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Influence of Electrolysis Variables on the Passivation Time of Copper Anodes in Copper Electrorefining

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ABSTRACT

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In the present work it is assumed that passivation of copper anodes is due, in sulphate solutions, to the precipitation of a copper sulphate layer on the surface. An equation describing dependence of the passivation time on the current density has been established under some simplifying assumptions.

The influence of the current density, solution composition, temperature and the solution flow rate on the passivation time has been investigated.

Experimental data are consistent, to a large extent, with the semi-empirical equation for passivation time suggested by the authors.

INTRODUCTION

A sudden rise of the anode potential (passivation) is occasionally observed during the process of copper electro-refining. This produces several deteriorating effects including an increase in cell voltage and an increase in energy consumption. Another consequence is the rise of the silver concentration in the electrolyte which is followed by a parallel rise of silver content in the cathodic copper [1,2]. Passivation has also been suggested to be a contributor to slime formation and thus to an increase of As and Sb content in the cathodic deposit and to the formation of excrescences on its surface [3–5].

Passivation is widely attributed to a decrease of the anode active area induced by the precipitation of copper sulphate [6–10]. It is also widely accepted that Ag, Pb and Ni, present as impurities in the anode copper, foster this process [1,11–17].

The susceptibility of the anode copper to passivation is often expressed by a "passivation time" t_p. This is a period of time after which, at constant applied

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current density, a sudden increase of the anode potential occurs. In general, the smaller the current density, the longer the passivation time. The nature of the curves showing this dependence suggests that below a certain current density which depends on the electrolysis conditions, passivation does not occur. This threshold value will be called a "permissible current density i_{pr}" in the following text. Note that it differs from the critical current density i_{cp} determined by the so-called galvano- or potentio-static experiments (Fig. 1a, b).

In the truly static experiments, after each change of the independent variable, one should wait until the other reaches its constant value. This sometimes takes several hours. In practice however, independent variables are commonly changed in pre-programmed steps in arbitrarily chosen time intervals, usually of short duration. As a result the values of the dependent variables do not correspond to their true steady-state values. The experiment performed in this way is in fact quasistatic and thus the values of i_{cp} determined are in consequence greater than values of i_{pr}. Departures from the steady state are even larger in the dynamic experiments (Fig. 1c).

Another factor which is an obstacle in the application of so determined i_{cp} values in the discussion of copper anodes behaviour, in the process of electrorefining, is the formation of the slime layer on the anode. This layer is principally composed of lead sulphate, cemented silver and fine grain copper powder. It grows as the anode dissolves and thus diminishes the active part of the anode surface. The transport of copper ions from the anode into the bulk of the solution is hindered by this layer. In effect it fosters precipitation of copper sulphate on the anode. The amount of slime is proportional to the mass of anodically dissolved copper and the latter is determined by the charge passed. As a result the formation of slime layer depends on the way in which experiments are performed.

The paper presented is a summary of some previous investigations on the influence of the temperature and copper concentration on the passivation time

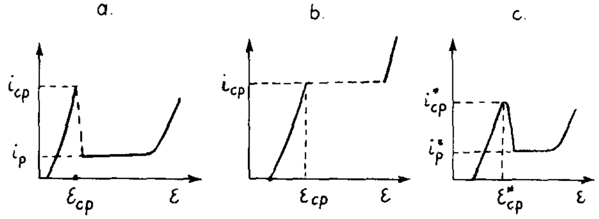

Fig. 1. Passivation of anodes. Experiments performed: a. potentiostatistically; b. galvanostatically; c. potentio- or galvano-dynamically.
i_{cp} = critical passivation current, i_p = passivation current, ϵ_{cp} = critical potential of passivation. Critical values i^*_{cp} and ϵ^*_{cp} determined in the dynamic experiments depend on the rates of change $d\epsilon/dt$ or di/dt of the independent variables.

[18–20]. In addition it contains data concerning the influence of sulphate ion concentration and the rate of electrolyte flow, on t_p. All these data have been used in this paper to verify a semi-empirical equation which the authors have established on the basis of an assumed model of the process.

EQUATIONS DESCRIBING DEPENDENCE OF THE PASSIVATION TIME ON THE CURRENT DENSITY

The dependence of the passivation time on the anodic current density is sometimes described by the empirical Eq. 1 [13,14,21].

$$\log t_p = a_1 + b_1 \log i_A \qquad (1)$$

An attempt to modify this equation, in such way that it expresses the fact that below a certain value of i_A passivation does not occur, leads to the revised Eq. 2.

$$\log t_p = a_2 + b_2 \log(i_A - i_{pr}) \qquad (2)$$

Statistical analysis of experimental results indicates that Eq. 2 describes the investigated dependence better than Eq. 1 [20]. However, both equations are empirical and as such lack fundamental justification.

