Recovery of Copper from Synthetic Solution by Cementation on Moving Bead of Zinc Spheres

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ABSTRACT

This work deals with the cementation of copper from sulfate solution on moving zinc beads as sacrificial metal using magnetic stirring. The efficiency of zinc beads in copper recovery has been estimated in terms of kinetic and apparent mass transfer coefficients according to operating parameters such as initial copper ion concentration, rotational speed, zinc beads diameter as well as temperature. Kinetic investigation showed that the copper cementation reaction follows a first order reaction and the activation energy was calculated. The rate of diffusion controlled cementation of copper ions was expressed in terms of the mass transfer coefficient; the data were correlated with the following dimensionless correlation: \( \text{Sh} = 0.7485 \text{Sc}^{0.33} \text{Re}^{0.53} \). The resulting samples of zinc beads surface and copper precipitate were characterized by two analysis methods, scanning electron microscopy (SEM) and X-Ray (EDX) which confirmed that about 99% of copper can be recovered from the sulfate solution.

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1. Introduction

The spontaneous reduction of a metal ion contained in a liquid phase onto a more electronegative solid metal, known as cementation, has recently gained a renewed interest for its application. This technique is successfully used for the recovery, reduction or elimination of metallic ions. The advantages of cementation lie in the fact that it is relatively simple easy to control, and low energy consumption. The process has been largely used in industry for a long time, not only in hydrometallurgy but also in industrial effluent treatments and purification of electrolytic baths. Cementation reaction is a heterogeneous process limited by diffusion through the mass transfer boundary layer. However, unlike, many other heterogeneous reaction systems, cementation reactions are unique in that the reaction product usually does not impede the reaction progress but rather frequently enhance the reaction kinetics. Researchers usually attributed this phenomenon to the electrochemical nature of cementation reaction and also to the structure of the cementsed deposit. 1-4

Copper ions or heavy metals generally, as pollutants, do not accumulate in the human body in massive amounts, though copper can cause illness or even death. So, copper and heavy metals that may be present in industrial wastewater must be removed. Cementation is one of the most effective and economic techniques for recovering toxic metals from industrial wastewater. The removal of copper ions by cementation has been studied by a number of researchers who used different methods to enhance the rate of cementation. 5,6

Zinc has been chosen as sacrificial metal because of its low cost and possible use in hydrometallurgical process. As cementation system like copper/zinc is known to be generally governed by mass transfer, the objective of chemical engineering is to increase both convective mass transfer and reaction surface in order to improve the cementation reaction. 7

The main objective of the present work is to investigate the cementation of copper ions on moving zinc beads under the influence of different operating parameters including copper concentration, rotational speed, zinc beads diameters and temperature. An additional objective is to develop the industrial application of the reaction in copper recovery processes. Scanning electron microscopy and energy dispersive X-ray spectrometry (EDX) were used to examine cementation reaction products.

2. Experimental Part

2.1 Materials

Analar grade copper sulfate (Adwic chemicals) and distilled water were used in preparation of a stock solution of copper. The concentration of the stock was confirmed with atomic absorption spectrophotometer. Then, dilutions were done. Zinc beads with high grade purity of 99.9% (J.T.Baker Inc.) were used. Its shape is spherical with a diameter of 0.54 cm and a weight of 0.5 g for each one.

2.2 Measures and analysis

The experiments were done by using Dragon digital (hotplate) magnetic stirrer MS-H-Pro with temperature sensor PT 1000. Samples (0.25 ml) are withdrawn in the storage tank. They are used in atomic absorption spectrophotometer at 324.8 nm wavelength of copper to determine dissolved copper concentration. Copper deposit is observed by scanning electron microscopy (SEM) technique and energy dispersive X-Ray fluorescence (EDX) technique to determine the chemical composition of Zn beads with a Jeol-JSM-5300 apparatus. Solution density and viscosity needed for data analysis were determined using hydrometer according to ASTM method D1298 and Ostwald viscometer respectively. Crison GLP 21 pH-meter was used to adjust pH of solutions. Diffusivity of CuSO4 was taken from literature 8-9 and was corrected for the change in temperature using Stokes-Einstein equation.

