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Model Based Analysis of Forced and Natural Convection Effects in an Electrochemical Cell

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ABSTRACT

High purity copper, suitable for electrical applications, can only be obtained by electro-winning. The hallmark of this process is its self-induced natural convection through density variations of the electrolyte at both anode and cathode. In order to accelerate the process, first its full dynamic complexity needs to be understood. Thus, an OpenFoam®-based 2D model has been created. This finite-volume multiphysics approach solves the laminar momentum and copper-ion species conservation equations, as well as local copper-ion conversion kinetics. It uses a Boussinesq approximation to simulate the species-momentum coupling, namely natural draft forces induced by variations of the spatial copper concentration within the fluid. The model shows good agreement with benchmark-cases of real-life electrochemical cells found in literature. An additional flow was imposed at the bottom of a small-scale electrochemical cell in order to increase the ionic transport and thereby increase the overall performance of the cell. In a small-scale electrochemical cell in strictly laminar flow, the overall performance could be increased and stratification decreased.

1. INTRODUCTION AND OBJECTIVE

Natural convection flow developed on vertical planes plays an essential role in unstirred electrochemical cells. Copper refining is the most important large-scale industrial application, where several 1 m high vertical electrodes are placed in baths. Sulfuric acid and other additives are frequently added to increase the conductivity of the electrolyte and support the electrochemical process. Wagner analysed the steady state ionic mass transfer due to natural convection along the vertical electrode [1], which leads to the limiting current density based on the boundary-layer theory. Ever since, numerous theoretical and experimental papers have been published on velocity profile of natural convection [2-3], concentration profile [4-6] and current density distribution [7-9]. Most of these studies focus on the cathode, with fewer focusing on the anode. In the past years, numerical studies have been conduced. Though most of the numerical studies are based on laminar flow, a few use turbulence models such as k-ε [10,11]. Solving the equation in laminar flow has the advantage of resolving the concentration boundary layer which simplifies the study of the electrochemical reaction. Kawai did several studies of electrochemical cells both experimentally and computationally with two vertical electrodes. He studied the transient behaviour of the natural convection at a constant current density [12]. Later, he focused on

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the ionic mass transfer in $CuSO_4$-H_2SO_4 solutions whereas the electric field and electrochemical reaction were solved as well [4-6, 10]. The results show a good agreement with the conducted experiments. Based on his results, Sakr [10] and Ehrl [17] tested the accuracy of his code in laminar flow.

Many computations in turbulent flow involve forced convection. A common case is having a parallel flow between 2 plates where no natural convection takes place. This case has been subject to several studies using different turbulence models [10-11, 18-20]. Even full industrial scale studies have been conducted to understand the flow conditions in a copper electrolysis bath [21-22].

The objective of this paper is to understand the effect of natural convection interacting with an additional flow in terms of kinetics. Therefore, a flow is injected at the bottom of a cell facing the lower part of the cathode.

In a first step, the accuracy of the OpenFoam® based natural convection model is tested on a Benchmark case experimentally and computationally conducted by Kawai [12]. In the second case, the impact of an additional flow is studied. Therefore, the kinetics have to be implemented by solving the Botler-Volmer equation and the electrostatic field has to be considered as well.. The domain is kept small, consequently the flow remains within the laminar regime. This basic model should help to understand the process within such an electrochemical system. However due to the difference in scale the results do not represent a full industrial scale plant.

2. MATHEMATICAL MODEL

The simulations are carried out in OpenFOAM®, version 4.1. The first case models considers transient natural convection and is based on the Benchmark case originally conducted by Kawai [12]. In a second model, the electrochemical reaction and electrostatics are considered as well.

2.1. Model 1: Natural Convection

The presented model, originally conducted by Kawai [12] and later validated by Sark[10], is used for validation of the modified Boussinesq solver. In the model, a constant homogeneous current density of 20 A/m² is applied between anode and cathode in a 0.6 M $CuSO_4$ aqueous solution.

Conservation of momentum is described by the incompressible Navier-Stokes equations for Newtonian fluids, equations 1, 2. The influence of the local density variations due to changes of concentration are accounted for by the Boussinesq approximation, whereas c_{ref} is the bulk concentration.

$$\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u}\nabla\mathbf{u} = -\frac{\nabla p}{\rho} + \nu\,\Delta\mathbf{u} + \beta\mathbf{g}(c - c_{ref}) \tag{1}$$

$$\nabla \cdot \boldsymbol{u} = \mathbf{0} \tag{2}$$

The ionic transport is based on diffusion and convection, equation 3.

