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DEVELOPMENT AND EVALUATION OF METHODS FOR CURRENT DENSITY DISTRIBUTION PREDICTION IN ELECTROCHEMICAL SYSTEMS

(13 RITE-EURAM PROJECT: BE-5187 CONTRACT NR: BRE2-CT92-0170)

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Abstract

The general objective of this project is to develop, compare and validate two new, complementary and generally applicable numerical methods to predict current density distributions in electrochemical cells in situations where mass transfer cannot be neglected and where hydrodynamics may be complex. These methods are based on the MultiDimensional Upwinding Method (MDUM) and the Boundary Element Method (BEM).

Models for dilute solutions with a maximum of 4 ions are considered. The project is limited to steady-state, two-dimensional and axisymmetrical problems. Measurements were obtained in a parallel plate reactor without and with a fence, in a constricted cell with a backward facing step and in a jet cell. The ferri-ferrocyanide system was used for limiting current measurements whereas the $CuSO_4/H_2SO_4$ system provided data ranging from secondary up to tertiary current density distributions.

Comparison with analytical solutions showed very good to excellent results. In general also measurements and numerical results were in satisfactory good agreement. In the case of limiting current density distributions the numerical results are closer to measurements even in complex flow situations. Comparison with current density distributions obtained in the copper solution revealed that it is of major importance to have a proper description of the electrochemical processes involved.

Introduction

The design and scale-up of electrochemical cells requires a model for accurately predicting the current and potential distributions in the electrolyte solution, this being the focus of analysis in the study of electrochemical systems [1]-[6]. The equations have to include the effects of

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diffusion, convection and migration of ions, which describe the mass transfer and charge transport processes [3] ,[7].

Once such general applicable numerical models are available, they can be applied to a variety of electrochemical processes. On one side to improve model identification of electrode processes e.g. measured with a Rotating Disc Electrode, and on the other side to perform optimal design of electrochemical processes with respect to composition and thickness of deposit, speed).

A substantial number of researchers tried to solve this problem, but almost all of them deal with simplified cases in which either migration or convection phenomena are ignored [8]- [13]. Treatment of the original problem without any simplification is quite complicated because of the non-linear behaviour and the complexity of the governing equations and the strong non-linear boundary conditions.

In this project, two new numerical methods have been developed to solve the mass and charge transport equations governed by diffusion, convection and migration. The Multi Dimensional Upwind Method (MDUM), originally developed at von Karman Institute (VKI) [14], [15], is modified by Vrije Universiteit Brussel (VUB) to deal with mass and charge transport. The Boundary Element Method (BEM) [16]-[1 8], has been adapted at Wessex Institute of Technology (WIT) to deal with high velocities and migration of ions. As a result, one has two totally different numerical methods to solve the model for diluted solutions.

The experimental data that are necessary for the validation of these numerical methods are provided by Laboratoire des Sciences du Génie Chimique (LSGC) and University of Exeter (UE). LSGC does measurements on the copper system in a parallel plate cell and a jet cell. Measurements of limiting current densities for the ferro/ferri system in a parallel plate electrochemical reactor without and with obstruction (fence, backward facing step, . ..) have been done in UE. Both experimental groups built up their own devices.

Technical description

Equations for multi-ion electrochemical systems

Starting from a dilute solution of I species in an unionised solvent at constant pressure and temperature, one can write down six equations describing transport of mass and charge [3],[7]. The flux of each dissolved species k due to diffusion, convection and migration is given by:

$$\overline{N}_k = - D_k \overline{\nabla} c_k + c_k \overline{v} - z_k u_k F c_k \overline{\nabla} U \quad , \qquad (1)$$

with c_k the concentration, z_k the charge, u_k the mobility, U the potential, D_k the diffusion coefficient, $\overline{v}$ the velocity of the solvent, and F the Faraday constant. The total current density is easily obtained by adding each ion flux multiplied by the corresponding charge per mole:

$$\bar{J} = F\sum_{k=1}^{I} z_k \bar{N}_k \quad , \tag{2}$$

with I the number of ions. For each species k one can state that at each point in the solution, the change of concentration is equal to the net input plus the local production due to chemical reactions. Conservation of charge is therefore expressed as follows:

$$\frac{\partial c_k}{\partial t} = -\bar{\nabla}.\bar{N}_k + R_k \quad . \tag{3}$$

with:

$\bar{\nabla}.\bar{N}_k$	the divergence of the flux vector,
R_k	the production rate of an ion (positive or negative) due to homogeneous reactions in the bulk of the solution.