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2.3 Procedure

Experiments were performed by stirring zinc beads and 100 ml of CuSO₄ solution in a cylindrical reactor of 10 cm diameter and 25 cm height fitted with a magnetic stirrer of 1 cm length and 0.5 cm diameter resting on the container bottom. The pH of the solution was fixed at 5.3. Experiments were carried out at different temperatures 301, 308, 313, and 318 K, stirring speed were 100, 250, 400, 500, and 700 rpm, initial copper ions concentration were 50, 75, 100, 150, and 200 mg/l, zinc spheres in the amount 1, 2, 3, and 4 g were used and the corresponding diameter were 1.08, 2.16, 3.24, and 4.32 cm respectively. 0.25 ml of the aliquots was taken from the solution of the reaction at different time intervals for analysis. The solution was filtered to separate the cemented copper as precipitate then washed by distilled water and left to dry at room temperature. Copper deposits on zinc beads and precipitated copper obtained after filtration were examined by SEM techniques.

3. Results and Discussions

3.1 Copper cementation kinetics

It is generally agreed that the rate-controlling step in the cementation process is usually the diffusion of copper ions to the zinc surface. In this case, the rate of change of copper concentration in the solution follows the following equation,

\[
\ln \left( \frac{C_o}{C} \right) = \frac{kA}{V} t
\]

(1)

where \( C_o \) is the initial concentration of copper ions (mg/l), \( C \) is the Cu²⁺ ions concentration (mg/l) in solution at time \( t \) (min), \( k \) is the mass transfer coefficient (cm s⁻¹) and is used to express the rate of cementation, \( V \) is the solution volume (cm³), \( A \) is the area of zinc beads (cm²) [number of zn bead × bead area], and \( t \) is the reaction time (min).

The rate of mass transfer is proportional to the copper concentration in solution and the exposed zinc area. During laboratory scale experiments were carried out in a temperature range from 301 to 318 K by shaking 100 ml of 50, 75, 100, 150, and 200 mg/l copper sulfate solution at an initial pH of 5.3. The reaction kinetics was evaluated by plotting \( \ln \left( \frac{C_o}{C} \right) \) against time as shown in Fig. 1. It is clear that the rate of cementation increases with increasing concentration, speed of rotation, zinc beads dosage, and increases also with increasing temperature, i.e., the cementation rate increases in the direction of precipitation of copper. The mass transfer coefficient of copper \( (k) \) was obtained from the slope of the plot and given in Table 1. The data show that \( k \) increases with increasing CuSO₄ concentration.

The increase in \( k \) with initial CuSO₄ concentration may be attributed to the fact that, as the initial concentration of noble metal in solution increases, the deposited copper tends to pass from a fine-grained, compact and barely porous structure to a coarse-grained porous structure, which increases surface roughness and so promote the formation of eddies, thus leading to an increase in the rate of mass transfer. The continued removal of copper ions with time indicates that the deposited copper layer is porous and allows copper ions to diffuse through it to react with zinc. Figure 1 also indicates that cementation reaction is a first-order reaction, which was verified by other authors.

The increase in the rate of cementation with increasing initial CuSO₄ concentration may be also caused by the following additional effects of initial Cu²⁺ concentration:

i) Cementation takes place through the galvanic cell:

\[ \text{Zn/CuSO₄/Cu} \]
in the absence of supporting electrolyte Cu²⁺ ions are transferred to the cathodic sites by diffusion and electrical migration both of which increases with increasing initial CuSO₄ concentration.1,6,11

ii) With increasing the initial Cu²⁺ concentration the porous copper deposits grow rapidly with a consequent increase in the cathode area. Since the reaction rate is controlled by the cathodic process,12 it follows that the rate of cementation as well as the mass transfer coefficient should increase with initial Cu²⁺ concentration.

The percentage of removal of copper is calculated from the relation:

\[
\% \text{removal} = \frac{(C_0 - C)}{C_0} \times 100
\]  

Figure 2 shows the effect of initial concentration of Cu²⁺ on the % removal of copper (which is equivalent to the rate of cementation). It is clear that the % removal is increased by increasing Cu²⁺ concentration.

