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Separation of Gold from Iodine–Iodide Solutions by Cementation on Zinc Particles

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ABSTRACT

Separation of gold from iodine–iodide solutions by cementation on zinc particles was studied. The effect of various parameters such as mixing rate, temperature, zinc particles size, and initial concentrations of gold–iodide complex and iodine were examined. The reaction was found to be under diffusion control at the conditions studied. Due to iodine side reactions, excess zinc consumption and a subsequent retardation of the cementation reaction rate were identified. A well-defined, conventional first-order kinetics model was established to explain the experimental findings.

INTRODUCTION

Cementation of zinc particles for gold and silver recovery, known as the Merill–Crowe process, is one of the most common contact-reduction processes in hydrometallurgy. Advantages of the process are fast reaction rate, low gold inventories, and ease of operation (1). However, leach liquor clarification, zinc cost, and reaction sensitivity to impurities of the leach liquor can make the zinc-particle technique less competitive with other process technologies, particularly carbon adsorption (1). Recently, Mintek researchers suggested that zinc cementation should be considered as an alternative process to electrowinning for direct treatment of carbon eluates in the CIP process (2).

Most of the articles published on the cementation of gold have dealt with aurocyanide solutions, since cyanidation remains the main industrial process for gold leaching from ores. The use of iodine–iodide solutions as an alternative lixiviant for gold leaching was proposed recently by a number of articles. The kinetics and the basic principles of the process have been studied (3–9), while the application of the process to ores in laboratories and mines has also been examined (10–12). The process seems to be considerably faster than the conventional cyanidation (5, 8), and it is selective concerning gold dissolution (6, 12). The main disadvantage seems to be the cost of the lixiviants. CIP application in the case of iodine solutions may be troublesome, as iodine tends to be adsorbed quantitatively onto activated carbon. The latter is used to characterize the activity of carbon with the so-called "iodine number" (6). Since iodine is sparingly recoverable from carbon, excess iodine consumption is expected. On the other hand, the application of the Merril–Crowe process may have advantages for the specific system. The process has been used effectively for gold removal from gold–bromide complex solutions (13).

The main effort of the present research work was to study the kinetics of gold cementation from iodine–iodide solutions in correlation with hydrometallurgical practice.

THEORETICAL APPROACH

The main simplified reactions involved in the gold–iodide complex zinc cementation system and their equilibrium constants [thermodynamic data from various sources (14–17)] are the following.

Main Reaction

1. Gold cementation:

$$2AuI_2^- + Zn \rightarrow 2Au + Zn^{2+} + 4I^- \qquad (pK = -45.42)$$

This reaction is expected to be quantitative and fast.

Side Reactions

2. Zinc dissolution by excess iodine:

$$Zn + I_2 \rightarrow Zn^{2+} + 2I^- \qquad (pK = -43.9)$$

This reaction is expected to be quantitative and fast.

3. Zinc dissolution due to the acidity of the solution:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

The influence of this reaction seems to be insignificant at the experimental pH (about 6).

4. Zinc dissolution in aerated solution:

$$Zn + 2H^+ + O_2 \rightarrow Zn^{2+} + 2H_2O$$

The influence of this reaction also seems to be insignificant in deaerated solution.

5. Gold cement dissolution:

$$2Au + I_3^- + I^- \rightarrow 2AuI_2^- \qquad (pK = 1.42)$$

At the standard experimental conditions the reaction is near equilibrium and the redissolution of gold cement seems to be negligible. Redissolution may occur at higher iodine concentrations.

6. Zinc hydroxide formation due to hydrolysis:

$$Zn^{2+} + 2H_2O \rightarrow Zn(OH)_2 + 2H^+$$

The influence of this reaction is expected to be insignificant at pH values near the neutral region (15).

7. Solid zinc iodide formation:

$$Zn^{2+} + 2I^- \rightarrow ZnI_2$$

The influence of this reaction seems to be negligible due to the high solubility of zinc iodide salt ($K_{sp} = 1.8 \times 10^7$).

In hydrometallurgical practice, several impurities such as copper, lead, and silver species may be involved with the cementation process. In the specific case of iodine–iodide lixiviants application, however, the presence of this species is negligible in the process liquors (10, 12).

