

Removal of Copper from Dilute Solutions by Cementation on Zinc in Baffled Batch-Agitated Vessels

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Rates of Cu^{++} removal from waste solution by cementation on zinc in a baffled-agitated vessel, lined with a cylindrical zinc sheet, were studied under different conditions of impeller rotation speed, initial copper concentration, temperature and time of cementation. It was found that the rate of Cu^{++} removal increases with increasing impeller rotation speed, initial concentration, temperature and residence time at pH 4. The cementation rate temperature dependence was found to be of Arrhenius type with an activation energy of 23 J mol^{-1} confirming the diffusion controlled nature of the reaction. Mass transfer study of the process has revealed that the data for the conditions: $57\,628 < Re < 485\,550$ and $638 < Sc < 1697$ fit the following dimensionless equation:

$$Sh = 0.035Re^{0.89} Sc^{0.33}$$

Key words:

Wastewater, cementation, copper removal, mass transfer, agitated vessels.

Introduction

Environmentalists concern over the presence of toxic heavy metals in the aquatic environment stems from the fact that these metals are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain. Furthermore, the presence of heavy metal ions in wastewater inhibits biodegradation of organic pollutants, which might be present in the wastewater. A variety of industries are responsible for the release of heavy metals into the environment through their wastewaters. Growing concern over the removal of heavy metals from wastewaters has stimulated many researchers to develop various treatment processes.

Copper, which is very detrimental for both, aquatic life and biological treatment of wastewater can be found in many wastewater sources including printed circuit board manufacturing, metal finishing industry e.g. pickling of copper and its alloys, electroplating and electroless plating, electropolishing, paint manufacturing, wood preservatives and printing operations.

Cementation is one of the most effective and economic techniques used for removing toxic and/or valuable metals from industrial waste solutions. Cementation is also used widely to purify leach liquors from more noble impurities in the electrowinning of metals from natural ores. The cementation reaction is a heterogeneous process in which electropositive less-toxic sacrificed solid metal is utilized for the recovery of electronegative

dissolved metal species. The metal displaced from the solution is deposited on the surface of the less noble metal which is simultaneously dissolved, *Wadsworth*¹ has reviewed the theory and application of the process.

The aim of the present work is to study the rate of copper removal from a synthetic waste solution, which simulates industrial waste by cementation on cylindrical zinc sheet lining the inner wall of a cylindrical agitated vessel. The vessel was provided with four baffles to enhance the rate of cementation via modifying the flow pattern in the agitated vessel.

Previous studies on cementation of copper on less noble metals have shown that the reaction is diffusion controlled.²

Accordingly, to increase the rate of cementation stirring is essential. Removal of Cu^{++} by cementation has been studied by many researchers who used different means of stirring such as rotating disc,^{3,4} rotating cylinder,⁵ gas sparging,^{6,7} fixed and fluidized bed,^{8,9,10} and surface vibration¹¹ (oscillation), to enhance the rate of cementation. Recently, *Nosier*¹² used mechanical stirring for removing Cd^{++} from waste solution by cementation on zinc cylindrical sheet lining the walls of unbaffled agitated vessel. He found that the rate of cementation increases with the 0.438th power of the impeller rotation speed.

Mishra and Paraguru^{28,29} and *Kuntyi et al.*³⁰ studied the kinetics of Cu^{++} concentration on Zn from sulphate solutions. *Karavasteva*³¹ studied the kinetics and deposit morphology of copper cementation onto zinc, iron, and aluminum.

Experimental technique

Fig. 1 shows the experimental set-up used in the present work, which consisted of 2 L cylindrical glass container lined with a cylindrical zinc sheet made of 99.9 % pure zinc. The container was fitted with a variable speed stirrer made of carbon steel and fitted with an axial flow impeller. The sheet had 13 cm diameter and 10 cm height. The outer surface of the zinc sheet, which contacted the wall of the cylindrical glass container, was isolated with epoxy resin. The impeller was 45° pitched blade turbine type of 4.5 cm diameter. The impeller was mounted centrally on a 25 cm shaft of the same material and was 2 cm from the vessel bottom. Both the impeller and the shaft were isolated with epoxy resin to avoid copper cementation on them. The shaft was connected to a variable speed motor. The rotational speed of the motor was adjusted by a variac and measured by an optical tachometer. Four vertical plexyglass strips of 1 cm width, perpendicular to the walls of the cylindrical zinc sheet, were fitted to the wall of the agitated vessel to act as baffles. The cylindrical glass container and its contents were immersed in a rectangular thermostated water bath to control its temperature. Before each run, a fresh zinc sheet was used, 1500 mL of fresh copper sulfate solution were introduced into the cylindrical vessel. The rate of cementation was followed by withdrawing five milliliters samples at 2–5 minutes intervals for Cu^{++} analysis. Copper analysis was carried out using idometry.¹³ A temperature range of 25–40 °C was used in carrying out the experiments. The copper-bearing solution was prepared

