

Simulation of hydrodynamics and inhibitor consumption in hydrometallurgical plants

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Mathematical models are presented for the consumption of the inhibitors of electrocrystallization in hydrometallurgical plants involved with the copper electrorefining and zinc electrowinning. Continuously-stirred tank reactors (CSTR) and plug flow reactors (PFR) in which first order chemical and electrochemical reactions take place are used in these models. The time dependent behaviours of the industrial plants are predicted. Tests with metallic tracers show the validity of the models. Possible uses in electrocrystallization studies are described.

Nomenclature

V	volume of a reactor (CSTR or PFR)	k_a, k_c	electrochemical reaction rate constant
V'	volumetric flow rate of the electrolyte entering the electrochemical cell	a	ratio between the surface area of an electrode immersed in a reactor and the volume of this reactor
α	ratio between the volumetric flow rate of the 'fresh' electrolyte fed in the holding tank and that of the electrolyte entering the electrochemical cell	S	surface area of an electrode
n	ratio between the volumetric flow rate of the electrolyte in the PFR located near the cathode and that entering the electrochemical cell	τ	ratio between the volume of a reactor and its volumetric flow-rate = spacetime of the reactor
m	ratio between the volumetric flow rate of the electrolyte in the PFR located between the electrodes and the cell walls (electrowinning model) and that entering the electrochemical cell	t	time
C_0	concentration of the reactant in the 'fresh' fed electrolyte	C	concentration
k	chemical reaction rate constant	r	rate of a chemical reaction per unit volume of reacting fluid
		r''	rate of an electrochemical reaction per unit surface area of the electrode
		subscripts: 1 to 7	reactor number
		a	anodic or anode
		c	cathodic or cathode

1. Introduction

Complex organic molecules are often present in the electrolytes of industrial electrorefining and electrowinning plants. These inhibitors of electrocrystallization modify the nucleation and growth processes of the metals at the cathode. Small changes of the concentration of these inhibitors may have important effects on the cathode current efficiency, on the morphology of the metallic deposit and also on cathode purity. Unfortunately, the inhibitor concentration is usually below the capability limits of simple analytical methods. Moreover, these inhibitors undergo complex degradation processes and it is not easy to establish the nature of the true active species, so that monitoring is very difficult.

Developing a model for the consumption of these organic molecules would certainly be a step forward. Such a model should take into account the hydrodynamics and the kinetics of the global degradation

reactions of the inhibitors. Data are available in the literature for electrorefining and electrowinning industrial cells [1-9] and for the most usual organic additives [10-15]. This paper deals mainly with the description and the development of such models which can be used to describe these processes and with the tests used to verify their validity.

2. Description of the models

It is assumed that the tankhouse of an electrolytic plant contains a large number of identical cells placed in series or in parallel.

The hydrodynamic model of the industrial plant deals with such a single cell (comprising a cathode, an anode and the electrolyte between these two electrodes) and the related recycling pipes and holding tanks. The dimensions of the cells, pipes and tanks are evaluated in order to maintain the same ratios between the surface of the electrodes and the volume

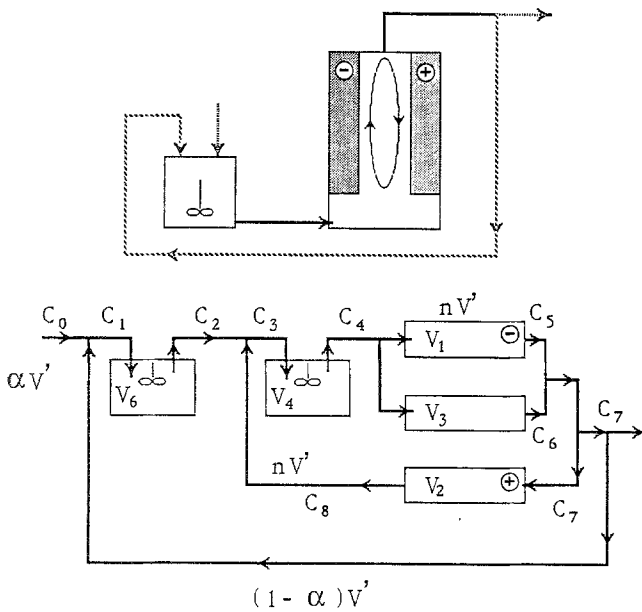


Fig. 1. Electrorefining flow-sheet and its simulation model.

