

Theoretical considerations of the cementation of copper with iron

by R. D. AGRAWAL*, Ph.D. (Met. Eng.), M.I.I.M. and M. L. KAPOOR*, Ph.D. (Met. Eng.), M.I.I.M.

SYNOPSIS

Cementation has been used extensively by chemists and metallurgists as an economical process for the purification and recovery of metals from dilute solutions.

The paper deals, firstly, with the thermodynamic aspects of cementation, and, secondly, with the effects of various process variables, such as temperature, stirring speed, initial concentration of copper ions, pH of the solution, atmosphere, and surface area of the precipitant metal, on the kinetics of the process in the light of the rate expressions.

SAMEVATTING

Sementering word op groot skaal deur skeikundiges en metallurge gebruik as 'n ekonomiese proses vir die suiwering en herwinning van metale uit verdunde oplossings.

Die referaat handel in die eerste plek oor die termodinamiese aspekte van sementering, en tweedens oor die uitwerking van verskillende prosesveranderlikes soos temperatuur, roerspoed, beginkonsentrasie van koperione, die pH van die oplossing, atmosfeer en oppervlakarea van die metaal wat neerslaan op die kinetika van die proses in die lig van die tempo-uitdrukkings.

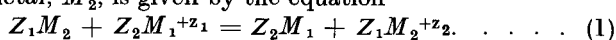
Introduction

Large tonnages of dilute copper-bearing solutions (0.5 to 3.0 g of copper per litre), produced principally from the *in situ*, dump, and percolation leaching of low-grade ores and mine wastes and from electrorefining operations, have become the potential source of copper in many parts of the world. Such solutions are too dilute in copper for direct electrowinning, gaseous reduction, or chemical precipitation. Cementation, which involves the precipitation of an electropositive metal from a solution by an electronegative one, is one of the most ancient, yet economical and efficient, hydrometallurgical processes for the recovery of dissolved metal values from such dilute solutions, as well as for the purification of leach liquors. This process is extensively applied to the removal of copper, cadmium, and thallium from zinc sulphate leach liquors, of copper from nickel sulphate leach liquors, and of gallium from aluminate leach liquors; and to the recovery of copper from dilute run-of-mine solutions, spent electrolyte, and leach liquors arising from low-grade copper ores, and to the recovery of gold and silver from cyanide solution.

A critical study of the published works on cementation indicates that most of the articles published until about 1960 deal only with plant practices, and that scientific investigations of cementation started only in the past decade and are mostly confined to the kinetics of cementation using disc or cylindrical samples of precipitant metal. Systematic work on the thermodynamics of the process has been reported only recently. This paper covers the fundamental aspects of the cementation reactions with reference to the copper-iron system.

Thermodynamics of Cementation

The basic cementation reaction between a cation, $M_1^{+z_1}$, present in an aqueous solution or melt and a metal, M_2 , is given by the equation



* University of Roorkee, Roorkee 247672, India.
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The system can essentially be visualized to consist of a set of short-circuited electrolytic microcells. If there is no solid-solution formation between M_1 and M_2 , the conditions for the cementation reaction to occur can be expressed as follows¹ by use of the Nernst equation and standard electrochemical notation:

$$\frac{[M_2^{+z_2}]^{1/z_2}}{[M_1^{+z_1}]^{1/z_1}} \frac{[f_{M_1^{+z_1}}]^{1/z_1}}{[f_{M_2^{+z_2}}]^{1/z_2}} \exp \left[\frac{F}{RT} (E_{M_2}^\circ - E_{M_1}^\circ) \right] \dots \quad (2)$$

where $f_{M_1^{+z_1}}$ and $f_{M_2^{+z_2}}$ are the activity coefficients of the ions $M_1^{+z_1}$ and $M_2^{+z_2}$ respectively, and $[M_1^{+z_1}]$ and $[M_2^{+z_2}]$ are the concentrations of the ions $M_1^{+z_1}$ and $M_2^{+z_2}$ respectively.

