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Mass transfer correlation of simultaneous removal by cementation of nickel and cobalt from sulfate industrial solution containing copper

Part I: Onto rotating zinc electrode disc

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Abstract

In this part I of our work, the kinetics study of simultaneous cementation of nickel and cobalt from industrial zinc sulfate solutions using a rotating zinc electrode disc was investigated. Experiments were carried out in the presence of copper to increase the low cementation rate of these elements (Ni and Co). The effect of temperature, metallic ions concentrations and electrode rotation speed was also investigated. The reaction of nickel cementation was found to be under diffusional control while that of cobalt was found under chemical control. The reaction rate was found to be strongly affected by the increase in the electrode surface area. Mass transfer study of the process was correlated by the equation: $Sh = 1.43Sc^{0.33}Re^{0.49}$.

The results obtained will be used to establish optimal conditions for the zinc production plant of ALZINC, Tlemcen, Algeria.

Keywords: Cementation; Copper; Cobalt; Zinc; Mass transfer

1. Introduction

The presence of metallic impurities in zinc electrolyte is a major concern for the zinc electrowinning process. When the impurity is more noble metal than zinc (such Ni and Co) it can deposit easily. These impurities in the electrolyte baths decrease the current efficiency causing the total or partial dissolution of the cathode during the electrolysis and lower the purity grade of zinc deposited [1–5]. This redissolution phenomenon has been interpreted in terms of the formation of local Zn–Ni and Zn–Co galvanic cells [2,6]. Therefore, adequate purification of the zinc electrolyte before electrowinning is essential. This purification is carried out by cementation which consists in the removal of metal impurities from the solution by spontaneous reduction to its elemental metallic state, for instance, Ni^{2+} can be removed from electrolytic solution by cementation on zinc according to the reaction:

$$Zn + Ni^{2+} \rightarrow Zn^{2+} + Ni \qquad (1)$$

Most of previous studies were carried out on the removal of copper, lead and silver from wastewater and rotating disc system has been widely adopted because the system presents a known and reproductible hydrodynamic [1,7–9]. The physical nature of metal deposits formed on the surface of cementation agents is one of the factors which influences the cementation rate and two different explanations have been proposed. The rate enhancement can result either from changes in deposit structure generating increases in surface area or from the presence of turbulences associated with increasing roughness of the deposit [1,10–12]. The negative change (cementation rate retarded) can result from the blocking effect produced by the deposit or from a redissolution of formed deposit caused by hydrogen evolution (corrosion reaction) [13].

In the most modern zinc production plants [14–18], these metallic impurities were removed by adding activators in view to enhance the cementation kinetics. Antimony and antimony compounds such as Sb, $KSbC_4H_2O_6{\cdot}1.5H_2O$, $Na_3SbS_4{\cdot}9H_2O$, Sb_2O_3, Zn–Al, Zn–Ca alloys, Zn–Sb–graphite, Cd–Cu–Sb, arsenic salts As_2O_3, etc. are widely used for activated cementation of cobalt and nickel.

Several mechanisms have been proposed to explain the role of copper and antimony in the enhancement of the removal of nickel and cobalt [19–22]. Some authors put forward the fact that

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Nomenclature

a	specific geometrical surface area (related to the volume of solution) (cm^{-1})
a_e	specific effective surface area (related to the volume of solution) (cm^{-1})
C	nickel or cobalt concentration at time t
C_0	initial concentration of nickel or cobalt
d	zinc disc diameter (cm)
D	nickel-ion diffusivity ($cm^2\ s^{-1}$)
k	local mass transfer coefficient ($cm\ s^{-1}$)
$\hat{k}$	apparent mass transfer coefficient ($cm\ s^{-1}$)
Re	Reynolds number ($=\Omega d^2/\nu$)
Sc	Schmidt number ($=\nu/D$)
Sh	Sherwood number ($=\hat{k}d/D$)
t	time (min)
T	temperature (K)
Greek letters	
μ	solution dynamic viscosity ($kg\ m^{-1}\ s^{-1}$)
ν	solution kinematic viscosity ($cm^2\ s^{-1}$)
Ω	angular velocity of rotating disc electrode ($rad\ s^{-1}$)

