

CEMENTATION KINETICS OF COPPER ON A ROTATING ZINC CYLINDER

Vladimír GLASER^a, Jan VÍDENSÝ^a and Miroslav KUŽELA^b

^a *Prague Institute of Chemical Technology,*

Department of Inorganic Technology, 166 28 Prague and

^b *Chemopetrol k.p., Benzina Prague*

Received April 4th, 1986

The authors followed the course of cementation of copper from sulphate solutions on a rotating zinc cylinder. Treatment of experimental data revealed that the coefficient of proportionality in the kinetic equation is not influenced by the Cu layer deposited on the zinc surface and is independent of the concentration of Cu(II) ions, but decreases with increasing concentration of ZnSO₄ in solution. The cementation reaction proceeds in the diffusion region and is of the first order with respect to the concentration of Cu(II) ions; the proportionality constant in the rate equation corresponds to the mass transfer coefficient.

In hydrometallurgical treatment of polymetallic ores, cementation reactions are used to remove undesirable cations from the solution. One of them is copper which is mostly cemented by zinc. The reaction depends on many factors, mainly temperature¹ and concentration of Cu(II) ions in solution¹⁻⁷, the presence and concentration of other ions^{1-3,5,6}, the thickness and character of the deposited copper layer on the zinc surface^{1,2,7}, and rate of stirring^{2,8}. To elucidate the influence of these factors, measurements were carried out in an isothermal batch reactor, in which the cementation took place on a rotating zinc cylinder. The experimental data were evaluated from the macrokinetic point of view. The influence of stirring will be the subject of a separate communication⁹.

EXPERIMENTAL

The course of cementation was followed in a batch reactor, which was a cylindrical organic glass vessel closed with a lid and provided with a coiled heating tube and vertical ribs at the inner wall surface (Fig. 1). An electric motor with variable speed, whose shaft reached into the lower third of the reactor, was fastened to the lid. A zinc cylinder with two symmetrically placed organic glass cylinders of the same diameter were fastened by a screw to the end of the shaft. The copper solution was deoxygenated by bubbling pure nitrogen before entering the reactor, and it was heated to the desired temperature in a separate vessel. Nitrogen was bubbled through the solution during the whole measurement through an inlet at the bottom and the temperature was maintained constant. The evaporated water was condensed by cooling and refluxed.

The zinc cylinder was cast from granulated zinc, turned to 35 mm diameter and 10 mm height, and provided with an axial hole. Its surface was degreased with gasoline before the experiment.

All chemicals and the granulated zinc were of reagent grade (Lachema, Brno).

The course of the reaction was followed polarographically by measuring the concentration of Cu(II) in samples taken from the reactor. We measured the influence of the rotation speed, temperature, and concentration of Cu(II) and Zn(II) ions. A zinc cylinder with pure surface was used for every reaction isotherm. The obtained dependences are shown in Figs 2–6.

THEORETICAL

The reaction under discussion is electrochemical in nature: Cu^{2+} ions accept electrons at those sites of the zinc electrode surface which function as cathode to form metallic copper, while zinc is dissolved at anodic sites to form Zn^{2+} ions. These processes are accompanied by transport of reactants from the bulk of the solution to the interface and *vice versa*.

To express the rate of transfer processes, we shall use the film model and assume that the processes of chemical nature can, as a whole, be considered as an irreversible reaction of the first order with respect to concentration of Cu^{2+} ions. The rate equations can then be written as follows.

1. Transfer of Cu^{2+} ions from the solution to the interface

$$j_A = k_{dA}(c_A - c_{As}), \quad (1)$$

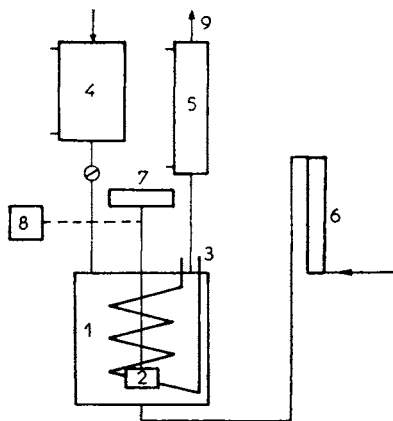


FIG. 1

Scheme of the apparatus. 1 Reactor, 2 zinc cylinder, 3 heating coil with vertical ribs, 4 vessel for tempering the solution, 5 water cooler, 6 rotameter, 7 electric motor, 8 revolution counter, 9 exhaust

