, pH 6.0, 318 K (45°C) and Ag:Zn equal to 1:3. Silver cementation increases whit the Ag:Zn weight ratio, pH and temperature* increases. The X-Ray and SEM-EDS results showed that the cementation product is formed by Ag and Zn.

I. INTRODUCTION

Silver is unique in its ability to react to light and produce images in applications such as photography and radiography (X -rays). This is released from the photographic film during the developing and printing processes and can be successfully recovered from the effluent resulting for reuse. Residual X ray fixer used in the developing process of x-ray films may contain from 5 to 12 g L^{-1} silver in solution [1]. The treatment of spent solutions from fixing process is presented as a technical problem due to the large volume generated; however, the cementation process may overcome this problem. Cementation involves the precipitation of an electropositive metal from solution by a metal more electronegative. This is one of the oldest, efficient and economical hydrometallurgical processes for the recovery of metal values in solution, and for the purification of leach liquors. This process has been widely used for removing Cu, Cd and Ta from leach liquor of zinc sulfate [2]. Actually, the conventional processes for gold and silver recovery from cyanide leach solution is the Merrill Crowe zinc dust cementation in which the efficiency of the reaction is significantly improved by removing dissolved oxygen from the system prior to zinc addition, using a vacuum deaeration technique 3. The advantages of cementation include simple control requirement, low energy consumption and recovery of valuable or toxic metals in a harmless and reusable form. The cementation processes have been constantly used and researched [3-6], some of them are batch agitated processes, other use reactors with disc rotating cylinder 4. Silver is the most studied metal using zinc as a cementing medium 3; however, researches to recover Au, Co, Cd, Cu and Ni have also been reported [3, 7-12]. It has been reported that the process has a first-order reaction, wherein the reaction is controlled by diffusion, together with the activation energy (Ea) [13].

The present work aims to determine the optimal conditions for the cementation process of silver from residual zinc X ray fixers, and propose an effective and feasible method to treat this effluents.

II. EXPERIMENTAL SECTION

Residual X ray fixers were used, chemically pure zinc powder, sodium hydroxide and sulfuric acid to adjust the pH of the solution. Previously the X ray fixers were characterized with the ICP method to determine their chemical composition. The cementation process was carried out using 1 L of solution in a glass reactor of 2 L. A hot plate (Barnstead/ Thermolyne Super-nova) equipped with temperature control and a mechanical stirring system with six-blade propeller type axial at 250 rpm was also used. The initial pH of the solution was measured and kept constant throughout the process. The volume of the solution was not affected by maintaining desired pH value because the amount of sodium hydroxide or sulfuric acid to adjust the pH of the solution was minimal. Zn powder was added and the progress of cementation was studied at different times during the reaction by obtaining successive samples of 10 mL and filtering with What man No. 42 filter paper. The end of the reaction was considered when it was not observed pH variation. The reaction progress was monitored by determining the Ag concentration with the ICP method performing the correction of Ag concentration by volume change.

The following Ag cementation with Zn trials was tested:

(a) 298 K (25°C) with the following Ag:Zn weight ratios: 1:1, 1:2, 1:3, 1:4, and 1:4, pH = 5.0 (pH of the initial solution). The required stoichiometric amount of zinc was calculated by the following reaction.

$$2Ag(S_2O_3)2^{[3-]} + ZnO = 2AgO + Zn^{[2+]} + 4(S_2O_3)^{[2-]} \qquad (1)$$

(b) At 298 K (25°C), Ag:Zn weight ratio constant and with the following pH values: 3, 4, 5, 6 y 7. The $[OH^-]$ concentration was calculated taking into account the solubility product constant of NaOH in water [14] and the pH of the alkaline solution according to the experimental temperatures.

(c) At Ag:Zn ratio and pH constants and with the following temperatures: 303K (30°C), 308 K (35°C), 313K (40°C) and 318K (45°C).

After the reaction the solution was filtered and the solid was dried and analyzed by scanning electron microscopy (SEM), and the solids were characterized by X-ray diffraction (XRD).

III. RESULTS AND DISCUSSION

A. Residual X ray fixers Chemical composition

The chemical analysis of Residual X ray fixers is shown in Table I. The chemical analysis of each element was carried out four times; the obtained standard deviation was about σ = 0.1422. All elements were determined by ICP method.