ratio Co:Sb = 1:1 is necessary permanent factor for satisfactory results during cementation [14]. The reactions involved in acidic solutions are [22]:

$$3Cu^{2+} + 2Sb + 4H_2O \Leftrightarrow 2HSbO_2 + 6H^+ + 3Cu \quad (2)$$

$$2HSbO_2 + 2Co^{2+} + 6H^+ + 5Zn \Leftrightarrow 2CoSb + 5Zn^{2+} + 4H_2O \quad (3)$$

$$2HSbO_2 + Co^{2+} + 6H^+ + 4Zn \Leftrightarrow CoSb_2 + 4Zn^{2+} + 4H_2O \quad (4)$$

However, cementation of metal ions more noble than zinc is not the only reaction that occurs. Hydrogen evolution is a competitive reaction during the process; and cemented copper and other metals more noble than zinc (Co, Ni) increase the hydrogen evolution. This hydrogen evolution causes the precipitation of basic zinc salts on the electrode surface and this leads to the formation of compact deposits which inhibit the rate cementation [23,24].

Practically, different schemes are applied but each of them has specific features, and it is not always applicable to the conditions of every zinc production process.

The objective of the present study is to determine the influence of the main parameters (temperature, metallic ion concentrations and electrode rotation speed) on kinetics and mass transfer of the process of simultaneous cementation of cobalt and nickel from simulated industrial solution in view to establish the optimal conditions for the cementation in the zinc production plant of ALZINC, Tlemcen, Algeria.

2. Experimental

The study for simultaneous cementation of Ni^{2+} and Co^{2+} ions was carried out using solution obtained after the first cementation (Table 1) of ALZINC corresponding to the average content of the main components within the following limits (exempt cadmium): Zn 160 $g\,l^{-1}$, Cu 200 $mg\,l^{-1}$, Co 10 $mg\,l^{-1}$, Ni 1.5 $mg\,l^{-1}$, Sb 0.5 $mg\,l^{-1}$, pH 2.5 ± 0.5. In the whole series of experiments, we have adjusted antimony content in the electrolyte to satisfy the condition that the ratio $Q_{Co}/Q_{Sb} = 1{:}1$ [14].

The equipment used for conducting the experiments consisted of a thermostated cementation cell with a constant solution volume of 200 ml. According to the conditions of zinc production plant of ALZINC the cementation process was investigated at 60–85 °C. We used rotating zinc disc of 0.2 cm^2 surface area and the pH value was maintained at 2.5 ± 0.5 by adding concentrated sulfuric acid. Before the start of each experiment the disc was polished with emery papers to the 1200 grit, then it was cleaned in dilute hydrochloric acid and finally rinsed with distilled water. The time dependence of nickel and cobalt concentration was followed during cementation by withdrawing a sample of 2 cm^3 from the cell at different time intervals and analyzed by atomic absorption spectrophotometer (Shimadzu AA 6500) controlled with a microcomputer.

The physical properties of the solution needed for data correlation such as viscosity and diffusion coefficient were evaluated. The kinematic viscosity was measured by Ubbelhode viscosimeter (Normandie Labo company) and the diffusivity of the solutions was obtained from the literature [1] and corrected for the temperature change using the Stokes–Einstein equation.