From this relationship it is clear that, for an understanding of the thermodynamics of cementation, a knowledge of the variation of the activity coefficient with the concentration of the ions in the solution is essential. The equilibrium constant K for the cementation reaction is given by the relation

$$K = \exp \left[\frac{Z_1 Z_2 F}{RT} (E_{M_2}^\circ - E_{M_1}^\circ) \right] \dots \quad (3)$$

The calculated value of K for the copper-iron system is $10^{26,37}$ at 25°C, which shows that theoretically copper should be completely removable from the aqueous phase. A critical study of the published works²⁻²⁷ on the kinetics of cementation shows that the thermodynamic properties of the aqueous phase considerably affect the course of the cementation process, and their study is therefore of considerable importance for an understanding of the reaction involved.

Agrawal¹ and Kapoor have studied the thermodynamics of the aqueous phase containing the mixed electrolytes that are generally present during the cementation of copper, and have arrived at the following conclusions.

- (i) The activity coefficient of copper sulphate in a single electrolyte system conforms to the Hückel relationship²⁸ and follows the expression

$$\log f = -\frac{2,405\sqrt{\mu}}{1+1,32\sqrt{\mu}} - 0,004\mu, \dots \dots \dots (4)$$

where μ is the ionic strength of the solution.

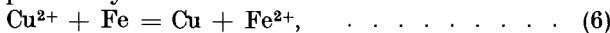
- (ii) The activity coefficient of ferrous sulphate in a single electrolyte system conforms to the Guggenheim relationship²⁹ and follows the expression

$$\log f = -\frac{2,511\sqrt{\mu}}{1+\sqrt{\mu}} + 0,194\mu. \dots \dots \dots (5)$$

- (iii) The activity coefficients of copper sulphate and ferrous sulphate are increased by the addition of sulphuric acid, and Harned's rule³⁰ is observed to be followed in both cases.
- (iv) The activity coefficient of copper sulphate is decreased by the substitution of ferrous sulphate for copper sulphate in its solution, whereas the activity coefficient of ferrous sulphate is increased by the substitution of copper sulphate for ferrous sulphate in its solution. Harned's rule³⁰ is observed to be obeyed in both cases.
- (v) The thermodynamic driving force for the cementation reaction is independent of pH and dependent on the concentrations of both copper sulphate and ferrous sulphate.

Kinetics of Cementation

The kinetics of cementation of copper with iron has been studied by several investigators^{1, 5, 6, 8, 17-23}. It has been suggested that the copper cementation reaction, expressed by



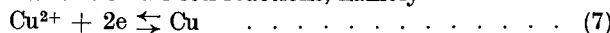
involves a series of transport and electrode processes. These can be broadly classified into three main processes:

- the transport of copper ions from the bulk of the aqueous phase to the solid metal surface,
- the electrode process at the interface between metal and aqueous phase, resulting in the precipitation of copper and the dissolution of iron, and
- the transport of ferrous ions from the interface to the bulk of the aqueous phase.

Transport processes can be classified further into a number of steps including bulk diffusion and the transport of ions to the outer Helmholtz plane (OHP) through the diffuse double layer (DDL). A schematic diagram depicting the various steps involved in the overall cementation reaction is given in Fig. 1. With the help of such a diagram, a quantitative analysis of the system has been made by a number of research workers³¹⁻³² and reviewed by Wadsworth³³ and Agrawal *et al.*³⁴.

Electrode Processes

The overall electrode process in cementation can be divided into half-cell reactions, namely



and

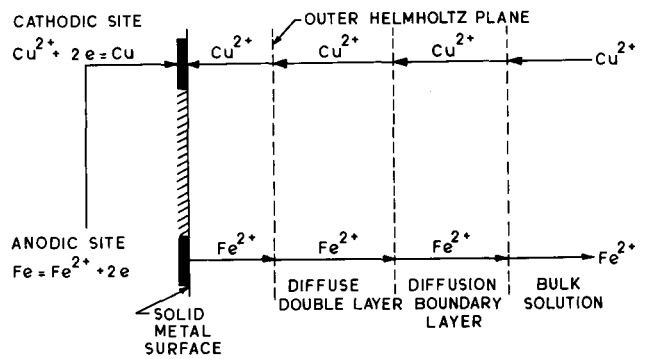


Fig. 1—Steps involved in the overall cementation reaction.