of electrolyte, in the plant and in the model. Values of parameters for the models will be based, as far as possible, on industrial estimates.

2.1. Electrorefining model

Due to density gradients at the electrode/electrolyte, interfaces [16-17], the electrolyte motion is oriented downward near the anode and upward near the cathode of an electrorefining cell. This is simulated by two plug flow reactors located near the electrodes (V_1 and V_2) and one plug flow reactor in the centre of the cell (V_3) (see Fig. 1).

It is assumed that the electrolyte in this latter reactor is concerned neither with the anodic nor with the cathodic reaction.

The V_4 CSTR is inserted to take into account the mixing volume at the bottom of the industrial cell. This volume is due to the smaller height of the electrodes than the height of the electrolytic cell itself. The V_6 CSTR represents the volume of the recycling pipes (with a $(1 - \alpha)V'$ flow rate) and of the holding tank.

The 'fresh' reactant is fed with a flow rate $\alpha V'$ and a C_0 concentration in this V_6 reactor. It is assumed that the flow rates and the volumes of the electrode reactors (V_1 and V_2) are identical.

Accordingly, two parameters are chosen for the electrorefining model: the flow rate and the volume of the cathodic plug flow reactor.

2.2. Electrowinning model

In an electrowinning plant, gas evolution may be observed at both electrodes (especially at the anodes). The electrolyte motion is oriented upward near the electrodes and downward between the electrodes or between the electrodes and the lateral walls of the cell. This is simulated by two PFR (V_1 and V_2) near the electrodes and one PFR (V_3) corresponding to the electrolyte volume located between the electrodes and the lateral cell walls. The electrolyte in this latter reactor is only concerned with chemical reactions (see Fig. 2).

The V_4 CSTR has the same meaning as in the

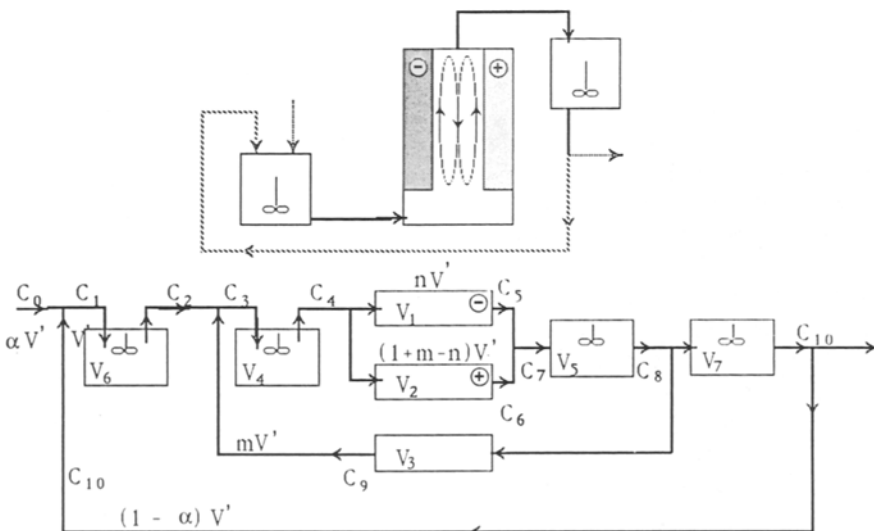


Fig. 2. Electrowinning flow-sheet and its simulation model.

electrorefining model but another CSTR (V_5) is inserted in the model to simulate the experimentally observed mixing zone in the upper part of the cell. In this zone, the two upward oriented flows are mixed together. The height of this mixing zone is estimated in industrial operating conditions.