3. Results and discussion

3.1. Kinetics results

The temporal evolution of the concentration shown in Fig. 1 is quite typical results obtained for different experimental con-

Table 1
Content of the main impurities of the industrial zinc sulfate solutions at different steps of the purification

	Before cementation ($mg\,l^{-1}$)	After the first cementation ($mg\,l^{-1}$)	After the second cementation ($mg\,l^{-1}$)	Behind the third cementation ($mg\,l^{-1}$)
Cu	800	250	<0.2	<0.2
Cd	300	300	<2.0	0.2
Sb	0.5	0.5	<0.05	<0.05
Co	10	10	<0.25	<0.25

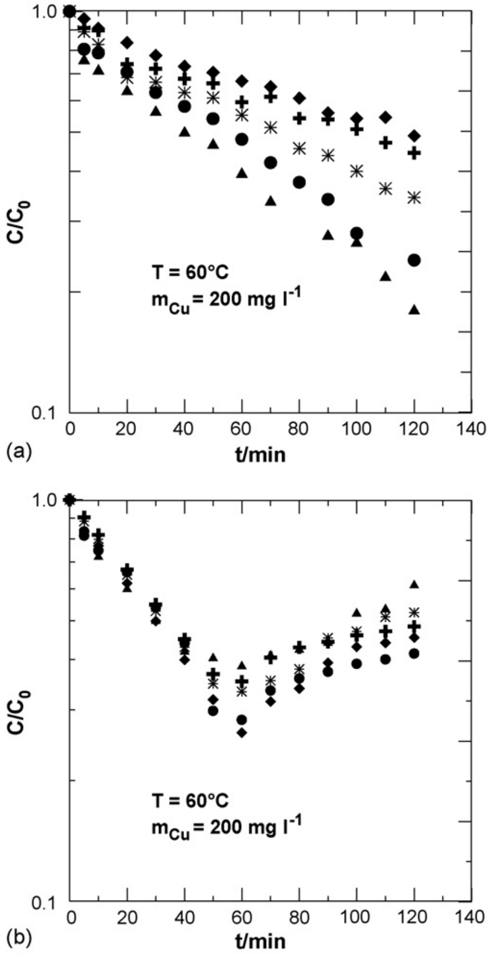

Fig. 1. Typical log(C/C_0) vs. time at different rotation speed: (a) nickel and (b) cobalt. (◆) 500 rpm; (✚) 1000 rpm; (✳) 2000 rpm; (●) 3000 rpm; (▲) 4000 rpm.

ditions. It can be observed (Fig. 1b) that in the course of time the degree of cementation of cobalt increases, reaches a maximum between 50 and 60 min and then decreases. The negative change can result from the blocking effect produced by the deposit or from a redissolution of formed cobalt deposit. This cobalt redissolution can occur by hydrogen evolution (corrosion) following the reaction $Co + 2H^+ = Co^{2+} + H_2$ or by cementation reaction of Ni^{2+} ions onto formed metallic cobalt deposit (Ni more noble than cobalt) following the reaction $Ni^{2+} + Co = Co^{2+} + Ni$. These phenomena might result in reducing the cementation process of cobalt [14–17,19].

It is seen also that, globally, the degree of cementation of nickel increases continuously with the increase of the duration of the process.

These plots show, for the cobalt, that rotation speeds have little effect on cementation rate (at least for the time less than 60 min) suggesting that the reaction is chemically rate limited, whereas the depletion of Ni^{2+} becomes more rapid with higher rotation speed and the first order kinetics is exhibited. Then the cementation of nickel can be expressed by

$$ka_e = -\frac{2.3}{t} \log\left(\frac{C}{C_0}\right) \tag{5}$$

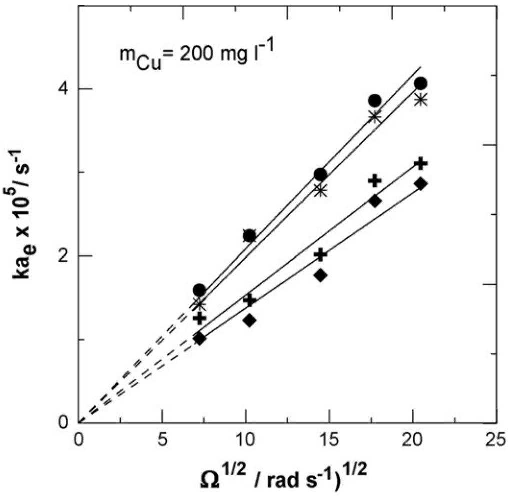

Fig. 2. Variation of ka_e as a function of rotation speed for different temperatures, in the case of nickel. (◆) 60 °C; (✚) 70 °C; (✳) 80 °C; (●) 85 °C.