For either of the half cells, the reaction kinetics can be considered separately in terms of the absolute reaction rate theory.

On the basis of this theory, one can derive the following expression for cathodic current density:

$$I_- = \lambda F Z C \leftarrow \neq \frac{kT}{h} \kappa; \dots \dots \dots (9)$$

the expression for anodic current density is

$$I_+ = \lambda F Z C \rightarrow \neq \frac{kT}{h} \kappa, \dots \dots \dots (10)$$

where I_- and I_+ are the cathodic and anodic current densities respectively, κ is the transmission coefficient, k is the Boltzmann constant, λ is the distance between

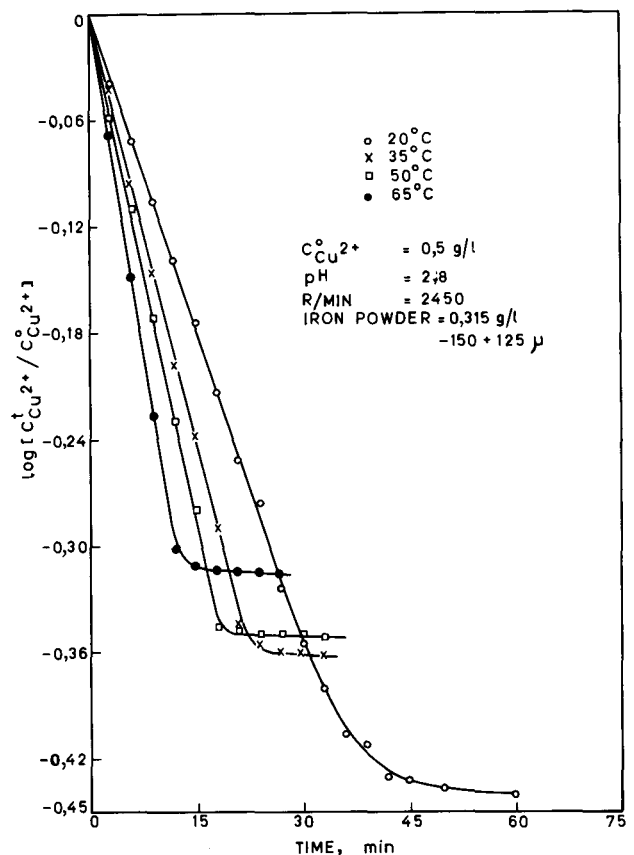


Fig. 2—The effect of temperature on the rate of cementation

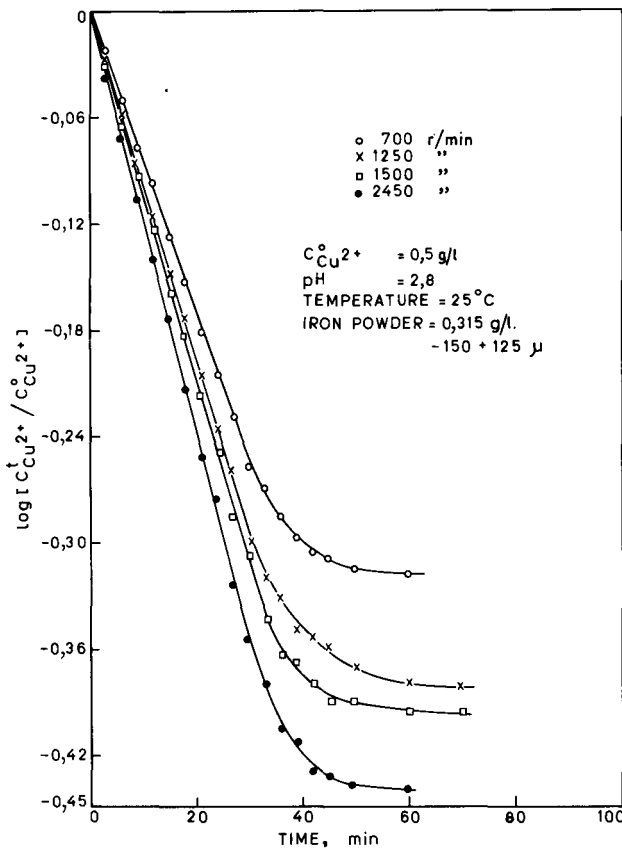


Fig. 3—The effect of stirring speed on the rate of cementation

the minima on either side of the activated state in the diagram of potential energy versus reaction coordinates, h is the Planck constant, and $\overleftarrow{C}^\ddagger$ and $\overrightarrow{C}^\ddagger$ are the concentrations of the activated complex for the cathodic and anodic directions respectively. These concentrations are expressed in terms of the equilibrium constant, K , as follows:

$$K = \frac{\overleftarrow{C}^\ddagger}{C_c} \dots \dots \dots (11)$$

and

$$K = \frac{\overrightarrow{C}^\ddagger}{C_a} \dots \dots \dots (12)$$

where C_a is the effective concentration of metal sites capable of reacting in the anodic direction and C_c is the concentration of cations at the OHP. Thus, the expression for the net current density, I , with $\kappa = 1$, can be written as