For the displacement reaction in Eq. (3):

\[
\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}
\]

The increase in the zinc concentration (Δ[Zn²⁺]) in solution at any time should exactly balance the decrease in copper concentration (Δ[Cu²⁺]). However, the reaction was not stoichiometric as typical set of results (Fig. 3) indicates that the rate of increases of the zinc concentration exceeded the rate of decrease of the copper concentration.13 The most likely cause of this imbalance is the retardation of H⁺ and dissolved oxygen along with Cu²⁺ deposition. Recalling the fact that cementation takes place through the galvanic cell: Zn/electrolyte/Cu, the following reaction likely to take place during cementation at the present pH 5.3.

![Figure 2](image2.png)

**Figure 2.** Relationship between % removal after 60 min and different initial copper ions concentration at different doses of zinc beads and.

![Figure 3](image3.png)

**Figure 3.** Change of zinc, copper and proton concentrations during a typical displacement reaction.

3.2 Influence of rotational speed

The rate of reaction was calculated from the slopes of the plots (Fig. 1) and tabulated in Table 1. It is clear from Figs. 4 and 5 that the rate of cementation represented by k and % removal increase with increasing speeds of rotation. Thus confirming the diffusion controlled nature of the cementation process.14,15 The data fit the equation:

\[
k = \alpha \omega^n
\]  

Values of n are 0.425, 0.420, 0.439, and 0.587 at 50 mg/l for 1, 2, 3, and 4 g of zinc beads respectively.

The exponent (n) is in good agreement with a diffusion-controlled cementation reaction under laminar conditions.16 The increase in the rate of cementation with increasing the rotational speed may be attributed to:

- The higher the rotational speed, the higher the solution momentum and the thinner the diffusion layer (δ) surrounding each zinc bead, since \( k = D/\delta \) it follows that k should increase. On the other hand,
the relative motion between the solution and the zinc beads may lead to boundary layer separation and turbulent wake formation in the rear of each bead, this turbulent wake contribute to enhancing the rate of mass transfer and the rate of cementation through surface renewal of the solution at each bead.9

3.3 Influence of zinc beads diameter

The influence of Zn beads diameter on the kinetics of copper cementation is illustrated in Fig. 4. As the dose of Zn beads increases, and consequently the diameter of moving beads Zn spheres increases, the mass transfer coefficient decreased as in Table 1 and Fig. 6. This may be attributed to the fact that as each bead rotates in solution a hydrodynamic boundary layer and diffusion layer are built on its surface. As the Zn diameter increases the average thickness of the hydrodynamic boundary layer increases with a consequent increase in the diffusion layer thickness; accordingly, the mass transfer coefficient decreases.15,18

3.4 Influence of temperature

Temperature is a key parameter in determining reaction rates and mechanisms; so, cementation process was performed at different temperatures: 301, 308, 313, and 318 K. The cementation kinetics is getting more significant as temperature increases. Typically, the apparent mass transfer coefficient rises within the temperature range to be 16.83 × 10⁻³, 19.74 × 10⁻³, 22.20 × 10⁻³, and 24.58 × 10⁻³ cm s⁻¹ for 301, 308, 313, and 318 K respectively at 700 rpm, 100 mg/l and 4 g Zn beads dose.9

As a consequence, the increase in the rate of cementation can be explained by evaluation of the change of physical properties with temperature (viscosity and diffusion coefficient), and part of it can be attributed to changes in deposit morphology; i.e. increasing solution temperature favors the copper cementation probably because the increase of temperature reduces solution viscosity with a consequent increase in Cu²⁺ diffusivity (D) according to the Stokes-Einstein equation.19

\[
\frac{\mu D}{T} = \text{Constant}
\] (9)

The increase in diffusivity with temperature also increases the mass transfer coefficient \( (k = D/\delta) \) and the rate of cementation.3,16

In order to confirm the diffusion controlled nature of the cementation reaction, an Arrhenius plot based on first-order kinetics was examined for the temperature range 301–318 K. Figure 7 is a plot of ln\( k \) against \( 1/T \) at 100 mg/l of initial copper ions and constant 700 rpm.

\[
\ln k = \ln A - \frac{E_a}{RT}
\] (10)