EXPERIMENTAL

The batch reactor for the suspended particle cementation experiments consisted of an airtight glass beaker (250 mL) equipped with four side baffles. The reactor was supported in a constant-temperature bath. The test solutions were purged with nitrogen prior to use, and a nitrogen atmosphere was preserved during the experiments. A paddle-type agitator mounted on the shaft of a Fisher Stedi-Speed stirrer was used to mix the suspension.

Gold–iodide complex solutions were prepared by dissolving pure, metallic gold in an iodine–iodide solution.

Zinc particles were prepared by electrolysis using pure zinc electrodes and separated by wet sieving to five fractions:

-1000 μm to $+710$ μm
-850 μm to $+500$ μm
-500 μm to $+212$ μm
-212 μm to $+125$ μm
-125 μm to $+75$ μm

The individual samples of zinc were cleaned with dilute (1 M) hydrochloric acid to remove any surface oxide film, washed with acetone, and dried in air before being introduced into the reactor.

During the experiments, 5 mL aliquots were withdrawn from the reactor at regular intervals and their concentrations in gold and zinc were determined by AAS (Perkin-Elmer model 2380 spectrophotometer). Since the samples withdrawn caused a significant volume change during every experimental run, the use of a corrected time was essential. "Corrected time" is that time which would have elapsed if the total solution volume had remained constant at its initial value. The procedure to calculate corrected time is described elsewhere (8, 18).

Unless otherwise stated, the standard experimental conditions were:

Initial solution volume = 200 mL
Rotational speed: 26.2 rad·s^{-1}
Initial gold–iodide complex concentration: 25 mg·L^{-1}
Zinc particles: 1 g (fraction size -850 μm to $+500$ μm)
Initial iodine concentration: 0.0025 M or 630 mg·L^{-1}
Initial iodide concentration: 0.005 M
Temperature: 25°C
Reaction time: 45 minutes
pH value around 6

RESULTS AND DISCUSSION

Long-Term Experiment

A long-term experiment (150 min) was carried out to check the kinetic behavior of the system at the standard conditions mentioned above. After completion of the first run, an additional quantity of the gold–iodide complex solution was added, the volume was corrected, and the experiment was prolonged for an additional 25 minutes. The second run was carried out to check the ability of zinc to cement more gold from solution. The results presented as gold–iodide complex concentration vs time are shown in Fig. 1(A). In Fig. 1(B) the results are plotted according to first-order kinetics since this is the generally accepted kinetic model for cementation systems (19). Gold recovery of more than 85% was observed after 150 minutes while the cementation ability of zinc remained almost unchanged. A first-order kinetics model seems to be a good fit for the experimental

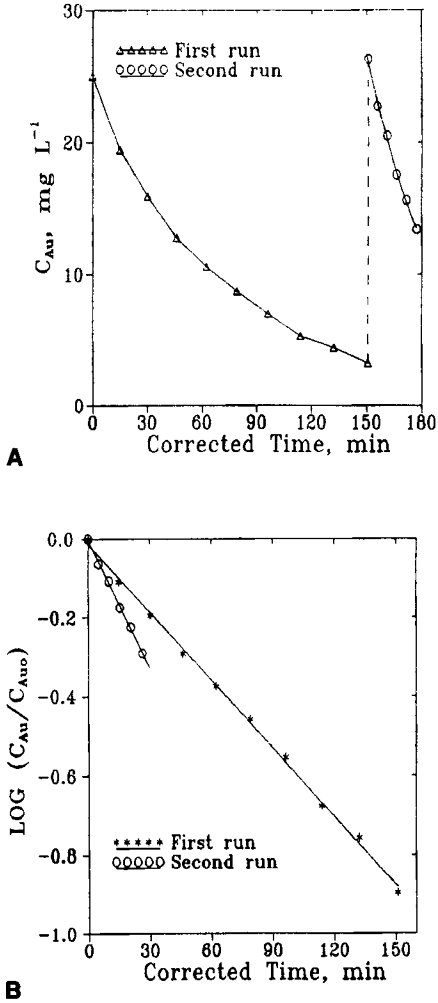

FIG. 1 (A): Gold–iodide complex concentration changes as a function of corrected time at standard conditions during the two long-term experimental runs. (B): The above data plotted in the form of first-order kinetics.

results during both runs. Since the major part of iodine was consumed during the first run, a subsequent increase of cementation rate was observed during the second run due to the reduction of interference caused by Reaction (2).