$$I = \overleftarrow{k} C_c \exp\left(\frac{(1-a)}{RT} ZFE\right) - \overrightarrow{k} C_a \exp\left(-\frac{a}{RT} ZFE\right) \dots \dots \dots (13)$$

where a is the transfer coefficient, and $\overleftarrow{k}' = \overleftarrow{k}'ZF\lambda$, $\overrightarrow{k} = \overrightarrow{k}'ZF\lambda$, and \overleftarrow{k}' and \overrightarrow{k}' are the specific rate constants for the cathodic and anodic directions respectively. With the introduction of I_0 , the equilibrium exchange

current density, the above expression takes the form

$$I = I_0 \left[\exp\left(\frac{(1-a)}{RT} ZF\eta\right) - \exp\left(-\frac{a}{RT} ZF\eta\right) \right] \exp\left(-\frac{(1-a)}{RT} ZF\Psi_0\right) \dots \dots \dots (14)$$

where η is the over potential, $(E - E_0)$, E_0 is the equilibrium electrode potential, and Ψ_0 is the potential at OHP.

Transport through the Diffuse Double Layer

In the DDL, the transport of ions takes place under simultaneous concentration and electrical potential gradient. If x' is the thickness of the DDL, the variation in potential from OHP in the direction of the bulk of the electrolyte is given, according to the Gouy-Chapman theory³⁵, by the relationship³⁶

$$\Psi_x = \frac{2RT}{|Z|F} \ln \cot h \frac{1}{2} (\delta\chi + a') \dots \dots \dots (15)$$

where,

$$a' = - \ln \tan h \left[Z \frac{F}{4RT} \Psi_0 \right] \dots \dots \dots (15)$$

where $2/\delta$ is the thickness of the DDL and Z is the absolute value of the electronic charge of the ions. Following Eyring and Eyring's treatment³⁷ and assuming the diffusion coefficient, D , of the ion to be independent of the concentration, one gets the following expression for

