ELSEVIER

Chemical Engineering Journal 68 (1997) 69–72

Chemical Engineering Journal

Short communication

On the numerical solution of an electrolytic convective–diffusion problem in an externally imposed force field

Kwangsin Kim [1], Thomas Z. Fahidy *

Department of Chemical Engineering, University of Waterloo, Waterloo, Ont., N2L 3G1, Canada

Received 17 February 1997; accepted 18 June 1997

Abstract

A numerical solution based on a finite-difference approximation to the nonlinear equation of an electrolytic convective diffusion problem, using a staggered-grid structure for the velocity and concentration field, is described. The effect of externally imposed magnetic force fields is manifested by additional driving terms in the ionic flux and momentum equations. The computed overall current density/magnetic flux density relationship may be represented by a simple power regression, in agreement with experimental findings. © 1997 Published by Elsevier Science S.A.

Keywords: Convective-diffusion; Electrolysis; Magnetic field

1. Introduction

Pursuant to the seminal work of Levich [1], convective diffusion problems became an integral part of the theory of transport phenomena, and acquired particular prominence in the analysis of concentration boundary layers existing in electrolytic solutions during the passage of electric current. Convective diffusion is routinely treated in textbooks of electrochemical engineering e.g. [2–7]. A variety of analytical and numerical solutions is available also in the journal literature, treating primarily linear problems.

A challenging case is presented by electrolytic systems where an external force field is coupled with the imposed electric field. Magnetic/electric field interactions are one example of this class of problems [8–11], often requiring unconventional techniques for the solution of the governing nonlinear differential equations. The purpose of this paper is to summarise a recently developed approach [10] to a particular convective diffusion problem arising in magnetically assisted electrolysis (magneto-electrolysis).

2. Problem formulation

The system consists of a rectangular electrolytic cell with parallel-plate vertical electrodes (one anode and one cathode) in the (x,z) plane. A uniform magnetic field, imposed horizontally in the z-coordinate direction, and perpendicularly to the uniform electric field in the y-coordinate direction, generates a magnetohydrodynamic body force in the vertical x-coordinate direction. This force modifies free convective conditions in the boundary layer adjacent to the electrode, by interacting with the gravity field. With appropriate simplifications of the constitutive (vectorial) relationships discussed earlier [10,11], the convective diffusion problem is reduced to a set of partial differential equations consisting of (i) the continuity equation

$$u_x + v_y = 0 \tag{1}$$

(ii) the ionic flux equation

$$uc_x + vc_y = Dc_{yy} + nFDB(uc_y + cu_y)/RT \tag{2}$$

and(iii) the momentum equation

$$\nu u_{yy} + g\alpha(c - c_0)/\rho_0 + nFBDc_y/\rho_0 = 0 \tag{3}$$

with associated boundary conditions set: $x=0$: $u=v=0$; $c=c_0$; $y=0$: $u=v=0$; $c=0$; and $y\to\infty$: $u=v=0$; $c\to c_0$. In Eq. (3) the buoyancy term is shorthand for $g\Sigma_k\alpha_k(c_k - c_{k0})/\rho_0$, carrying ionic densification coefficients and ionic concentrations, in order to avoid confusion arising from grid subscripts during discretisation (Section 3.4). The subscripted variables in Eqs. (1)–(3) denote partial derivatives, with the exception of ρ_0.

* Corresponding author. Tel.: +1 519 885 1211, ext. 3310; fax: +1 519 746 4979; e-mail: tfahidy@cape.uwaterloo.ca

[1] Present address: Radiation Safety Group, Nuclear Energy Research Laboratory, Korea Electric Power Research Institute.

PII S1385-8947(97)00077-6

From the viewpoint of electrochemical engineering, the prime figure of merit of convective diffusion is the magnitude of the current density at the electrode:

$$J = |nFDc_y|_{y=0} \tag{4}$$

requiring the additional computation of the concentration gradient at the electrode surface.