Table 1: Chemical composition of Residual X ray Fixers

Element	*Content (mg L^{-1})*
Al	556.98
Cu	0.18
Pb	0.20
K	5,244.19
Ag	5,165.21
Na	7,023.26
S	172,558.14

B. Potential-pH diagram

Pourbaix diagrams can be used to identify the conditions required to dissolve a solid compound in an aqueous solution at a given temperature and pressure as well as estimate the solid and aqueous products of the dissolving reaction. The EpH module of the FACTSage thermodynamic software [15] enables to generate isothermal Eh vs. pH (Pourbaix) diagrams for one-, two or three-metal systems using data retrieved from the compound databases that also include infinitely dilute aqueous data. This module can also calculate these diagrams not only at 98.15 K (25ºC) but also at higher temperatures. This advantage of FACTSage is used to estimate the effect of temperatures and pH on the stability of the species with Zn and Ag in an aqueous solution.

Figure 1 and Figure 2 shows the potential-pH diagram at 298.15 K (25°C) and 318 K (45 °C) for the Ag-Zn-H_2O system calculated with the FACTSage software. The molality of all the aqueous species in this system has been fixed at m = 1.

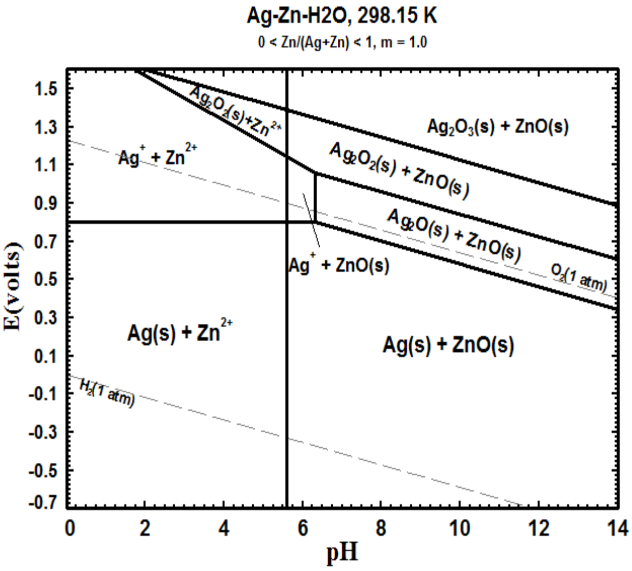

Figure 1: Potential-pH diagram for the Ag-Zn-H_2O system at 298.15 K (25°C)

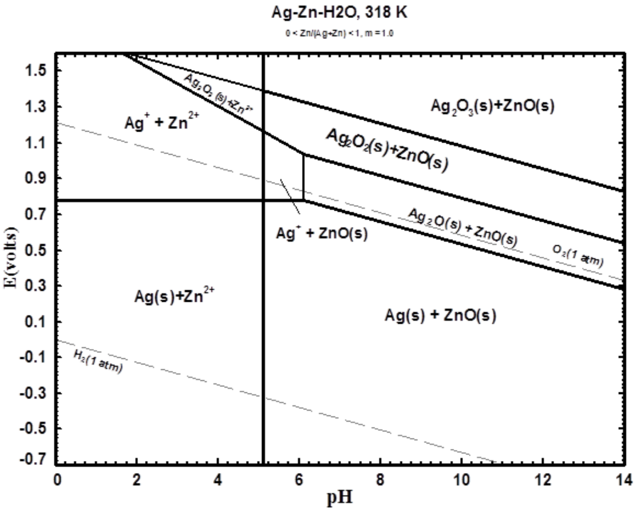

Figure 2: Potential-pH diagram for the Ag-Zn-H_2O system at 318 K (45 °C)

Water is only stable in the region bounded by the dashed lines. The equilibrium conditions that can be utilized for the leaching of minerals or any solid compound in aqueous solutions at ambient temperature are constrained to those defined by the region of water stability. Figure 1 shows that Ag(s) is stable when pH of the liquid solution is between 0 and 14 and almost all the E values where water is stable. At 298.15 K (25ºC), Zn^{2+} ion is stable when pH is less than 5.65, whereas ZnO(s) is stable at pH higher than 5.65, and at 45ºC (Figure 2) the pH limit of the stability of Zn^{2+} and ZnO(s) is about 5.09.