In an electrolyte, the conductivity is so large that free charges do not exist. Therefore the following expression holds:

$$\sum_{k=1}^{I} z_k c_k = 0 \quad . \tag{4}$$

Equation (4) is not valid very close to the electrodes where the double-layer exists. The phenomena taking place in the double layer will be encompassed in the non-linear boundary conditions. Combination of equations (1) to (4), together with some mathematical manipulations leads to the following well known system of equations describing transport of mass and charge in dilute electrolytes:

$$\frac{\partial c_k}{\partial t} + \bar{v}.\bar{\nabla}c_k = \overline{z_k}F\nabla.(u_k\overline{c_k}\nabla U) \overline{+} \nabla.(D_k\bar{\nabla}c_k) + R_k \quad , \tag{5}$$

$$\sum_{k=1}^{I} z_k c_k = 0 \quad . \tag{6}$$

This set contains I+1 equations which, after solution, will give the I+1 unknowns, c_k and U. Obviously, even in the case of an infinitely dilute electrolyte, a complex system of coupled partial differential equations has to be solved. ‘

In the case of an infinitely dilute electrolyte, the velocity field $\bar{v}$ in (5) can be determined in advance since the fluid dynamic equations are not coupled with the electrochemical ones. This velocity field is obtained by solving either analytically or numerically the continuity and the Navier-Stokes equations given below:

$$\bar{\nabla}.\bar{v} = 0 \tag{7}$$

$$\frac{\partial \overline{v}}{\partial t} + \left(\overline{v}.\overline{\nabla}\right)\overline{v} = \frac{1}{\rho}\overline{\nabla}p + \nu\Delta\overline{v} + \overline{g} \qquad (8)$$

Obtaining a numerical solution of these equations was the task of VKI. To that purpose also MDUM was used.

Numerical methods to solve the Navier-Stokes equation

The Multi Dimensional Upwind Method consists in a subdivision of the two-dimensional geometry into a number of arbitrarily distributed triangles, called elements. In each element the unknowns have a linear representation. The size and distribution of the triangles allow to approximate properly local variations of the unknowns by small piecewise linear functions. Such a division of the geometry into a grid is also applied in the Finite Element Method (FEM) and is much more flexible than the regular grids needed for the Finite Difference Method (FD).

Another interesting aspect of the MDUM is that it enables to model situations with very high Péclet numbers using a restricted number of elements. More detailed information on MDUM can be found in [14], [15].

In the frame-work of this project a new (and original) formulation has been adopted to solve the Navier-Stokes equations. This method is described in detail in [19].

Numerical methods to solve the equations describing transport of mass and charge in diluted electrochemical systems

The MultiDimensional Upwinding Method

The Multi Dimensional Upwinding Method (MDUM), originates from the field of fluid mechanics (see above). It is an alternative approach to both finite element methods and finite volume methods and has been extended to the equations describing transport of mass and charge in dilute electrochemical systems. A very detailed description of the MultiDimensional Upwinding Method applied in electrochemistry can be found in [20] -[22].

The Boundary Element Method

The second method developed to solve equations (5) and (6) is the Boundary Element Method (BEM). In this approach, the velocity field is divided into an average and a perturbation, and the fundamental solution of the diffusion-convection equation for constant velocity is applied. The perturbation velocity and migration terms are included through a domain discretization. Papers [23]-[27] give a very detailed description of this method.

Experiments done to obtain data for the evaluation of the numerical codes

Measurements done on the copper system

LSGC investigated the electrochemistry of copper deposition by linear voltammetry at a rotating disk electrode. Using the Nernst film model, experimental curves yielded values for diffusion coefficient of the electroactive species and for the kinetic parameters of the deposition. The anodic dissolution of copper, occurring at the counter electrode of the cell, was also investigated using voltammetric techniques.

A two-meter long parallel plate flow cell has been designed in strong collaboration between LSGC and UE. Installed in a flow rig, the cell allows the measurements of local current densities, for given operating conditions. The design of the cell allows the flow to establish at the entrance of the electrode gap. Various flow disruptions such as a fence and a backward facing step can be placed in the cell. Two metal plates (350 mm long, 100 mm wide) act as electrodes and two rows of micro electrodes are inserted in the working electrode, upstream and downstream the disruption. A data acquisition system allows the simultaneous recording of data from up to 32 micro electrodes. Subsequent treatment of raw data is ensured by a computer connected to the set-up. It is refered to [28] for more detailed information.

Furthermore, a jet cell was designed and built for the measurement of current density profiles on a copper electrode facing the submerged jet of an electrolyte solution. The large dimensions of the cell allow the micro electrodes to be located with accuracy in front of the 30 mm diameter jet flowing downwards. The cathode is a 300 mm diameter copper disk and distributions can be measured using 42 micro electrodes. A copper disk located in the upper part of the cell acts as the anode. The cell has been tested for various conditions of the Reynolds number, cell voltage and dimensionless distance from the nozzle outlet to the copper plate. More detailed information can be found in [29].

Measurements done on the ferro/ferri system

A vertical, 2.03 m tall cell, with an inlet section of 1.03 m, and exit section length 0.34 m was used as measuring device. The working cathode was a 0.35 m long nickel plate 0.1 m wide and set in one wall of the channel while the anode was a 0.41 m long plate set opposite the cathode with an interelectrode spacing of 0.01 m. The physical properties of the electrolyte system were determined and the cathode reaction was the reduction ofFe(CN)63 - to Fe(CN)6 4- from a K3Fe(CN)6 / K4Fe(CN)6 / NaOH / H20 electrolyte. Mass transfer coefficients for the cathodic reaction were calculated from the measured limiting currents and were carried out under natural, mixed and forced convection conditions.