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = \Delta c \tag{3}$$

The solution consists of Cu^{2+} and SO_4^{2-} ions in an aqueous solution. Electro neutrality demands the same concentration for Cu^{2+} and SO_4^{2-} at any spatial position within the fluid, equation 4. Therefore, only one species has to be considered.

$$0 = \sum_i c_i z_i \tag{4}$$

The boundary conditions for the ionic flux at the anode and cathode corresponds to the applied current as described in equation 5. At all other boundary the ionic flux is zero, equation 6.

$$\frac{\partial c}{\partial \boldsymbol{n}} = \frac{j}{DFz} \tag{5}$$

$$\frac{\partial c}{\partial \boldsymbol{n}} = \boldsymbol{0} \tag{6}$$

2.2. Model 2: Impact of an Additional Flow

In the second model, the steady state behaviour of an electrochemical cell is studied whereas electrical effects such as migration, electrochemical reaction and the electric field are considered as well. Any reactions within the domain Ω are expressed by the source term R. However, in our case the reactions are only taking place at the boundary, thus $R(\Omega) = 0$. The species transport can be defined, see equation 7, where N is the ionic flux.

$$0 = \frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{N} + \mathrm{R} \tag{7}$$

The ions within the diluted $CuSO_4$ solution are exposed to an electric field. The ionic flux consists of convection and diffusion. Due to gradients within the electric field migration will occur as well, equation 8.

$$\boldsymbol{N} = c\boldsymbol{u} - D\nabla c - \frac{zFD}{RT} c\nabla\, \phi \tag{8}$$

The current is assumed to be transported by electrical conduction, whereas κ is the electric conductivity of the fluid, equation 9.

$$\nabla\phi \sum_i \frac{F^2 z_i D_i c_i}{RT} = \kappa\nabla\phi = \boldsymbol{j} \tag{9}$$

Because there are no current sources or sinks within the system, the current has to be conserved, as shown in equation 10. Thereby, the system is closed and we can define the equation for the electric potential ϕ, equation 11.

$$\nabla \cdot \boldsymbol{j} = 0 \tag{10}$$

$$\nabla \cdot \kappa \nabla \phi = 0 \tag{11}$$

The electrochemical reaction is taking place at the boundary. The anodic reaction is assumed to be infinitely fast and is not of much interest in the presented study. The potential distribution is assume to be uniform at both electrodes, whereas the potential at the anode is set to zero, $\phi(anode) = 0$.

The cathodic reaction is described by the Botler-Volmer equation 12, which depends on the local concentration c and over potential η.

$$j = \mathrm{j}_0 \left(\frac{c}{c_{ref}}\right)^{\gamma} \left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(\frac{\alpha_c F}{RT}\eta\right)\right) \tag{12}$$

The over potential is the difference between applied voltage ΔV and local electric potential at the boundary, thereby ohmic resistance is considered, equation 13.

$$\eta = \Delta V - \phi \tag{13}$$

The electric current expressed by the Bother-Volmer equation results in an ionic flux. Both ionic transport and electrochemical reaction have to be in balance at the boundary, equation 14.

$$\frac{\partial c}{\partial \boldsymbol{n}} zDF = \mathrm{j}_0 \left(\frac{c}{c_{ref}}\right)^{\gamma} \left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(\frac{\alpha_c F}{RT}\eta\right)\right) \tag{14}$$

In order to find a stable solution, the equation is linearized to the first cell in the domain, whereas δ is the normal distance to the first cell. The boundary concentration is obtained by solving the equation by the Newton's method, equation 15.

$$\frac{c(\delta) - c}{\delta} \cdot DFz = \mathrm{j}_0 \left(\frac{c}{c_{ref}}\right)^{\gamma} \left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(\frac{\alpha_c F}{RT}\eta\right)\right) \tag{15}$$

The total current at both anode and cathode has to be the same to ensure the conservation of current as described in equation 10. Thus, we can define the anodic reaction with an uniform current density distribution, equation 16.

$$\frac{\partial c}{\partial \boldsymbol{n}} D = \frac{1}{A_{cathode}} \int_{A_{anode}} \frac{\partial c}{\partial \boldsymbol{n}} D dA \tag{16}$$

Table 1: Simulation parameters for case 1 (see 3.1) and case 2 (see 3.2)

Simulation parameter	**Value**	**Units**
ν	1.21x10-6	m^2/s
$D_{Cu^{2+}}$	7.12x10-10	m^2/s
$D_{SO_4^{2-}}$	1.06x10-9	m^2/s
D	4.42x10-10	m^2/s
β	1.4x10-4	m^3/mol
j_0	0.76 [16]	A/m^2
α_a	1.5 [23]	
α_c	0.5 [23]	
T	293.15	K

3. RESULTS

Natural convection plays a major role concerning the the ionic transport within an electrochemical cell. To test the accuracy of the modified Boussinesq solver within OpenFOAM®, simulations on a Benchmark case are performed.