An attempt has been made to obtain an equation which describes the dependence of t_p on i_A on the basis of the suggested mechanism of the process [18–20]. It has been assumed that passivation occurs when the copper ion concentration in the vicinity of the anode surface attains the value corresponding to the saturation point of the copper sulphate. The simplest case, i.e. anodic dissolution of pure copper, is discussed. The assumed scheme is presented in Fig. 2.

In this figure J_I, the rate of anodic dissolution, is proportional to the current density; J_{II} is the flux of the copper ion transport from the anode to the bulk of solution. When $J_I > J_{II}$ then C^*, the concentration of copper ions in the vicinity of the anode surface, rises gradually to the saturation value C_s.

Several simplifying assumptions, presented below (a–d), are necessary to obtain Eq. 3 below.

(a) Existence of a diffusion layer δ of constant thickness is postulated. Taking into account the geometry of the cell and of the electrolyte flow, which imitate the conditions of the refining process, the concept of the diffusion layer has no precise physical meaning. The symbol δ in the equations presented should be treated as a coefficient which, as in the case of the diffusion layer, decreases with the diminishing viscosity of the solution and also with the rise of its flow rate.

(b) It is assumed that the transport of copper ions in the vicinity of the anode surface is determined solely by diffusion. Migration is neglected on account of the high sulphuric acid concentration in the refining electrolyte.

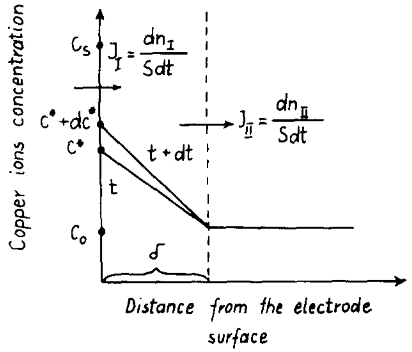

Fig. 2. Hypothetical distribution of copper ions in the vicinity of the anode surface. C_s = concentration of copper ions in saturated solutions, C_o = concentration of copper ions in the bulk of the solution (practically constant throughout the electrolysis), C^* = concentration of copper ions at the anode surface at the time t and respectively $C^* + \mathrm{d}C^*$ at the time $t + \mathrm{d}t$, δ = diffusion layer, J = flux of the copper ions.
Boundary conditions: $t = 0$, $C^* = C_o$; $t \to t_p$, $C^* \to C_s$.

(c) A linear drop of copper ion concentration is assumed in the diffusion layer, as well as independence of the coefficient D on concentration.

(d) It is assumed that the whole surface of the anode is equally accessible to the passivation process.

(e) The constant value of J_I is due to the fact that the experiments are performed galvanostatically.

Copper ion concentration in the bulk of the solution C_o has been kept constant during the experiments (soluble anode).

Equation 3 is obtained after taking all these assumptions into account.

$$\frac{DzF}{\delta}(C_o - C_s)\frac{1}{i_A} + 1 = \exp\left(-\frac{2D}{\delta^2}t_p\right) \qquad (3)$$

This equation includes the idea of the permissible current:

$$\lim_{t_p \to \infty} i_A = \frac{DzF}{\delta}(C_s - C_o) = i_{pr} \qquad (4)$$

Pomosov and collaborators have obtained a similar equation in a different way [4,21].

Combination of the Eqs. 3 and 4 leads to Eq. 3a

$$\log\left(1 - \frac{i_{pr}}{i_A}\right) = -\frac{2D}{2.302\delta^2}t_p = b_3 t_p \qquad (3a)$$

These equations can be verified in several ways.

(a) It follows from Eq. 3a that, at constant temperature, concentration of reagents, flow rate of the solution, i.e. when i_{pr} is constant, the passivation time should be a linear function of log $(1-i_{pr}/i_A)$.

(b) Equation 4 indicates that i_{pr} should be a linear function of copper concentration in the electrolyte C_o, when all other variables are kept constant.

(c) The concentration of copper C_s, in solutions saturated with $CuSO_4$, depends on the total concentration of the sulphate ions $\sum C_{SO_4}$ (introduced into the solution with $CuSO_4$ and with H_2SO_4), and on temperature. At constant temperature is $C_s = I/\sum C_{SO_4}$, where I is the solubility product of $CuSO_4$. Taking this last fact into account one can transform Eq. 4 into Eq. 4a.

$$i_{pr} = \frac{DzF}{\delta}\left(\frac{I}{\sum C_{SO_4}} - C_o\right) \tag{4a}$$

This implies that when C_o, temperature and other variables are kept constant, i_{pr} should be a linear function of the reciprocal value of $\sum C_{SO_4}$.