The cell was operated with a single plane fence obstruction of variable height (3 mm, 5 mm, and 7.5 mm) situated 100 mm from the leading edge of the cathode and local mass transfer distributions were measured at different flow rates. Double obstructions of the same fence *heights* were also applied for the experiments. Also a 5 mm backward facing step was used and in separate experiments the obstructions were also placed on the opposite wall. Local mass transfer coefficients for the cathodic reaction were calculated from the measured limiting currents. More detailed information can be found in [30] -[33].

Results

Comparison between BEM and analytical solutions

In this example results obtained with BEM will be compared with the analytical values. The test case is a one dimensional limiting current density analysis of a binary electrolyte with one reacting ion (ion 1). The geometry consists of a parallel plate cell with metal dissolution at x = O and metal deposition at x = L. The electrical cathode potential (V_c = O) is imposed and the anode potential V_a is variable. Suppose the current density at both electrodes is given by the following Butler-Volmer equation:

$$J_n = J_o\left(\frac{c_1}{c_{1b}}\right)^{\gamma}\left| e^{\alpha_1\frac{nF}{RT}(V-U)} - e^{-\alpha_2\frac{nF}{RT}(V-U)} \right. , \quad \} \tag{9}$$

Test aredone for $D_1 = D_2 = 10^{-5}cm^2s^{-1}$, n = 1, $z_1 = +1$, $z_2 = -1$, L = 1 cm, c_{1b} = 0.1 M, V_a = **O** V, V_c = -0.1 V and T = 25^{0}C. **The** parameters for the electrode reaction are $J_o = 10\text{-}^{2A}cm^{-2}$, $\gamma = 1$, $\alpha_1 = \alpha_2 = 0.5$.

The one dimensional analytical solution for the concentration and potential is given by [34]:

$$c_1 = Ax + B , \tag{10}$$

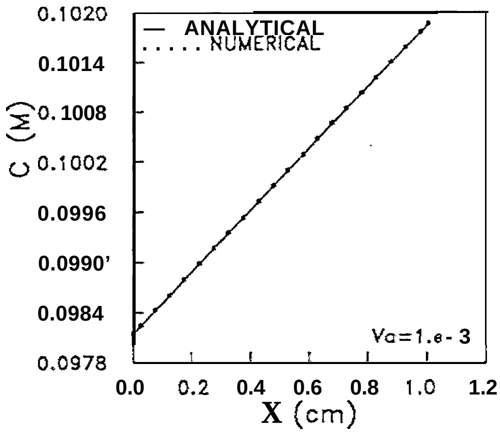
$$U = K\ln(Ax+B)+D , \tag{11}$$

with $K = -RT/z_2F$ and A, B and D depending on V_a **as** listed in the table below:

V_a	A	B	D
1.010-3	3.716110-6	9.814210-5	2.391210-1
5.010-3	3.671410-5	8.164310-5	2.440910-1
1.010-2	$1.4397\ 10^{-4}$	$2.8014\ 10^{-5}$	2.741410-1

Results for the concentration and potential distribution obtained with BEM are presented in figures 1 to 6. The agreement between the numerical and analytical solution is perfect for all values of V_a.

Numerical data resulting from MDUM, not presented in this report, matched equally well with the analytical solution.



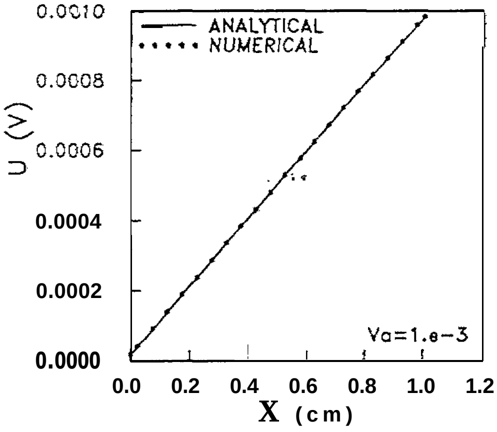
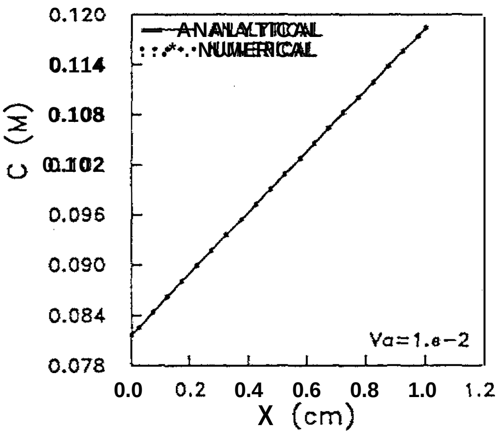


