Simulations of Turbulent Flow, Mass Transport, and Tertiary Current Distribution on the Cathode of a Rotating Cylinder Electrode Reactor in Continuous Operation Mode during Silver Deposition

Mario Rosales and José L. Nava*

Department of Geometric and Hydraulic Engineering, University of Guanajuato, Guanajuato, Guanajuato 36000, Mexico

This work presents numerical simulations of turbulent flow, mass transport and tertiary current distribution on the cathode of a rotating cylinder electrode reactor (RCE) in a continuous operation mode. A configuration of a RCE with electrolyte inlet at the bottom and the electrolyte exit at the top was employed. Silver electrodeposition (12.15 mol m\(^{-3}\) (1300 ppm) Ag(I), 883.5 mol m\(^{-3}\) (23000 ppm) CN\(^-\), pH 13 and 150 mS cm\(^{-1}\) conductivity) was used as a test system. Bulk electrolysis in the RCE was performed at a constant potential of \(-1.2 \text{ V} \) vs. SCE, which ensured complete mass transport control. A constant volumetric inflow rate of 0.1 L min\(^{-1}\) at the RCE inlet was employed. CFD simulations were obtained solving the RANS equations with the standard k–\(\varepsilon\) turbulence model. For mass transport simulations, the averaged diffusion-convection equation was solved. For the simulations of tertiary current distribution, wall functions were employed. The tertiary current distribution on the RCE interface along the z-coordinate presented one border effect close to the electrolyte inlet, afterwards, even current distribution was obtained. The border effect is created by the abruptly silver concentration depletion at the electrolyte inlet. Good agreement between mass transport correlation and current distribution simulations with experimental data were attained.

The rotating cylinder electrode electrochemical reactor (RCE) is a geometry widely used in the following studies: metal ion recovery,\(^1\)–\(^6\) alloy formation,\(^2\)–\(^4\) corrosion,\(^6\)–\(^8\) effluent treatment,\(^9\)–\(^13\) and Hull cell studies.\(^14\) The RCE is employed for metal ion removal because this cell allows metal removal from 10,000 to 10 ppm,\(^15\) i.e. this reactor has been used to recover cadmium,\(^9\)–\(^10\) copper,\(^11\)–\(^13\) nickel,\(^17\) silver,\(^18\) tin,\(^19\) and zinc.\(^20\) The RCE generates turbulent convection at \(Re > 100\), where peripheral velocity, \(u\), normally lies in the range 0.6–20 m s\(^{-1}\). In previous studies carried out by our group the influence of using four-plate, six-plate, and a concentric cylinder as counter electrode on the turbulent flow in batch\(^16\) and continuous\(^2\)–\(^2\) operation mode have been deeply discussed. In the former paper, the formation of three turbulent Taylor vortex flow for the four-plate and six-plate arrangements was developed, however, these vortexes did not appear in the concentric arrangement. The presence of the Taylor vortex flow was attributed to the turbulence promoted by the plates. Whereas in continuous mode, for the six plate arrangement, only one turbulent Taylor vortex appeared, owing to the electrolyte inflow and outflow modifying the flow pattern in the RCE.

On the other hand, the turbulent mass transport is imposed by the angular rate of the inner cylinder and the applied limiting current density.\(^2\)–\(^2\)–\(^2\)–\(^2\) When the flow pattern is developed entirely in the RCE, the parameters of mass transport can be determined by a dimensionless group correlation of the form:\(^2\)–\(^2\)

\[ Sh = a R e ^ b S c ^ {0.56} \]  

where the Sherwood number \(Sh = k_s d / D\) describes mass transport by forced convection, the Reynolds number \(Re = ud / \nu\) is an indicator of the fluid flow regime, and the Schmidt number \(Sc = \nu / D\) relates the electrolyte transport properties. Here, \(k_s\) is the mass transfer coefficient in cm s\(^{-1}\), \(d\) is the rotating cylinder electrode diameter in cm, \(D\) is the diffusion coefficient of the electroactive species in cm\(^2\) s\(^{-1}\), \(u\) is the peripheral velocity imposed by the rotation of cylindrical electrode in cm s\(^{-1}\), and \(\nu\) is the kinematic viscosity of the electrolyte in cm\(^2\) s\(^{-1}\). Many papers have showed that mass transport correlation, described by Equation 1, is best determined through analysis of experimental data, i.e. following the concentration during bulk electrolysis or measuring the limiting current using metal ion deposition. Table I exemplifies this later. Based on the analysis of the mass transport correlation, the value of the experimental coefficient \(a\), is associated with cell dimensions, electrode shape, and electrolyte properties,\(^1\)–\(^2\)–\(^2\)–\(^2\) whereas exponent \(b\) is attributed to the flow pattern performed on the smooth\(^2\) and roughened RCE interfaces.\(^2\)–\(^2\) It is important to highlight that \(b\) is strongly influenced by the morphology of the metal deposits, i.e. \(b > 0.9\) is a typical value associated to rough metal deposits.\(^2\)–\(^2\) The above results have been obtained in RCE in batch mode of operation. Nevertheless, the mass transport characterization during metal recovery in the RCE in continuous mode is rather limited.