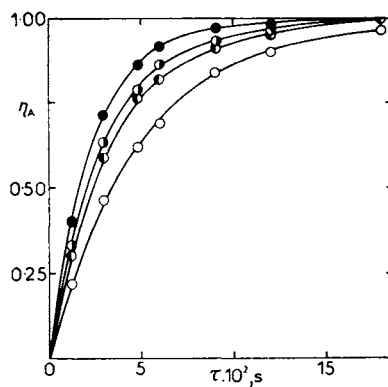


FIG. 2

Cementation isotherms obtained at various speeds of rotation of the zinc cylinder. Solution of $1.57 \text{ mol m}^{-3} \text{ CuSO}_4$, 65°C ; revolutions *per minute*: ○ 500, ● 800, ● 1 000, ● 1 330

where j_A denotes diffusion current density of Cu^{2+} ($\text{mol m}^{-2} \text{s}^{-1}$), k_{dA} mass transfer coefficient for Cu^{2+} (m s^{-1}), c_A and c_{As} concentrations of Cu^{2+} ions in the bulk and at the zinc cylinder surface (mol m^{-3}).

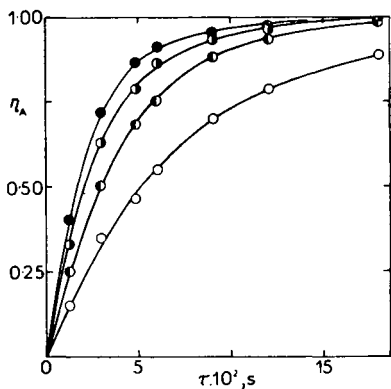


FIG. 3

Cementation isotherms obtained at various temperatures. Solution of 1.57 mol m^{-3} CuSO_4 , 1 000 rpm; Temperature: \circ 40, \odot 50, \bullet 65, \bullet 80°C

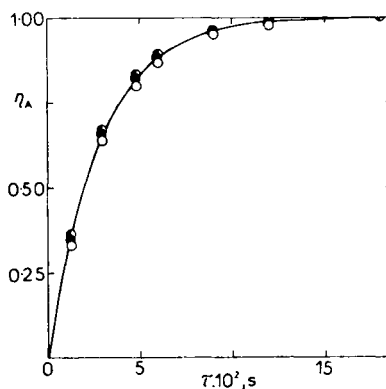


FIG. 4

Cementation isotherms obtained at various concentrations of CuSO_4 ; 1 000 rpm, 65°C; concentration of CuSO_4 : \circ 1.57, \odot 4.71, \bullet 7.85 mol m^{-3}

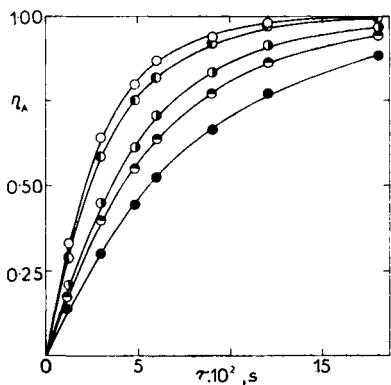


FIG. 5

Cementation isotherms obtained at various concentrations of ZnSO_4 . Concentration of CuSO_4 1.57 mol m^{-3} , 1 000 rpm, 65°C; concentration of ZnSO_4 : \circ 0.0, \bullet 4.59, \bullet 7.65, \bullet 12.20, \bullet 15.30 mol m^{-3}

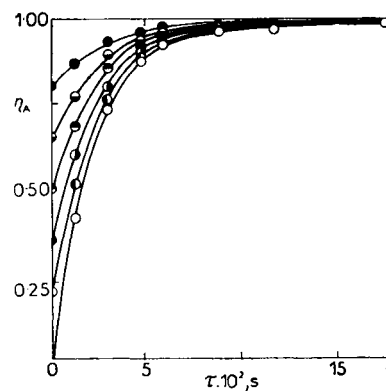


FIG. 6

Cementation isotherms obtained with a solution of CuSO_4 after the reaction proceeded to a certain stage. Starting concentration of CuSO_4 1.57 mol m^{-3} , 1 330 rpm, 65°C; degree of prereacting of the CuSO_4 solution: \circ 0.0, \bullet 0.2, \bullet 0.35, \bullet 0.5, \bullet 0.65, \bullet 0.8

2. Surface reaction at the zinc electrode

$$r_A = k_A c_{As}, \quad (2)$$

where r_A denotes the surface reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$) and k_A rate constant (m s^{-1}).

3. Transfer of Zn^{2+} ions from the interface to the bulk solution

$$j_R = k_{dR}(c_{Rs} - c_R), \quad (3)$$

where j_R denotes diffusion current density of Zn^{2+} ions ($\text{mol m}^{-2} \text{s}^{-1}$) and k_{dR} mass transfer coefficient for Zn^{2+} (m s^{-1}).