Figure 1. Concentration distribution for V_a = **0.001**

Figure 2. Potential distribution for V_a = 0.001



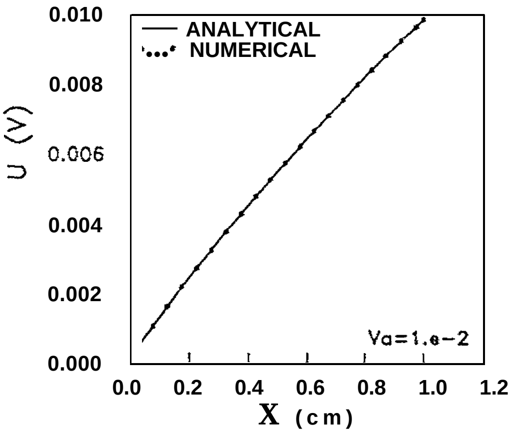
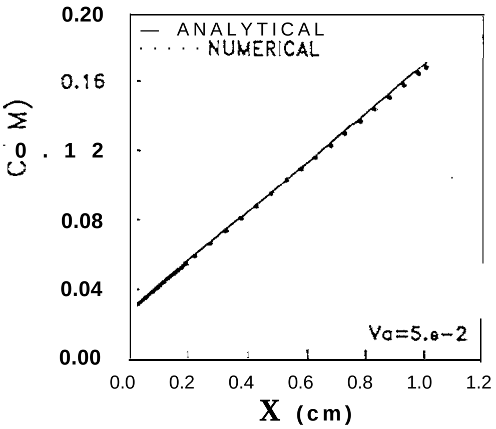


Figure 3. Concentration distribution for V_a = 0.01

Figure 4. Potential distribution for V_a = 0.01



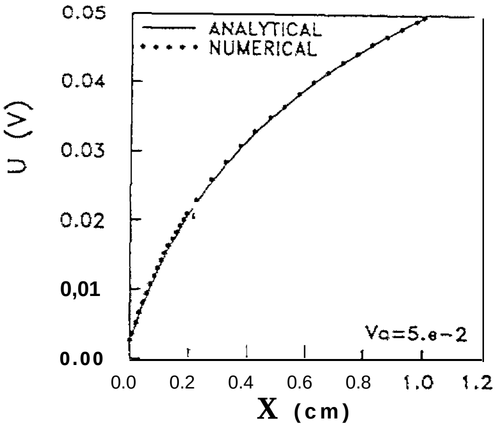


Figure 5. Concentration distribution for V_a = 0.05

Figure 6. Potential distribution for V_a = 0.05

Comparison between MDUM and experimental data

Limiting current analysis in the ferri/ferro system

Limiting current experiments done by UE on the ferri/ferro system have been compared with the numerical data obtained with MDUM. Two different geometries are considered: a parallel plate reactor without obstruction (with analytical solution for the velocity field) and a parallel plate reactor with a 5 mm fence (with numerical solution for the velocity field obtained with the fluid flow solver developed at VKI).

The geometries used for the numerical simulation are given in figures 7 and 8. The length of the cathode and anode is 352 mm and the distance between the plates is 10 mm. At both inlet and outlet a 50 mm insulating part has been introduced to deal with the edge effects occurring at the electrodes.

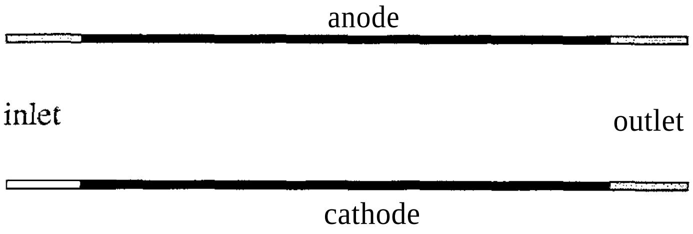


Figure 7. Parallel plate channel without fence

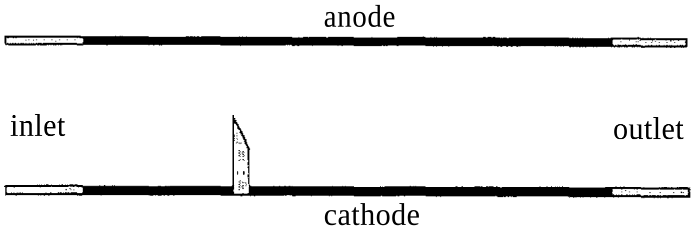


Figure 8, Parallel plate channel with 5 mm fence

The electrolyte is 0.005 M $K_4Fe(CN)_6^{3-}$, 0.01M $K_4Fe(CN)_6^{4-}$ and 0.5 M NaOH at 20°C. The physical properties of the electrolyte at this temperature are:

Density : $p = 1020.5$ kg/m^3
Viscosity: $\mu = 1.105\ 10^{-3}$ kg/ms
Diffusivity of ferricyanide ion: $D = 6.631\ 10^{-10}$ m^2/s

resulting in a Schmidt number ($Sc = \mu/\rho D$) of 1633. The Reynolds is defined as follows:

$$Re - \frac{d_e < v > \rho}{\mu}, \qquad (12)$$

with <v> the average velocity and d_e = 4wh/(w+h), the duct equivalent diameter depending on the height (h) and the width (w) of the cross section at the inlet of the channel. The width of the channel being 100 mm, this results in a value for d_e of 18.2 mm.