The above equation was used to calculate the product ka_e deduced from the slope of straight lines in Fig. 1. A distinction has to be made between the two terms a and a_e representing specific geometrical surface area and specific effective surface, respectively [11,25]. It is not possible to know the value of a_e. However, this is not a problem for design because, as shown by Eq. (5), k and a_e do not have to be known separately but only as the product ka_e.

In the present paper all the kinetic results are presented in the form of ka_e, then the mass transfer in the cell is analyzed by introducing an apparent mass transfer coefficient $\hat{k}$ which is defined by

$$\hat{k} = \frac{ka_e}{a} \tag{6}$$

The values of ka_e, obtained from the slope of straight lines in Fig. 1a (case of Ni ions) using Eq. (5), are plotted in Fig. 2 versus the square root of the electrode rotation speed. The increase in product ka_e with increasing angular speed of rotation is in agreement with a diffusion controlled of the nickel cementation process. The data fit the equation:

$$ka_e = \mathrm{Cste}\,\Omega^{0.5} \tag{7}$$

Fig. 3 shows that increasing solution temperature enhances the rate of cobalt cementation, whereas the degree of nickel cementation is influenced to a smaller extent. The enhancement of the temperature reduces solution viscosity with a consequent increase in reducible ions diffusivity according to the Stokes–Einstein equation [26,27]:

$$D = \text{constant} \times \frac{T}{\mu} \tag{8}$$

To lend support to the diffusion-controlled and the chemical-controlled mechanisms of nickel and cobalt cementation, respectively, the product ka_e was plotted as a function of the Kelvin temperature in Fig. 4. The slopes of these plots yield an activation energies of 24 and 60 kJ mol^{-1} for nickel and cobalt, respectively. Activation energies of these magnitudes are indica-

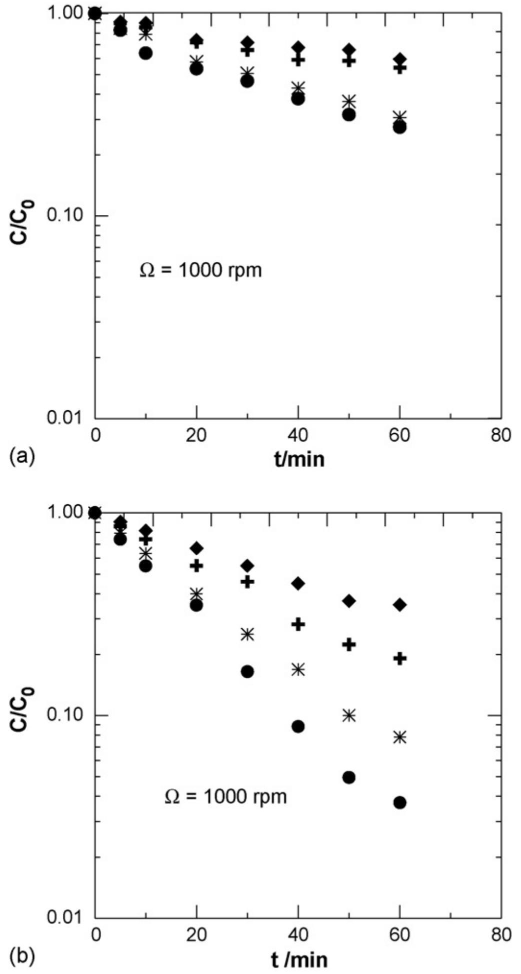

Fig. 3. Temperature effect on nickel and cobalt cementation: (a) nickel and (b) cobalt. (♦) 60 °C; (✚) 70 °C; (✳) 80 °C; (●) 85 °C.