In the pseudostationary state, the rates of these processes are equal to one another, hence the rate of the cementation reaction referred to unit surface area of the zinc electrode can be expressed by any one of them:

$$-(1/S)(d\eta_A/d\tau) = j_A = r_A = j_R. \quad (4)$$

In treating the kinetic data, it is convenient to refer the reaction rate to a unit volume of the reactor. We shall express it from Eq. (2), where the value of c_{As} follows from the equality of the expressions (1) and (2). Thus,

$$r_V = c_A^0(d\eta_A/d\tau) = k_A k_{dA}/(k_A + k_{dA})(S/V) c_A = k c_A. \quad (5)$$

Here, r_V denotes the cementation rate ($\text{mol m}^{-3} \text{s}^{-1}$), c_A^0 concentration of Cu^{2+} ions in the bulk at $\tau = 0$ (mol m^{-3}), η_A conversion of Cu^{2+} ions defined as $(c_A^0 - c_A)/c_A^0$, V volume of reactor (m^3), k coefficient of proportionality (s^{-1}), and S surface area of the zinc cylinder (m^2).

If the coefficient k can be considered constant during the cementation reaction in a given range of the solution composition, Eq. (5) can be integrated after separation of variables and expressing c_A as function of the conversion η_A to give

$$\eta_A = 1 - e^{-k\tau}, \quad (6)$$

an exponential reaction isotherm in η_A - τ coordinates. If the reaction proceeds in the kinetic region, the coefficient k is equal to $k_A S/V$, while in the diffusion region it is equal to $k_{dA} S/V$.

In the pseudostationary state, the overall cementation rate can be expressed from equations (1) or (3) as well. Thus, we obtain

$$r_V = c_A^0(d\eta_A/d\tau) = k_{dA}(S/V)(c_A - c_{As}) \quad (7)$$

or

$$r_v = c_A^0(d\eta_A/d\tau) = k_{dR}(S/V)(c_{R_s} - c_R) \quad (8)$$

as alternatives to Eq. (5).

RESULTS AND DISCUSSION

To evaluate the experimental data, we used the differential form of the kinetic equation. The integral η_A - τ curves were, to this end, expressed by the empirical equation

$$\ln [1/(1 - \eta_A)] = a + b\tau + c\tau^2. \quad (9)$$

The constants a , b , and c were evaluated and the values of $d\eta_A/d\tau$ were obtained by numerical differentiation as function of the conversion η_A . After multiplication by the initial concentration of Cu^{2+} ions, the reaction rates r_v were calculated. These data served to calculate the coefficient k from Eq. (5). The values of k were approximately constant for a given reaction isotherm, the deviation being within 10%. This is comparable with the scatter of experimental data. On neglecting these deviations, the course of the isotherms in the integral form can be expressed by Eq. (6).

The fact that the coefficient k in the kinetic equation does not depend significantly on the conversion η_A allows us to conclude that the copper layer deposited on the surface of the zinc cylinder has no influence on the cementation rate. This is in accord with reaction isotherms obtained with solutions whose composition corresponded to a certain stage of the reaction (Fig. 6). The calculated values of k from these isotherms are:

| | | | | | | |
|-------------------------------|-----|-----|------|-----|------|-----|
| η_A | 0 | 0.2 | 0.35 | 0.5 | 0.65 | 0.8 |
| $k \cdot 10^3, \text{s}^{-1}$ | 4.4 | 4.3 | 4.2 | 4.2 | 4.1 | 4.2 |

The dependence of the reaction rate r_v at the beginning of the isotherm on the initial concentration of Cu^{2+} ions is shown in Fig. 7. The linear form of this dependence shows that the coefficient k is constant in the given range of c_A^0 values.

The course of the reaction isotherms at various speeds of rotation of the zinc cylinder (Fig. 2) shows that transport of the participating ions to the interface influences the rate of the cementation reaction. This is in accord with the value of apparent activation energy, 26 kJ mol^{-1} , obtained by evaluating the dependences in Fig. 3 by means of the Arrhenius equation.

The influence of the concentration of Zn^{2+} ions in solution on the initial cementation rate can be seen from Fig. 8. The reaction isotherms underlying these data were measured at the same concentration of Cu^{2+} ions, hence the coefficient k shows a similar trend as the values of $(r_v)_{\tau \rightarrow 0}$. Since the concentrations of Zn^{2+} ions were

rather high, their effect on the reaction rate and on the coefficient k can be attributed to decreasing rate of transfer of the participating ions at the interface with increasing concentration of Zn^{2+} .