Results for the channel without obstruction

In this case, an exact (analytical) solution for the velocity field and the current density is available. Comparisons are shown for Reynolds numbers equal to 55,300 and 1200 resulting in an average velocity of 0.33, 1.80 and 7.2210-2 m/s (figures 9 to 11).

The approximated analytical (Levecque) and numerical solutions match very well for all values of Re. At low Re (55), the numerical values are significantly higher than the experimental one. This can be explained by the influence of natural convection, not taken into account in the model. At higher Re (300, 1200), the experimental and numerical data match very well.

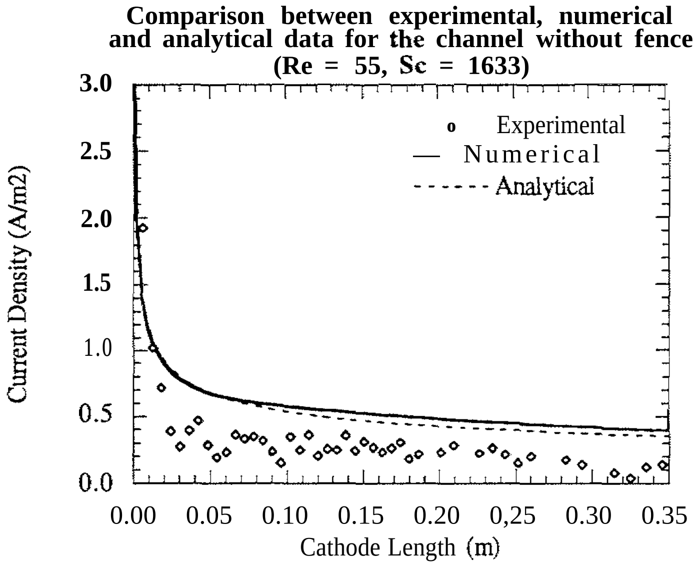


Figure 9.

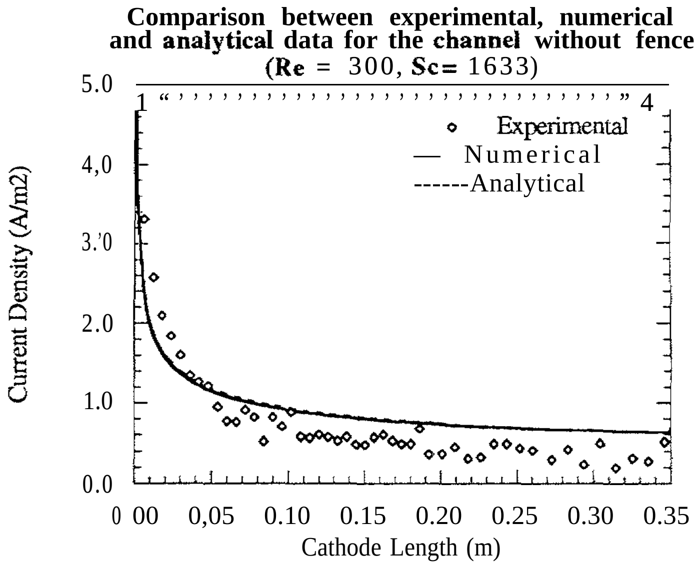


Figure 10-

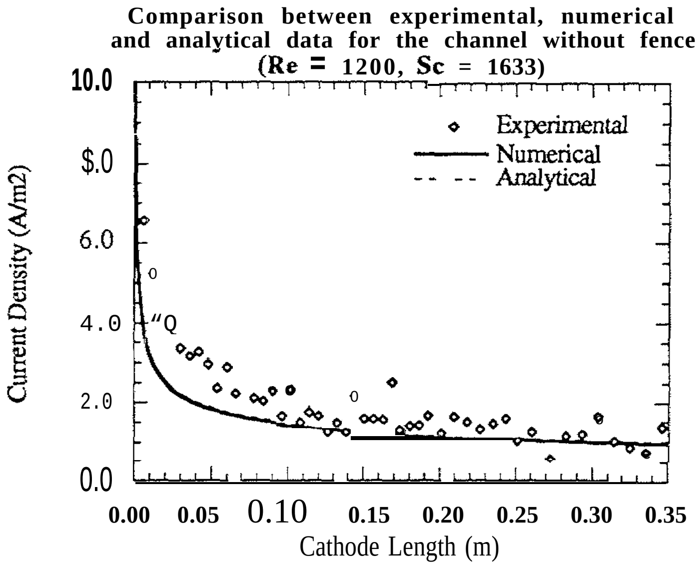


Figure 11.