(d) The determination of C_s and i_{pr} values at different temperatures presents the possibility of verifying Eq. 4. An obstacle is that both D and δ depend on temperature, D rises and δ decreases as temperature is increased.

Assuming that the thickness of the diffusion layer δ is proportional to the viscosity of the solution, and taking into consideration the dependences of viscosity and diffusion coefficient on temperature: $\eta = \eta_0 \exp(\alpha/T)$; $D = D_0 \exp(-\beta/T)$, one can transform Eq. 4 in the form (4b).

$$\log \frac{i_{pr}}{C_s - C_o} = a_4 - \frac{b_4}{T} \tag{4b}$$

(e) The coefficient δ representing the thickness of the "diffusion layer" should decrease with the rise of the flow rate of the electrolyte. Hence it follows from Eq. 4 that i_{pr} should rise when the flow rate increases.

EXPERIMENTAL

Experimental conditions were chosen to mimic the industrial process of copper electrorefining.

Two series of experiments were performed at constant temperature. The first series was done with solutions of constant sulphate ion concentration $\sum C_{SO_4}$ ca. 2.43 *M* and of different concentrations of copper ions 0.16–0.94 *M*; i.e. ca. 10–60 g Cu l^{-1}. The second was done in solutions of constant copper concentration 0.63 *M* i.e. ca. 40 g Cu l^{-1} and of different sulphate ion concentrations ca. 0.85–2.43 *M*.

All chemicals used were of analytical grade. The anode (30×30×10 mm) was cast from electrolyte copper. It was situated in the middle of the cell between two cathodes (60×60 mm) which were 90 mm apart.

The cell contained 1 l of solution circulating at a rate of 13.5 l h^{-1}. One series was performed at 6.8 l h^{-1}. The flow rate of the electrolyte was greater than in industrial processes. Electrolyte was pumped from the bottom of the cell and delivered to the surface at the opposite corner.

The rotating disc method, which usually allows quantitative description of the transport rate, was unfortunately useless in the experiments performed. The roughness factor of the anode surface, at current densities of several hundreds of A m^{-2}, rises rapidly with the time of electrolysis. It makes a discussion of the process in terms of the rotating disc theory impossible.

The current density, calculated with respect to the geometric area of the anode, was kept constant within ± 4 A m^{-2}. The potential difference between the electrodes was measured and registered continuously. Passivation was announced by a sudden rise of this parameter.

RESULTS AND DISCUSSION

Some examples of the experimental results are presented in Figs. 3 and 4. Each point in these figures represents an average of between 2 and 6 experiments. Results of all experiments were used to calculate the data which are collected in Table I.

The curves in Figs. 3 and 4 seem to indicate that below a certain value of the anodic current density, which depends on concentration, temperature etc., passivation does not occur.

Attempts were made to verify, on the basis of experimental data, the dependence of t_p on i_A indicated by Eq. 3a. To do this the values of i_{pr} for each series of experiments needed to be known. Determination of these values from the curves shown in Figs. 3 and 4 was inaccurate. To overcome this obstacle a statistical method was applied. Different, arbitrarily chosen, i_{pr} values were introduced into Eq. 3a. It was found that for each series of experiments a characteristic i_{pr} value existed which corresponded to the maximum value of the correlation coefficient. The results of these calculations, for a series of experiments performed in solutions of different concentrations of copper ions, are presented in Fig. 5. The derived i_{pr} values, for all series of experiments, are shown in Table I.

The high values of the correlation coefficients seem to confirm the existence of the dependence of log $(1 - i_{pr}/i_A)$ on t_p, predicted by Eq. 3a.

The linear dependence of i_{pr} on copper concentration in the solution C_o, presented in Fig. 6, is also in agreement with Eq. 4.