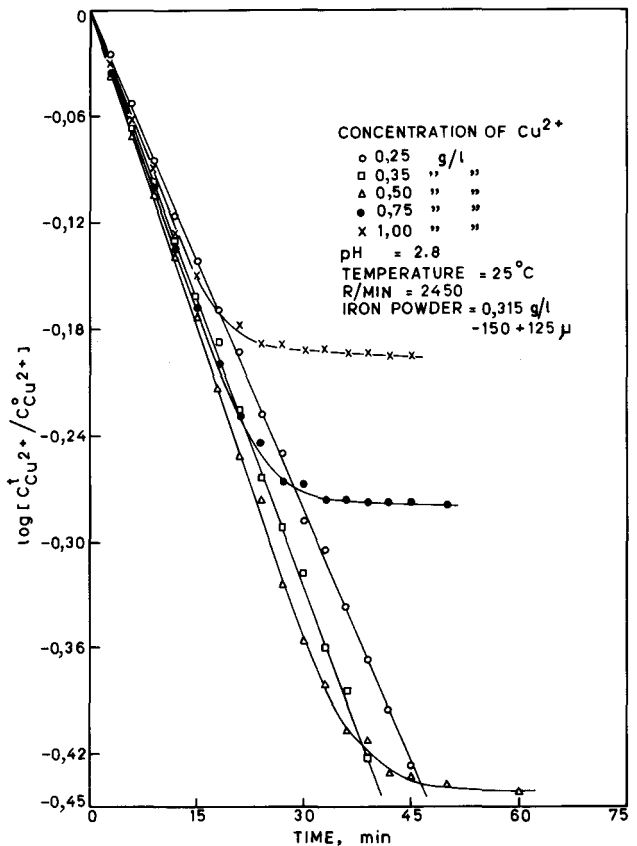


Fig. 4—The effect of initial copper concentration on the rate of cementation

the transport of ions from the DDL towards OHP under steady state conditions:

$$\frac{I}{ZF} = \frac{\delta DC_D}{2\Omega} - \frac{\delta DC_C}{2\Omega} \exp \left[-\frac{ZF}{RT} \Psi_0 \right], \quad (17)$$

where C_D is the concentration of reducible cation at the diffuse double layer.

Transport through the Boundary Layer

The transport of an ion from the bulk of the solution phase to the particle surface involves the transport of chunks of solution to the boundary-film surface by the eddies in the solution. Using Fick's second law of diffusion, which is defined as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (18)$$

and boundary and initial conditions expressed as

$$C = C_b \text{ at } x = 0 \quad \text{for } t = 0 \quad (19)$$

$$C = C_D \text{ at } x = 0 \quad \text{for } t > 0 \quad (20)$$

$$C = C_b \text{ at } x = L \quad \text{for } t > 0 \quad (21)$$

where C_b and C_D are the bulk and surface concentrations of the ion respectively and L is the thickness of the boundary layer, one arrives at the following expression for the instantaneous rate of mass transfer, J , from the solution to the interface:

$$\frac{I}{ZF} = J = (C_b - C_D) \frac{D}{L} \left(1 + 2 \sum_{n=1}^{n=\infty} \exp \left(-\frac{n^2 \pi^2 D t}{L^2} \right) \right) \quad (22)$$

The mean mass transfer rate can be obtained from the above expression on the assumption of the Higbie model³⁸ (i.e. that either all the surface-renewing chunks of fluid are exposed at the boundary layer surface for the same time, t_e) or of Danckwert's model³⁹ (i.e. a random age distribution). In either case, one can write the above equation in the following form:

$$\frac{I}{ZF} = J = K_m (C_b - C_D), \quad (23)$$

where K_m is the mean mass transfer coefficient that will have different expressions for the two cases.

Generalized Rate Equation

The combination of equations (14), (17), and (23) under steady-state conditions leads to the following expression for the rate of cementation:

$$\frac{I}{ZF} = \frac{\lambda \overleftarrow{k} C_b \exp \left(\frac{(1-\alpha)}{RT} ZFE \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) - \lambda \overrightarrow{k} C_a \exp \left(-\frac{\alpha}{RT} ZFE \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right)}{\exp \left(\frac{(1-\alpha)}{RT} ZF\Psi_0 \right) + \lambda \overleftarrow{k} \left(\frac{2\Omega}{\delta D} + \frac{1}{K_m} \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) \exp \left(\frac{(1-\alpha)}{RT} ZFE \right)} \quad (24)$$