Results for the channel with a 5 mm fence

The fence is placed at 0.1 m from the beginning of the electrode. Comparisons have been done for Reynolds numbers equal to 55, 180 and 300, with the velocity field computed by VKI. Flow pattern results at different velocities are presented below from figures 12 to 14.

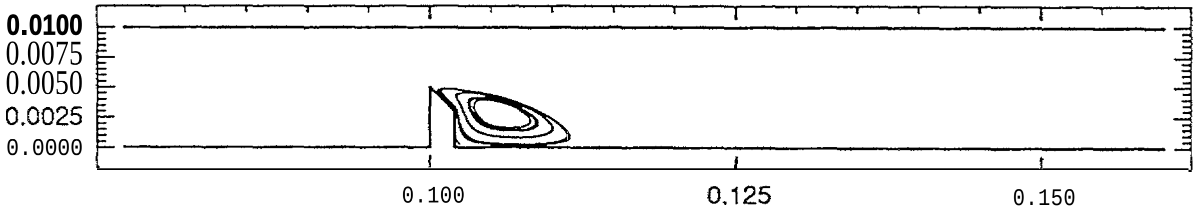


Figure 12. Flow pattern for parallel plate channel with 5 mm fence at Re = 55

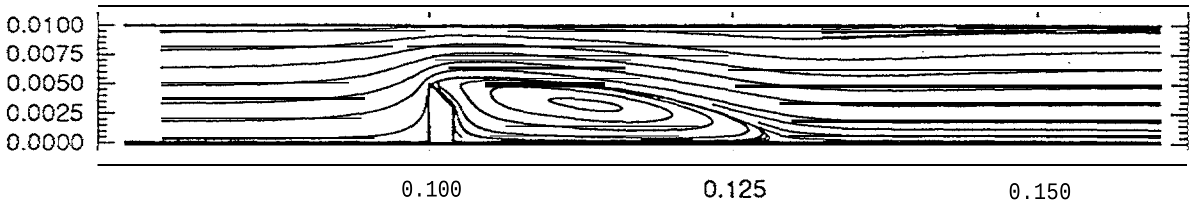


Figure 13. Flow pattern for parallel plate channel with 5 mm fence at Re = 180

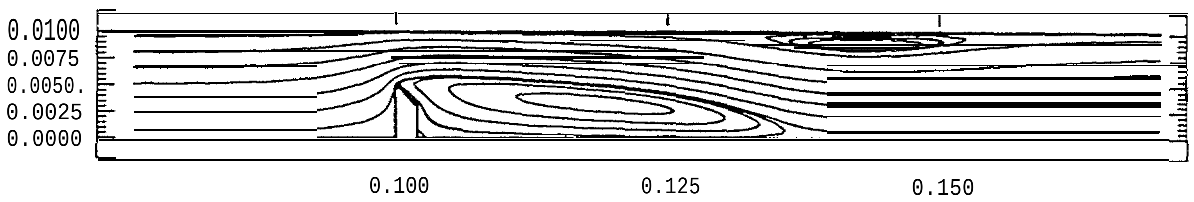


Figure 14. Flow pattern for parallel plate channel with 5 mm fence at Re = 300

Comparison between experimental and numerical data for this geometry is presented from figures 15 to 17. The analytical solution for the channel without fence gives an idea of the solution in the regions far away from the fence (inlet and outlet). For all values of Re one can remark that the numerical solution in those regions is as excellent as before.

The influence of the peak on the numerical data is clearly visible: the higher the value of Re, the higher the peak value and the peak position of the current density. One can observe that the peak position of the current density and the reattachment point downstream the fence on the lower wall fall together.

Comparison between numerical and experimental yields the same conclusions as in the channel without fence. At low Reynolds number (55), the numerical data are considerably higher than the experimental ones, probably due to the effect of natural convection.

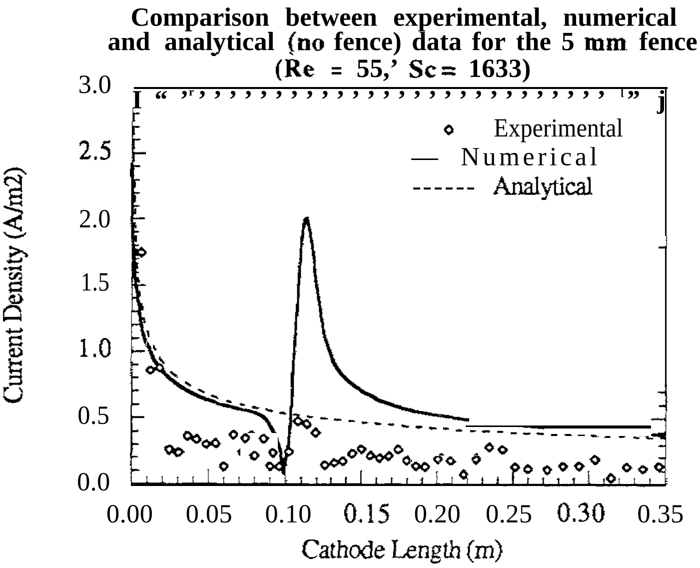


Figure 15.