In Fig. 2 a comparison is made between the zinc concentrations measured during a cementation experiment in the complete absence of iodine and the predicted ones from the stoichiometry of Reaction (1). It is obvious that zinc is dissolved almost exclusively by the cementation reaction at the experimental conditions studied, and that in the absence of iodine, the role of other zinc side reactions is negligible.

In hydrometallurgical practice the presence of residual iodine in the leaching liquors will be unavoidable. Thus, all other experiments were carried out in the presence of iodine. In Fig. 3 the influence of the mixer's rotational speed is studied (initial iodine concentration 0.0025 M or 630 mg·L^{-1}). First-order kinetics seems to fit the experimental data well for all experiments.

The measured zinc concentrations during the long-term runs plotted as a function of corrected time are shown in Fig. 4(A). Based on the original assumption that zinc dissolution is mainly due to iodine reduction on the surface of zinc particles and gold cementation, we may accept that changes of iodine concentration are connected with the net zinc concentration changes. The latter is defined as the portion of dissolved zinc resulting from iodine attack. By the stoichiometry of Reaction (2), we have:

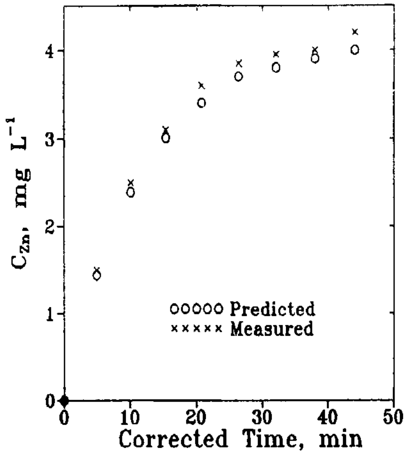

FIG. 2 Predicted and measured zinc concentrations as a function of time during gold–iodide complex cementation in the absence of iodine.

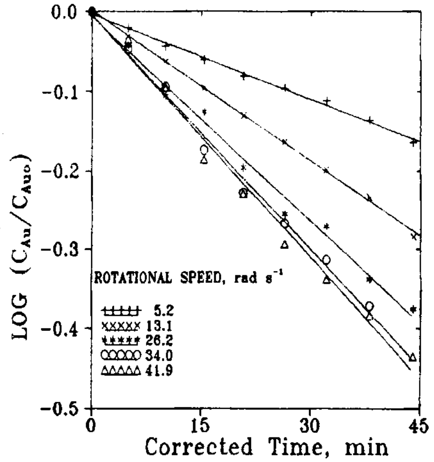

FIG. 3 Gold–iodide complex concentration changes, plotted according to first-order kinetics, as a function of time during cementation at various mixer rotational speeds at standard experimental conditions.

$$C_{Zn} = a(C_{I0} - C_I) \tag{1}$$

where C_{Zn} = net zinc concentration at any time t, calculated by subtracting the zinc quantity produced by gold cementation from the total zinc measured in solution, mg·L^{-1}

a = stoichiometric coefficient according to Reaction (2) (a = 0.259)

C_I = iodine concentration at any time t, mg·L^{-1}

C_{I0} = initial iodine concentration at t = 0, mg·L^{-1}

Assuming that iodine reduction by zinc follows first-order kinetics, iodine concentration at any time t (C_I) is given by

$$C_I = C_0 \exp(K_I \mathrm{A}_{I0} t) \tag{2}$$

where K_I is the apparent iodine reduction rate constant, cm^{-2}·min^{-1}.

By prediction from Eq. (1), zinc dissolution may be expressed by

$$C_{Zn} = C_{Zn0}[1 - \exp(K_I \mathrm{A}_{I0} t)] \tag{3}$$

where C_{Zn0} is the maximum zinc concentration assuming complete consumption of iodine, predicted from the stoichiometry of Reaction (2).

According to Eq. (3), a linear relation must exist between $\log[(C_{Zn0} - C_{Zn})/C_{Zn0}]$ and t.