3. The numerical solution scheme

3.1. Basic notions

Due to the magnetic field interaction terms in the ionic flux and the momentum relationships, Eqs. (1)–(3) do not possess an analytical solution. An attractive numerical solution method involves an iterative (Gauss-Seidel type) computation scheme for the (u,v) velocity field and the electrolyte concentration c. Typically, one velocity component is iterated until convergence is reached, then the other velocity component is iterated using the converged value of the first one. The procedure is repeated for the electrolyte concentration. The next set of iterations starts with the converged values of variables from the previous iteration set and the procedure is repeated until changes in values of all variables fall within a preset error-tolerance range.

3.2. The steady-state approach

A conventional path is to discretise Eqs. (1)–(3) by appropriate finite-difference approximations to derivatives, and to solve the discretised equations by a Gauss-Seidel iteration scheme [12], using simultaneous overrelaxation [13–15]. A systematic search for stable and efficient algorithms indicates that the momentum equation solved for velocity component u has an acceptable rate of convergence with any positive overrelaxation parameter, although parameters larger than unity are, in principle, preferable for fast convergence. The particular numerical value of the overrelaxation parameter is, however, of little importance here, since the ionic flux equation cannot be solved in this manner, even if it is transformed into a unidimensional initial-value diffusion equation, by letting u be the equivalent of time, and treated by a backward time-difference algorithm (which normally guarantees convergence). The relative (and a priori unknown) distance of the initial guess set for u, v and c from their true values also determines if divergence occurs. In summary, a conventional steady-state approach is ineffective for the solution of the equation set. The time-transient methods shown in Section 3.4 combined with a staggered-grid structure leads, however, to a successful solution.

3.3. The staggered-grid structure

The usefulness of the staggered-grid principle has been shown e.g. [16,17] in dealing with the numerical solution of equations prone to instability. If the faces of a control area are located in the middle of two adjacent nodes, then at any arbitrary value of y the continuity equation over the control area is integrated to $u_{i+1/2} - u_{i-1/2} = 0$, since $u_x = 0$. By applying a piecewise-linear profile to u at the midway locations, i.e. by setting

$$(u_{i+1} + u_i)/2 - (u_i + u_{i-1})/2 = 0 \tag{5}$$

the discretised form

$$u_{i+1} - u_{i-1} = 0 \tag{6}$$

is obtained. The condition of equality of velocities at alternate nodes instead of adjacent ones implies the use of a coarser grid, hence a somewhat diminished accuracy. More seriously, Eq. (6) can easily be satisfied by unrealistic (e.g. 'zigzag') velocity fields leading to physically absurd results. However, the staggered-grid principle can successfully be applied if the velocity nodes are placed on the faces of the control area, while nodes for the other variables are kept at the centre of the control area. The additional programming required (e.g. with certain interpolations between the two grid position sets) is a small price to pay for the gain of the stability.

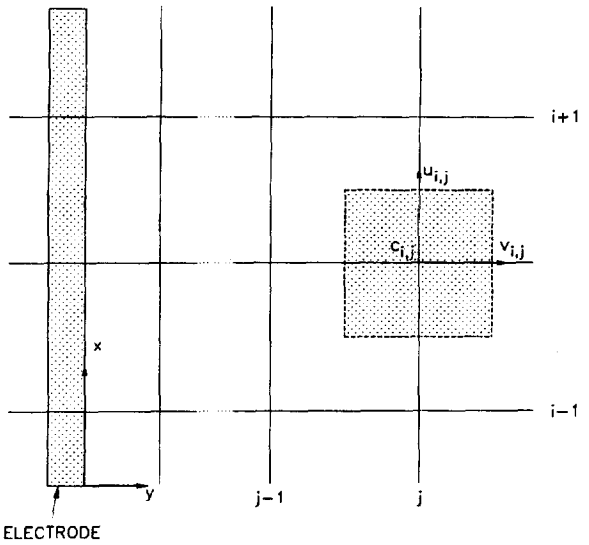

Fig. 1. The staggered-grid structure employed in the numerical solution.

The approach is illustrated in Fig. 1. The u-grid is shifted upward by a half-grid size such that the $u_{i,j}$ positions are on the top face of the i,j-control area. The v-grid is shifted to the right by a half-grid size such that the $v_{i,j}$ positions are located on the right face of the i,j-control area. The concentration grid remains unchanged, i.e. its nodes are located at the centre of the control area. The electrode surface is aligned with the v-grid to set the nodes associated with surface velocity onto the electrode surface facing the electrolyte. The final discretised form of the continuity equation:

$$(u_{i,j} - u_{i-1,j})/\Delta x + (v_{i,j} - v_{i,j-1})/\Delta y = 0 \tag{7}$$

is stable and wavy velocity field solutions, which can appear without a staggered-grid configuration, are avoided.