Simulation of mass transport at RCE reactors have been performed in 2D and 3D. Rivero et al.\(^2\) presented the mass transfer simulation in the copper deposition system solving the averaged diffusion-convection equations. Bauer et al.\(^2\) proposed a 3D convective–diffusion–migration model for multi-ion transport processes in a concentric RCE cell under turbulent flow conditions. It is important to mention that these papers have been focused on modeling the RCE in batch operation mode. In a previous communication\(^3\) we modeled the current distribution on the RCE, where we evidenced homogeneous current distributions for the secondary and tertiary problems, using four-plate, six-plate or concentric cylinder as counter electrodes indistinctly. Other authors have modeled the tertiary current distributions at RCE solving the diffusion-convection equation during the copper electrodeposition.\(^2\)–\(^2\) Worth mentioning, existing studies on this RCE have not paid much attention to the particular simulations of mass transport and tertiary current distribution in continuous mode of operation. Also, the morphology of metal deposits on the cathode of a RCE in continuous mode has not yet been reported, thus being difficult to draw conclusions that can be generalized to other heavy metals. The CFD simulation of hydrodynamics, mass transport, and tertiary current distribution in a RCE in continuous operation mode is mainly useful for scaling-up from the laboratory to pilot size in wastewater treatment applications and metal recovery.

*E-mail: jhm@ugto.mx

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0351711jes] All rights reserved.
Table I. Mass transport correlations (Sh = aRebSc0.356) at RCE reactor.

| Electroactive species | Operation mode | Anode | D (cm² s⁻¹) × 10⁵ | a | b | Ref. |
|-----------------------|----------------|-------|-------------------|---|---|-----|
| Cu(II)                | Batch          | Concentric | 0.594          | 0.079 | 0.9 | 24  |
| Cu(II)                | Batch          | 4 plate    | 0.594          | 0.012 | 0.95 | 21  |
| Cu(II)                | Batch          | 6 plate    | 0.594          | 0.014 | 0.91 | 21  |
| Cu(II)                | Batch          | Concentric | 0.594          | 0.022 | 0.91 | 21  |
| Cu(II)                | Batch          | 6 plate    | 0.594          | 0.0081 | 0.91 | 25a |
| Cu(II)                | Batch          | 4 plate    | 0.594          | 0.014 | 0.88 | 25b |
| Ag(I)                 | Batch          | 6 plate    | 2.2            | 0.11  | 0.99 | 18  |
| Ag(I)                 | Continuous     | 6 plate    | 2.2            | 0.006 | 0.97 | This work |

aThis correlation was obtained in RCE with an inter-electrode gap of 2.4 cm.
bThis correlation was obtained in RCE with an inter-electrode gap of 3.2 cm.

For the first time, we model and simulate the turbulent flow, mass transport and the tertiary current distribution on the RCE, in continuous operation mode. A configuration of the RCE with an electrolyte inlet at the bottom and the electrolyte exit at the top was employed. The silver electrodeposition from cyanide electrolyte is used as a test system. CFD simulations of turbulent flow were obtained solving the RANS equations with the standard k-ε turbulence model. For turbulent mass transport simulations, the averaged diffusion-convection equation was solved. For the simulations of tertiary current distribution concentration wall functions were employed. Transport equations were solved numerically in 3D by finite element method. The theoretical mass transport correlation and current distribution were validated with experimental data.

Description of the RCE

Figure 1a shows a schematic diagram of the RCE reactor configuration in continuous mode. The acrylic reactor body has an internal diameter of 9.5 cm and 15 cm in height. A 316-type stainless steel cylinder with a 3.8 cm diameter and a length of 11 cm was used as a cathode. Six Ti-IrO₂ plates were attached to the reactor wall and interconnected and were used as anodes. Each plate was 13 cm long, 2 cm wide and 0.3 cm thick. The Ti-IrO₂ anode plates were fabricated in-house by the Pechini method. The electrolyte inlet is located at the bottom center of the reactor (with a diameter of 1 cm). The electrolyte outlet (EO), which consists of six windows (with dimensions of 3 cm arc length and 2 cm height), was located at the top of the reactor at a height of 10 cm, between the spaces of the six-plate Ti-IrO₂ anode, see Figs. 1b and 1c. An acrylic electrolyte collector is located at the top of the reactor wall at a height of 9 cm (see Figure 1a); it contains the following dimensions: 20.5 cm diameter and 7 cm height. It is important to note that there is an electrolyte collector outlet at the bottom, with a diameter of 1.27 cm. An IKA RW, 20 digital electric motor of variable velocity, was used to rotate the inner cylinder. Table II shows the dimensions of the RCE used in this paper.

Formulation of Numerical Simulation

A constant volumetric flow rate of 1.7 cm³ s⁻¹ (0.1 L min⁻¹) giving a mean flow rate of 0.037 cm s⁻¹ (performed at the gap area

Figure 1. (a) Exploded view of the RCE reactor with electrolyte collector. (b) Isometric view of the reactor body without the electrolyte collector. (c) Isometric view of the acrylic reactor body highlighting the electrolyte inlet and electrolyte outlet manifolds. EO is the electrolyte outlet located around the wall of the reactor body.
between inner rotating cylinder and reactor walls) was tested here. The rotational speeds at the RCE surface were 100, 200, 300, 400, and 600 rpm (peripheral velocity of 10.5, 20.9, 31.4, 41.9, and 62.8 cm s\(^{-1}\); \(Re\) of 7600, 15100, 22700, 30200, and 45400, respectively). It is important to highlight that the peripheral velocities predominate in two magnitude orders over the inflow electrolyte rate. Consequently, the mass transport is controlled ultimately by the electrode rotation speed.