As $I_{Cu} = -I_{Fe}$ for a system at steady state, one can arrive at the following equation for the mixed potential, E_m , in the system, which can be defined as the potential

at which the rate of copper deposition would be equal to the rate of iron dissolution:

$$\left[\frac{A_c \left[\lambda \overleftarrow{k}_{Cu} C_{b,Cu} \exp \left(\frac{(1-\alpha)}{RT} ZFE_m \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) - \lambda \overrightarrow{k}_{Cu} C_{a,Cu} \exp \left(-\frac{\alpha}{RT} ZFE_m \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) \right]}{\left[\exp \left(\frac{(1-\alpha)}{RT} ZF\Psi_0 \right) + \lambda \overleftarrow{k}_{Cu} \left(\frac{2\Omega}{\delta_{Cu} D_{Cu}} + \frac{1}{K_{m,Cu}} \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) \exp \left(\frac{(1-\alpha)}{RT} ZFE_m \right) \right]} + \frac{A_a \left[\lambda \overleftarrow{k}_{Fe} C_{b,Fe} \exp \left(\frac{(1-\alpha)}{RT} ZFE_m \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) - \lambda \overrightarrow{k}_{Fe} C_{a,Fe} \exp \left(-\frac{\alpha}{RT} ZFE_m \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) \right]}{\left[\exp \left(\frac{(1-\alpha)}{RT} ZF\Psi_0 \right) + \lambda \overrightarrow{k}_{Fe} \left(\frac{2\Omega}{\delta_{Fe} D_{Fe}} + \frac{1}{K_{m,Fe}} \right) \exp \left(\frac{ZF}{RT} \Psi_0 \right) \exp \left(\frac{(1-\alpha)}{RT} ZFE_m \right) \right]} \right] = 0 \quad (25)$$

where A_c is cathodic area and A_a anodic area. From a knowledge of the various parameters in the above equation, one can obtain the mixed potential, E_m , as a function of the concentration of various ions in the bulk of the solution. Using this value of mixed potential, one can calculate the rate of cementation from equation (24).

Discussion

Although equations (24) and (25) consider the effect of transport through various layers and the electrochemical reaction at the electrode on the overall kinetics of the system in general, one of these steps — the slowest step in the whole process — controls the overall rate of the reaction. Equation (24) can be simplified accordingly.

From the results of an electrochemical investigation of copper cementation by iron, Rickard and Fuerstenau⁸ noted that a tenfold increase in current density shifts the anodic potential of iron dissolution by only 0.03 mV, which leads to the conclusion that the anodic process does not form the slowest step. With this observation, the overall rate equation reduces to the expression

$$\frac{I}{ZF} = \frac{C_b \left[1 - \exp \left(\frac{\Delta G}{RT} \right) \right]}{\left[\frac{1}{K_m} + \frac{2\Omega}{\delta D} + \frac{1}{\lambda \overleftarrow{k}} \exp \left(-\frac{(1-\alpha)}{RT} ZFE \right) \exp \left(-\frac{\alpha}{RT} ZF\Psi_0 \right) \right]}, \quad (26)$$

where $\Delta G = -ZF \Delta E$ and ΔE is the thermodynamic driving force for copper reduction. Since the thermodynamic equilibrium constant for the cementation reaction is very large ($10^{26,37}$), the equilibrium constant for the back reaction that refers to the dissolution of copper

will be very small, and the above expression therefore simplifies to

$$\frac{I}{ZF} = \frac{C_b}{\left[\frac{1}{K_m} + \frac{2\Omega}{\delta D} + \frac{1}{\lambda k} \exp\left(-\frac{(1-a)}{RT} ZFE\right) \right] \exp\left(-\frac{a}{RT} ZF\Psi_0\right)} \quad (27)$$

The denominator in the above expression stands for the sum of the resistances of the various processes in series. The first term in the denominator stands for the resistance to transport through the diffusion boundary film, the second term refers to the resistance to transport through the DDL, and the third term stands for the resistance to surface reactions. Polarization studies by Rickard and Fuerstenau⁸ and Agrawal¹ have proved that the boundary resistance is the predominant one. Under these conditions the overall rate equation takes the simple form

$$\frac{I}{ZF} = C_b K_m A = -V \frac{dC}{dt}, \quad (28)$$

where A is the surface area of the precipitant metal and V is the volume of the solution. K_m in the above expression is related to the diffusion coefficient of copper ions, which, among other factors, is the function of the activity coefficient of copper.