3.4. Numerical solution via the time-transient method

The effect of the initial guess set on convergence is eliminated by the adoption of the time-transient method [18] with certain refinements. A second and equally important property of this approach is that the initial values of all variables and parameters are physically known at zero time, hence no 'guesstimation' is necessary. The transient portion of the solution provides the unsteady-state behaviour of the system, allowing an analysis of convection dynamics. This information is additional to the steady-state solution, which is, nevertheless, the primary goal of the numerical solution.

The procedure is further simplified if density changes are ignored, except in the buoyancy force appearing in the momentum equation. The discretised form may be written as

$$U_{i,j}=u_{i,j}+\Delta t\{\nu[(u_{i,j+1}-2u_{i,j}+u_{i,j-1})/(\Delta y)^2] - \alpha(c_{i,j}-c_0)g+(zFDB/\rho_0)(c_{i,j+1}-c_{i,j})/\Delta y\} \quad (8)$$

where $U_{i,j}$ denotes the computed value of $u_{i,j}$ at the end of a time step. The discretised form of the ionic flux equation becomes

$$C_{i,j}=c_{i,j}+\Delta t\{D[(c_{i,j+1}-2c_{i,j}+c_{i,j-1})/(\Delta y)^2] - u_{i,j}(c_{i+1,j}-c_{i-1,j})/2\Delta x-v_{i,j}(c_{i,j+1}-c_{i,j-1})/2\Delta y + (zFBD/RT)[c_{i,j}(u_{i,j+1}+u_{i-1,j+1} - u_{i,j-1}-u_{i-1,j-1})/4\Delta y + u_{i,j}(c_{i,j+1}-c_{i,j-1})/2\Delta y]\} \quad (9)$$

where $C_{i,j}$ denotes the computed value of $c_{i,j}$ at the end of each time step. This is a complicated equation due to the necessity of interpolation to compensate for the staggered grid.

The solution of Eqs. (7)–(9) is obtained as follows. First, Eq. (8) is solved for u and the obtained values are employed in solving Eq. (9) for c. Solving Eq. (7) for v, in terms of the u and c values just obtained, completes a time step. The procedure is repeated for each time step until steady state is reached. Finally, the current density is calculated from the discretised form of Eq. (4):

$$J=|nFD(c_{i,0}-c_{i,1})/\Delta y| \quad (10)$$

Steady state is assumed to have been reached if the computed current density change between adjacent time steps is within a preset error limit.

3.5. Numerical aspects

The stability of the numerical solution depends strongly on the grid size. In principle, Δx and Δy should be large and Δt should be small, but for sufficient accuracy, the grid state should also be small. A good compromise between speed, stability and accuracy was found by using a 100×100 grid for the space coordinates, and a time step of 0.001 s. Steady state was assumed when the current density between two adjacent time steps changed less than 1 $\mu A\ cm^{-2}$ (the measured current density range is 200–2300 $\mu A\ cm^{-2}$). Depending on the relative strength of free convection (i.e. on the magnitude of the densification coefficients) the time-transient profiles reached steady state at about 200 simulated seconds (strong convection; acidic cupric sulphate electrolyte), or about 600 simulated seconds (weak convection; alkaline ferri/ferro-cyanide electrolyte).

An important result of the numerical solution is that it provides proof for the soundness of the power relationships between current density and magnetic flux density

$$J=J_0+aB^m \quad (11)$$

possessing r^2 values close to unity. Regression analysis of experimental current density data [10,11] corroborates the form of Eq. (11), where the numerical values of a and m depend on the nature and the composition of the electrolyte. Thus, the simplified model offers a reasonable approximation to the real-life behaviour of a certain class of magnetically assisted convective diffusion systems.