The dependences of the cementation rate on the speed of rotation of the zinc cylinder, on the temperature and concentration of Zn^{2+} ions suggest that transfer processes play a decisive role in the cementation; and it may be assumed that they are the controlling processes. Under this assumption, the quantity c_{As} in Eq. (7) can be neglected against c_A and the equation takes then the same form as Eq. (5), the coefficient k being equal to the product of the transfer coefficient k_{dA} and the term S/V :

$$r_v = k_{dA}(S/V) c_A. \quad (10)$$

The values of k found as the ratio of r_v/c_A can thus be recalculated by using the known value of S/V to give k_{dA} .

Since the Cu^{2+} and Zn^{2+} ions are similar in character, we may assume that their transfer coefficients are also similar, *i.e.*

$$k_{dA} \approx k_{dR}. \quad (11)$$

The rate of cementation is also expressed by Eq. (8) which for the initial state, where the solution contains only Cu^{2+} ions, gives

$$(r_v)_{\tau \rightarrow 0} = k_{dR}(S/V) c_{Rs}^0 \quad (12)$$

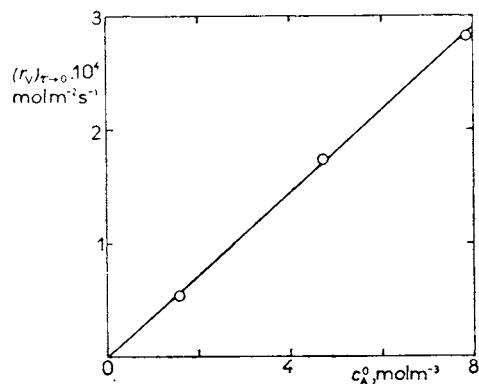


FIG. 7

Initial value of the reaction rate as function of the concentration of Cu^{2+} ions in the starting solution of $CuSO_4$; 1 000 rpm, 65°C

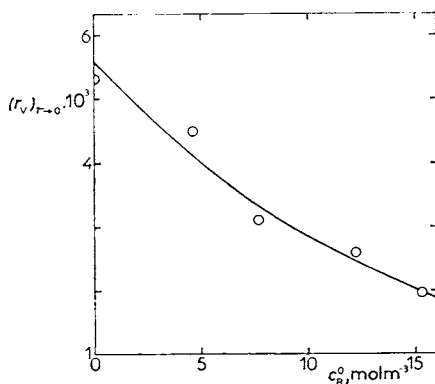


FIG. 8

Initial value of the reaction rate as function of the concentration of $ZnSO_4$ in the starting solution. Concentration of $CuSO_4$ 1.57 mol. $\cdot \text{m}^{-3}$, 1 000 rpm, 65°C

and, with respect to Eq. (11),

$$(r_v)_{\tau \rightarrow 0} = k_{dA}(S/V) c_{R_s}^0. \quad (13)$$

On comparing this equation with Eq. (10) we obtain $c_{R_s}^0 = c_A^0$. When the reaction proceeds, the second term in Eq. (8) comes into play and it increases until c_R becomes equal to c_A^0 .

In the case where Zn^{2+} ions are present already in the starting solution, an analogous consideration leads to the equation

$$c_{R_s}^0 = c_R^0 + c_A^0. \quad (14)$$

Since the content of zinc ions increases during the reaction from c_R^0 to $c_R^0 + c_A^0 - c_A$, Eq. (8) can be written in the form

$$r_v = k_{dA}(S/V) [c_{R_s}^0 - (c_R^0 + c_A^0 - c_A)] \quad (15)$$

which is equivalent to Eq. (10) and satisfies the experimental data.

It can be concluded that cementation of copper from its sulphate solutions with zinc is controlled by the rate of transfer of the participating ions at the interface. Its rate is given by a kinetic equation for an irreversible first-order reaction with respect to the concentration of Cu^{2+} ions, where the proportionality constant has the meaning of the mass transfer coefficient. Its value can be considered constant for a given reaction isotherm.

REFERENCES

1. Strickland P. H., Lawson F.: Proc. Aust. Inst. Min. Met. No. 236, 25 (1970).
2. Straten F. W., Ehret W. F.: J. Am. Chem. Soc. 61, 1798 (1939).
3. Power G. P., Ritchie I. M.: Mod. Aspects Electrochem. 11, 199 (1975).
4. Miller J. D., Beckstead L. W.: Metall. Trans. 4, 1967 (1973).
5. Centnerszwer M., Heller W.: Z. Phys. Chem., A 161, 113 (1932).
6. Margulis F. V., Rodin I. V.: Zh. Prikl. Khim. (Leningrad) 53, 1001 (1980).
7. Strickland P. H., Lawson F.: Proc. Aust. Inst. Min. Met. No. 246, 1 (1973).
8. Sareyed-Dim N. A., Lawson F.: Trans. Inst. Min. Met. 85, C 1 (1976).
9. Glaser V., Vídenský J., Kužela M.: Chem. Prum. 4, 178 (1987).

Translated by K. Micka.