3.1 Case 1: Natural Convection

To test the accuracy of the code, the results are compared with the Benchmark case originally conducted by Kawai [12]. Thereby, the transient behaviour of both flow and concentration is analysed. A constant current density of $20 A/m^2$ is applied between two vertical electrodes. The model is described in chapter 2.1 and the domain is shown in figure 1.

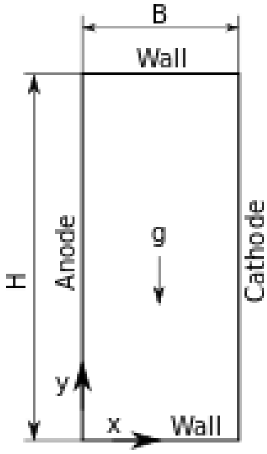

Figure 1: Electrochemical cell with vertical parallel electrode of Kawai [12], H = 10 mm, B = 1 mm

Density variations within an electrochemical cell lead to a natural convection between two vertical electrodes. The resulting velocity field after 50s simulation time is shown in figure 2.

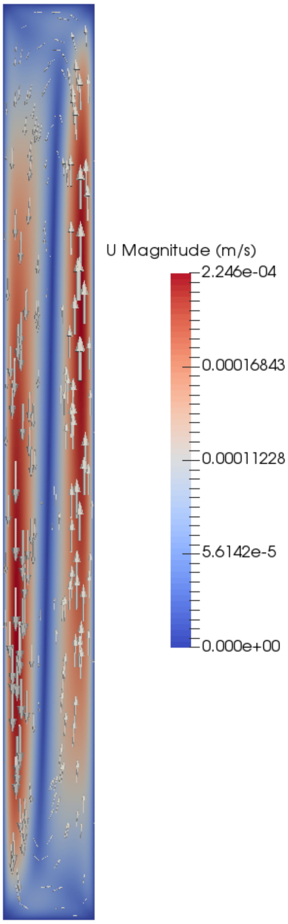

Figure 2: Velocity field of the electrochemical cell, 0.6M $CuSO_4$ solution, B = 1 mm, H = 10 mm, J = 20,0 A/m², t = 50 s.

The velocity profile at mid height of the cell captures the natural convection nicely. The low cupper concentration at the cathode leads to a low density, creating a flux facing upwards, whereas the higher copper concentration at the anode creates a downward facing flow. The velocity increases in a parabolic function from the wall and reaches a maximum at 0.15 B. Then, it decreases linearly towards the bulk concentration. At the cathode an antisymmetric velocity profile is observed. The space variation of the vertical velocity component after 50 seconds of simulation time is shown in figure 3.

At the beginning of the process, the boundary concentration at mid height increases proportionally to the square root of time. Within the first approximately 50 seconds, the transport is based on diffusion until a maximum deviation of ca. 37mol/m^3 from the bulk concentration is reached at both anode and cathode. As time passes, natural convection starts to contribute to ionic transport more significantly and the boundary concentration decreases towards the bulk concentration.

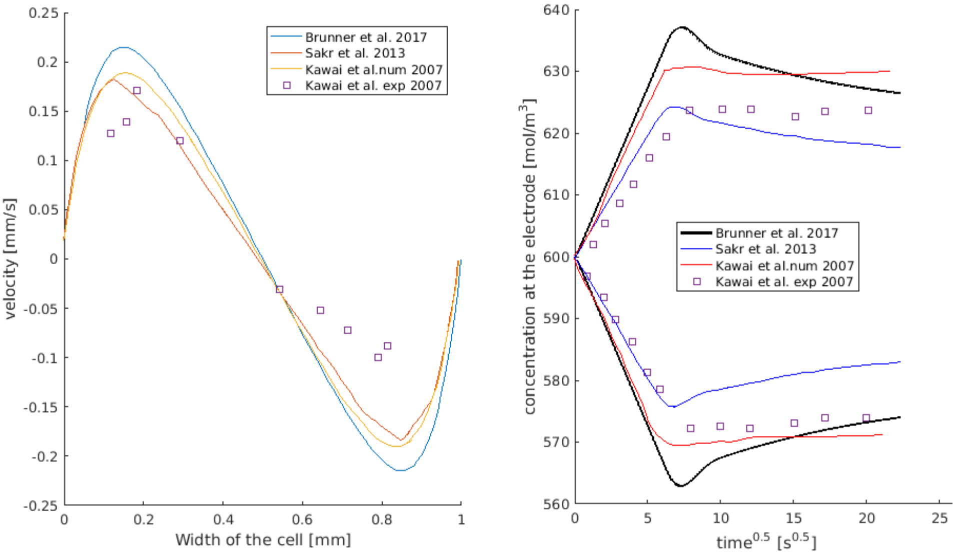

Figure 3: On the left side: Spatial dependent vertical velocity at mid height of 0.6 M $CuSO_4$ solution. On the right side: Boundary concentration at mid height of the electrode. B=1mm, H=10mm, J=20A/m^2, t=50s. The data is compared with literature results [10,12].