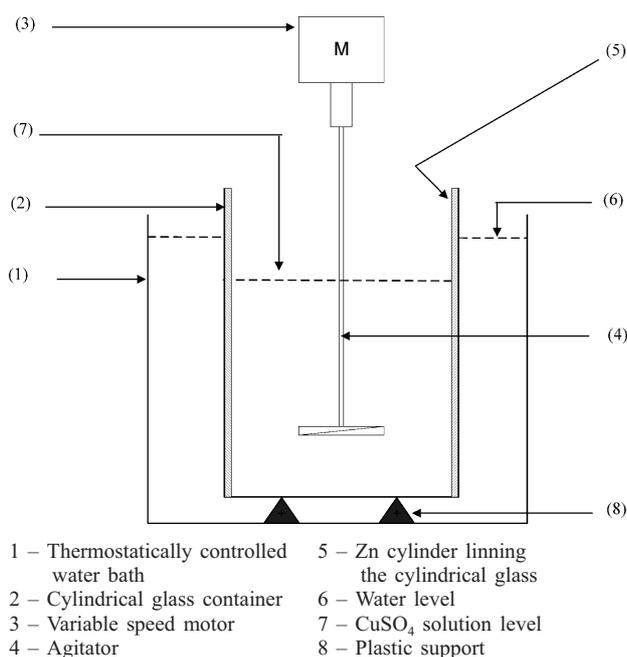


Fig. 1 – Experimental Apparatus

using A.R grade copper sulfate and distilled water. The initial Cu^{++} mass fraction used in this study were $w = 150, 300, \text{ and } 450 \cdot 10^{-6}$ as Cu^{++} . The speed of impeller rotation ranged from $n = 500$ to 3000 min^{-1} , pH of the solution was adjusted at 4 by adding droplets of dilute H_2SO_4 and/or dilute NaOH to avoid formation of copper hydroxyl complexes, which may interfere and inhibit cementation rate for neutral and alkaline solution.¹⁹

Results and discussion

The mass transfer coefficient of the diffusion controlled cementation of Cu^{++} on Zn was determined under different conditions from the batch reactor material balance equation:

$$-Vdw/dt = k_dAw \quad (1)$$

which integrates to

$$\ln \frac{w_0}{w} = \frac{k_d A}{V} t \quad (2)$$

Figure 2 shows a typical $\ln \frac{w_0}{w}$ vs t plot at different speed of rotation, the mass transfer coefficient was calculated from the slope $k_d A/V$.

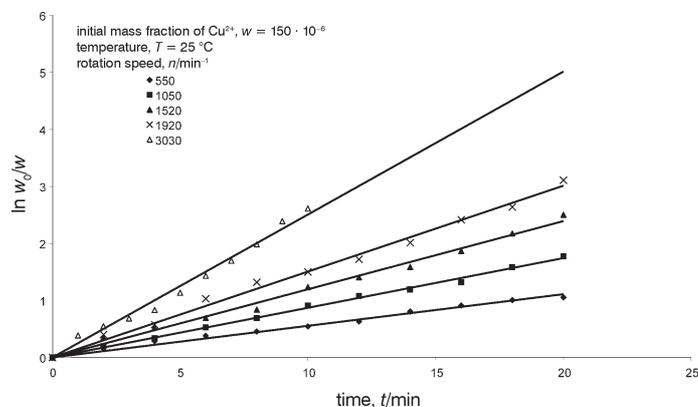


Fig. 2 – Typical $\ln w_0/w$ vs t plot at different rotational speeds

Figure 2 shows that the mass transfer coefficient increases with increasing the angular speed of rotation as a result of the decrease in the diffusion layer thickness at the zinc surface, the data of fig. 2 fit the equation:

$$k_d = B \omega^{0.89} \quad (3)$$

The high ω exponent 0.89 reflects the turbulent nature of the flow, induced by the presence of baffles as compared to the value 0.438 obtained by *Nosier*,¹² who used unbaffled agitated vessel to cement Cd^{++} on Zn using a set up and conditions sim-

ilar to those used in the present work. In the absence of baffles tangential (swirl) flow predominates in the agitated vessel.¹⁵ Installing baffles in the agitated vessel, as in the present work, eliminates the ineffective swirl flow in favor of the other more effective types of fluid motion such as axial and radial flow. The present finding on the enhancing effect of baffles agrees with previous heat and mass transfer studies conducted in baffled and unbaffled agitated vessels.¹⁶