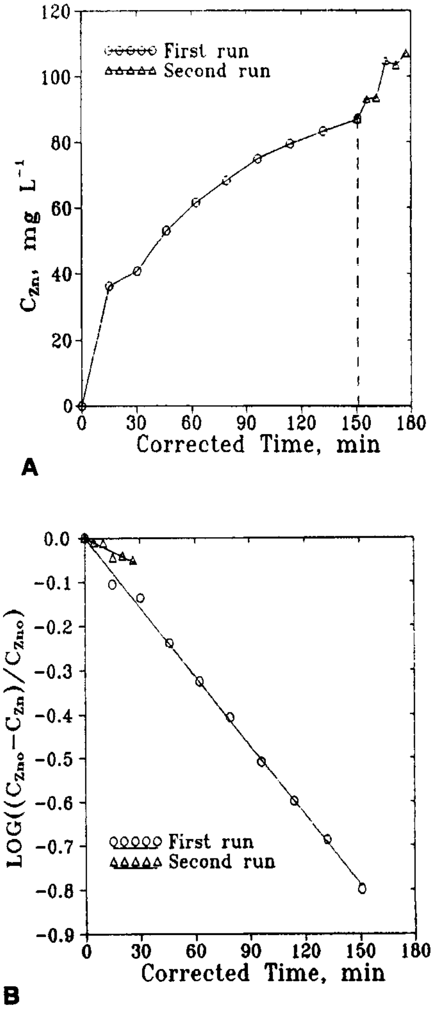

FIG. 4 (A): Net zinc concentration changes as a function of corrected time at standard conditions during the two long-term experimental runs. (B): The above data plotted in the form of first-order kinetics.

The zinc concentrations measured during the long-term runs are plotted according to the above relation in Fig. 4(B). The linear relation observed confirms the proposed mechanism. A retardation of the zinc production rate during the second run is attributed to the presence of less iodine. In

Fig. 5 a study of the influence of the mixer's rotational speed is given. The results are presented in the form of $\log[(C_{\mathrm{Zn}0} - C_{\mathrm{Zn}})/C_{\mathrm{Zn}0}]$ as a function of time. A linear relation fits well the data from all experimental runs.

Mixer's Rotational Speed and Temperature Effect

A series of experiments was carried out to determine the effect of the mixer's rotational speed on the rate of gold cementation. The rotational speeds studied were between 0 and 41.9 $\mathrm{rad \cdot s^{-1}}$. The calculated apparent rate constants for gold cementation and net zinc production (based on first-order kinetics), are plotted as a function of the square root of the rotational speed in Fig. 6(A) and Fig. 7(A), respectively. The linear relationship observed between the square root of the rotational speed and the respective apparent rate constants is characteristic of systems controlled by diffusion.

The effect of the temperature on the apparent cementation and iodine reduction rate constants is essential to know in order to calculate the activation energy of the reactions. The temperature varied between 15 and 45°C. Arrhenius plots for the gold cementation and net zinc production systems are shown in Fig. 6(B) and Fig. 7(B). The activation energy values were found to be 17.3 and 13.8 $\mathrm{kJ \cdot mol^{-1}}$ for gold cementation and net zinc production, respectively, which are representative of reactions under diffusion control.

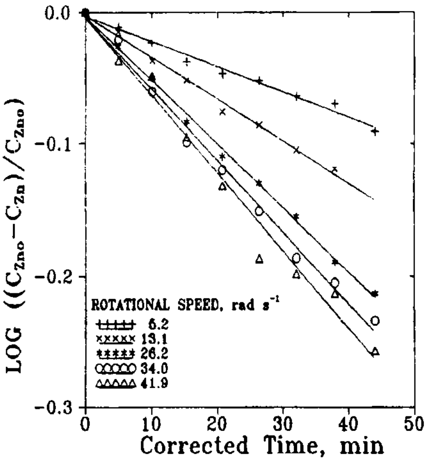

FIG. 5 Net zinc concentration changes, plotted according to first-order kinetics, as a function of time during cementation at various mixer rotational speeds at standard experimental conditions.