4. Final remarks

The numerical solution scheme presented in this paper may readily be adapted to convective diffusion problems arising from the imposition of arbitrary force fields. In the instance of space- and/or time-dependent physical parameters, the algorithmic structure would be more complex on account of additional terms in the constitutive equations, hence a more sophisticated staggered-grid configuration may be necessary. The time-transient approach would be advantageous for both steady-state and unsteady-state solutions inasmuch as the same numerical scheme could be utilised without major modifications.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors are grateful to Professors G.D. Raithby and R.B. Simpson of the University of Waterloo for their valuable suggestions.

Appendix A. Nomenclature

a	regression parameter (Eq. (11))
B	magnetic flux density (T)
C	value of c at the end of a time step (mol m^{-3})

c electrolyte concentration; c_0 its value in the electrolyte bulk (mol m^{-3})
D electrolyte diffusivity (m^2 s^{-1})
F Faraday's constant (96 487 C mol^{-1})
g acceleration due to gravity (981 cm s^{-2})
J current density; J_0 its value in the absence of a magnetic field (A m^{-2})
m regression parameter (Eq. (11))
n valency
R universal gas constant (8.3144 J K^{-1} mol^{-1})
r^2 coefficient of determination (regression analysis)
T temperature (°C)
t time (s)
u velocity component along the x-coordinate (m s^{-1})
v velocity component along the y-coordinate (m s^{-1})
x coordinate along the vertical electrode height (m)
y coordinate normal to the vertical electrode (m)
α densification coefficient (kg mol^{-1})
Δ increment
ν kinematic viscosity (m^2 s^{-1})
ρ density; ρ_0 its value in the electrolyte bulk (kg m^{-3})

Subscripts

i node position in the x-direction
j node position in the y-direction
k ionic species
x partial derivative with respect to the x-coordinate
y partial derivative with respect to the y-coordinate
z coordinate along the horizontal electrode width

References

[1] V.G. Levich, Physicochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, 1962, pp. 39–184.
[2] J.S. Newman, Electrochemical Systems, Prentice Hall, Englewood Cliffs, 1973, Part C, pp. 215–253; 1991, Part D, pp. 297–377.
[3] F. Coeuret, A. Storck, Elements de Génie Electrochimique, Lavoisier, 1984, ch. 3, pp. 91–128.
[4] I. Roušar, K. Micka, A. Kimla, Electrochemical Engineering, Elsevier, Amsterdam, 1986, vol. I, part C, pp. 227–344; vol. II, part D, pp. 13–103.
[5] K. Scott, Electrochemical Reaction Engineering, Academic Press, London, 1991, section 7.4.1.1, pp. 428–432.
[6] G. Prentice, Electrochemical Engineering Principles, Prentice Hall, Englewood Cliffs, NJ, 1991, ch. 6, pp. 151–176.
[7] T.Z. Fahidy, Principles of Electrochemical Reactor Analysis, Elsevier, Amsterdam, 1985, ch. 7, pp. 165–189.
[8] T.Z. Fahidy, J. Appl. Electrochem. 13 (1983) 553.
[9] R.A. Tacken, L.J.J. Janssen, J. Appl. Electrochem. 25 (1995) 1.
[10] K. Kim, A study of magnetoelectrolysis coupled with natural convection, Ph.D. Thesis, University of Waterloo, Waterloo, 1994.
[11] K. Kim, T.Z. Fahidy, J. Electrochem. Soc. 142 (1995) 4196.
[12] W.H. Press, B.F. Flanney, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes, Cambridge University Press, New York, 1987, pp. 652–659.
[13] E.A. Volkov, Numerical Methods, Hemisphere, New York, 1990, section 21, pp. 150–155.
[14] R.S. Varga, Matrix Iterative Analysis, Prentice Hall, Englewood Cliffs, 1962, ch. 3, pp. 56–61.
[15] J.S. Vandergraft, Introduction to Numerical Computations, Academic Press, New York, 1978, section 68, pp. 216–229.
[16] S.V. Patankar, Numerical Heat Transfer and Fluid Flow, Hemisphere, New York, 1980, pp. 118–120.
[17] Wei Shyy, Computational Modeling for Fluid Flow and Interfacial Transport, Transport Processes in Engineering 5, Elsevier, New York, 1994, ch. V, section 4.1, pp. 133–136.
[18] B. Carnahan, H.A. Luther, J.O. Wilkes, Applied Numerical Methods, Wiley, New York, 1969, ch. 7, pp. 429–530.