Figure 7 shows the dependence of i_{pr} on the reciprocal values of the total concentration of sulphate ions. Linearity, which follows from Eq. 4a, is fulfilled when the concentration of H_2SO_4 in the electrolyte is higher than 0.2 M. It may be that the sudden decrease of i_{pr}, observed in the solutions of low acid concentrations, occurs as the result of the coprecipitation of hydroxysalts, or

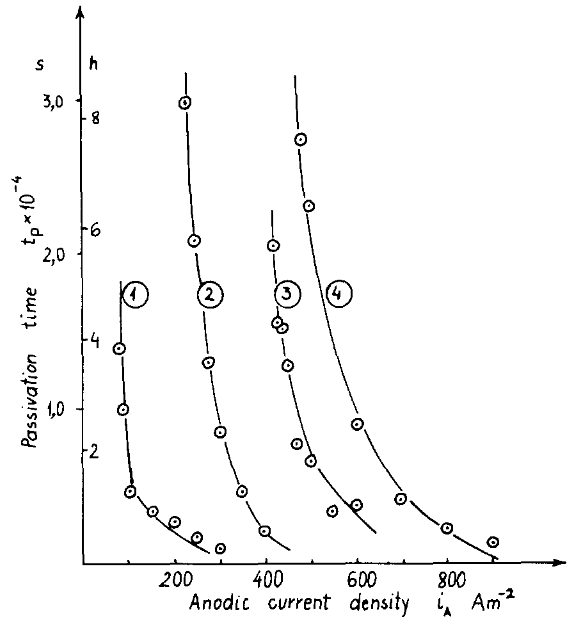

Fig. 3. Dependence of the passivation time of the copper anodes on the current density, in solutions of different copper ion or sulphate ion concentrations.

Curves 1–3; $\sum C_{SO_4} = 2.43$ M and concentrations of copper respectively 0.94, 0.63 or 0.16 M (ca. 60, 40 or 10 g Cu l^{-1}).

Curves 2 and 4: $C_0 = 0.63$ M (ca. 40 g Cu l^{-1}), concentration of sulphate ions $\sum C_{SO_4} = 2.43$ or 1.23 M. Temperature: 30 °C, solution flow rate: 13.5 l h^{-1}.

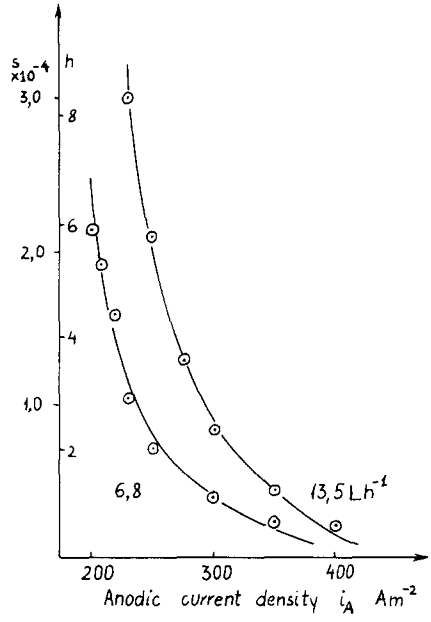

Fig. 4. Dependence of the passivation time of the copper anodes on the current density. Results of experiments performed at different flow rates of the electrolyte.

$C_0 = 0.63$ M (ca. 40 g Cu l^{-1}); $\sum C_{SO_4} = 2.43$ M (ca. 175 g H_2SO_4 l^{-1}); temperature: 30 °C.

TABLE I

Passivation of the copper anodes in the sulphate solutions
$\log(1-i_{pr}/i_A)=a+bt_p$ (3b);
i_A=anodic current density, A m^{-2}; t_p passivation time, s;
i_{pr}=permissible current density, A m^{-2}

Variable		Density d (kg m^{-3})	Dynamic viscosity (mPa s)	Number of experiments (n)	Coefficients		i_{pr} (A m^{-2})	Correlation coefficient	$\bar{i}_{pr}{}^1$ (A m^{-2})	$i_{mx}{}^2$ (A m^{-2})
					a	$b\times10^5$				
A. $\Sigma C_{SO_4}=2.43\pm0.00$ M; temperature 30 ± 0.2 °C; electrolyte flow rate 13.5 l h^{-1}; volume of the cell 1 l										
Cu (M)										
0.16		1150	13.8	21	-0.33 ± 0.02	-5.75 ± 0.20	408	0.9759	410 ± 21	773 ± 74
0.31		1167	14.8	26	-0.52 ± 0.05	-6.09 ± 0.51	400	0.8546	410 ± 26	589 ± 64
0.47		1178	15.8	15	-0.37 ± 0.02	-5.48 ± 0.16	305	0.9876	306 ± 10	540 ± 36
0.63		1194	16.2	13	-0.29 ± 0.01	-2.55 ± 0.04	210	0.9958	210 ± 4	435 ± 15
0.94		1126	17.5	19	-0.09 ± 0.04	-8.47 ± 0.61	77	0.9141	87 ± 17	-
B. $C_o=0.63$ M Cu; temperature 30 ± 0.2 °C; electrolyte flow rate 13.5 l h^{-1}; volume of the cell 1 l										
Concentration										
C_{SO_4} (M)	H_2SO_4 (M)									
0.83	0.2	1110	11.7	13	-0.28 ± 0.01	-1.91 ± 0.07	358	0.9859	360 ± 17	765 ± 60
1.23	0.6	1131	12.0	12	-0.28 ± 0.01	-2.78 ± 0.07	435	0.9931	438 ± 17	905 ± 49
1.63	1.0	1154	13.0	18	-0.24 ± 0.01	-4.53 ± 0.10	365	0.9921	368 ± 16	857 ± 64
2.03	1.4	1800	14.4	10	-0.24 ± 0.02	-4.98 ± 0.10	248	0.9962	247 ± 8	581 ± 54
2.43	1.8	1194	16.2	13	-0.29 ± 0.01	-2.55 ± 0.05	210	0.9958	210 ± 4	436 ± 15
2.43^3	1.8	1194	16.2	20	-0.25 ± 0.01	-3.85 ± 0.13	185	0.9773	186 ± 9	421 ± 38