The V_6 and V_7 CSTRs represent, respectively, the volume of the waiting tank (in which the 'fresh' reactant is fed) and the volumes of the recycling pipes and of the cooling tank (from which electrolyte is extracted and is sent to the leaching stage).

It is assumed for the zinc electrowinning model that in the laminar regime, the linear velocities of the electrolyte in the PFRs V_1 and V_2 are proportional to the gas volume produced at each electrode [20].

Accordingly, for this electrowinning model, the same two parameters as for electrorefining are chosen.

2.3. Reaction models

The detailed degradation reactions of the inhibitors of electrocrystallization, like thiourea and gelatin, are very complex and some discrepancies appear in the literature concerning the degradation processes and products in industrial operating conditions. Nevertheless, data for global degradation reactions are available [10–15].

Three types of global reaction are proposed:

– a first order chemical reaction ($M \rightarrow R$) with a kinetic constant k .

– a cathodic reaction ($M + xe^- \rightarrow S$) occurring at its diffusion limiting current density with a kinetic constant k_c .

– an anodic reaction ($M \rightarrow T + ye^-$) occurring at its diffusion limiting current density with a kinetic constant k_a .

This model is only valid for low concentration reactants and not for the main ions of the electrolyte.

So, the rate of the chemical reaction per unit volume of reacting fluid is:

$$r_M = \frac{1}{V} \frac{dN_M}{dt} = -kC_M \quad (1)$$

the rate of the cathodic reaction per unit surface of cathode is:

$$r_M^c = \frac{1}{S_c} \frac{dN_M}{dt} = -k_c C_M \quad (2)$$

and the rate of the anodic reaction per unit surface of anode is:

$$r_M^a = \frac{1}{S_a} \frac{dN_M}{dt} = -k_a C_M \quad (3)$$

The transient behaviour of a plug flow reactor (of length L) in which these three reactions occur is described by the following equation:

$$\frac{dC_M}{dt} + \frac{L}{\tau} \frac{dC_M}{dx} + \left(k + k_a \frac{S_a}{V} + k_c \frac{S_c}{V} \right) C_M = 0 \quad (4)$$

If $a_c = S_c/V$ and $a_a = S_a/V$, the solution of this equation is:

$$C_M(L, t) = C_M(0, t - \tau) e^{-(k+k_a a_a+k_c a_c)\tau} \quad (5)$$

The transient behaviour of a continuously-stirred tank reactor in which the three reactions occur is described by the following equation:

$$\tau \frac{dC_M}{dt} + (1 + (k + k_a a_a + k_c a_c)\tau) C_M = C_{M_0} \quad (6)$$

The solution of this equation is:

$$C_M = \frac{C_{M_0}}{1 + (k + k_a a_a + k_c a_c)\tau} \times (1 - e^{-[1+(k+k_a a_a+k_c a_c)\tau]t/\tau}) \quad (7)$$

2.4. Systems of equations

Two systems of equations may be proposed for each model: the system corresponding to the steady-state of the plant and the system corresponding to the transient behaviour of the plant. Only the latter system is presented here, taking into account that the steady-state system of equations may be extrapolated from the transient system. The sets of equations include material balance equations at the nodes of the models (equations (8), (10), (14), (16), (18), (22)) and reactor equations (equations (5) or (7)) for every reactor present in the models.