This is explained because the equilibrium between Zn ions and ZnO in aqueous solution is expressed by:

$$4H^+ + 2ZnO = 2Zn^{2+} + 2\,H_2O \quad \Delta G^\circ 298.15K\ (25^\circ C) = -127517.2 \qquad (2)$$

The Gibbs free energy expression for this reaction if H+ and Zn2+ do not occur in their standard states is expressed as:

$$\Delta\, G = \Delta G^\circ + RT\,\ln\left(\frac{[Zn^{2+}]^2}{[H^+]^4}\right) \qquad (3)$$

This equation can be changed using $\log_{10}$, the pH which is equal to -$\log_{10}(H^+)$, and assuming that the $[Zn^{2+}]$ = 1 mol/kg of water:

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$$\Delta G = \Delta G° + 22834.88(pH) \qquad (4)$$

It is clear that

If pH = 5.5843, then $\Delta G = 0$ and Zn^{2+} and ZnO are in equilibrium

If pH < 5.5843, then $\Delta G < 0$ and Zn^{2+} is more stable than ZnO

If pH > 5.5843, then $\Delta G > 0$ and ZnO is more stable than Zn^{2+}

Cementation Kinetic

A. Effect of zinc concentration

In most cases, the cementation reactions follows first order reaction kinetics and generally are limited by diffusion of the noble metal ion through the mass-transfer boundary layer. Most of the cementation reactions are found to be first-order diffusion process [16] with respect to the noble metal ion, and the reaction velocity constant, km, for such a reaction may be computed from the general first-order rate equation:

$$\frac{dc}{dt} = \frac{-kmAC}{V} \qquad (5)$$

If km in not concentration dependent and the area in unchanging, equation (5) is integrated resulting in the integrated fisrt-order reaction.

$$log\frac{C}{C_0} = -\frac{-kmAC}{2.3V} \qquad (6)$$

Where km is the reaction velocity constant (cm s^{-1}), which, among others factors, is the function of the activity coefficient of silver. A is the surface area of cementing metal (cm^2), V is the solution volume (cm^3), t is time (s) and C and C_0 are the noble metal concentrations at time t and the initial concentration at time = 0 respectively.

The required amount of zinc was calculated by the reaction (1), and it is shown in Table 2 together with different Ag:Zn weight ratios. Table 2 also shows the calculated surface area values for each studied weight ratio such was measured using the BET technique (quatasorb Model 0S10, Quanta chrome Corporation).

Table 2: Weight ratios, weights and surface area of Zn powder.

Weight ratio (Ag:Zn)	*Mass Zn ($g\ L^{-1}$)*	*Surface area Zn ($cm^2\ g^{-1}$)*
1:1	1.38	1161
1:2	2.76	2324
1:3	4.54	3484
1:4	5.88	4942
1:5	7.56	6371

Figure 3 shows the results obtained for cementing of Ag using the amounts of Zn powder shown in Table 2, pH: 5.0 and 250 rpm of agitation. Silver recovery is expressed as:

$$Ag_{recovery} = \left[\frac{C^o_{Ag} - C^t_{Ag}}{C^o_{Ag}}\right]100 \qquad (7)$$

Where $C°_{Ag}$ is the initial silver content in the aqueous solution and C^t_{Ag} is the silver content in the solution at a given time. The reaction progress at time t was monitored by determining the Ag concentration with the ICP method (C^t_{Ag}).

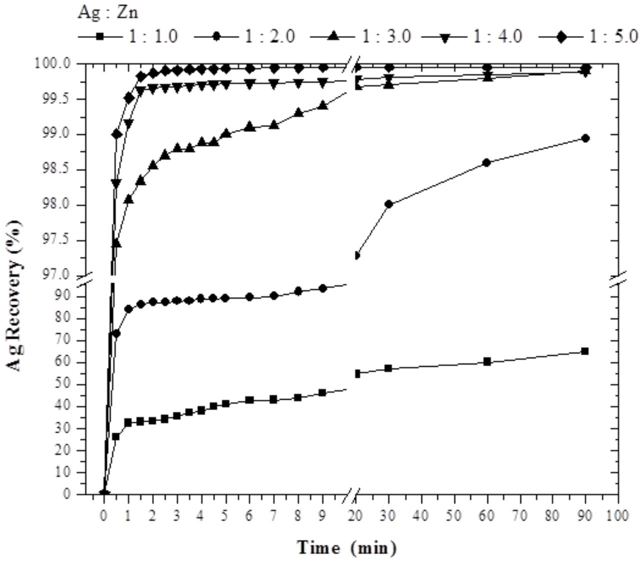


Figure 3: Ag recovery. Effect of zinc concentration.