Several models have been applied to describe the turbulent flow in rotating inner cylinder geometries such as the Reynolds stress model (RSM),\textsuperscript{31} the mixing length model,\textsuperscript{32} the \(k - \omega\) model\textsuperscript{33} and the \(k - \varepsilon\) model.\textsuperscript{22,36} Particle image velocimetry (PIV) measurements have been performed to validate the velocity field for the RSM model.\textsuperscript{31} Droplet size distribution experiments have been performed to validate the mixing length model,\textsuperscript{32} and the \(k - \omega\) model has been validated against empirical equations.\textsuperscript{33} It is important to mention that Droplet size distribution experiments have been performed to validate the velocity field for the RSM model.\textsuperscript{31} Particle image velocimetry (PIV) measurements have been performed to validate the velocity field for the RSM model.\textsuperscript{31} In regions contiguous to the wall, and due to its effects, velocities decrease quickly and are dissimilar to the model because the turbulence model is applicable to high Reynolds numbers. Wall functions, based on universal velocity distribution, are typically used to solve this problem,\textsuperscript{22,26,36–42} avoiding the need for fine grid resolution in near-wall regions. The wall function for the turbulent layer is:\textsuperscript{22,26,36–42}

\[
u^+ = 5.5 + \frac{1}{k} \ln y^+ \quad [7]
\]

where \(y^+\) is the dimensionless velocity normal to the wall, \(k\) is the von Karman constant and \(y^+\) is the dimensionless distance from the wall to the boundary layer, \(y^+ = \mu_t \kappa / \mu\), where \(\mu_t\) is the friction velocity, \(\kappa = c_{\mu}^{1/4} \kappa\) and \(\gamma\) is the thickness of the wall.\textsuperscript{38,39}

The corresponding boundary conditions to solve Equations 2 to 6 are:

- A normal inflow velocity at the electrolyte inlet, \(u = -U_0 n\).
- Where \(U_0\) is the average velocity at the electrolyte inlet and \(n\) is the normal unit vector; in this paper the calculation for the inlet values of \(U_0\) and \(\kappa_0\) were obtained from the turbulent intensity \(I_T\), and the turbulent length scale \(L_T\), by the next simple formulas: \(U_0 = 3/2(U_0 I_T)^{2/3}\) and \(\kappa_0 = C_p^{1/2} / L_T^{3/2}\). In this paper \(I_T\) was fixed at 0.05 and \(L_T\) was determined by \(L_T = 0.07 r\), where \(r\) is the electrolyte inlet radius of 0.5 cm.
- Decreasing shear stress at the fluid surface, 
  \[ -P + (\mu + \mu_T)(\nabla u + (\nabla u)^T) n = 0, u \cdot n = 0. \]
- A normal stress equal to a pressure at the electrolyte outlet, 
  \[ -P + (\mu + \mu_T)(\nabla u + (\nabla u)^T) n = -n P_0, \text{Where } P_0 \text{ is the pressure at the electrolyte outlet}. \]
- Moreover, at the electrolyte exit \(\nabla u \cdot n = 0 \) and \(\nabla \cdot n = 0.\)
- A normal stress equal to a stress that results from the tangential velocity vector in the RCE surface, 
  \[ -P + (\mu + \mu_T)(\nabla u + (\nabla u)^T) n = -\rho \omega^2 u_{\text{tang}}, \text{where } u_{\text{tang}} = -u_{n} \frac{\omega R_o u_n}{u_n \cdot u_n}. \]
- In this work \(u_n\) is the velocity vector of the moving wall given by \(R_o\), where \(R\) is the radius of the RCE and \(\omega\) is the angular velocity.
- Velocity \(u_x^+\) at a \(y^+\) distance from solid surface, for all other boundaries. The values of \(y^+\) were fixed at 11.1. This value is located in the fully turbulent region.\textsuperscript{41}

### Table II. Parameters of the RCE.

| Parameter                        | Value          |
|----------------------------------|----------------|
| Electrolyte volume within the reactor, \(V_R\) | 559.4 cm\(^3\) |
| Reactor diameter                 | 9.5 cm         |
| RCE diameter, \(d\)              | 3.8 cm         |
| RCE length (in contact with solution) | 10 cm         |
| RCE area (in contact with solution), \(A_{RCE}\) | 119.38 cm\(^2\) |
| Distance of RCE from the bottom   | 0.3 cm         |
| Length and width of the counter electrodes | 13 cm x 2 cm     |
| Plates (attached to the reactor walls) | 2.85 cm        |
| Counter electrode area (in contact with solution), \(A_{ACE}\) | 120 cm\(^2\) |
| Electrolyte inlet diameter       | 1 cm           |

![Figure 2. Simulation domain and tetrahedral mesh for the continuous RCE.](image)