C. $C_o = 0.52$ mol Cu kg^{-1}; $C_{H_2SO_4} = 1.50$ mol kg^{-1} (ca. 175 g l^{-1}); $\sum C_{SO_4} = 2.02$ mol kg^{-1} (ca. 2.40 mol l^{-1}); electrolyte flow rate 13.5 l h^{-1}; volume of the cell 1 l

Temperature, t (°C)									
20	1197	19.5	15	-0.10 ± 0.01	-1.94 ± 0.06	55	0.9852	58 ± 9	292 ± 71
30	1194	16.2	13	-0.29 ± 0.01	-2.55 ± 0.03	210	0.9958	210 ± 4	434 ± 14
40	1184	11.8	16	-0.34 ± 0.02	-5.03 ± 0.12	399	0.9909	400 ± 16	742 ± 58
45	1179	10.9	14	-0.40 ± 0.01	-2.16 ± 0.06	650	0.9886	651 ± 10	1075 ± 32
50	1175	9.3	13	-0.45 ± 0.01	-2.06 ± 0.04	850	0.9962	850 ± 10	1313 ± 26

[1] $\bar{i}_{pr} = \Sigma i^*_{pr}/n$ where: $i^*_{pr} = [1 - 10^{(a+bt_p)}]$; n = number of electrolysis series; i_A = anodic current densities corresponding to the passivation times t_p determined in separate experiments; "a" and "b" are coefficients of the Eq. 3b.

[2] Statistical analysis of the experimental data indicates that the semi-empirical Eq. 3a should be completed by the addition of the coefficient "a" of Eq. 3b. This means that t_p aims at 0 (instantaneous passivation) when $i_A \rightarrow i_{pr}/1 - 10^a = i_{mx}$.

[3] Series of the electrolysis performed at the electrolyte flow ate 6.8 l h^{-1}.

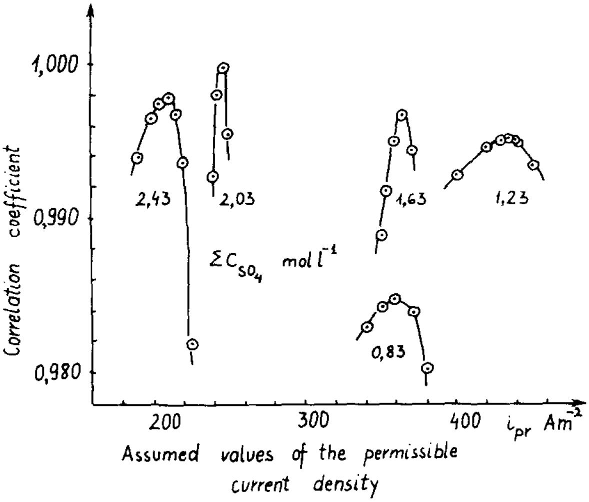

Fig. 5. Dependence of the correlation coefficients of Eq. 3a on the assumed values of the permissible current densities. Results of the experiments, which have been performed in solutions of constant copper concentration $C_0 = 0.63\ M$ and of different sulphate ion concentrations, have been used in these calculations. Temperature: 30 °C; flow rate of the electrolyte: 13.5 l h^{-1}.