It is observed that using the Ag:Zn weight ratios 1:1 and 1:2 produce less than 95% of silver cemented in 10 minutes of process, while is higher than 96% using Ag:Zn weight ratios of 1:3, 1:4 and 1:5 in less than 1 minute. This is due to the high surface area of the zinc powder added. The silver ions are readily reduced by zinc due to the difference in standard reduction potentials:

$$Ag^{2+} + e^{-} = Ag^{+} \quad E^{o}= 1.77\ V \tag{8}$$

$$Zn^{2+} + 2e^{-} = Zn \quad E^{o}= -0.763\ V \tag{9}$$

Under standard conditions the cementation reaction is the shown in reaction (1) with E° = 0.1923 V.

It is worth to note that if the electrochemical potential of the cell is greater than zero (positive), then the change in Gibbs free energy (ΔG) is negative, and the reaction may proceed spontaneously as written.

Figure 4 shows the logarithm of the fraction of Ag cemented vs. cementation time. (Calculated with equation (6)). According to the equation (6) the plot is been to be linear in the first 15 minutes, indicating that this reaction is firs order, which has been verified by others authors [3, 17,18]. Where the process is tightly controlled by hydrodynamic conditions within the reactor, so it is confirmed that the process is controlled by mass transfer solution to the surface film of the zinc particles.

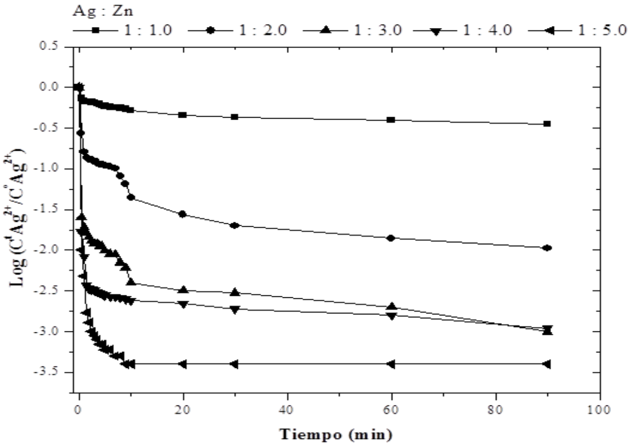
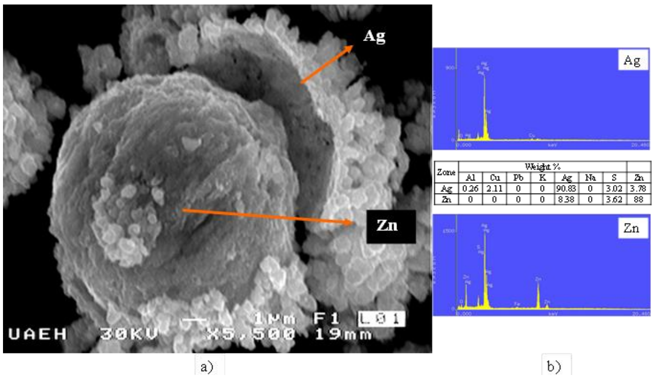


Figure 4: Effect of zinc concentration on the rate of cementation.

It can be seen that there is a slight increase in the rate constant with increasing amount of Zn. However have been reported 2 that in some cases the structure and morphology of the reaction product can have a significant effect on passivating the surface. The Figure 5 shows a micrograph of the cemented silver obtained by SEM-EDS with Ag:Zn 1:3, pH 6.0 and temperature of 303K (30°C) where zinc and silver are observed in the same particle. The effect of the mechanical propeller separates the Ag that forms around the Zn particle, and comes off easily; therefore, for each reaction time a new Zn surface area is exposed.



Zone	Weight %							
	Al	Cu	Pb	K	Ag	Na	S	Zn
Ag	0.26	2.11	0	0	90.83	0	3.02	3.78
Zn	0	0	0	0	8.38	0	3.62	88

Figure 5: a) SEM micrograph of Ag cementation with Zn. b) EDS analysis of the reaction.