(a) Isometric view and (b) lateral view in the y-z plane.
Mass transport.—In a stable flow system (steady state) for the RCE, under turbulent flow conditions, with an electrochemical system with no chemical reaction in bulk solution and considering the migration term of the Nernst–Planck equation to be negligible because of high concentration of background electrolyte, the following averaged diffusion-convection equation is derived:26,37
\[ -\mathbf{u} \cdot \nabla C + \nabla \cdot (D + DT) \nabla C = 0 \]  
where \( C \) is the averaged concentration of the ionic species and \( DT \) the turbulent diffusion coefficient. To perform the mass transport simulation it is necessary to evaluate \( DT \), which can be obtained from the turbulent Schmidt number \( (Sc_T = \mu_t / (\rho DT)) \). The eddy diffusivity or turbulent diffusivity is determined following the approach used by Rivero et al.,26 considering an analogy between heat and mass transport, which allows the use of the Kays–Crawford model15 as an improvement for turbulent Schmidt number calculation, according to Equation 9:26,37
\[ Sc_T = \left( \frac{1}{2Sc_{CT\infty}} + \frac{0.3}{\sqrt{Sc_{CT\infty}}} \frac{\mu_T}{\rho D} - \frac{0.3}{\rho D} \right)^2 \times \left( 1 - \exp \left( -\rho D / \left( 0.3 \mu_T \sqrt{Sc_{CT\infty}} \right) \right) \right)^{-1} \]  
where \( Sc_{CT\infty} = 0.85 \). It is worth mentioning that the local values of \( Sc_T \) obtained by our simulations (at 7600 < \( Re < 45400 \)) were between 0.850 to 0.852. The latter value confirms that the Schmidt number did not strongly depend on turbulent viscosity under the hydrodynamics conditions considered here.

Equations 8 and 9 are valid in the bulk fluid region, separated a \( y^+ = \delta^+ \) dimensionless distance from the wall (see Figure 3). To describe the concentration distribution close to the wall, the Launder–Spalding distribution has been adapted to the mass transport problem by means of the analogy with heat transport, giving close agreement between experimental and theoretical mass transport results.26,37,44 This Launder-Spalding-like model employs the standard wall functions described by Equations 10 and 11 to link the viscosity affected region between the wall and the fully turbulent zone:
\[ C^+ = Sc_T^{1/3} \left( \frac{1}{\kappa} \ln y^+ + 5.5 + P_T \right) \]  
where the dimensionless concentration \( C^+ \) is defined as
\[ C^+ = \frac{C_{1,w} - C_i}{C_{1,w}^{1/4} k^{1/2}} \]  
where \( C_{1,w} \) is the concentration on the wall surface, \( C_i \) the concentration at a distance \( y^+ \) from the wall and \( N_{i,w} \) the diffusion flux adjacent to the wall.

The variable \( P_T \) in Equation 11 relates the change in mass transport resistance from the viscous sublayer to the turbulent layer and is typically determined by means of the next empirical equation that has presented good results in mass transport simulations:26,37,44
\[ P_T = A \left( \frac{Sc}{Sc_T} \right)^{3/4} - 1 \]
where \( A \) is determined from experimental data. It should be noted that the empirical parameter \( A \) in Equation 13 was adjusted at 11, using trial and error to obtain the best fit between experimental and theoretical mass transport coefficients in the RCE in continuous operation mode for all the Reynolds numbers studied here.

The boundary conditions to solve the Equation 8 on the mass transport model are set up as follows:

- \( C = C_0 \), at the reactor inlet, where \( C_0 \) is the electrolyte inlet concentration.
- \( n \cdot (-D \nabla C) = 0 \), at the reactor outlet.
- \( C^+ \) concentration wall function given by Equations 11 and 12 at a \( y^+ \) distance from RCE surface.
- Zero flux, \( n \cdot (-D \nabla C + u C) = 0 \), in all other boundaries.

The \( u \) values to solve Equation 8 were taken from the solution of the RANS equations.

Tertiary current distribution.—In dilute solutions the current density \( J \) at any point inside the RCE reactor was determined from the gradient of local potential, \( \phi \) according to Ohm’s Law:14,28
\[ J = -\kappa \nabla \phi \]
where \( J \) is the current density vector and \( \kappa \) is the electrolyte conductivity and \( \phi \) the electric potential. The potential distribution in the electrolyte was described by the Laplace equation:14,28
\[ \nabla^2 \phi = 0 \]
Depending on the characteristics of boundary conditions on the working electrode, three types of current distribution models can be specified.28 The corresponding boundary conditions to solve Equation 15, the tertiary current distribution problem, are set up as follows:14,28

- \( -\kappa \frac{\partial \phi}{\partial n} = -j_i(\frac{C_i}{C_i^{bc}}) \exp(\frac{\eta}{\eta T}) \), at the working electrode (cathode, RCE).
- \( -\kappa \frac{\partial \phi}{\partial n} = -j_{rec}(\frac{4kT}{\Delta E_{rec}}) \), at the counter electrode.
where ξ is the normal to the surface, j₀ is the exchange current density, η is the overpotential at the electrode, bₜ is the cathodic Tafel slope, jₚ is the average current density on the RCE (in practice, the current intensity is the same between the working and counter-electrode), Aₑₑₚ is the area of working electrode, and Aₑₑₚ is the area of counter electrode. The Cᵣ and Cᵣₚ values were taken from the solution of the averaged diffusion-convection equation.