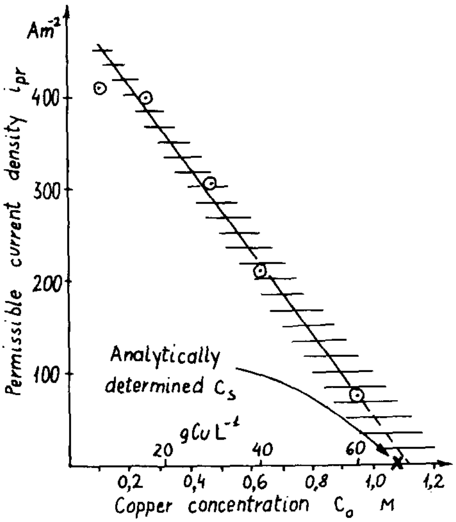

Fig. 6. Dependence of the permissible current density on the copper concentration in the electrolyte. $\Sigma C_{SO_4} = 2.43\ M$; temperature: 30 °C; flow rate of the electrolyte: 13.5 l h^{-1}.
$i_{pr} = (508.5 \pm 18.1) - (457.7 \pm 31.8) C_0\ \mathrm{A\ m^{-2}}$.

even of oxide formation, at the anode. This would mean a change in the passivation mechanism.

To verify Eq. 4b, the concentrations C_s, of the solutions saturated at differ-

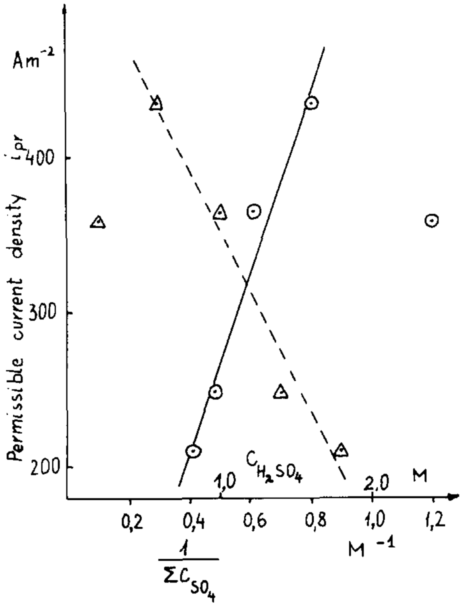

Fig. 7. Dependence of the permissible current density on the reciprocal value of the sulphate ions concentrations (circles) and on the sulphuric acid concentration (triangles). $C_0 = 0.63$ *M*; temperature; 30 °C; flow rate of the electrolyte: 13.5 l h^{-1}.

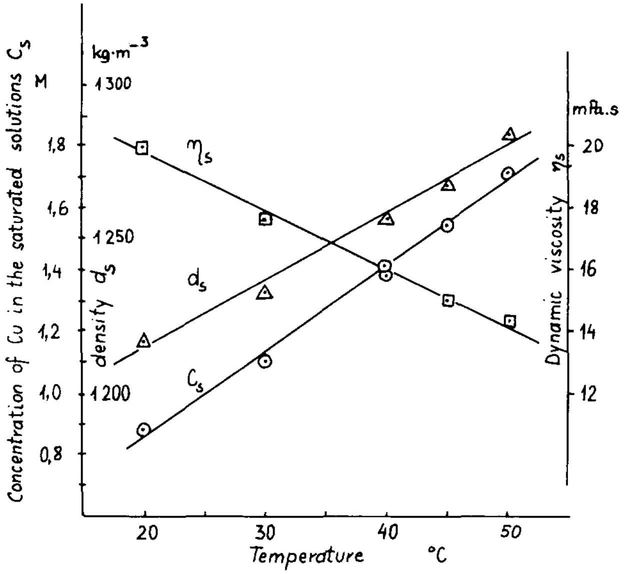

Fig. 8. Solutions of $CuSO_4$ and H_2SO_4, of constant sulphate ion concentration ΣC_{SO_4} = ca. 2.4 *M*, saturated with $CuSO_4$. Dependence of the copper concentration, and of the density and viscosity of solutions, on the temperature.

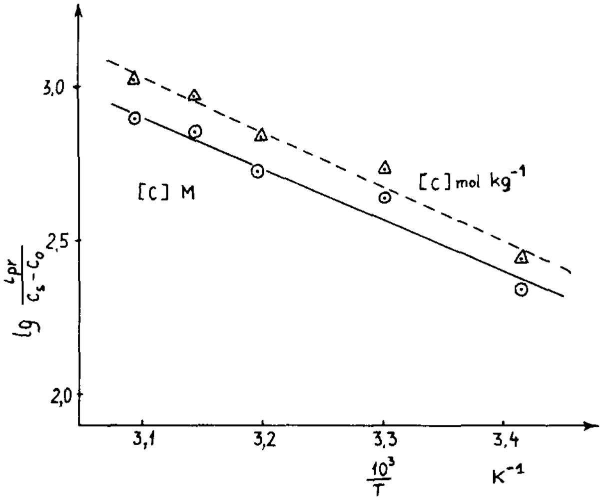

Fig. 9. Verification of Eq. 4a.
$C_o = 0.52$ mol Cu kg^{-1} (ca. 0.63 M), $\sum C_{SO_4} = 2.02$ mol kg^{-1} (ca. 2.4 M; ca. 175 g H_2SO_4 l^{-1}).