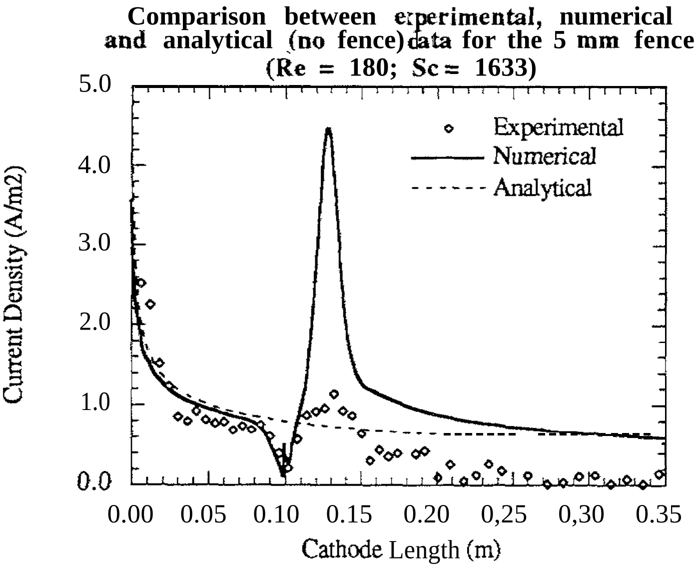


Figure 16.

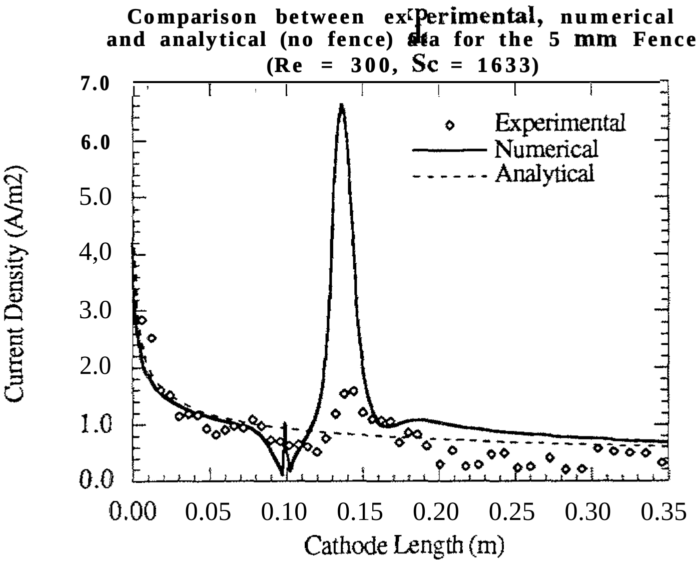


Figure 17.

At higher values of Re (180, 300), the numerical and experimental data at the inlet match well. The peak position of the current density for both data sets match very well, the current density at this position being about 4 times higher for the numerical solution.

Mass and charge transfer analysis in the copper system

LSGC provided experimental data for a wide range of applied cell voltages, electrolyte solutions and average velocity. Results for the channel without fence are presented here.

The physical properties of the electrolyte solutions and the electrode kinetics have been determined. The diffusivity of the cupric ion is 6.1 $10^{-10}\ m^2/s$, the current density at both electrodes is given by $J = J_a + J_c$, with:

$$J_a = +J_{oa}\left(\frac{c_{oa}}{c_b}\right)^{\gamma_a} \exp\left\{\frac{+\alpha_a zF}{RT}\left(V_a - U_a - E^{\infty}\right)\right\},$$
$$J_c = -J_{oc}\left(\frac{c_{oc}}{c_b}\right)^{\gamma_c} \exp\left\{\frac{-\alpha_c zF}{RT}\left(V_c - U_c - E^{\infty}\right)\right\}, \qquad (13)$$

and J_{oa} =5.6 A/m², $J_{oc} = 40.7 A/m^2$, et, =0.5, $\alpha_c = 0.21$, $\gamma_a = \gamma_c = 0.75$ and E^{∞} depending on the electrolyte solution.

Computations for solutions of 0.01 M $CuSO_4$ and 0.013 M $CuSO_4$ in 0.1 M H_2S 04 at Reynolds numbers of 230 and 1200 respectively have been done. These values correspond to average velocities of 1.3 and 6.510-2 m/s. Results are presented for two different values of the applied voltage (Re 230: figures 18-19 and Re 1200: figures 20-21), resulting in currents below and in limiting current conditions. For the latter one, also a comparison with the Levecque solution has been done. This is possible since a large amount of supporting electrolyte is present.