For the electrorefining model (see Fig. 1), the equations are:

$$C_1(t) - (1 - \alpha)C_7(t) = \alpha C_0 \quad (8)$$

$$\frac{C_1(t)}{1 + k\tau_6} (1 - e^{-(1+k\tau_6)t/\tau_6}) - C_2(t) = 0 \quad (9)$$

$$C_2(t) - (1 + m)C_3(t) + mC_8(t) = 0 \quad (10)$$

$$\frac{C_3(t)}{1 + k\tau_4} (1 - e^{-(1+k\tau_4)t/\tau_4}) - C_4(t) = 0 \quad (11)$$

$$e^{-(k+k_c a_c)\tau_1} C_4(t - \tau_1) - C_5(t) = 0 \quad (12)$$

$$e^{-k\tau_3} C_4(t - \tau_3) - C_6(t) = 0 \quad (13)$$

$$nC_5(t) + (1 + m - n)C_6(t) - (1 + m)C_7(t) = 0 \quad (14)$$

$$e^{-(k+k_a a_a)\tau_2} C_7(t - \tau_2) - C_8(t) = 0 \quad (15)$$

and for the electrowinning model (see Fig. 2):

$$C_1(t) - (1 - \alpha)C_7(t) = \alpha C_0 \quad (16)$$

$$\frac{C_1(t)}{1 + k\tau_6} (1 - e^{-(1+k\tau_6)t/\tau_6}) - C_2(t) = 0 \quad (17)$$

$$C_2(t) - (1 + m)C_3(t) + mC_8(t) = 0 \quad (18)$$

$$\frac{C_3(t)}{1 + k\tau_4} (1 - e^{-(1+k\tau_4)t/\tau_4}) - C_4(t) = 0 \quad (19)$$

$$e^{-(k+k_c a_c)\tau_1} C_4(t - \tau_1) - C_5(t) = 0 \quad (20)$$

$$e^{-(k+k_a a_a)\tau_2} C_4(t - \tau_2) - C_6(t) = 0 \quad (21)$$

$$nC_5(t) + (1 + m - n)C_6(t) - (1 + m)C_7(t) = 0 \quad (22)$$

$$\frac{C_8(t)}{1 + (k + k_c a_{5c} + k_a a_{5a})\tau_5} \times (1 - e^{-(1 + (k + k_c a_{5c} + k_a a_{5a})\tau_5)t/\tau_5}) - C_8(t) = 0 \quad (23)$$

$$e^{-k\tau_3} C_8(t - \tau_3) - C_9(t) = 0 \quad (24)$$

$$\frac{C_8(t)}{1 + k\tau_7} (1 - e^{-(1 + k\tau_7)t/\tau_7}) - C_{10}(t) = 0 \quad (25)$$

where τ_i is the spacetime in the i th reactor.

In the steady-state, these equations are linear and are easy to solve. On the contrary, due to the lag times introduced by the plug flow reactors, the transient systems are not linear. To solve this problem, the highest common factor, τ , of the space-times in the plug flow reactors is calculated. The time scale is then considered as a sequence of time intervals ($t_n, t_n + \tau = t_{n+1}$). In these time intervals, the sets of equations are linear. The concentration at any time may then be obtained taking into account the steady initial conditions and the preceding steps.

2.5. Determination of the model parameters

The criterion used to determine the model parameters is to keep in the models the same diffusion limiting current densities for the reactants as in the industrial cells. These are directly related to the hydrodynamics near the electrodes.

To determine the hydrodynamic conditions near the industrial cathodes, the tracer method was used [18–20]. The tracer must have well known kinetic

parameters, may not modify the industrial process to be studied even at measurable concentration, must be more noble than the main metal to be deposited and must be codeposited at its diffusion limiting current density throughout the deposition cycle. Silver for copper electrolysis and cadmium for zinc electrolysis to satisfy these requirements. The limiting current density of the tracer was obtained by chemical analysis of the cathodic deposit.

In a laboratory channel cell [19] with forced electrolyte flow (behaviour approximating a plug flow reactor), the relationship between the diffusion limiting current density of the tracer and the linear velocity of the electrolyte was determined. Assuming that the linear velocity in this channel cell corresponds to the linear velocity of the electrolyte in the plug flow reactor of the model, it is possible to determine the flow rate in the cathodic plug flow reactor of the model in order to maintain the same diffusion limiting current density of the tracer and, accordingly, the same hydrodynamic conditions as in the industrial cell.