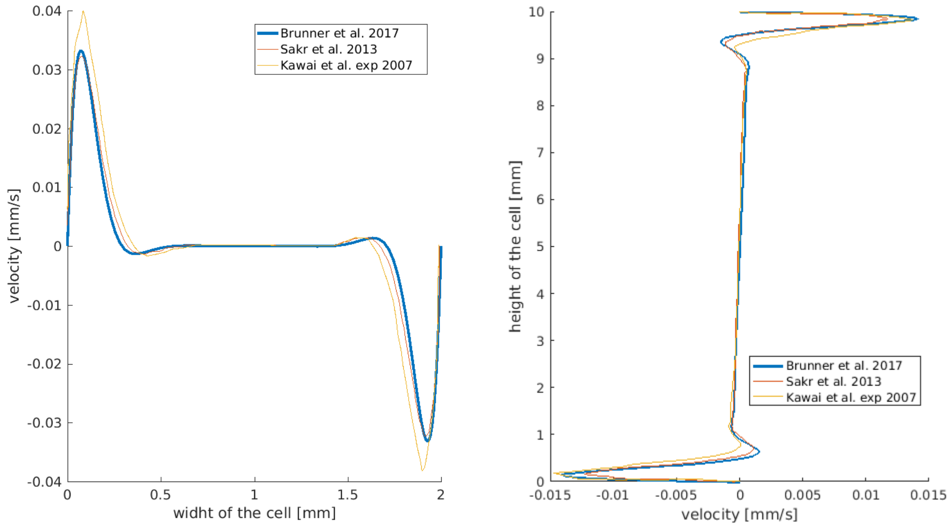

Figure 4: Spatial dependent horizontal velocity at mid height on the left and spatial dependent vertical velocity profile on the right side. The data is compared with literature results [10,12]. Cupper concentration 0.6M $CuSO_4$, B=2mm, J=20 A/m^2, t=2000s

After 6000s in a 2mm wide cell with the same constant applied current density an almost steady state is reached. The initially strong natural convection has significantly decreased, a boundary layer has been formed, and the inner movement has significantly decreased.

To show the validity of the code, both velocity profiles and boundary concentrations are compared with the experimental and computational results by Kawai et al [1] and Sakr et al [2]. The presented results show a good qualitative and quantitative agreement for both velocity and concentration as shown in figure 3 and 4.

3.2. Case 2: Impact of an Additional Flow

In most unstirred electrochemical cells, the ionic transport is limited by natural convection. All equation for the used model are described in chapter 2.2. To increase the ionic transport, an additional flow is introduced, which is aimed to support the existing natural convection. The flow is injected at the bottom below the cathode as it is shown in figure 5. A 2-D baffle to ensure no direct backflow from inlet and outlet is placed in the centre of the cell. It reaches from the bottom towards the height at which the bottom edge of the cathode is located.

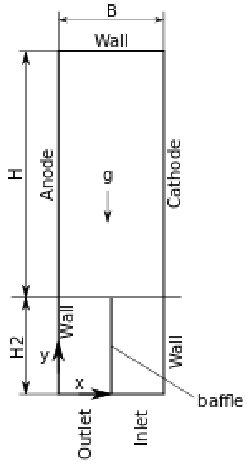

Figure 5: Electrochemical cell with vertical parallel electrode with inlet and outlet, H=4mm, B=0.5mm, H2=1mm

The ionic flux over the boundary can be obtained by solving the electrochemical reaction as described in the previous chapter.

The flow at the bottom going from anode to cathode is interrupted due to the additional forced convection. As its magnitude increases, a back flow forms from cathode to anode and inlet to outlet respectively.

The additionally imposed flow has little impact on the qualitative structure of the copper-ion concentration field, electric potential and vertical velocity distribution. Figure 7 and 8 show the space variation of those properties at 3 different heights, 0.125H, 0.5H, 0.875H. The field values are shown in figure 6. The boundary concentration at the cathode is almost 0 at all positions at the cathode as a result of the strong electrochemical reaction and limitation by transport. Due to the low concentration in immediate vicinity of the cathode the electrical conductivity decreases and high gradients as well as potentials are observed. At the lower end of the cathode the incoming flux has no developed concentration boundary layer. Thus, the kinetics and current is very high, leading to a maximum in the electric potential field.