**Simulation.**—All model equations were solved numerically in 3D by finite element method using the software COMSOL Multiphysics version 5.1 on a computer with two Intel Xeon 2.30 GHz processor, 96 GB of RAM, and 64-bit operating system.

Turbulent flow Equations 2 to 6 were solved using calculation options by default: stationary solver with Geometric Multigrid iterative methods for u, P and for the turbulence model variables, k and ε, and a relative tolerance of 1 × 10⁻⁵. After that, we confirmed the solution at different mesh sizes until the typical solution around these mesh elements was unaffected. The simulation domain, with 843041 tetrahedral mesh elements (Figure 2), was used in all calculations presented here. The simulation time was about 205 minutes.

The solution of the mass transport Equations 8 and 9 took into account the local velocity vectors and turbulent kinematic diffusivity from the solution of the RANS equations. The simulation time was of about 5 minutes.

The solution of potential distribution, Equation 15, requires the previous mass transport calculations, highlighting the values of Cᵣ (at y’ = δ”) and Cᵣₚ. These values were determined by substituting Equation 11 in Equation 12 (see Figure 3), with Nᵣₚ = jₚ/εF, where z is the number of electrons transferred in the reaction (z = 1) and F is Faraday constant 96,485 C mol⁻¹. The simulation time was about 15 minutes. The RCE reactor parameters and the values of electrolyte transport properties and kinetic parameters used in the numerical calculations are shown in Table II and Table III.

**Experimental.**

The solution employed in this paper (12.15 mol m⁻³ (1300 ppm) Ag(I), 883.5 mol m⁻³ (23000 ppm) CN⁻, pH 13 and 150 mS cm⁻¹ conductivity) resembles the rinse wastewater of the plating silver process. At these electrolyte conditions the complex Ag(CN)−₂ is predominant. The solution was prepared with analytical grade reagents.

**Equipment.**—The characteristics of the RCE used in this work were described in Description of the RCE section. Figure 4 shows a schematic representation of the experimental system used for silver electrodeposition, which was composed by an electrolyte reservoir made of polycarbonate with maximum capacity of 2.5 L, a pump (0.25 HP Owaki Co. LTD, a valve for flow rate control, a flowmeter (0.1 L min⁻¹ to 1 L min⁻¹ WHITES Industries) and a RCE reactor. The electrodes were connected to the potentiostat-galvanostat (BioLogic Instruments SP-150) with EC-Lab software coupled to a VMP-3 model booster (20 V to 10 A) both from BioLogic Instruments. The electrode potentials were measured vs. a saturated calomel reference electrode (sat. SCE), Radiometer Analytical model XR100. The SCE was coupled to a Luggin capillary. The silver concentrations were determined by Atomic AA using a Perkin Elmer model Analyst 200. Microanalysis of obtained silver deposits was carried out using a scanning electron microscopy (SEM) JEOL model JSM 6010 PLUS/LV.

**Methodology.**—Mass transport characterization.—The potential range where the Ag(I)/Ag(0) process is limited by mass transport was found to be in the potential range of −1.35 ≤ E ≤ −1.15 V vs. SCE (Figure 5). This polarization curve was constructed by rotating disk electrode (RDE) studies; the methodology for RDE tests has been previously reported by our group. Hence, in this paper, the electrolyses in the RCE were performed by maintaining a constant
potential of $-1.2$ V vs. SCE, to guarantee mass transport control. The rotational speeds at the RCE surface were 100, 200, 300, 400, and 600 rpm (giving $Re$ of 7600, 15100, 22700, 30200, and 45400, respectively). A constant volumetric flow rate of 1.7 cm$^3$ s$^{-1}$ (0.1 L min$^{-1}$) giving a mean flow rate of 0.037 cm s$^{-1}$ was tested here. The silver ions concentration at the RCE surface achieved a steady state after 30 minutes of electrolysis in continuous operation mode. The concentration during electrolysis was determined by AA analysis. After electrodeposition tests, the silver deposit on the RCE was detached carefully from the electrode, using a spatula. Around the center of the RCE, 10 rectangles of 0.3 cm$^2$ at 10 different heights of 0.3, 0.5, 0.9, 1.75, 3.8, 4.2, 5.2, 5.6, 7.7 and 8.9 cm, of the total height of the formed deposit, were scratched and weighed. In order to obtain the normalized experimental weight ($W/W_{ave}$) of silver deposits, the average deposit weight ($W_{ave}$) was evaluated as follows:

$$ W_{ave} = \frac{1}{L} \int_0^L W dL $$

where $L$ is the arc length of the RCE surface or the length in the z-coordinate of the RCE surface, and $W$ is the local experimental weight. The ratio ($W/W_{ave}$) should be equal to the value of the normalized current density ($j/j_{ave}$). In the same way, the one-dimensional average current density was determined, except that $W$, in Equation 16, is substituted by the local current density $j$.