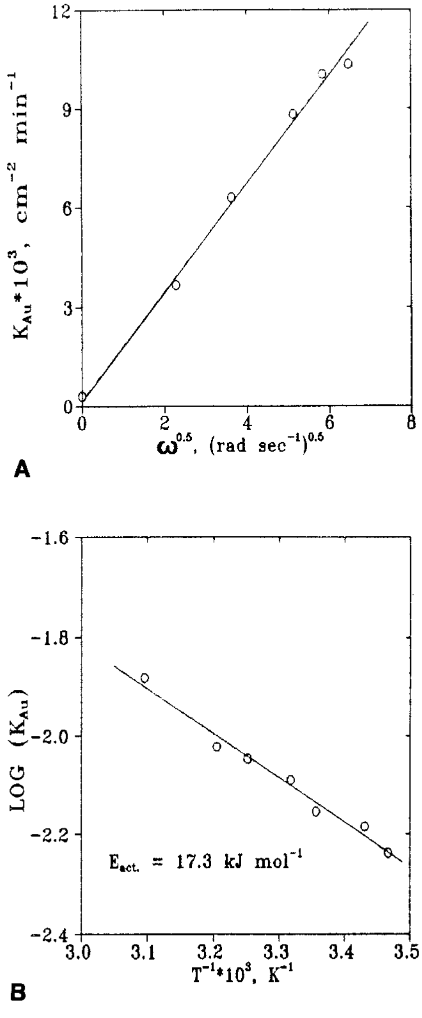

FIG. 6 (A): Apparent gold cementation rate constants as a function of the radical of rotational speed. (B): Arrhenius plot for gold–iodide complex cementation.

Zinc Particle Size Effect

A series of experiments was conducted to examine the influence of zinc particle size on gold cementation and zinc dissolution apparent rate constants. In Figs. 8(A) and 8(B) the calculated rate constants are plotted

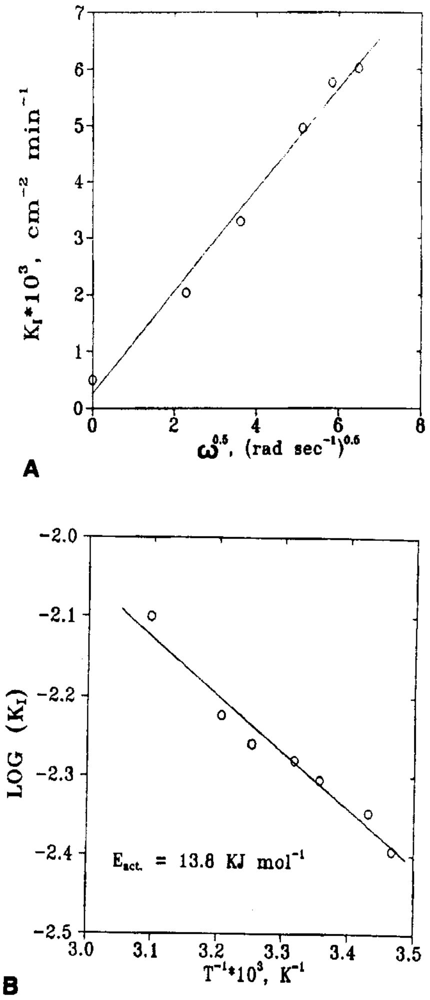

FIG. 7 (A): Apparent net zinc dissolution rate constants as a function of the radical of rotational speed. (B): Arrhenius plot for net zinc dissolution.

as a function of the inverted geometrical mean of each particle's size fraction. The geometrical mean was used since it gives a more representative value of the average diameter of nonuniform particles (1).

According to the proposed kinetic model, a linear relationship should exist between the apparent rate constants and the respective initial anodic