Figure 6 shows the X-ray diffraction pattern of the cementation products. These results confirm the formation of two phases corresponding to Ag (JCPD file 4-783) and Zn (JCPD file 4-831).

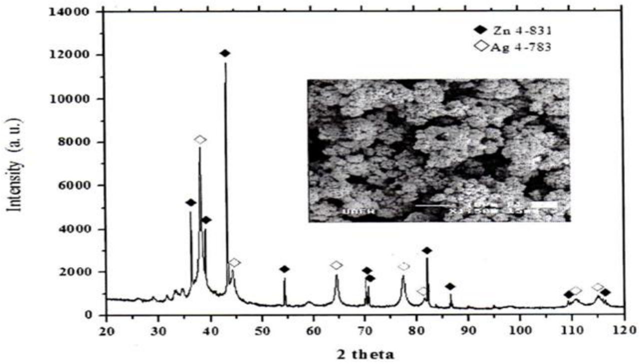


Figure 6: X-ray diffraction pattern of silver cementation products.

B. pH effect

Figure 7 shows the results for the pH effect on silver cementation with zinc powder realized with Ag:Zn weight ratio equal to 1:3, agitation: 250 rpm and pH values of 3, 4, 5, 6 and 7. Is observed that by acidic pH the Ag recovery decreases. This is due to the increased competition between Ag ions and hydrogen ions for discharge sites on the metal surface at higher concentrations of hydrogen ions:

$$Zn + 2H^{2+} = Zn^{2+} + H_2 \qquad (10)$$

Which can proceed to higher extent at low pH, the surface area available for the cementation reaction is decreased. The hydrogen so produced is likely to block the metal surface because of it slow desorption step [2].

Figure 8 shows the effect of solution acidity on the rate of cementation with Zn powder, it shows that speed cementation decreases when the pH decreases. The decrease of the rate constant with increasing acidity of the solution can be attributed mainly to the effect of hydrogen ions mentioned above.

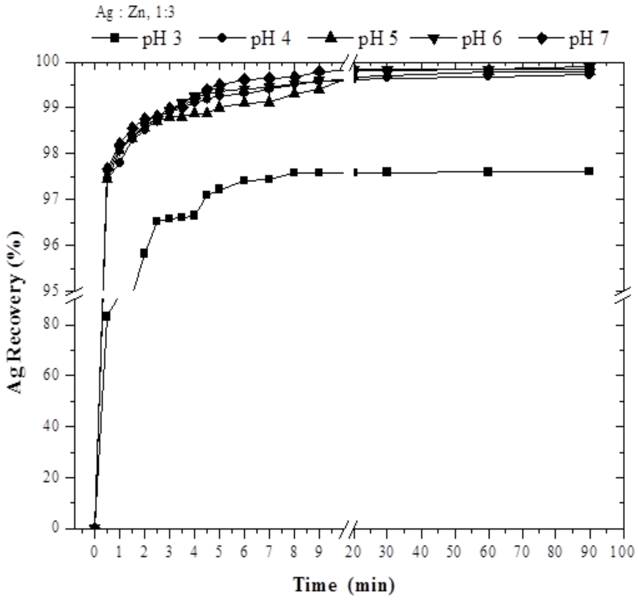


Figure 7: Ag recovery. Effect of Ph.

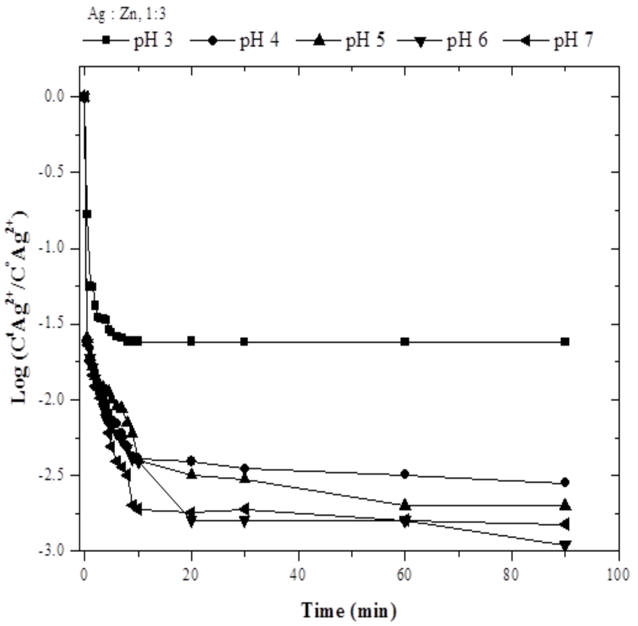


Figure 8: Effect of solution acidity on the rate of cementation.