Thus, there is only one remaining parameter for the two models: the volume of the cathodic plug flow reactor. The sensitivity of the models to the chosen value of this volume is calculated in steady-state conditions for the tracer ions considered as the reactant. The calculated values are compared with the experimental values measured in industrial operating conditions. As may be seen in Fig. 3, for the copper electrorefining model, the theoretical steady-state silver concentration in the electrolyte outlet is nearly constant and very close to the experimental value whatever the volume of the cathodic reactor is, except when this volume becomes comparable to the volume of the diffusion film near the cathode.

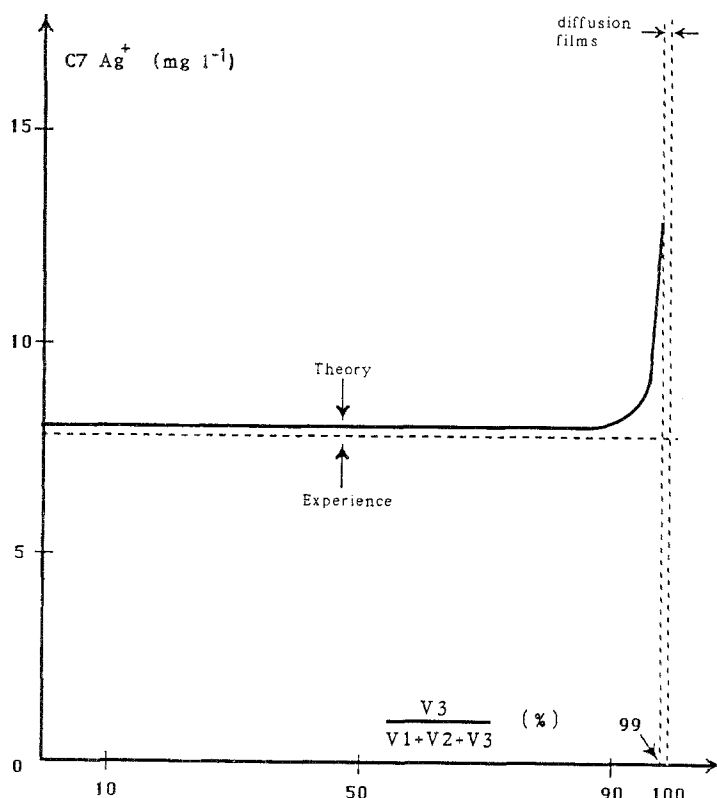


Fig. 3. Copper electrorefining model. Steady-state silver concentration in the electrolyte overflow versus the volume of the reactor V_3 . Solution inlet: 30 ml h^{-1} at 2 g/l Ag^+ .

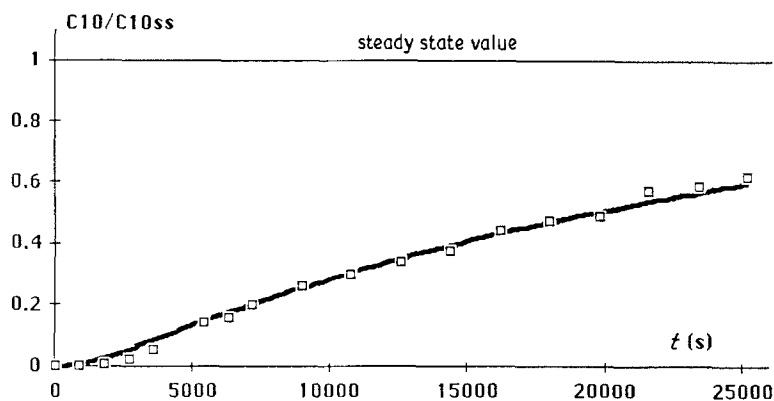


Fig. 4. Reduced lithium concentration in the electrolyte outlet as a function of time during zinc electrowinning. Curve: calculated concentration. Points: experimental concentration. Solution inlet: 1.95 l/h at 101.0 mg/l Li^+ . Total volume of the experimental set-up: 24.71.