From the slope of this plot, the activation energy of the cementation reaction \( (E_a) \) was calculated. The results indicated that, the present data fit the Arrhenius equation with activation energy 17.83 kJ mol⁻¹ which shows that the cementation process is diffusion controlled.3,4,20

The thermodynamic activation activation parameters namely, enthalpy of activation \( \Delta H^\circ \), entropy of activation \( \Delta S^\circ \) and free energy of activation \( \Delta G^\circ \) were calculated from the following equations:5,9,18

\[
\Delta H^\circ = E_a - RT
\] (11)

\[
\Delta S^\circ /R = \ln A - \ln \beta eT/h
\] (12)

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\] (13)

where \( A \) is the frequency factor, \( \beta \) is the Boltzmann constant, \( e \) is 2.7183, \( h \) is Plank’s constant, \( R \) is ideal gas constant \( (J\ mol^{-1}K^{-1}) \), and \( T \) is the absolute temperature (K).
Table 2. Thermodynamic activation parameters at 700 rpm, 100 mg/l initial copper ion concentration and 4 g Zn beads dose.

<table>
<thead>
<tr>
<th>Temp. K</th>
<th>ΔHº (kJ/mol)</th>
<th>ΔSº (J/mol·K)</th>
<th>ΔGº (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>15.33</td>
<td>-228.04</td>
<td>83.96</td>
</tr>
<tr>
<td>308</td>
<td>15.27</td>
<td>-228.23</td>
<td>85.56</td>
</tr>
<tr>
<td>313</td>
<td>15.23</td>
<td>-228.36</td>
<td>86.70</td>
</tr>
<tr>
<td>318</td>
<td>15.18</td>
<td>-228.49</td>
<td>87.84</td>
</tr>
</tbody>
</table>

The data of thermodynamic parameters are listed in Table 2. These data show positive sign for ΔHº, reflecting the endothermic nature of cementation process; highly negative values of ΔSº indicating a more ordered system. The positive values of ΔGº mean that the cementation reaction of copper onto zinc is non spontaneous reaction. At all temperatures ΔHº and ΔSº compensate each other to produce little change in ΔGº.

3.5 Data correlation

Since the cementation reaction is a mass transfer process and in order to evaluate the hydrodynamic effect over the mass transfer in our work, the method of dimensional analysis is used to correlate all data. The mass transfer coefficient can be correlated to different variables by the functional equation:

\[ k = f(\mu, \rho, D, N, d) \]  \hspace{1cm} (14)

Dimensional analysis leads to the dimensionless equation:

\[ Sh = \alpha Sc^{0.33} Re^{0.6} \]  \hspace{1cm} (15)

where \( Sh \) is the Sherwood number, \( Sh = kd/D \), describes mass transport by forced convection; \( Sc \) is Schmidt number, \( Sc = \mu/\rho D \) relates the electrolyte transport properties, \( Re \) is the Reynolds number, \( Re = \rho Vd/\mu \) is an indication of the fluid flow regime, \( \alpha \) and \( \beta \) are constants, \( d \) is the diameter of zinc beads in cm, \( \rho \) is the density of solution (g/cm³), \( V \) is the rotational velocity = \( ad/2 \), \( \omega \) is the angular velocity (rad s⁻¹), \( \mu \) is the viscosity of solution (g cm⁻² s⁻¹), \( D \) is the diffusion coefficient (cm² s⁻¹), \( k \) is the mass transfer coefficient (cm s⁻¹). The exponent of \( Sc \) was fixed at 0.33 following previous theoretical and experimental studies in mass transfer. For Reynolds number (\( Re \)) values between 1.11 × 10⁴ < \( Re \) < 7.77 × 10⁵. The calculated apparent mass transfer coefficient was plotted as Sherwood number (log \( Sh/Sc^{0.33} \)) against Reynolds number (log \( Re \)). Figure 8 shows that plotting of log \( Sh/Sc^{0.33} \) vs. log \( Re \) a slope of 0.53 was obtained. The data can be represented with average deviation of ±13.16 by the equation:

\[ Sh = 0.7485R^{0.51}Sc^{0.33} \]  \hspace{1cm} (16)

