

# **PROGRAM BOOKLET**

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# ROOM E.0.12 - Friday May 29th, 2009

# Fluid Mechanics 4 (Chair : C. Lacor, VUB)

10.40 - 11.00	High Order Upwind Residual Distribution Schemes on Isoparametric Curved Elements M. Vymazal - N. Villedieu - T. Quintino - H. Deconinck, VKI			
11.00 - 11.20	Highly Transient Mixed Flows with Air/Water Interactions: Homogeneous Equilibrium Model and Friction Correlations F. Kerger - P. Archambeau - S. Erpicum - B.J. Dewals - M. Pirotton, ULg			
11.20 - 11.40	A new library of multigrid solvers for large-scale CFD calculations M. Rasquin - G. Degrez - H. Deconinck, ULB and VKI			
11.40 - 12.00	Effective modelling of mass transfer in electrochemical reactors using a hybrid spectral/finite-elements method M. Krivilyov - M. Rasquin - R. Laguerre - G. Degrez - J. Fransaer, KULeuven and ULB			
12.00 - 12.20	Hydrogen micromix combustion - Introductory study - Cold flow E. Recker - W. Bosschaerts,RMA			

# ROOM E.O.11 - Friday May 29th, 2009

# Structural Mechanics 4 (Chair : S. Cescotto, ULg)

10.40 - 11.00	Lateral-torsional and lateral-distortional buckling of I-section members with web openings D. Sonck - J. Belis - G. Lagae - W. Vanlaere - R. Van Impe, UGent
11.00 - 11.20	An adapted dynamic programming algorithm for the identification of moving forces EM. Lourens - G. Lombaert - G. Degrande - G. De Roeck, KULeuven
11.20 - 11.40	The buckling behaviour of steel cylinders with engaged columns W. Vanlaere - D. Sonck - D. Callewaert - R. Van Impe - G. Lagae, UGent
11.40 - 12.00	Global size and shape optimization of trusses S. Arnout - G. Lombaert - G. De Roeck, KULeuven
12.00 - 12.20	Rate Dependent Moment-Curvature Relations for the Progressive Collapse Analysis of RC Structures B. Santafé - T.J. Massart - Ph. Bouillard - J. Vantomme, RMA and ULB
12.20 - 12.40	Nested inverse method for mechanical material parameter identification using DIC and FE computed deformation fields B. Belkassem - S. Bossuyt - H. Sol, VUB

# Modeling of mass transfer in (electro)chemical reactors using a hybrid spectral/finite-elements method

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Abstract: A numerical tool for the analysis of the mass transfer in the purely turbulent regime in (electro)chemical reactors of the Taylor-Couette type is suggested. Comparison of the preliminary results of modeling with the empirical formula of Eisenberg shows a good agreement.

Keywords: combined FEM/spectral methods, electrochemistry

#### I.INTRODUCTION

Turbulent flow is a phenomenon which is encountered in many chemical and electrochemical processes that usually include conjugate transfer of heat, mass and electric charge. For example, forced flow is used to enhance the deposition rate during electrolytic deposition on surfaces. However, as the fluid flow influences the concentration of ions and hence the local current density on the electrode the quality of a deposited layer strongly depends on the proper control of the flow conditions. Therefore, study of flow in electrochemical reactors is of practical importance and numerical simulation is one of the promising tools. Experimental studies of transport phenomena in electrochemical processes were performed by different authors [1,2,3] but only a few studies are devoted to 3D numerical modeling. A comprehensive study was performed in [4] where LES modeling was used for the description of the fluid flow in a reactor with a planar geometry. Experiments using the Taylor-Couette reactor (Fig.1) with a rotating cylindrical electrode (RCE) are also common in electrochemistry and this geometry is used in our research.

Due to curvature and centrifugal acceleration, instabilities develop, producing annular vortices called Taylor vortices, which eventually lead to fully turbulent flow with increasing of the Reynolds number. Based on the three dimensionless parameters identified by Chandrasekhar [5], multiple flow structures have been reported for this geometry. The first parameter is the ratio of the inner to outer cylinder diameters denoted by  $\eta = r_i/r_o$ . The second one corresponds to the Reynolds number based on the gap between the two cylinders:  $\operatorname{Re} = \omega r_i (r_o - r_i)/\nu$ , where v is the kinematic viscosity. The reactor's height  $h/(r_o - r_i)$  scaled by the gap width  $s = r_o - r_i$ corresponds to the last parameter. In the present analysis, the inner cylinder rotates while the outer one is at rest. Our objective was to develop a numerical tool for the analysis of the mass transfer in the purely turbulent regime in reasonable computational time. Such a tool can assist or even replace experimental studies where data on mass transfer are difficult to extract with classical electrochemical methods. This work is an extension of our previous work [6] where only the fluid flow was studied.