The results of thermodynamic investigations have shown that the effect of ferrous sulphate on the activity coefficient of copper sulphate is very small, and one can therefore assume that the activity coefficient of copper sulphate remains practically constant during a cementation run. Also, the total ionic strength of the solution remains constant during a cementation run. Thus, the diffusion coefficient, and hence the mass transfer coefficient, behave as a constant during a cementation run. The integration of the above expression therefore leads to the following expression:

$$\log \left[\frac{C_{Cu^{2+}}^t}{C_{Cu^{2+}}^0} \right] = -\frac{AK_m}{2,303V} t, \quad (29)$$

where $C_{Cu^{2+}}^t$ stands for the concentration of copper at time t , and $C_{Cu^{2+}}^0$ for the initial concentration of copper ions in solution. A is the surface area of the precipitant metal, and V is the volume of the solution. For the present case, namely the cementation of copper, the plots between $\log (C_{Cu^{2+}}^t/C_{Cu^{2+}}^0)$ versus time for temperature, stirring speed, and initial concentration of copper ions in solution as parameters are shown in Figs. 2 to 4.

In accordance with equation (29), the plots in Figs. 2 to 4 are seen to be linear, indicating that this reaction is first order, which has been verified by other workers. An analysis of the results of various investigations^{1, 5, 6, 17-23} has shown that the overall rate of reaction has low activation energy (in the range 3 to 6 kcal/mol) and is strongly dependent on the hydrodynamic conditions of the bath. This also confirms the conclusion that the rate of cementation is controlled by mass transport through the boundary film.

For a quantitative evaluation of the effect of stirring on the rate of cementation, a dimensional analysis technique

was used and gave the following mathematical relation¹:

$$Sh = f(Re, Sc), \quad (30)$$

where

$$Sh = \frac{K_m L'}{D}, \quad Re = \frac{\rho' \theta L'}{\mu'}, \quad \text{and } Sc = \frac{\nu}{D}.$$

Here, ρ' is the density of the solution, μ' is the viscosity of the solution, L' is the characteristic length and is a measure of the size of the system, θ is the velocity of the fluid, and ν is the kinematic viscosity of the solution. As L' , D , μ , and ν are constant for a given solution, equation (30) can be rewritten as

$$K_m = B(\text{rpm})^a, \quad (31)$$

where a and B are constants. Constant a is evaluated from a plot of K_m (obtained from the slope of the plots of Fig. 3) against stirring speed. This has been done in Fig. 5, which gives the value of $a = 0,264$. This value of slope is in agreement with the value reported in the literature⁴⁰.

A plot of the rate constant versus the log of initial copper ion concentration, calculated from the slope of the plots in Fig. 4, is shown in Fig. 6. It is seen that initially the rate of cementation increases as the initial concentration of copper ions increases up to about 0,5 g/l. This is due to an increase in the ionic diffusivity of copper at higher concentrations. However, the rate of cementation decreases with further increase in the initial concentration of copper ions in solution. No satisfactory explanation is yet available for this latter effect.

In accordance with equation (29), the rate constant should, ideally, be independent of the initial concentration of copper ions. Since such behaviour is not observed, the rate constant is referred to as a pseudo rate constant.