It would be of interest to compare the present ω exponent with the value derived from theoretical considerations. Using *Kolmogoroff's* theory of isotropic turbulence, *Calderbank* and *Moo-Young*¹⁷ derived the following relationship for the mass transfer coefficient in terms of specific energy dissipation (ϵ)

$$k_d \propto Sc^{-0.66} (\gamma)^{0.25} \quad (4)$$

the power consumption in baffled tanks at $Re > 10000$ is given by¹⁵

$$P = K_T n^3 d^5 \rho / g_c \quad (5)$$

i.e. $\epsilon \propto (n)^3$ substituting for ϵ in equation (4) we get

$$k_d \propto Sc^{-0.66} \gamma^{0.25} n^{0.75} \quad (6)$$

since $\omega = 2\pi n$, it follows from equation (6) that

$$k_d \propto \omega^{0.75} \quad (7)$$

The higher exponent 0.89, obtained in the present work compared to the theoretical value 0.75 obtained from *Kolmogoroff's* theory of isotropic turbulence, may be attributed to the increase in surface roughness resulting from copper deposition on the cylindrical zinc sheet; surface roughness enhances the rate of mass transfer through turbulence promotion and increasing the diffusional area.^{18,20,21,22}

Figure 3 shows that the mass transfer coefficient increases with temperature according to *Arrhenius* equation with an activation energy of 23 J mol⁻¹.

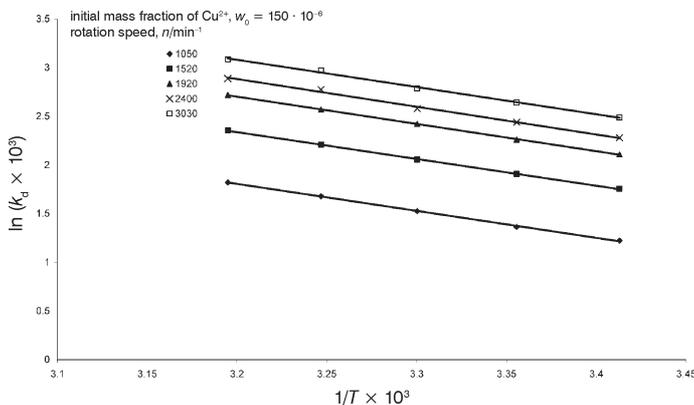


Fig. 3 – Arrhenius plot of the experimental results

The rate of cementation tends to increase with decreasing solution viscosity^{6, 24} probably because of the increase in Cu⁺⁺ diffusivity owing to the decrease in the diffusion layer thickness according to the relation: $k_d = \frac{D}{\delta}$, where δ is the diffusion layer thickness and D is the diffusivity.

The value of the activation energy confirms the diffusion controlled mechanism of the cementation reaction.²³ The value is in a fair agreement with the value obtained by *Strickland* and *Lawson*.²⁷ To correlate the present data using a dimensionless equation, the dimensionless groups Sh , Sc and Re usually used in correlating mass transfer data in agitated vessels were used.

Fig. 4 and 5 show that the present data for conditions $57628 < Re < 485550$, $638 < Sc < 1697$ fit the equation:

$$Sh = 0.035 Re^{0.89} Sc^{0.33} \quad (8)$$

the above equation can be also written in the form of:

$$k_d = 0.035 D^{0.66} d_c^{-1} \rho^{0.56} n^{0.89} d^{1.78} \mu^{-0.56}$$

with an average deviation of $\pm 14\%$.