Fig. 1. Sketch of the reactor with Taylor-Couette geometry.

#### II.MODEL

Mass transfer in an electrochemical reactor with Taylor-Couette geometry is modeled using a hybrid spectral/finiteelement method [7-10]. This method assumes periodicity in one direction so the spectral approach is used for discretization of governing equations in the azimuthal direction. In the transverse direction discretization is performed by means of finite elements allowing complex axisymmetric geometries. No subgrid model was applied so the modeling was a pure DNS type. The governing equations are (i) incompressible Navier-Stokes for the velocity and pressure fields and, (ii) convection-diffusion equations for the concentration fields. We advance the governing equations in time in a 2<sup>nd</sup> order accurate manner, by setting the following continuity, momentum and scalar variable residuals  $R_C^{n+1}$ ,  $\mathbf{R}_M^{n+1}$  and  $R_{\phi_i}^{n+1}$  correspondingly to zero at each new time

 $\mathbf{K}_{M}^{n,i}$  and  $K_{\phi_{i}}^{n,i}$  correspondingly to zero at each new time step n+1:

$$R_{\rm C}^{n+1} = \nabla \cdot (\mathbf{u}^{n+1}) = 0, \qquad (1)$$
  
$$R_{\rm M}^{n+1} = \frac{(\mathbf{u}^{n+1} - \mathbf{u}^n)}{\Delta t} + \nabla p^{n+1/2} - \frac{1}{2 \operatorname{Re}} \nabla^2 (\mathbf{u}^{n+1} + \mathbf{u}^n)$$

$$+\left(\frac{3}{2}\right)\left(\frac{1}{2}\right)\left(\left(\mathbf{u}^{n}\cdot\nabla\right)\mathbf{u}^{n}+\nabla\cdot\left(\mathbf{u}^{n}\otimes\mathbf{u}^{n}\right)\right)\right)$$
(2)

$$-\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left\{\left(\mathbf{u}^{n-1}\cdot\nabla\right)\mathbf{u}^{n-1}+\nabla\cdot\left(\mathbf{u}^{n-1}\otimes\mathbf{u}^{n-1}\right)\right\}=0,$$

$$\mathcal{R}_{\phi_i}^{n+1} = \left(\frac{\phi_i^{n+1} - \phi_i^n}{2}\right) / \Delta t - \frac{1}{2\operatorname{Pe}} \nabla^2 \left(\phi_i^{n+1} + \phi_i^n\right) + \left(\frac{3}{2}\right) \nabla \cdot \left(\mathbf{u}^n \phi_i^n\right) - \left(\frac{1}{2}\right) \nabla \cdot \left(\mathbf{u}^{n-1} \phi_i^{n-1}\right) = 0.$$
(3)

where **u** is the flow velocity, *p* is the pressure,  $\Delta t$  is the time interval of iteration and Pe is the Péclet number  $Pe = \omega r_i (r_o - r_i)/D_i$ ,  $\phi_i$  and  $D_i$  are the concentration and the diffusion coefficient of the *i*-th chemical component. Herein, the pressure, viscous and diffusion terms are treated in an implicit manner using the Crank-Nicolson scheme, whereas the convective terms are treated explicitly using the Adams-Bashforth method. The convective terms in Eq. (2) and (3) are written in the sqew-symmetric and divergence forms correspondingly [10].

The azimuthal direction is periodic for the considered geometry. It is natural then to represent any flow unknown q (where q represents either the pressure p, or any component of the velocity vector  $\mathbf{u}$ , or the scalar variable  $\varphi_i$ ) by means of a truncated Fourier series in this direction. In cross planes formed by the two remaining directions, we introduce a finite element representation on a structured triangular mesh (i.e. P1 elements). This mesh was generated from quadrilateral finite elements oriented along the radial, tangential and vertical isolines by splitting each quadrilateral element in two triangular one. Since we have a natural period of  $2\pi$  in the azimuthal direction, such hybrid spectral/FE approach approximates variables using the following discretization method written in the cylindrical coordinate system  $(r, \theta, z)$ :

$$q^{n}(r,\theta,z) = \frac{1}{N_{\theta}} \sum_{k=-N_{\theta}/2+1}^{N_{\theta}/2} \sum_{j=1}^{N_{nod}} Q_{k,j}^{n} N_{j}(r,z) e^{ik\theta}, \qquad (4)$$

where  $i = \sqrt{-1}$ ,  $N_0$  is the number of modes in the expansion,  $Q_{k,j}^n$  are the Fourier coefficients associated with the *j*-th element at the *n*-th time step. Herein, to ensure the real-valuedness of the solution, the Fourier coefficients must obey the symmetry relation  $Q_k = Q_{-k}^*$ .