C. Temperature effect

Figure 9 shows the effect of temperature solution on the kinetics of Ag cementation. It can be seen that the silver recovery increases whit the temperature increases. Experimental investigations [2-6] indicate that most cementation reactions are controlled by a mass transfer process. For almost all the cementation process systems the apparent activation energy is in the range 2 – 6 kcal mol^{-1} which suggest that the cementation reactions are limited by mass transfer in the aqueous phase. Figure 10 shows the effect of temperature on the rate of cementation with Ag:Zn weight ratio equal to 1:3 ratio, pH 6 and 250 rpm of agitation. This results are consistent with those reported by others authors [2], also the reaction is strongly dependent on the hydrodynamic conditions of the bath. This also confirms that the rate cementation is controlled by mass transport through the boundary film.

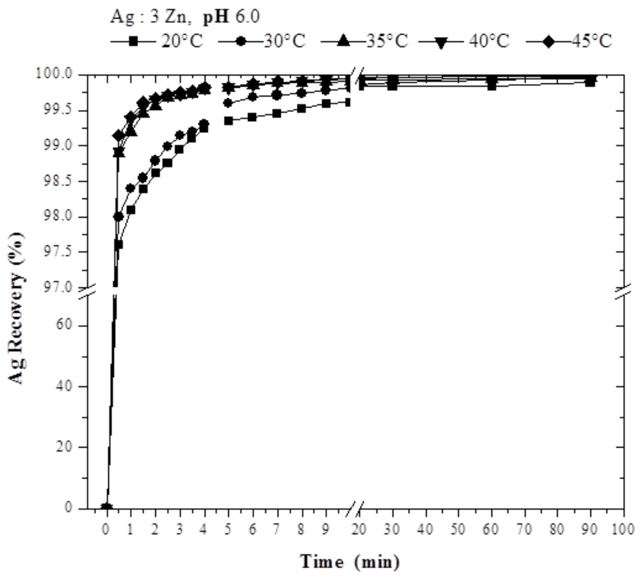


Figure 9: Ag recovery. Effect of reaction temperature.

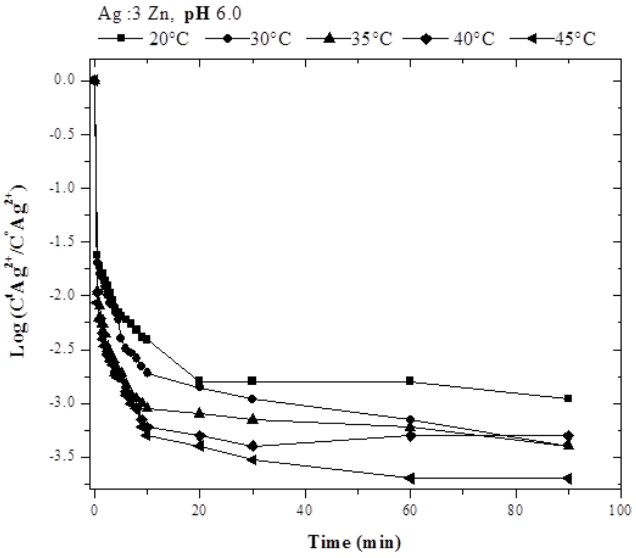


Figure 10: Effect of temperature on the rate of cementation

IV. CONCLUSIONS

The effects of pH, temperature and zinc content on the rate of Ag cementation with Zn of residual X ray fixers were studied. Zinc can be used effectively for the recovery of silver ions from X ray fixers. The X ray fixers have a silver concentration of 4.55 gL^{-1}. The optimal conditions for the Ag cementation process whit Zn were: Ag:Zn weight ratio equal to 1:3, pH: 6.0 and at 318 K (45°C) to get Ag recoveries of 99.99 %. It was observed that pH's less than 4 and zinc concentrations lower than the ratio 1:3 diminish the kinetics of the cementation process and the silver recovery. The X-ray diffraction pattern of the cementation products showed the formation of two phases corresponding to Ag and Zn. The potential-pH diagram presented that the cementation process leads to metallic silver together with residual unreacted zinc.

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