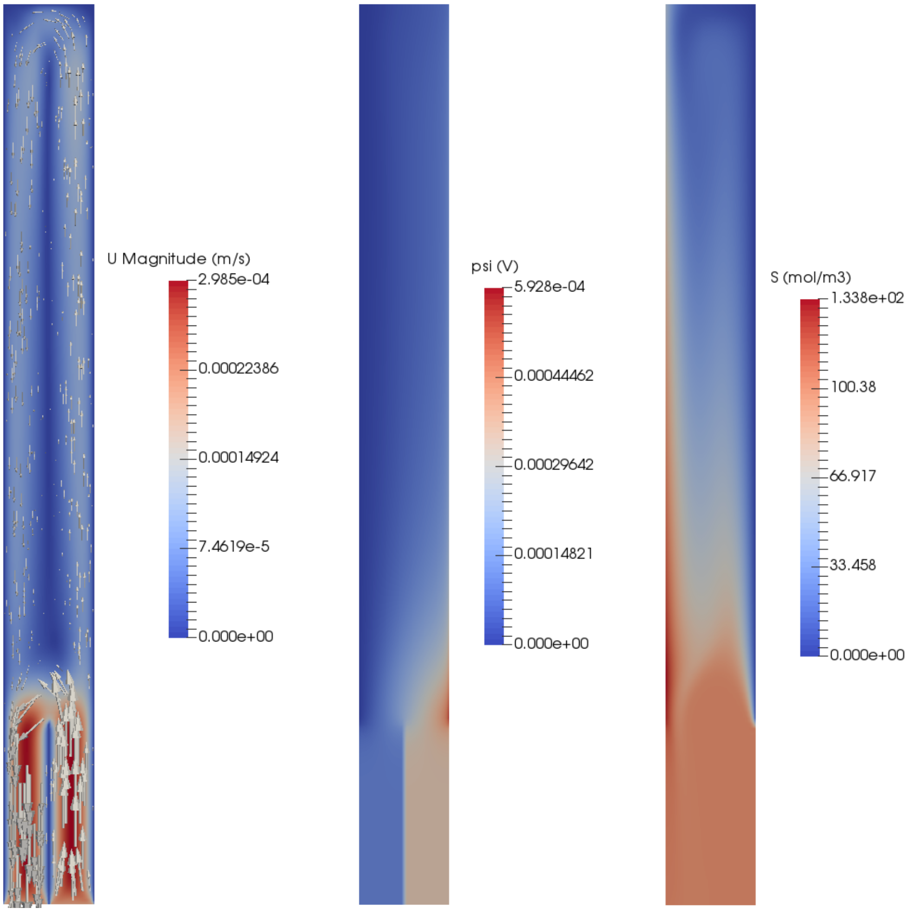

Figure 6: velocity, electric potential and copper concentration field for 0.08mm/s

Kinetics depend on the boundary concentration. At any given electric potential, ionic transport and electrochemical reaction have to balance. Figure 9 shows the boundary concentration of the cathode as a function of height. At low voltages both electrochemical reactions and ionic transport are important. At an applied voltage of 0.1V this yields to an average boundary concentration of 0.1089 (=10.9% c_{ref}) for a low inlet velocities. At 0.08 mm/s the relative average concentration increases up to 0.1247 as the convective transport becomes more dominant, allowing higher boundary concentration and thereby higher reaction rates. As voltage increases the electrochemical reaction becomes much stronger and the ionic transport becomes the limiting factor. Thereby, the boundary concentration approaches 0 at an applied potential of 0.2V resulting in an average concentration of 3.3*10-5 for u=0.008mm/s and 4.46*10-5 for u=0.08mm/s respectively. At this point, increasing the voltage would further lower the concentration, however it wouldn't not have any significant impact on the ionic transport, thus the limiting current density is reached. Any further increase can only be achieved by increasing the transport.