Results and Discussion

Figure 6a shows the simulated velocity field, calculated at 600 rpm and volumetric inflow rate of 0.1 dm$^3$ min$^{-1}$ (1.7 cm$^3$ s$^{-1}$). The slide plots show the velocity field at the front of the counter electrode and at the front of the reactor walls in planes $x$-$z$ and $y$-$z$, respectively. A turbulent Taylor vortex flow appeared near to the RCE surface; the extreme velocities are set in the middle of the RCE, at 5.3 cm height. In addition, the presence of low-velocity regions close to the reactor wall was present. In previous communications Rivero et al. and Pérez and Nava reported the presence of three Taylor vortex flow for the RCE in batch mode. The only one theoretical turbulent Taylor vortex flow obtained here is attributed to the continuous operation mode, which modifies the electrolyte flow field. In previous research carried out by our group this vortex (with a similar RCE and a ratio height-gap of 3.5) was experimentally visualized. Figure 6b shows the simulated Ag(CN)$_2^-$ concentration field, which was evaluated after 18 seconds of electrolysis at $E = -1.2$ V vs. SCE and 600 rpm with volumetric inflow rate of 0.1 dm$^3$ min$^{-1}$ (1.7 cm$^3$ s$^{-1}$); the slide plots illustrate small variations of Ag(CN)$_2^-$ concentration located in the domain of Taylor vortex; more discussion about this concentration graph is presented below.

In order to validate the mass transport simulations, experimental bulk electrolysis was performed in the RCE in continuous operation mode at $E = -1.2$ V vs. SCE at 7600 $\leq$ $Re$ $\leq$ 45400 with constant inflow velocity of 1.7 cm$^3$ s$^{-1}$. Figure 7 shows normalized decay of the experimental silver concentration at the exit of the RCE as a function of Reynolds number, which lead to determine the mass transport coefficients by means of the mass balance given by Equation $17$.

$$ C_{out}/C_0 = 1/(1 + (k_wA_{RCE}/q)) $$

where $C_{out}$ and $C_0$ are the concentrations of Ag(CN)$_2^-$ ions at the outlet and inlet of the reactor, and $q$ is the inflow rate. From the analysis of Figure 7 the silver concentration decay is faster as the $Re$ increases, as expected. The experimental $k_w$ values were comprised $1.75 \times 10^{-3}$ and $1 \times 10^{-2}$. Then, the experimental and theoretical mass transport correlation was obtained with the subsequent determination of the $Sh$ number.

Figure 8 shows the comparison of mass transport correlation obtained by bulk electrolysis and by simulations; moreover, these correlations were compared to those previously obtained by our group, in batch operation mode and in the same electrochemical system. The details of the theoretical assessment of mass transport correlation are explained in the Appendix. We can observe close agreement between mass transport simulations and experimental data in Figure 8. There-
Therefore, the mass transport characterization was averaged taking into account both the experimental data and predictions; in this context, the coefficient value $a = 0.006$, while the exponent $b = 0.97$. These numerical values differ to those obtained in batch conditions, where $a = 0.11$ and $b = 0.99$. The fact that the mass transport is greater in batch mode, is attributed, on the one hand, to hydrodynamic patterns (i.e. three Taylor vortexes appeared in batch mode, while only one appears in continuous mode); on the other hand, the silver deposits obtained here are well-defined grains (see micrograph of Figure 9), while dendritic deposits are obtained in batch mode. It is well known that dendritic deposits enhance interfacial micro-turbulence, which reveals the greatest $b$ values in batch mode. The lower $a$ values obtained here are attributed to the continuous operation mode.

Figures 9a, 9b and 9c exhibit SEM images of silver deposits at heights of 0.75, 5 and 7.35 cm in the $z$-coordinate respectively, in a continuous mode of operation at $E = -1.2 \, V$ vs. SCE ($\eta = -0.5 \, V$), $Re = 45400$ with constant inflow velocity of $1.7 \, cm^3 \, s^{-1}$. These images show deposits in the form of grains exhibiting the same shape and orientation, despite the decrease in size of the $z$-coordinate from Figures 9a to 9b. The average grain sizes are $13 \, \mu m$ at 0.75 cm, $10.8 \, \mu m$ at 5 cm and $10.6 \, \mu m$ at 7.35 cm, highlighting that at 0.75 cm (Figure 9a) the deposits are the largest. Meanwhile, there are no significant differences in the deposit sizes between Figures 9b and 9c. The maximum grain lengths are $20 \, \mu m$. It is important to mention that there is not deposit size distribution in the $z$-coordinate in batch mode.