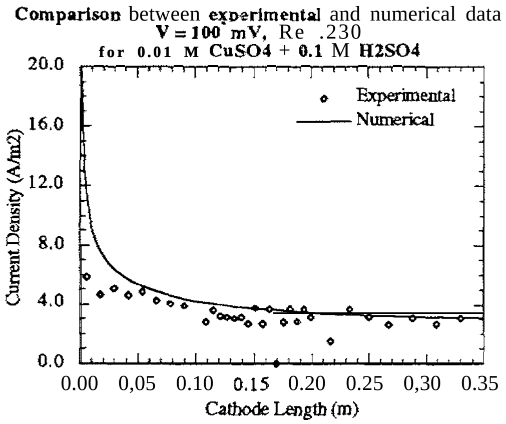


Figure 18.

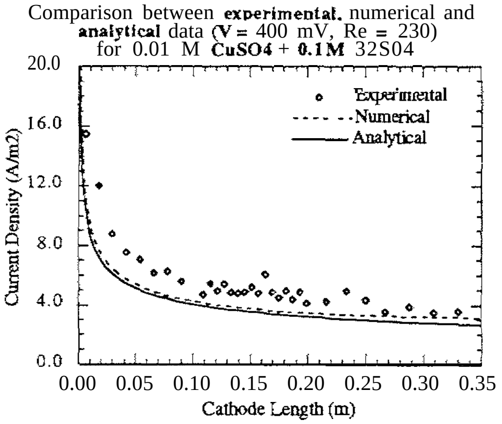


Figure 19.

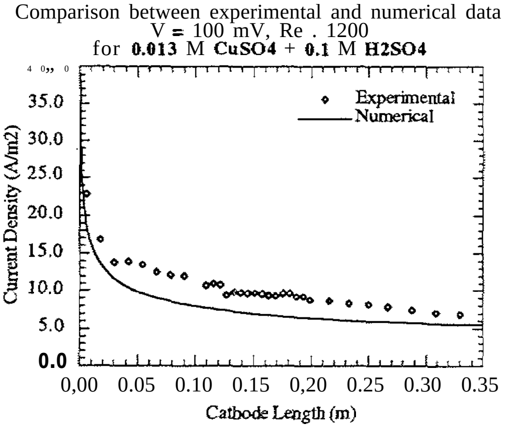


Figure 20.

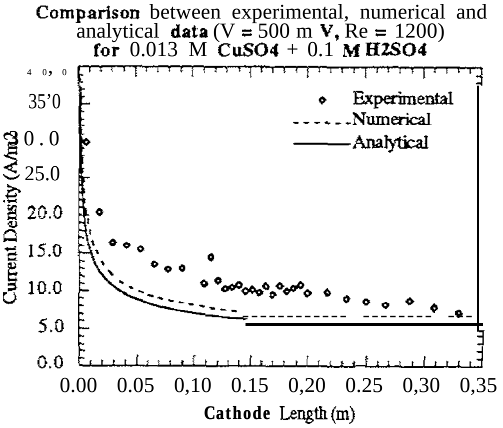


Figure 21.

Good results are obtained for both values of the Reynolds number and for currents below and in limiting conditions. For Reynolds equal to 1200, the experimental limiting current is about 38% higher than the numerical one, against only 17% for the lower Reynolds number. This is probably caused by a higher copper deposition (higher current density) at the micro electrodes, resulting in a larger surface of the electrodes and consequently in a current density that is overestimated.

Conclusions

Two totally new numerical methods have been developed enabling the solution of the “Dilute solution model” describing in a general way transport of mass and charge transport in diluted solutions. In that model a computed velocity field can be applied such that complex situations can be treated. In regions where no concentration variation is observed, the equations reduce to the so called potential model describing only charge transport in the solution.

Numerous test have been done to access the validity of the electrochemical and the fluid flow solvers. The amount of available experimental data being very large, not all of them have been compared with numerical calculations.

Comparison with analytical solutions (if available) showed very good to excellent results.

Experimental data performed in a channel without fence were simulated and gave very good results, especially at higher Reynolds numbers were the effect of natural convection, not taken into account in the model, is negligible.

Geometries with a complex hydrodynamic behaviour (parallel plate channel with fence) have been investigated. In this case the velocity had to be computed first. Again, the experimental and numerical current density matched well.

Data obtained with experiments done below and in limiting current conditions have been compared with the results from the numerical models and yield good results, especially at lower Reynolds numbers where the influence of copper deposition at the micro-electrodes is rather small.

Based on these results, the consortium applied for a new project in the framework of the Brite-Euram III programme. The proposal submitted received an Al ranking and was accepted for funding.

Referring to this conclusions it was felt that a further collaboration was needed such that the fundamental research could be continued. The aim is to elaborate and evaluate the dilute solution model in order to describe with more precision industrial electrode processes with the following features:

1. extension to three dimensions (3D),
2. application of much more ions (2D),
3. electrode processes with parallel reactions (2D),
4. homogeneous reactions in the solution (2D),
5. electrode growth (2D),
6. resistive electrodes (2D),
7. temperature effects (2D).

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