In further calculations, the volume V_3 is neglected in the electrorefining model and is restricted to the electrolyte volume located between the electrodes and the cell walls in the electrowinning model.

With the same values of the parameters, the models are further tested in the transient state for a non-reactive tracer (lithium ions). A very good agreement between theoretical and experimental values is observed (see Fig. 4 for zinc electrowinning). This confirms particularly the presence of the reactor V_5 (mixing zone in the upper part of the cell) in the zinc electrowinning model.

3. Possible uses of the models

So far, these models have been used to study the degradation of thiourea in copper electrorefining and of gelatin in zinc electrowinning [21–22].

For the thiourea degradation, data for the kinetic parameters of the degradation process are available, so that it was possible to simulate the transient behaviour of the copper electrorefining plant for different initial conditions (see Fig. 5).

Curve 0 is obtained when the electrolyte solutions contains no inhibitor at the start of the electrolysis. In this case, the thiourea concentration in the electrolyte outlet reaches 90% of the steady-state value after less than 3.5 h. It is interesting to note that this delay time is smaller than that obtained if the electrolytic cell is considered as a perfect CSTR (spacetime equal to 4 h).

Curve 1 is obtained with the initial concentration of thiourea in all the circuit equal to the steady-state concentration in the outlet of the cell.

Finally, curve 1* is obtained with an initial con-

centration in the cell equal to its steady-state concentration and an initial concentration in the holding tank equal to its own steady-state value. It is only with these initial conditions that the inhibitor concentration in the electrolytic cell is constant from the beginning of the electrolysis and, thus, that electrocrystallization starts under the control of a well defined inhibiting effect. This is particularly important for small scale experiments in research laboratories.

For the gelatin degradation, data for the kinetic degradation parameters were not available in the literature but experimental observations in industrial operating conditions showed that the life time of gelatin during a batch electrolysis was about 4 h. The electrowinning model was then adapted for a batch electrolysis. It was supposed that the chemical degradation of gelatin was negligible (k equal to 0) and that, globally, the kinetic parameters for the anodic and the cathodic degradation reactions were identical. Different sets of values for these parameters were introduced into the model and the transient behaviours were computed. The gelatin concentration decreased to 10% of its initial value after a 4 h batch electrolysis when the electrochemical parameters were equal to $2.5 \times 10^{-6} \text{ ms}^{-1}$. These values were then used to simulate the transient behaviour of the zinc electrowinning plant. The initial gelatin concentrations in all the reactors had to be set precisely before electrolysis in order to maintain a constant inhibitor concentration in the electrochemical cell.

4. Conclusion

Hydrodynamic models combining continuously stirred tank reactors and plug flow reactors have been used in

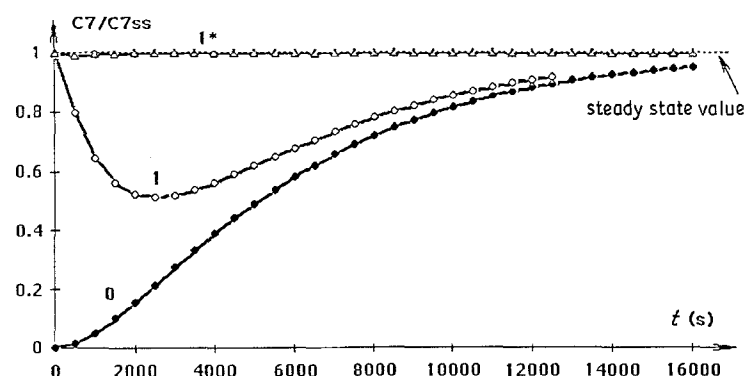


Fig. 5. Reduced thiourea concentration in the electrolyte outlet as a function of time during copper electrorefining. $V' = 4.45 \text{ l/h}$ — Volume of the cell: 17.81.