The rate of cementation was found to decrease with a decrease in pH from 2,8 to 1,5. This is due to the in-

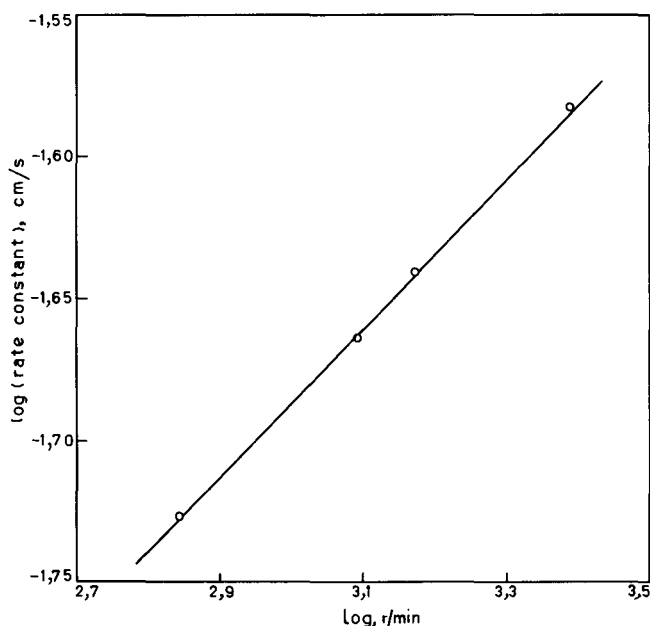


Fig. 5—Graph of log (rate constant) versus log (r/min) for copper cementation

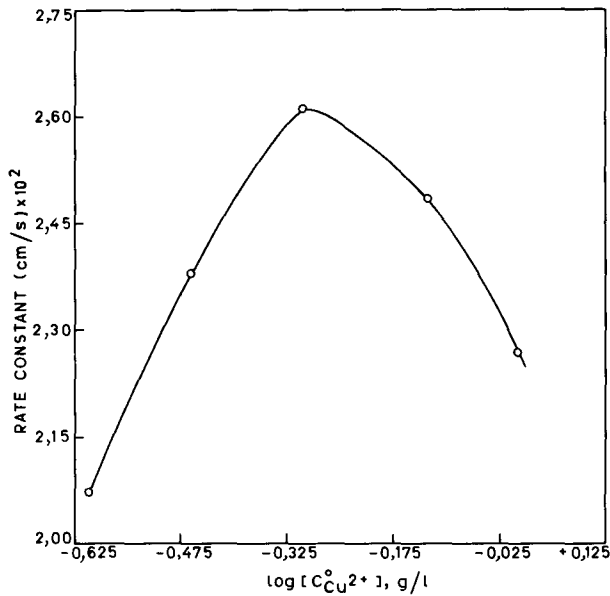
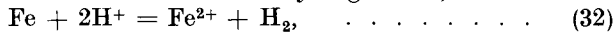


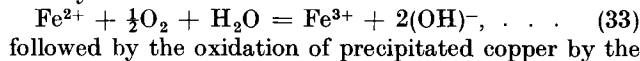
Fig. 6—Graph of rate constant versus log [C_{Cu²⁺}]

creased competition between copper ions and hydrogen ions for discharge sites on the metal surface at higher concentrations of hydrogen ions. Owing to the following reaction between iron and hydrogen ions,

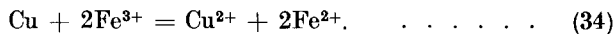


which can proceed to a higher extent at low pH, the surface area available for the cementation reaction is decreased. The hydrogen so produced is likely to block the metal surface because of its slow desorption step⁴¹.

It is clear from equation (29) that the rate of cementation increases with an increase in the surface area of the precipitant metal. The use of a hydrogen atmosphere, in place of a nitrogen atmosphere, has hardly any effect on the rate of cementation. However, in air or in an oxygen atmosphere, there is a slight decrease in the rate of cementation as a result of the formation of ferrous ions by the reaction



followed by the oxidation of precipitated copper by the reaction



Conclusions

The cementation of copper with iron is a first-order reaction with respect to the concentration of copper ions in solution, and the overall rate of cementation is controlled by mass transport in the aqueous solution. The rate of cementation increases with increasing temperature, stirring speed, surface area of the precipitant metal, and pH. However, there is an optimum value for the initial concentration of copper ions in solution for which the rate of cementation is highest.

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