The above equation can be used to predict the rate of cementation under a given set of conditions, it can also be used to calculate the cylindrical area

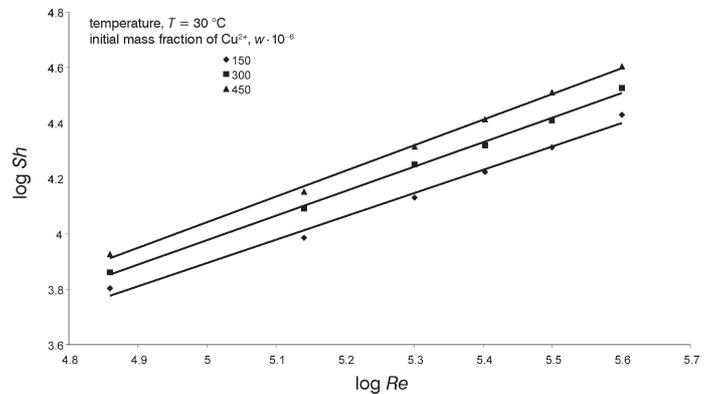


Fig. 4 – log Sh vs. log Re at different initial mass fraction of Cu⁺⁺

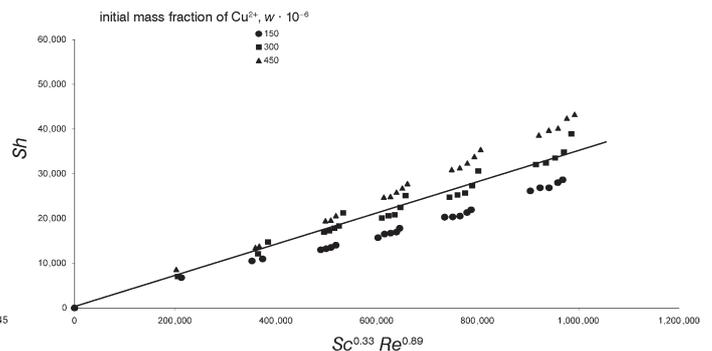


Fig. 5 – Overall mass transfer correlation

required to give a certain rate of cementation at a given rotation speed. In obtaining equation (8) the exponent of Sc was fixed at 0.33 following previous mass transfer studies,²⁵ impeller diameter was used as a characteristic length in calculating Re , while the cylindrical diameter was used as a characteristic length in calculating Sh .

Conclusion

(1) The present results have shown that baffled agitated vessel with axial flow impeller is a powerful tool for conducting diffusion controlled cementation reactions. The reactor can be operated batch wise or as a continuous stirred tank reactor. In the latter case a low solution rate should be used to increase the residence time of the solution in the reactor. The high residence time and the high mass transfer coefficient combine to increase the degree of conversion per pass.

(2) The mass transfer data obtained from rates of cementation under different conditions were correlated using the dimensionless equation:

$$Sh = 0.035 Re^{0.89} Sc^{0.33}$$

Which can also be written in the form:

$$k_d = 0.035 D^{0.66} d_c^{-1} \rho^{0.56} n^{0.89} d^{1.78} \mu^{-0.56}$$

The above equation can be used in the design and operation of the suggested reactor.

(3) Rates of cementation were found to increase with increasing temperature according to *Arrhenius* equation with an activation energy of 23 J mol⁻¹, which confirms the diffusion controlled mechanism of the cementation reaction.

List of symbols

- A – cylindrical sheet surface area, m²
 B – constant (equation (3))
 w_o, w – initial Cu⁺⁺ mass fraction and mass fraction at any time, 10⁻⁶
 D – diffusion coefficient of Cu⁺⁺ into Zn surface, m² s⁻¹
 d – impeller diameter, m
 d_c – cylindrical sheet diameter, m
 E_a – activation energy, J mol⁻¹
 E° – standard e.m.f. of the galvanic cell through which cementation takes place, J mol⁻¹
 F – Faraday's constant, 9 648 456 · 10⁴ C mol⁻¹
 g_c – Newton's – Law proportionality factor
 K – equilibrium constant
 k_d – mass transfer coefficient, m s⁻¹
 K_T – constant which depends on the impeller type (equation (5))

- n – impeller rotation speed, min⁻¹
 P – mechanical power consumed in rotating the impeller
 R – gas constant
 T – temperature, °C
 t – time, min
 V – volume of the solution in the reactor, m³
 v – linear velocity of the impeller
 z – charge number
 Re – Reynolds number ($\rho n d^2 / \mu$)
 Sc – Schmidt number ($\mu / \rho D$)
 Sh – Sherwood number ($k_d d_c / D$)
 ΔG – free energy of the reaction, J mol⁻¹
 ΔG° – standard free energy of the reaction, J mol⁻¹
 ρ – solution density, kg m⁻³
 μ – solution viscosity, Pa s
 ε – specific power dissipation, m² s⁻¹
 γ – kinematic solution viscosity (μ / ρ), m² s⁻¹
 δ – diffusion layer thickness, m
 ω – angular speed of rotation ($\omega = 2\pi n$), min⁻¹

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