#### **III.NUMERICAL IMPLEMENTATION**

It can be shown that the above approach allows decoupling the 3D non-linear problem (see Eqs. (1)-(3)) into a series of decoupled 2D non-linear problems, one for each Fourier mode. Coupling still occurs through the (nonlinear) convective terms, which are however treated explicitly and therefore do not complicate the (costly) linear solution phase. For the complete detail of the discretization procedure, the reader is referred to [8-10]. The discretized equations can be easily computed directly in terms of the Fourier components, except for the convective terms, which couple each Fourier mode to all others. The convective terms are therefore computed in physical space and then transformed to Fourier space using the Fast Fourier Transform (FFT) algorithm. The basic idea behind this pseudo-spectral solution procedure is as follows:

- evaluate the convective terms in physical space, using the previously calculated u<sup>n</sup> and u<sup>n-1</sup>;
- transform these terms to Fourier space using the FFT algorithm;
- set up the linear problems corresponding to each Fourier mode;
- apply appropriate boundary conditions for each Fourier mode;
- 5. solve the linear systems to obtain the updated solution unknowns  $Q_{k,j}^{n+1}$  in Fourier space;
- 6. apply the inverse Fourier transform to obtain the updated unknowns  $q^{n+1}$  in physical space.

This algorithm has been implemented for use on distributed memory parallel computers. The finite element mesh is divided into a number of partitions, which are stored on different processors. Before each linear solve, data belonging to each Fourier mode is gathered on a separate processor, such that all 2D linear solves can be performed simultaneously, but in a sequential manner (one linear solve per processor).

In our study, the concentration field is treated as a passive scalar and described by a convection-diffusion equation Eq. (3) which first requires computation of the velocity field from the hydrodynamic part given by Eqs. (1)-(2). It assumes that the concentration fields depend on the flow field but the flow field is not influenced by the concentration fields. Both convection-diffusion and hydrodynamic equations are solved at different instances of the code and they are coupled via dynamic data exchange at every time step using the MPI technique. This structure of the code yields an optimal distribution of load according to available computational resources. In other words, Navier-Stokes and passive scalar equations can be solved on the same or different processors.

#### **IV.RESULTS**

The model Eqs. (1)-(3) have been used for the simulation of fluid flow and mass transfer at different regimes. First, a hypothetical electrochemical solution with an unphysical diffusion coefficient of  $D=10^{-3}$  m<sup>2</sup>/s was simulated at a Reynolds number of Re=80 and a Schmidt number of Sc= $\nu/D$ =0.001 ( $\nu$  is the kinematic viscosity), Fig. 2. Since the Schmidt number is small, this test corresponds to problems where mass transfer is controlled by diffusion, i.e. Pe<<1 (Pe=Re Sc). As can be seen from Fig. 2, the numerical solution coincides with the analytical solution [3]:

$$C = \frac{C_{\eta} \ln(r_{o}/r) + C_{r_{o}} \ln(r/r_{i})}{\ln(r_{o}/r_{i})}.$$
 (5)



Fig. 2. Comparison between the analytical Eq. (5) and numerical solutions at Re=80 and Sc=0.001 given by the dimensionless concentration  $C/C_0$  as a function of dimensionless radial position  $(r-r_t)/s$ , where  $C_0$  is the nominal concentration.