The present Re exponent, 0.53 is in good agreement with a diffusion-controlled cementation reaction under laminar flow conditions.³,⁸,¹⁶

3.6 Morphological study

Scanning electron Microscopy (SEM) was used to examine the morphology of the cemented copper. This examination confirmed the change in the Zn beads surface as a consequence of the cementation process. All experiments proceeded at 301 K, 500 rpm, 60 min and 4 g of zinc dose and changing the initial copper ions concentration. Figure 9(a) before cementation, SEM showed a smooth surface of zinc beads. After 60 min of cementation reaction with respect to 50 and 200 mg/l of initial copper ions concentration, Figs. 9(b) and 9(c) reveal that the copper deposits seem to be in complete layer composed of globular crystallines with cluster shaped with numerous holes, which have been created. Accordingly, the increase in the copper cementation rate is strongly due to the morphology changes of deposit. The rate enhancement can result either from changes in deposit structure generating increase in the reactive surface area, or from the laminated flow associated increasing roughness of the deposit.

Also, as a product of cementation process, SEM was done on filtrated copper powder after the reaction. The solution was filtered to separate the cemented copper as a precipitate. These results show
that the cementation of copper by zinc beads under the experimental condition is an efficient method for the recovery of copper from cemented solution. Figures 9(d) and 9(e) for separated copper precipitate reveal that, at low initial copper ions concentration, the precipitate has a tendency to form coarse particles with small dentic structure. By increasing the initial copper ions concentration to 200 mg/L, the precipitate became highly dentic with Cauliflower shape.5,22

3.7 EDX spectroscopy study

The presence of copper onto zinc beads was confirmed with EDX analysis which was conducted with a very small electron beam as shown in Fig. 10 and Table 3. We have chosen the reaction of 500 rpm, 200 mg/L, 4 g of zinc at 301 K for studying by using the energy dispersive X-ray (EDX) because it achieved the optimum conditions of copper ions removal. The reaction was terminated after 60 min, and the zinc beads were dried at room temperature to avoid any unexpected effects of the high temperature. The majority of the surface was zinc. So, further cementation of copper is possible; also, that can be considered another reason that the rate of the reaction and the percent of removal increase with increasing initial copper concentration. The presence of sulfur onto the surface of zinc beads is a result of the presence of SO$_4^{2-}$ ions in the solution of the reaction.

3.8 Industrial application

The purity of the precipitated copper powder after filtration obtained from the present work was 99%, and the remaining was sulfur as a result of the presence of CuSO$_4$ in the solution. The percentage of recovery of copper ions was about 99% at 500 rpm, 200 mg/L and 4 g of zinc beads. The purity of the product copper was confirmed by using EDX analysis as shown in the following Fig. 11 and Table 3. The resulting copper powder has the potential of being used in paint industry as a pigment, in producing metallic composites by the powder metallurgy technique and as a catalyst for organic synthesis.

Table 3. Element compositions of pure zinc beads and precipitated copper after cementation.

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Zn</th>
<th>S</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc beads</td>
<td>61.3</td>
<td>1.3</td>
<td>37.4</td>
</tr>
<tr>
<td>Precipitated Cu</td>
<td>—</td>
<td>1.3</td>
<td>98.7</td>
</tr>
</tbody>
</table>

4. Conclusions

In this paper, attention was focused on copper cementation on moving beads of zinc spheres, as a sacrificial metal. Our purpose was to evaluate the effect of different operating parameters on this process. The enhancement in the rate of mass transfer was found to depend mainly on the initial copper ion concentration, rotational speed, zinc beads dosage and temperature. For higher rate of mass transfer, we should have higher initial copper ion concentration, rotational speed and temperature. The larger zinc beads diameter, the lower rate of mass transfer. The dimensionless equation obtained from this study can be used in the design and operation of laminar cementation reaction. The SEM examination confirmed the change in the Zn beads surface as a consequence of the cementation process. These results show that the cementation of copper by moving beads under the used experimental conditions is an efficient method for recovery and separation of copper from cemented solution. The percentage of cemented copper reaches about 99% with very high purity confirmed by EDX analysis.

References