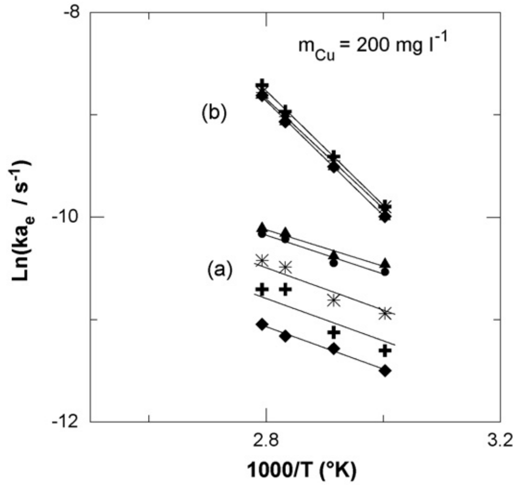

Fig. 4. Arrhenius plot of the experimental results: (a) nickel and (b) cobalt. (♦) 500 rpm; (✚) 1000 rpm; (✳) 2000 rpm; (●) 3000 rpm; (▲) 4000 rpm.

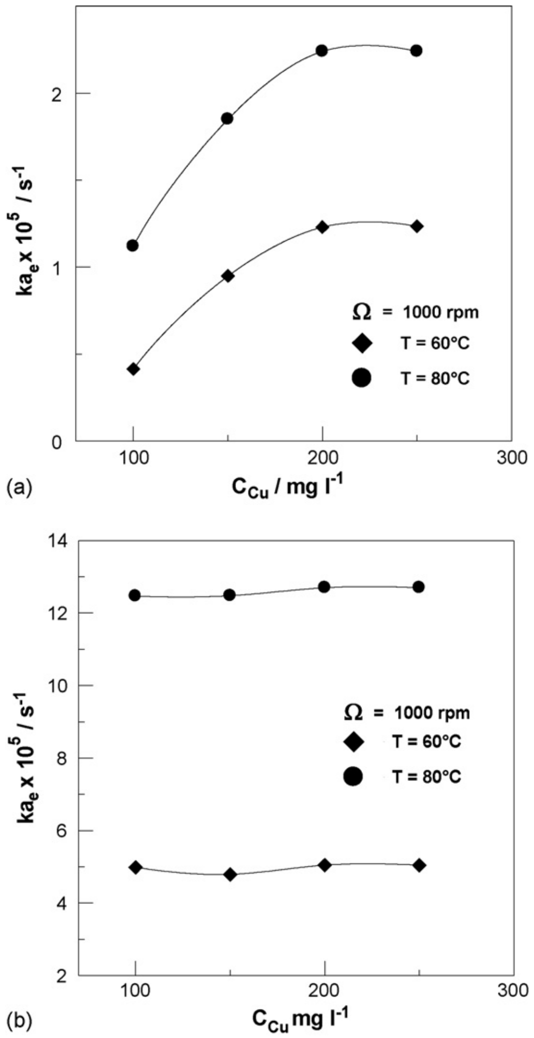

Fig. 5. Influence of copper content on cobalt and nickel cementation: (a) nickel and (b) cobalt.

tive that the reaction of nickel is diffusion-controlled and the cobalt deposition is chemically controlled [28–32]. These results are consistent which those found above (the rate of Ni cementation increases with increasing the rotation rate of the electrode while the rate of Co cementation is independent of the agitation).

The presence of copper in the solution is necessary for the cementation of nickel and cobalt. Cobalt gets cemented as a result of the action of micro-couple Zn–Cu. Fig. 5 shows the influence of copper content on the degree of cementation of nickel and cobalt in our industrial sulfate solution for two temperature values. The results showed that adding copper to the solution activates, to a greater extent, the cementation of nickel and to a smaller extent the cementation of cobalt. The optimal concentration of copper found to improve the cementation process is equal to 200 mg l^{-1}.