The main study was performed for the ferri-ferrocyanide solution containing the supporting electrolyte 100 mM NaOH with a pH of approximately of 13. The properties of this solution are: the diffusion coefficient is  $D=5.6\times10^{-10}$  m<sup>2</sup>/s, a valency number n=1, a nominal concentration  $C_0=10$  mM, a kinematic viscosity  $v=10^{-6}$  m<sup>2</sup>/s (yielding a large Schmidt number Sc=1785). The following electrochemical reaction is considered at RCE which is the inner (rotating) cylinder:

$$\operatorname{Fe}(\operatorname{CN})_{6}^{3-} + e^{-} \to \operatorname{Fe}(\operatorname{CN})_{6}^{4-}.$$
 (6)

The estimated thickness  $\delta_c$  of the concentration boundary layer is given as a function of the Reynolds number in Table 1. This parameter varies between 166 and 20 µm as the rotation rate goes from 50 to 1000 rpm so a fine mesh is needed for adequate resolution of the concentration layer near the electrode. The adaptive mesh was used to resolve this issue with the stretch factor of 1.05 in the direction perpendicular to the electrode surface. As a result, the radial length of the finite element near the electrode was 2 µm which provides sufficient accuracy in all calculations, Fig. 3. The concentration boundary layer is located completely inside the hydrodynamic boundary layer and the mesh captures variations of both the hydrodynamic and concentration variables.

An analytical solution for the diffusion-convection problem at Re>1 does not exist. Our simulations yield good agreement with the empirical relationship of Eisenberg [11] which gives the limiting current density j as a function of the rotation speed:

$$j = 0.0791 \, n \, \mathrm{F} \, C_0 \, U_{rot} \left(\frac{2r_l U_{rot}}{\nu}\right)^{-0.3} \left(\frac{\nu}{D}\right)^{-0.644}, \quad (7)$$

where F is Faraday's constant,  $U_{rot}$  is the tangential velocity at the rotating electrode. Equation (7) is valid in a wide interval of Reynolds numbers.

#### TABLE I

Estimated thickness  $\delta_C$  of the diffusion layer near the rotating electrode as a function of the rotation speed  $\omega$  and the Reynolds number Re. The radial length  $\delta_r$  of the smallest FE element is given for comparison. The calculations are performed for a 10 mM ferri-ferrocyanide solution containing 100 mM of NaOH.

<i>w</i> , rpm	Re	$\delta_{C}, \mu m$	$\delta_r$ , $\mu$ m
50	910	166	
100	1820	102	
200	3640	63	2
500	9100	33	
1000	18200	20	



Fig. 3. The dimensionless concentration  $C/C_0$  and dimensionless tangential velocity  $U_{\theta}/U_{rol}$  ( $U_{rol}$  is the tangential velocity at the rotating electrode) as a function of distance from the rotating electrode. Data are extracted from the solution averaged in time at Re=9100. The radial positions of the mesh nodes are depicted as vertical lines.



Fig. 4. Comparison of the numerical data with the empirical Eisenberg's relation Eq. (7) at the Reynolds numbers Re<10000. The dimensions of the reactor are: r<sub>i</sub>=6 mm, r<sub>o</sub>=35 mm, h=50 mm. The properties of the solution are: 10 mM ferri-ferrocyanide solution containing 100 mM NaOH as

mM ferri-ferrocyanide solution containing 100 mM NaOH as supporting electrolyte,  $D=5.6\times10^{-10}$  m<sup>2</sup>/s, n=1,

$$v = 10^{-6} \text{ m}^2/\text{s}.$$

In our simulations the limiting current density was calculated as

$$j = -n \operatorname{F} D \nabla C , \qquad (8)$$

where  $\nabla C$  is the gradient of concentration averaged in time near the surface of the electrode. The numerical solution has a better agreement with Eisenberg et al. at small rotation speeds, Fig. 4. At high rotation speeds, the difference between solutions is about 10%. These simulations have been performed in the axisymmetrical mode. Further calculations in full 3D should evidence if the disagreement comes from inaccuracy of the mathematical model or discretization scheme. The discretization scheme contains a specific relaxation parameter which allows increasing the time step at the expense of accuracy. Since characteristic time and space scales of the mass transfer by diffusion are few order of magnitude smaller than the scales of convection at Sc>>1, we used a high value of the relaxation parameter to study mass transfer at a long time. Decreasing of this parameter and the time step may be a possible solution to improve agreement with the relation of Eisenberg.

#### V.CONCLUSIONS

- 1. The presented results are the first step towards the full-scale simulations of turbulent mass transfer in a rotating cylinder geometry. The method is capable of modeling turbulent mass transfer in the bulk of the reactor what affects the local concentration and current distributions in the vicinity of the electrode.
- 2. DNS results showed a good agreement with both analytical [3] and experimental results [11,12]. The presented technique is especially useful for modeling of systems for which the Schmidt number Sc~1 where analytical and empirical models are not available.

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