Figure 10 shows the theoretical concentration profile along $z$-coordinate assessed at $\gamma^+ = 11.1$ from the RCE surface at $Re$ comprised between 7600–45400, at $E = -1.2 \, V$ vs. SCE, highlighting that the silver concentration at $z = 0$ decreases from 11.4 to 4.5 mol m$^{-3}$ as a function of $Re$. The concentration profiles decrease fast, in the $z$-coordinate, between 0 cm $z$ 1.5 cm, then at $z > 1.5$ cm the concentration slightly decreases until it becomes asymptotic. The silver concentration depletion as a function of hydrodynamics is attributed to an enhancement of the mass transport flux with hydrodynamics. The Ag(CN)$_2^-$ concentration profile along the $z$-axis, at $Re = 45400$, confirms the silver deposit size distribution obtained at the same Reynolds
number (Figure 9), which is created by the electrolyte inlet and outlet in the continuous operation mode. The above considers that the concentration is greater at the entrance, which favors deposit growth. In the ordinate axis we graph the current data considering that the equilibrium concentration is constant. The normalized current distributions did not show any difference with hydrodynamics (at constant overpotential). In the tertiary current distribution problem, where the concentration of Ag(CN)₂⁻ on the electrode surface is zero, the current density increases with hydrodynamics but if the electrolyte flow pattern is similar, as was the case of turbulent flow obtained here, the current density profile shape remains unchanged; in this way, the normalized ĵ/J₀ vs. z/h plot was independent of hydrodynamics. A border effect appeared close to the electrolyte inlet, at the bottom of the RCE (0 < z/h < 0.1), subsequently at z/h > 0.1, a homogeneous current distribution (close to unity) is obtained. In a previous paper we modeled the tertiary current distribution in a similar RCE reactor, but in batch mode. In that work, a homogeneous tertiary current distribution was obtained and no electrical edge effect was detected at the bottom; the absence of electrical edge effect is conditioned by the position of the rotating cylinder, which is very close to the reactor base. Accordingly, in the RCE studied here the edge effect is solely attributed to the depletion of silver ions at the inlet section of the electrolyte. The quasi even current distribution in the RCE (at 0.1 < z/h < 1) is developed by the symmetry between RCE and counter electrodes; the RCE and counter electrodes are equidistant and they have the same height, h = 10 cm. This is contrary to results obtained with working electrodes embedded in isolated surfaces, where edge effects predominate close the isolators.

To validate the current distribution model, silver deposit weights, obtained by bulk electrolysis at Re = 45400 (at E = −1.2 V vs. SCE, η = −0.5 V), were plotted as function of normalized length (symbols). Close agreement between experimental and theoretical data was obtained, which also coincides with the micrographs shown in Figure 9. Finally, homogeneous current distribution along the arc length of the RCE was confirmed by theoretical and experimental data (not shown herein), which coincides with that obtained in a previous communication.

Conclusions

For the first time, the hydrodynamics, mass transport, and tertiary current distribution in a RCE in a continuous mode of operation under turbulent flow conditions were calculated. A configuration of RCE reactor with electrolyte inlet at the bottom and the electrolyte exit at the top was employed. The mass transport correlations showed excellent agreement between simulations and experimental data for the RCE, obtaining values of a = 0.006 and b = 0.97. Well-oriented silver deposit grains were obtained in continuous mode, contrary to the dendritic deposits obtained in batch mode.

The tertiary current distribution on the RCE interface along the z-coordinate presented one border effect near the electrolyte inlet, at the bottom of the RCE, afterward, a homogeneous current distribution was obtained. The edge effect is created by the abrupt silver concentration depletion at the entrance of the electrolyte. Silver deposit profiles, obtained by bulk electrolysis, corroborated the numerical simulations of current distribution.

The mathematical model implemented here can be useful as a starting point for scaling-up the RCE from laboratory to industrial size for wastewater treatment applications and metal recovery; although the inputs for simulations must consider the corresponding properties and parameters of the electrochemical system.

Acknowledgments

M. Rosales is grateful to CONACyT for the scholarship No. 412713 granted. J. L. Nava acknowledges the Universidad de Guanajuato for financial support through the project No. 8862016. Special thanks should go to Sandra Mosqueda for her help in the electrolysis tests.

Appendix: Theoretical Assessment of Mass Transport Correlation

The limiting current intensity was determined by the integration of the mass transport flux, \( N_1 \), over the RCE surface:

\[
I_L = zF \int_{A_{RCE}} (N_1 \cdot n) dA_{RCE}
\]  

[\text{A1}]

where \( I_L \) is the limiting current, \( N_1 \) is taken from the solution of the averaged diffusion-convection equation (Equation 8). Then, the mass transport coefficients can be assessed using the limiting current density, \( J_L = I_L / A_{RCE} \) according to:

\[
k_m = \frac{J_L}{zC_b}
\]

[\text{A2}]

where \( C_b \) is the silver concentration in the bulk. It is important to remark that \( C_b \) was fitted equal to the inlet concentration (\( C_0 = 12.15 \text{ mol m}^{-3} \)), and owing to this fact, it provided...
the best fitting with experimental mass transport coefficients. Then, the correlation $Sh = aRe^bSc^{0.396}$ was constructed.