order to simulate complex phenomena such as the degradation of the inhibitors of electrocrystallization in electrorefining and electrowinning plants. Computer programs have been developed to calculate the transient and the steady-state behaviour of these compounds. The models have been tested and the hypothesis proved to be reasonable. Interesting fundamental and applied observations have been derived such as the transient behaviour of thiourea in a copper electrorefining plant and the values of the kinetic degradation parameters of gelatin in a zinc electrowinning plant. The main conclusion of these simulations is that it is very important to fix correctly the initial inhibitor concentration in the whole plant when studying the influence of this inhibitor at a pilot or micro-pilot scale.

Further developments including more complex reaction schemes (second order chemical reactions, cyclic reactions) are presently under study.

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References

- [1] D. J. Pickett, 'Electrochemical reactor design', Elsevier Amsterdam (1979).
- [2] L. H. Mustoe and A. A. Wragg, *J. Appl Electrochem.* **13** (1983) 507.
- [3] R. E. White, M. Bain and Raible, *J. Electrochem. Soc.* **130** (5) (1983) 1037.
- [4] F. Lapique and A. Storck, *J. Appl. Electrochem.* **15** (1985) 925.
- [5] K. Scott, *J. Appl. Electrochem.* **15** (1985) 659.
- [6] T. V. Nguyen C. W. Walton, R. E. White and J. Van Zee, *J. Electrochem. Soc.* **133** (1), (1986) 81.
- [7] M. J. Mader, C. W. Walton and R. E. White, *J. Electrochem. Soc.* **133** (6), (1986) 1124.
- [8] T. V. Nguyen, C. W. Walton and R. E. White, *J. Electrochem. Soc.* **133** (6) (1986) 1130.
- [9] J. T. Mulvale and T. Z. Fahidy, *Electrochim Acta* **31** (1986) 173.
- [10] P. Javet, N. Ibl and H. E. Hinterman, *Galvanotechnik und Oberfl.* **8** (1967) 231.
- [11] P. Javet, N. Ibl and H. E. Hinterman, *Electrochim. Acta* **12** (1967) 781.
- [12] P. Javet and H. E. Hinterman, *Electrochim. Acta* **14** (1969) 527.
- [13] A. Szymaszek, J. Biernat and L. Pajdowski, *Electrochim. Acta* **22** (1977) 359.
- [14] K. Tshula, Ph.D. Thesis, Université Libre de Bruxelles, Belgium (1983).
- [15] H. S. Jennings and F. E. Rizzo, *Met. Trans.* **4** (1973) 921.
- [16] Y. Awakura and Y. Kondo, *J. Electrochem. Soc.* **123** (8) (1976) 1184.
- [17] Y. Awakura, Y. Takenaka and Y. Kondo, *Electrochim. Acta* **21** (1976) 789.
- [18] T. J. O'Keefe, J. S. Cuzmar and S. F. Chen, *J. Electrochem. Soc.* **134** (1987) 547.
- [19] M. Degrez and R. Winand, *Electrochim. Acta* **29** (1984) 365.
- [20] H. M. Wang, S. F. Chen, T. J. O'Keefe, M. Degrez and R. Winand, *J. Appl. Electrochem.* **19** (1989) 174.
- [21] M. Degrez, J. L. Delplancke and R. Winand, 'Inhibitor behaviour simulation in copper electrorefining and zinc electrowinning', AIChE Meeting, New York (1987).
- [22] J. L. Delplancke, M. Degrez and R. Winand, 'Simulation of hydrodynamics and inhibitor consumption in electro-metallurgical plants', 173rd Electrochemical Society Meeting, Atlanta (May 1988).