$$\log \frac{i_{pr}}{C_s - C_o} = (8.10 \pm 0.46) - \frac{1674 \pm 143}{T} \text{ when } [C] \text{ in } M$$

$$= (8.60 + 0.43) - \frac{1797 \pm 134}{T} \text{ when } [C] \text{ in mol kg}^{-1}.$$

ent temperatures with $CuSO_4$, needed to be known. Unfortunately the data in the literature are practically useless for this purpose. They describe either the solubility of $CuSO_4$ in water or the solubility in sulphuric acid solutions of different concentrations. In both cases the condition of a constant concentration of sulphate ions, which is essential for our passivation experiments, is not fulfilled.

To determine the required values of C_s an excess of dehydrated $CuSO_4$ was introduced into sulphuric acid solutions of different concentrations. The system was stirred, at constant temperature, until a constant concentration of copper ions in the solution was reached. Plotted the copper concentrations, obtained in this way, against the concentrations of sulphate ions, it was possible to interpolate C_s values which corresponded to the value of $\sum C_{SO_4} =$ ca. 2.4 M. The C_s values obtained and the values of the solution densities d_s are plotted against temperature in Fig. 8.

Figure 9 which presents the dependence of log $i_{pr}/C_s - C_o$ on the reciprocal value of the absolute temperature seems to confirm validity of eq. 4b.

Another factor which speaks for the validity of Eq. 4, and hence of the assumptions underlying it, is the fact that C_s values determined analytically (1.095 M at 30 °C) coincide with values obtained by extrapolation of the line in Fig. 6 to $i_{pr} = 0$ (1.111 ± 0.012 M).

Experiments have proved also that the time of passivation, and the permissible current density, increase with the rise of the electrolyte flow rate. It is one of the premises ensuing from the Eq. 3 where the coefficient δ, which represents thickness of the "diffusion layer" should be a diminishing function of the electrolyte flow rate. This coefficient depends also on the geometry of the cell, on the pattern of the electrolyte flow etc. Therefore the authors consider that attempts to describe quantitatively the influence of the electrolyte flow rate on the passivation are purposeless in the experimental work done.

CONCLUSIONS

The semi-empirical Eq. 3, which describes the dependence of the passivation time on the current density has been derived on the basis of an assumed mechanism of anode passivation in the process of copper electrorefining. The existence of a permissible current density, and its physical meaning, follow from this equation.

Transformation of the Eq. 3 into Eqs. 4, 4a and 4b confirmed the expected influence of copper ion concentration, sulphate ion concentration, temperature and solution flow rate, on the passivation time and on the value of the permissible current density.

The following facts seem to confirm validity of the derived equations and at the same time speak for the suggested model of the process and for acceptability of the simplifying assumptions:

(a) High values of the correlation coefficients prove the existence of the linear dependence of the passivation time on $\log(1-i_{\mathrm{pr}}/i_{\mathrm{A}})$ predicted by Eq. 3.

(b) It has been found that in agreement with Eq. 4 the permissible current density, determined in solutions of constant sulphate ion concentration, is a linear function of the copper ion concentration (Fig. 6).

(c) The concentration of copper determined analytically in solutions saturated with $CuSO_4$ at constant $\sum C_{SO_4}$, is in good agreement with that obtained by the extrapolation of the linear dependence of the permissible current density on the concentration of copper ions, to $i_{\mathrm{pr}}=0$ (see Eq. 4 and Fig. 6).

(d) Results of experiments in solutions of different sulphate ion concentration prove that dependence of i_{pr} on the reciprocal value of sulphate ion concentration is fulfilled over a wide range of $\sum C_{SO_4}$ (see Fig. 7).

(e) Experiments performed at different temperatures confirm the linear dependence of $\log\,[i_{\mathrm{pr}}/(C_{\mathrm{s}}-C_{\mathrm{o}})]$ on the reciprocal value of the absolute temperature (see Fig. 9).

(f) Both the passivation time and i_{pr} decrease when the solution flow rate decreases. This is in agreement with Eq. 3.

However there are also some unexplained facts which do not fit the suggested model of the process. These include:

(a) Statistical analysis of the experimental results reveals the existence of a coefficient "*a*" (Table I, Eq. 3b) which is not anticipated by the Eq. 3a. Interpretation of this term seems to indicate the existence of another threshold value of the current density i_{mx} which causes instantaneous passivation.