References

1. D. R. Gabe, G. D. Wilcox, J. González, and F. C. Walsh, *J. Appl. Electrochem.*, 28, 759 (1998).
2. J. Low, C. Ponce de León, and F. C. Walsh, *Aust. J. Chem.*, 58, 246 (2005).
3. F. C. Walsh, *Hydrometallurgy*, 33, 367 (1993).
4. F. C. Walsh and D. R. Gabe, *Process Saf. Environ. Prot.*, 68, 107 (1990).
5. F. C. Walsh, in *Electrochemical Technology for A Cleaner Environment*, J. D. Genders and N. L. Weinberg, Editors, p. 101, The Electrosynthesis company Inc., New York (1992).
6. N. A. Gardner and F. C. Walsh, in *Electrochemical Cell Design*, R. E. White, Editor, p. 225, Plenum Press, New York, (1984).
7. F. C. Walsh, G. Kear, A. H. Nahli, J. A. Wharton, and L. F. Arenas, *Corros. Sci.*, in press (2017).
8. F. C. Walsh, *Pure Appl. Chem.*, 73, 1819 (2001).
9. J. M. Grau and J. M. Bisang, *J. Chem. Technol. Biotechnol.*, 77, 465 (2002).
10. G. Chen, *Sep. Purif. Technol.*, 38, 11 (2004).
11. F. Rivera, I. González, and J. L. Nava, *Environ. Technol.*, 29, 817 (2008).
12. S. Matlalcuatzi and J. L. Nava, *Water Sci. Technol.*, 65, 1406 (2012).
13. F. J. Almazán, F. V. Caballero, M. R. Cruz, E. P. Rivero, and I. González, *Electrochim. Acta*, 77, 262 (2012).
14. C. T. J. Low, E. F. L. Roberts, and F. C. Walsh, *Electrochim. Acta.*, 52, 3831 (2007).
15. J. E. Terrazas, S. Gutiérrez, A. Alatorre, C. Ponce de León, and F. C. Walsh, *Electrochim. Acta*, 56, 9357 (2011).
16. J. M. Grau and J. M. Bisang, *J. Appl. Electrochem.*, 37, 275 (2007).
17. M. Tesillo, S. Alonso, F. F. Rivera, E. P. Rivero, and I. González, *ECS Trans.*, 20, 313 (2009).
18. J. L. Arredondo, F. F. Rivera, and J. L. Nava, *Electrochim. Acta*, 147, 337 (2014).
19. J. C. Bazan and J. M. Bisang, *J. Appl. Electrochem.*, 34, 501 (2004).
20. J. St-Pierre, N. Masse, E. Frechette, and M. Bergeron, *J. Appl. Electrochem.*, 26, 369 (1996).
21. F. F. Rivera and J. L. Nava, *Electrochim. Acta*, 52, 5868 (2007).
22. M. Rosales, T. Pérez, and J. L. Nava, *Electrochim. Acta*, 194, 338 (2016).
23. D. R. Gabe, *J. Appl. Electrochem.*, 4, 91 (1974).
24. D. R. Gabe and F. C. Walsh, *J. Appl. Electrochem.*, 14, 565 (1984).
25. F. F. Rivera, J. L. Nava, M. T. Oropeza, A. Recéndiz, and G. Carreño, *Electrochim. Acta*, 55, 3275 (2010).
26. E. P. Rivero, P. Granados, F. F. Rivera, M. Cruz, and I. González, *Chem. Eng. Sci.*, 65, 3042 (2010).
27. G. Bauer, P. Gamnitzer, V. Gravemeier, and W. A. Wall, *J. Comput. Phys.*, 251, 194 (2013).
28. T. Pérez and J. L. Nava, *J. Electroanal. Chem.*, 719, 106 (2014).
29. C. P. Fabian, P. Mandin, M. Ridd, and M. Sheehan, *ECS Transactions*, 2, 303 (2006).
30. M. Tesillo, S. Alonso, F. F. Rivera, and J. L. Nava, *Electrochim. Acta*, 51, 4067 (2006).
31. D. L. Marchisio and A. A. Barressi, *Chem. Eng. Sci.*, 58, 3579 (2003).
32. D. Eskin, S. D. Taylor, and D. Yang, *Chem. Eng. Sci.*, 161, 36 (2017).
33. W. M. J. Batten, N. W. Bressloff, and S. R. Turnock, *Int. J. Numer. Methods Fluids*, 38, 207 (2002).
34. R. Enciso, L. A. Padilla, C. Ojeda, J. A. Delgadillo, and I. Rodríguez, *Int. J. Electrochem. Sci.*, 7, 12181 (2012).
35. P. M. Wild, N. Djilali, and G. W. Vickers, *J. Fluids Eng.*, 118, 116 (1996).
36. T. Perez and J. L. Nava, *Int. J. Electrochem. Sci.*, 8, 4690 (2013).
37. E. P. Rivero, M. R. Cruz, F. J. Almazán, and I. González, *Chem. Eng. Res. Des.*, 100, 422 (2015).
38. P. S. Bernard and J. M. Wallace, *Turbulent Flow: Analysis, Measurement and Prediction*, p. 304, John Wiley & Sons, New Jersey (2002).
39. K. H. Verssteeg and W. Malalasekera, *An Introduction to Computational Fluid Dynamics: The Finite Volume Method*, p. 41, Prentice Hall, London (1995).
40. T. Pérez, C. Ponce de León, F. C. Walsh, and J. L. Nava, *Electrochim. Acta*, 154, 352 (2015).
41. H. Schlichting and K. Gersten, *Boundary-layer theory*, MC Graw-Hill, New York (1979).
42. E. P. Rivero, F. F. Rivera, M. R. Cruz, E. Mayen, and I. González, *Chem. Eng. Res. Des.*, 90, 1969 (2012).
43. B. Weigand, J. R. Ferguson, and M. E. Crawford, *Int. J. Heat Mass Transfer*, 40, 4191 (1997).
44. F. J. Trujillo, T. Satinski, and A. A. Adesina, *Chem. Eng. Sci.*, 64, 1143 (2009).
45. D. R. Gabe and F. C. Walsh, *J. Appl. Electrochem.*, 13, 3 (1983).
46. W. R. Parrish and J. Newman, *J. Electrochem. Soc.*, 117, 43 (1970).
47. J. L. Santos, V. Geraldes, S. Velizarov, and J. G. Crespo, *Chem. Eng. J.*, 157, 379 (2010).