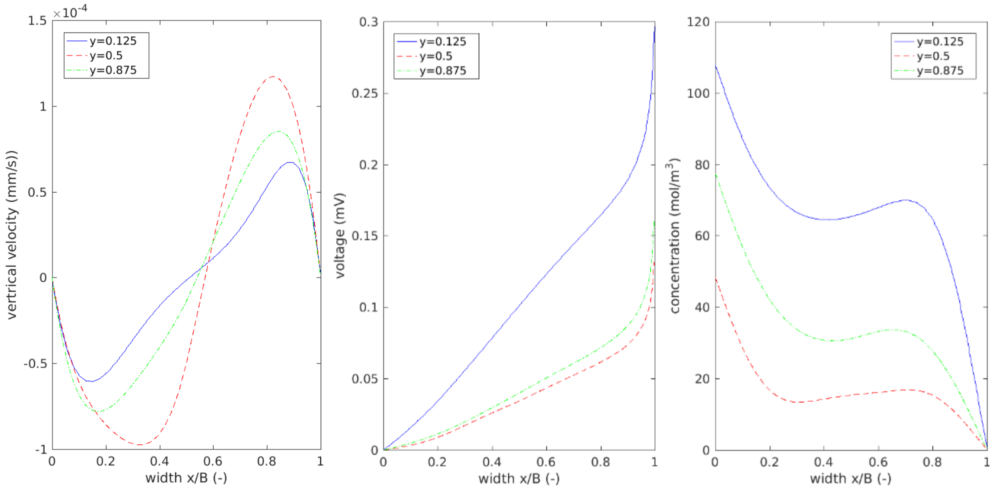

Figure 7: vertical velocity, electric potential and cupper concentration at 3 different heights, 0.125H, 0.5H, 0.875H with respect with the width of the cell at constant inlet velocity of 0.008mm/s

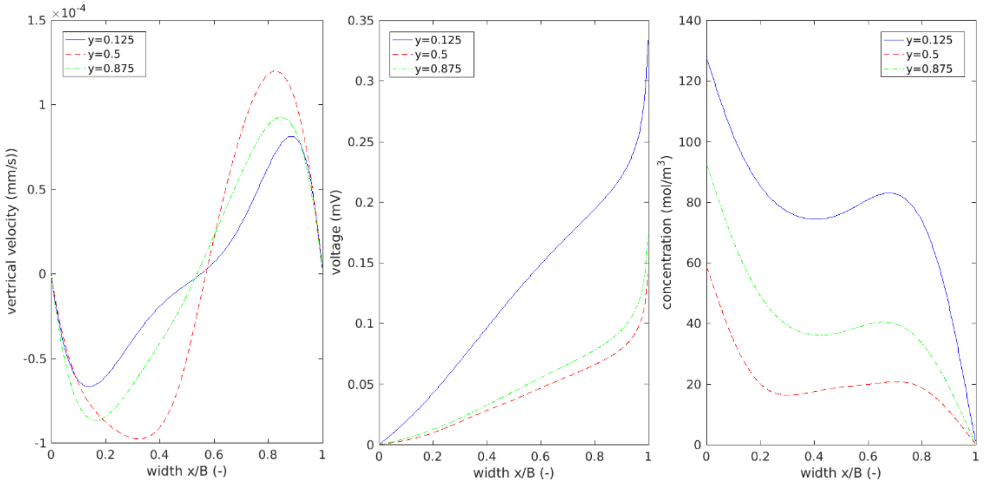

Figure 8: vertical velocity, electric potential and cupper concentration at 3 different heights, 0.125H, 0.5H, 0.875H with respect with the width of the cell at constant inlet velocity of 0.08mm/s

The local current density is highly coupled with the local copper-ion concentration due to the Botler-Volmer equation. Because the boundary concentration is higher at any spatial point with a higher inlet velocity we observe an increased current density as well.

The spatial dependence of the reaction rate on the cathode is shown in figure 10 for different inlet velocities and voltages. Very high current densities are observed at the bottom edge of the cathode. This is the result of two effects.

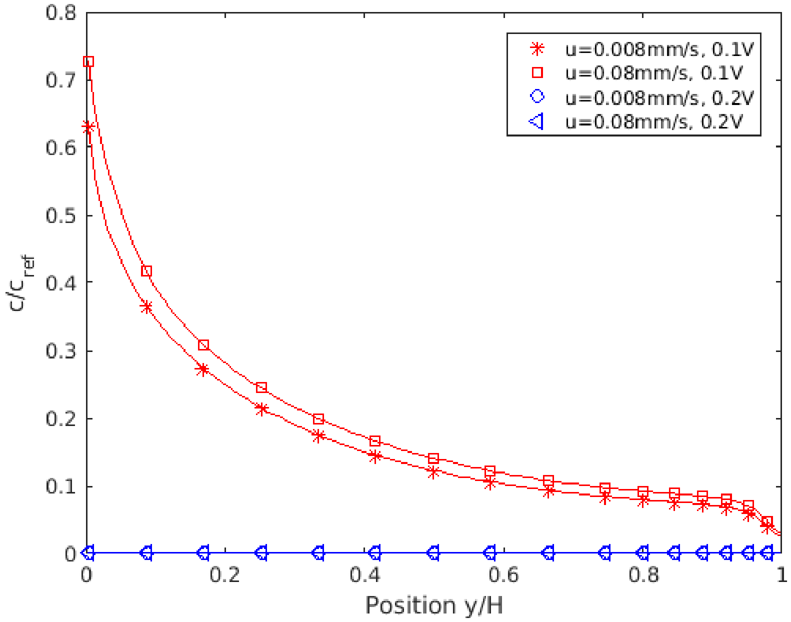

Figure 9: Cu concentration at cathode with respect to height for different inlet velocities 0.08mm/s, 0.008mm/s and different applied voltages: 0.1 ,0.2 V