(b) The linear dependence of i_{pr} on the reciprocal value of the sulphate ion concentration $\sum C_{SO_4}$, following from Eq. 4a, breaks down when the concentration of sulphuric acid is low (see Fig. 7). This is probably the result of the change of mechanism of passivation, possibly coprecipitation of hydroxysalts together with $CuSO_4$ or alternatively the formation of oxides in the anodic process.

(c) It is distressing that there is no evident dependence of the coefficients "*a*" and "*b*" (Eq. 3a and 3b) on the electrolysis variables.

LIST OF SYMBOLS

C_o	concentration of copper in the bulk of the solution
C_s	concentration of copper in the saturated solutions
C^*	concentration of copper ions in the vicinity of the anode surface
$\sum C_{SO_4}$	total concentration of the sulphate ions
D	diffusion coefficient
δ	thickness of the diffusion layer
ϵ_{cp}	critical potential of passivation
i_A	anodic current density
i_{cp}	critical current density
i_{mx}	current density which causes instantaneous passivation
i_p	density of the passivation current
i_{pr}	permissible current density (passivation occurs at current densities higher than i_{pr})
I	solubility product of $CuSO_4$
J_I	the rate of anodic dissolution
J_{II}	the flux of copper ion transport from the anode to the bulk of solution
t_p	passivation time
T	absolute temperature
η	dynamic viscosity of the solution

REFERENCES

1 Graumann, D., Fischer-Bartelek, C. and Schab, D., 1972. Neue Hüte, 17: 71.
2 Sędzimir, J., 1984. Arch. Metall., 29: 195.
3 Jun, A., Pomosov, A. and Pyrina, N., 1971. Cvet. Met., 44: 25.
4 Pomosov, A., Jun, A. and Murasova, J., 1973. Cvet. Met., 46: 9.
5 Pomosov, A., Jun, A. and Murasova, J., 1974. Cvet. Met., 17: 19.
6 Biswas, A. and Davenport, W., 1980. Extractive Metallurgy. Pergamon, Oxford.
7 Bajmakov, J. and Zhurin, A., 1963. Elektroliz w Gidrometałłurgii. Nancz. Techn. Izdat., Moskwa.

8 Azuma Kazuomi, Nakamura Tsuyoishi and Kurachi Mitsuo, 1978, 1981. Nippon Kogyo Kaishi, 94: 1083, 347; 97: 1125, 1205; quoted in Chem. Abstr., 1979 (90): 129 421a; 1983 (98): 224 119.

9 Abe, S., Burrows, B. and Ettel, V., 1980. Can. Metall. Q., 19 (3): 289; quoted in Chem. Abstr., 1981: 164 480 p.

10 Srinivasan, G., Adaikkalam, P., Radhakrish, P., Srinivasan, R., Ramachandran, P. and Naganatkan, K., 1982. J. Electrochem. Soc. India, 31 (1): 60; quoted in Chem. Abstr., 1982: 204 929x.

11 Leckich, E. and Levin, A., 1963. Cvet. Met., 36: 29.

12 Krzysztofowicz, K., Hanus, D. and Baranek, W., 1972. Rudy i Metale Niezelazne, 16: 99.

13 Hanus, D. and Krynicki, J., 1977. Pr. Inst. Met. Nieżelazne., 6: 135.

14 Shiga Shoji, Nahaoka Todao, Tanigava Toru and Inada Takashi, 1979. Furukvava Denku Jiho, 10: 1.

15 Abe Shinichiro and Goto Sakichi, 1981. Nippon Kogyo Kaishi, 97: 1126, 1289; quoted in Chem. Abstr., 1983: 130 334s.

16 Gruner, M., Jurev, B. and Łuneva, O., 1983. Zh. Prikł. Chim., 56: 1895.

17 Abe Shinichiro and Goto Sakichi, 1984. Nippon Kogyo Kaishi, 100: 1155, 429; quoted in Chem. Abstr., 1986: 215 193s.

18 Sędzimir, J. and Gumowska, W., 1986. Rudy i Metale Nieżelazne, 31: 419.

19 Sędzimir, J. and Gumowska, W., 1987. Zeszyty Naukowe AGH, 1138; Metaluriga i Odlewnictwo, 109: 215.

20 Sędzimir, J. and Gumowska, W., 1989. Arch. Metall., 34: 17.

21 Gmelins, 1955. Handbuch der Anorganischen Chemie. Weinheim, Vol. 60, Teil A.