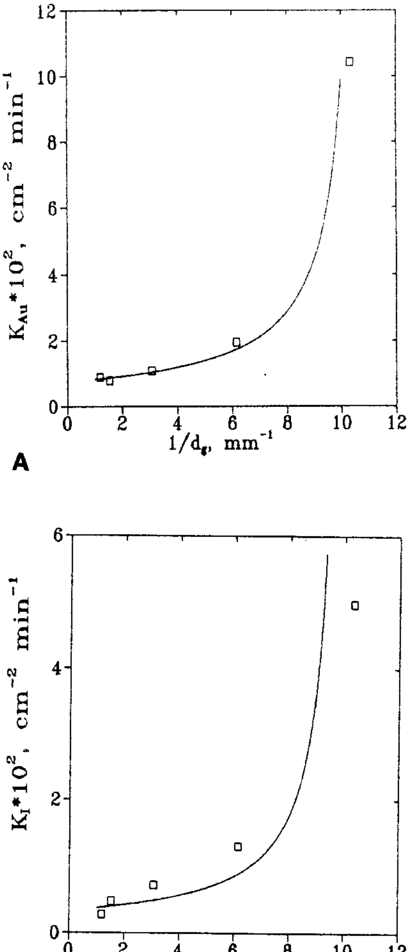

FIG. 8 (A): Apparent gold cementation rate constants as a function of the particles' geometrical mean diameter. (B): Apparent net zinc dissolution rate constants as a function of the particles' geometrical mean diameter.

surface:

$$K_i = k_i A_{i0} \tag{4}$$

where i refers to gold or iodine.

Assuming that the zinc particles are spherical with a diameter equal to the geometrical mean of the respective fraction, the total particle surface will be given by

$$A_0 = nE = m/(\rho\pi d_g^3/6)\pi d_g^2 = 6m/\rho d_g = C/d_g \tag{5}$$

where n = number of zinc particles
E = each particle surface
m = zinc particles mass, 1 g
ρ = zinc density, 7.14 g·cm^{-3}
π = 3.14
d_g = geometrical mean of particle fraction diameter

Considering Eqs. (4) and (5), the apparent rate constant is expected to be a linear function of $1/d_g$. A nonlinear regression analysis of the experimental data gave the following mathematical relation:

$$K_i = 1/(a_i d_g + b_i) \tag{6}$$

where a_i and b_i are constants.

The simulation curves are drawn in Figs. 8(A) and 8(B) according to Eq. (6).

At larger particle diameters the product $a_i d_g$ is considerably higher than b_i, and the second constant may be omitted in calculating the expected linear correlation between rate constant and the inversion of particle diameter. As the size of the particles decreases, the product $a_i d_g$ and the constant b_i have comparable values, giving a substantial increase to the rate constants. This behavior is related to the hydrodynamics of the specific reactor. As the size of the particles decreases, more particles leave the bottom of the reactor and are suspended in the solution, increasing the reaction rate.

The gold cementation yield, as expected, increases considerably as the size of the particles decreases from 56.2% (−850 μm to +500 μm) to 94% (−125 μm to +75 μm) in 45 minutes.

Initial Gold–Iodide Complex and Iodine Concentration Effect

The distribution of the initial total anodic active surface between the two parallel reactions (gold cementation and zinc dissolution) depends on the rate at which each reagent reaches the zinc particle's surface. Thus, we can accept that

$$r_{\mathrm{Au}}/r_{\mathrm{I}} = k_{\mathrm{Au}}C_{\mathrm{Au0}}/k_{\mathrm{I}}C_{\mathrm{I0}} = A_{\mathrm{Au0}}/A_{\mathrm{I0}} \tag{7}$$

Since

$$K_i = k_i A_{i0} \tag{8}$$

we may write

$$K_{Au}C_{Au0}/K_IC_{I0} = A^2_{Au0}/A^2_{I0} \tag{9}$$

By substituting A_{an0} for $A_{Au0} + A_{I0}$ and making the proper transformations, we have

$$A_{Au0} = A_{an0}\{K^{0.5}_{Au}C^{0.5}_{Au0}/[C^{0.5}_{I0}K^{0.5}_{I} + K^{0.5}_{Au0}C^{0.5}_{Au0}]\} = A_{an0}C_{Au0}F_{Au} \tag{10}$$