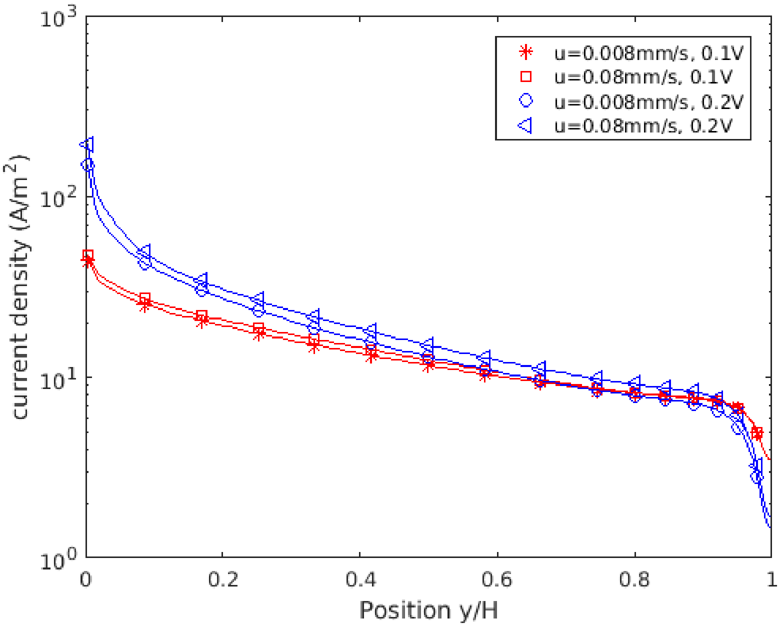

Figure 10: Spatial dependent current density at cathode for different inlet velocities 0.08 mm/s, 0.008 mm/s and different applied voltages: 0.1V, 0.2V.

- The incoming flow has the bulk concentration and no concentration boundary layer has been formed yet.
- Due to the small scale, ohmic resistance plays a minor role. Thus there is no significant reduction of the over potential η due to the flowing current.

High reaction rates at the bottom of the cathode at high applied voltages allows the boundary layer to grow much faster than with low voltages, leading to faster current density decrease beyond the starting point. At 0.1V the electrochemical reaction is much slower therefore the initial current density drop is weaker and the boundary layer forms more slowly. This results in more homogeneous current density distribution.

Towards the top, a second drop occurs. The upper wall prevents the natural convection from continuing further upward, thus the ionic transport is significantly reduced. The absence of natural convection at the top increases stratification as well, therefore we see the same drop at the same position 0.95 for current density and concentration. The incoming flow has a positive influence on the stratification within the cell. It keeps the same structure but at a slightly increased level, see figure 11.

An obvious result of consistent higher current densities occurring at higher current densities with higher inlet velocity is a higher overall performance of the entire cell, figure 12. The velocity specific increase at low values <0.01 mm/s is higher. Than the effect stagnates at higher velocities even though it sill increases. The limiting current density is reached at 0.2V. Applying a higher current results in a slightly higher current density over the cell.