3.2. Mass transfer correlation and comparison

When cementation kinetic laws are shown to be diffusion control (linear dependence of ka_e with $\Omega^{1/2}$, Fig. 2), the rate of mass transfer to a plane rotating disc in laminar flow is given by

$$J = \mathrm{Cste} D^{2/3} \Omega^{1/2} \nu^{-1/6} C^0 = kC_0 \qquad (9)$$

where C_0 is the initial concentration of reducible ions in solution.

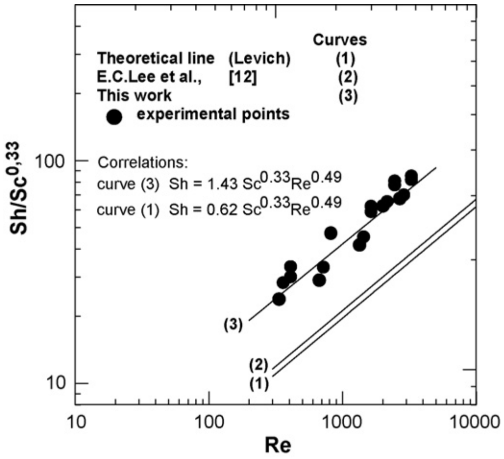

Fig. 6. Experimental data-mass transfer correlation and comparison of our experimental results with those of literature.

This is the well known theoretical Levich expression which can be written in dimensionless form as

$$Sh = \mathrm{Cste} Sc^{0.33} Re^{0.5} \tag{10}$$

In order to evaluate the hydrodynamic effect over the mass transfer in the cell, the dimensional analysis suggests the search of correlation in the following form:

$$Sh = \mathrm{Cste} Sc^{a} Re^{b} \tag{11}$$

Taking into account the surface evolution, the apparent mass transfer coefficient was introduced. This parameter, in fact, was found to play a significant role in the cementation process. For Reynolds number (*Re*) values between 300 and 3300 and the corresponding Schmidt values between 921 and 1238, the calculated apparent mass transfer coefficient was plotted as Sherwood number (*Sh*) against Reynolds number in Fig. 6. The data can be represented, with average deviation of ±10%, by the equation:

$$Sh = 1.43 Sc^{0.33} Re^{0.49} \tag{13}$$

In obtaining the above equation the exponent of the Schmidt number in the general mass transfer correlation was fixed at established value of 0.33 [33]. The present *Re* exponent 0.49, is in good agreement with a diffusion-controlled cementation reaction under laminar flow condition. However, the values of Sherwood number, derived from experimental data, are larger than that for theoretical values deduced from the Levich equation (Fig. 6). The dotted line 3 (experimental data), indicates that experimental values of Sh_{exp} are 2.3 times higher comparatively to the to the theoretical values (Sh_{th}) deduced from Levich equation. Such results agree with an increase of effective surface area of zinc surface caused by the deposit.

4. Conclusion

The following general conclusions may be drawn with respect to the codeposition of nickel and cobalt onto rotating zinc disc in industrial sulfate solution with the presence of copper as accelerator:

1. the nickel cementation reaction conformed to first order kinetics and was diffusion-controlled (the reaction rate variation was linear with the square root of the electrode rotation speed). The cobalt cementation reaction was chemically controlled (it was independent of stirring speed and presented an activation energy of 60 kJ mol^{-1}). After 75 min of cementation, the cobalt deposit dissolves reversibly caused probably by the hydrogen evolution or/and by cementation reaction of Ni^{2+} ions onto formed metallic cobalt deposit (Ni more noble than cobalt) following the reaction $Ni^{2+} + Co = Co^{2+} + Ni$. Adding copper (200 $\mathrm{mg\,l^{-1}}$) to the solution activates, to a greater extent, the cementation of nickel and, to a smaller extent the cementation of cobalt.
2. The experimental data for the simultaneous cementation of Ni and Co onto zinc are well correlated in terms of the mass transfer as follows:

$$Sh = 1.43 Sc^{0.33} Re^{0.49}$$

These experimental results are 2.3 times higher comparatively to the theoretical values deduced from Levich equation. These differences reflect the deposit morphology variation (enhancement of effective surface area of zinc surface caused by the deposit).

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