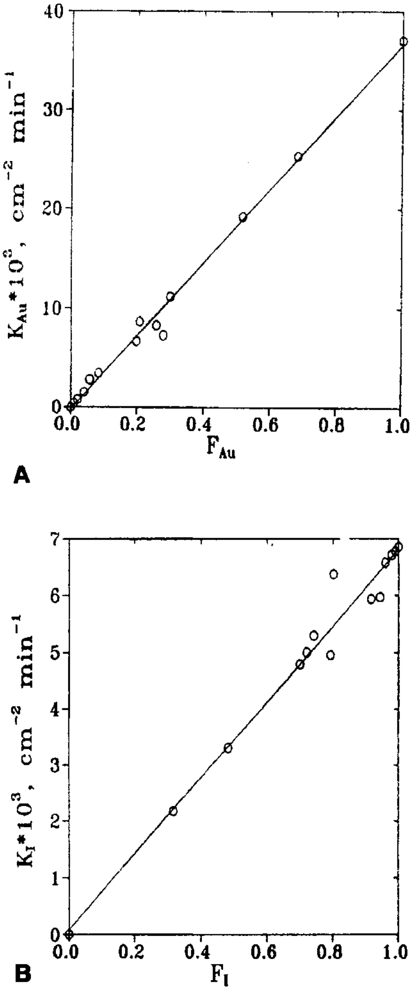

FIG. 9 (A): Apparent gold cementation rate constants as a function of the F_{Au} parameter. (B): Apparent net zinc dissolution rate constants as a function of the F_I parameter.

Finally, the respective apparent rate constants are given by

$$K_i = k_i A_{i0} = k_i A_{\mathrm{an}0} F_i \tag{11}$$

In Figs. 9(A) and 9(B) the experimental results of various experiments conducted at different initial gold–iodide complex and iodide concentrations are plotted as a function of F_i. As expected, a well-established linear correlation exists, showing that the relative diffusion rate of the gold complex and iodine species, from the bulk of the solution to the zinc particle's surface, controls the cementation rate.

CONCLUSION

The cementation zinc particles may be effectively used for gold separation from gold–iodide complex bearing solutions.

The reaction seems to be under diffusion control. As the size of the particles and iodine concentration decrease, the reaction rate increases considerably.

The presence of elementary iodine causes excess zinc dissolution and, subsequently, retardation of the cementation reaction rate. In hydrometallurgical practice it would be desirable to consume all the iodine present in the lixiviant during the ore leaching stage.

A first-order kinetic model was established to explain the experimental findings. Mathematical relations were established to connect the reaction rates with mixing rate, zinc particle size, and initial gold complex and iodine concentrations.

NOMENCLATURE

a	stoichiometric coefficient according to Reaction (1)
$A_{\mathrm{an}0}$	total initial anodic surface of zinc particles
A_{Au}	anodic surface including active sites for gold cementation at a given time t, cm^2
$A_{\mathrm{Au}0}$	initial anodic active surface offered for gold cementation, cm^2
$\mathrm{A}_{\mathrm{I}0}$	initial anodic active surface offered for iodine reduction, cm^2
C_{Au}	gold–iodide complex concentration at a given time t, $\mathrm{mg \cdot L^{-1}}$
$C_{\mathrm{Au}0}$	initial gold–iodide complex concentration, $\mathrm{mg\ L^{-1}}$ or $\mathrm{mg \cdot cm^{-3}}$
C_{I}	iodine concentration at given time t, $\mathrm{mg \cdot L^{-1}}$ or $\mathrm{mg \cdot cm^{-3}}$
$C_{\mathrm{I}0}$	initial iodine concentration, $\mathrm{mg \cdot L^{-1}}$ or $\mathrm{mg \cdot cm^{-3}}$

C_{Zn}	net zinc concentration at a given time t, $mg{\cdot}L^{-1}$ or $mg{\cdot}cm^{-3}$
C_{Zn0}	zinc concentration calculated from the initial iodine concentration from the stoichiometry of Reaction (2)
d_g	geometrical mean of particle fraction diameter, cm
E	particle surface, cm^2
K_{Au}	gold cementation apparent rate constant, $cm^{-2}{\cdot}min^{-1}$
K_I	apparent iodine reduction rate constant, $cm^{-2}{\cdot}min^{-1}$
k_{Au} or k_I	diffusional rate constant, min^{-1}
m	zinc particles mass, g
n	number of zinc particles
π	3.14
ρ	zinc metal density, $g{\cdot}cm^{-3}$
r_{Au}	gold cementation rate, $mg{\cdot}cm^{-3}{\cdot}min^{-1}$
r_I	iodine reduction rate, $mg{\cdot}cm^{-3}{\cdot}min^{-1}$

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