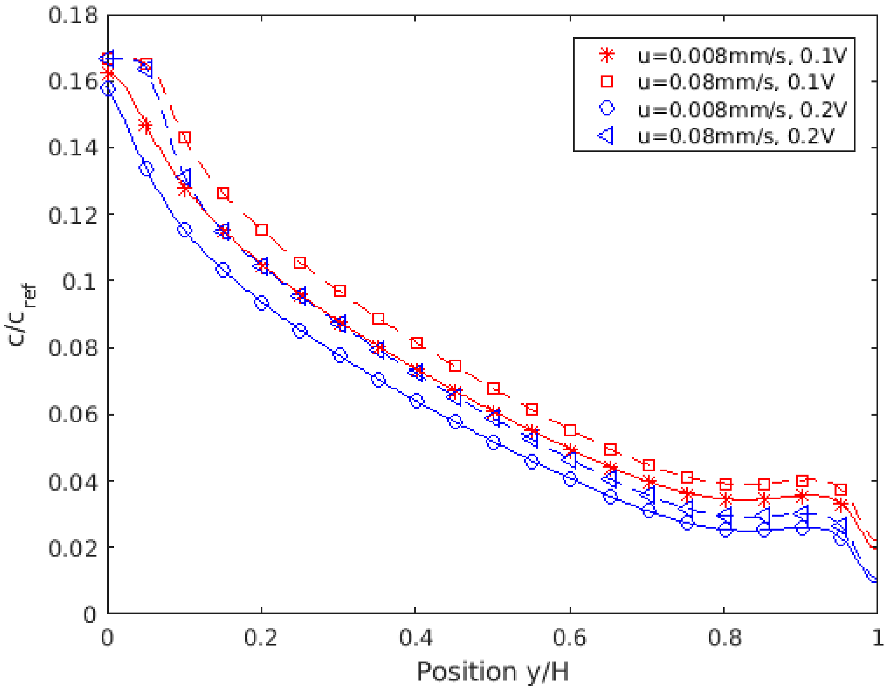

Figure 11: Spatial dependent Cu concentration at mid width for different inlet velocities 0.08mm/s, 0.008mm/s and different applied voltages: 0.1 ,0.2V

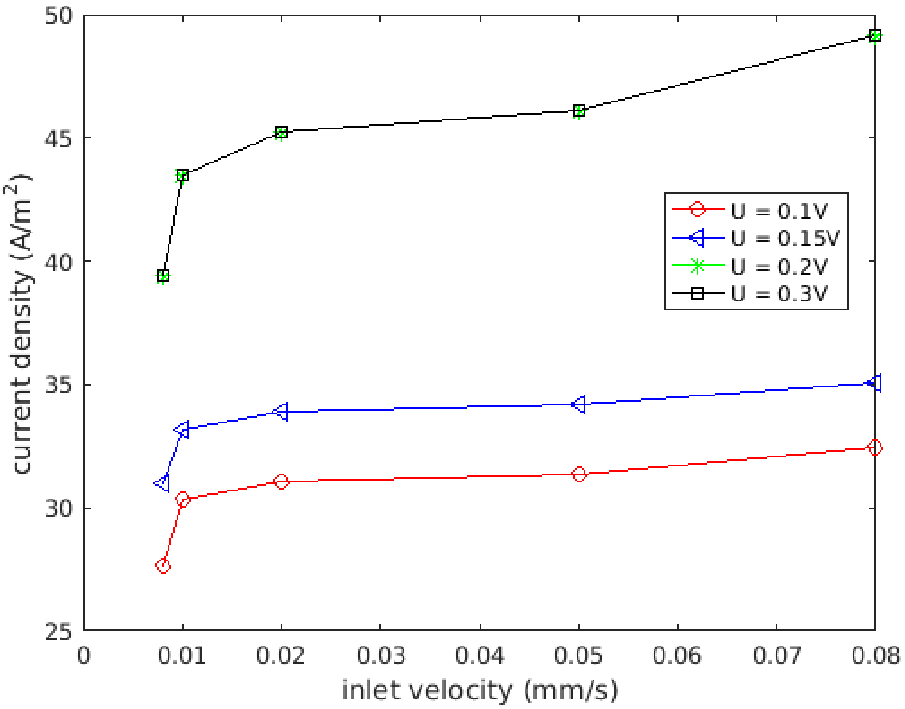

Figure 12: Overall performance of the electrochemical cell for different voltages and inlet velocities

4. CONCLUSIONS AND OUTLOOK

A numerical study on an electrochemical cell has been performed. In a first step the validity of the code was tested on a small electrochemical cell with a constant current density. The results agree with the data found in literature [1,2].

In the second step, the electrochemical reaction was considered in the model and an additional flow was introduced at the bottom facing towards the bottom edge of the cathode. With increasing magnitude of the incoming flux, the stratification of the cell is reduced and the ionic transport is increased. Both factors result in an improvement in both local and overall performance. Therefore, injecting an additional flow at the bottom of an electrochemical cell where natural convection dictates, increases cell performance. This holds true for small scale test cells and laminar flow conditions. No conclusion can be drawn for a full size industrial copper electrolysis process. Therefore, intense studies involving turbulent flow modelling are needed.

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NOMENCLATURE

c	*(mol/m³)*	Concentration
c_{ref}	*mol/m³*	Bulk concentration of the electrolyte
D	*m²/s*	Diffusion coefficient
F	*96485 sA/mol*	Faraday constant
j	*A/m²*	Current density
N	*mol/m²*	Ionic flux
P	*Pa*	Pressure
R	*8.314 J/molK*	Universal gas constant
s	*s*	Time
u	*m/s*	Velocity
z	*(-)*	Valency of an ionic species
α_a	-	Anodic transfer coefficient
α_c	-	Cathodic transfer coefficient
β	*m³/mol*	Densification coefficient
δ	*m*	Distance to the boundary cell center
ρ	*kg/m³*	Density
η	*V*	Over potential
Φ	*V*	Electric potential
κ	*S/m*	Electric conductivity