Electrical and Bubbly Flow Modeling of a Molten Salt Electrolysis Cell

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Abstract: A laboratory-scale electrolysis cell for the recovery of metals is simulated with COMSOL Multiphysics. Two models are implemented: an electrical model simulating the current density (reaction rate) distribution at the electrodes and a laminar bubbly flow model which solves for the electrolyte velocity induced by gas bubble production at the anode. A parametric study on the mesh refinement, the anode-cathode distance (ACD) as well as the bubble diameter (D_b) is carried out. Quite heterogeneous current distributions are simulated at the electrodes' surface, with strong edge effect at the cathode. At the anode, a more uniform current is however obtained when increasing ACD. The bubbly flow model suggests that significant electrolyte convective motions between the electrodes are favoured for small values of both ACD and D_b.

Keywords: Electrolysis, metal refining, electric modelling, bubbly flow.

1. Introduction

Electrolysis is a common electrochemical technique for gas production or metal recovery. In the latter process, the metal to be recovered is dissolved in an aqueous or a molten salt-based electrolyte and is deposited at the surface of an electrode when an electric current is prescribed to the cell [1].

Due to the high level of complexity of such processes, involving several physical phenomena that are strongly coupled to each other such as charge transfer, mass transfer, fluid dynamics, heat transfer and (sometimes) electromagnetics, the use of multiphysics simulation can be of great help to get insights into the underlying mechanisms. It can also be a predicting tool that can be used for optimising the design of an electrolysis cell [2-4].

In the present paper, we described an electrical and a computational fluid dynamics model of a newly developed lab-scale cell used for the recovery of metals in a molten salt electrolytic solution. For confidentiality reasons, the chemical composition of the electrolyte as well as the reactions taking place at the electrodes are not given. The influence of several parameters such as the mesh refinement, the anode-cathode distance or the gas bubble diameter on the numerical results are analysed.

2. Physics

2.1 Cell operation

The cell studied here is a lab-scale high-temperature electrolysis cell that can be used for the recovery of metals, alloys or rare earths. It works with a single compartment filled with a molten salt electrolyte, containing the species to be recovered and in which are immersed the anode and the cathode. The metal is being deposited as a solid or a liquid at the cathode surface while some gas evolves at the anode due to the molten salt decomposition. Bubble formation at the anode is the major source for electrolyte motions since very little natural convection is expected in this small-scale cell.

2.2 Geometry

The geometry of the cell studied here is 2D-axisymetric. It comprises a central cathode rod surrounded by a cylindrical anode, as depicted in fig 1. The anode-cathode distance (ACD) is a varying parameter of the model.
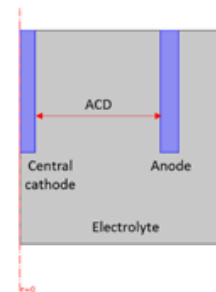

Figure 1. 2D-axisymetric geometry of the Cell

2.3 Electrical model

- Equation

The steady-state electrical behaviour of the cell is modelled under the secondary current approach, using the *Electrical Current* physics interface. The charge conservation equation is solved for in all domains:

$$\nabla . \vec{j} = 0$$

where $\vec{j}$ is the current density vector, which is expressed by the Ohm's law:

$$\vec{j} = -\sigma \vec{\nabla} V$$

where σ is electrical conductivity of the materials (electrodes and electrolyte) and V the electric potential.

- Boundary conditions

A normal current density, which is determined by the value of the total current I to be applied to the cell, is applied at the top boundary of the anode, while the potential V is set to zero at the top boundary of the cathode.

At the electrode/electrolyte interface, the faradaic current densities (j_A at the anode and j_C at the cathode) are defined by Butler-Volmer kinetics relations corresponding to the secondary current distribution theory:

at the anode/electrolyte interface:

$$j_A = i_{0(A)} (e^{\frac{0.5F}{RT}\eta_A} - e^{-\frac{0.5F}{RT}\eta_A})$$

at the cathode/electrolyte interface:

$$j_C = i_{0(C)} (e^{\frac{0.5F}{RT}\eta_C} - e^{-\frac{0.5F}{RT}\eta_C})$$

where $i_{0(A)}$ [resp. $i_{0(C)}$] is the exchange current density of the anodic [resp. cathodic] reaction, η_A [resp. η_C] is the anodic [resp. cathodic] overpotential, F is the Faraday's constant (= 96 485 C.mol^{-1}) and T the temperature.
The electrode overpotentials are defined by:

at the anode/electrolyte interface:
$$\eta_A = V - \phi - \Delta E^0$$

at the cathode/electrolyte interface:
$$\eta_C = V - \phi$$

where V and ϕ are the potential, taken at the electrode/electrolyte interface, of the solid phase and the liquid phase, respectively, and ΔE^0 is the difference in the standard potentials of the two reactions (= decomposition voltage).

2.4 Bubbly flow model

A transient bubbly flow model, implemented with the *Laminar Bubbly Flow* physics interface, simulates the electrolyte motions due to gas evolution at the anode. It consists in a diphasic laminar flow model for which the gas fraction is solved for together with the electrolyte velocity and pressure. The slip model is based on a pressure-drag balance with the hypothesis of small spherical bubble.

The three unknown to be solved are the liquid velocity u_l, the pressure p and the so-called "effective gas density" $\phi_g \rho_g$.

- Boundary conditions

Conditions of gas evolution and no slip condition for the liquid are set at the anode surface:

$$-n. N_{\rho_g \phi_g} = \frac{j_A M_g}{3F}$$

$$u_l = 0$$

j_A is the anodic current given by the Butler-Volmer expression, M_g is the molecular mass of the gas and F is the Faraday's constant, coefficient 3 in the denominator refers to 3 electrons being transferred in the anodic half-reaction to form a gas molecule and n refers to the normal vector of the surface.
A zero pressure reference is arbitrarily defined on a single point of the electrolyte surface and a tangential liquid flow is set all along at the top surface of the electrolyte.

A symmetry condition is defined on the symmetry plane of the half cell.

2.5 Resolution scheme

A unidirectional coupling between the electrical model and the bubbly flow model is assumed. In this approach, the electrical behaviour of the cell determines the electrolyte motions (the bubble

formation rate being determined by the value of the anodic current density j_A) but conversely the electrical model is not influenced by the bubbly flow model.

As a consequence, the steady-state electrical model is first computed, which gives the values of the potential throughout the cell as well as the value of the current densities. In a second step, the transient bubbly flow equations are solved for using the previously calculated j_A as input and considering an initial liquid velocity $u_l = 0$ everywhere. A quasi-steady state is reached after several tens of seconds, typically for t > 50 s.

This PDE system is solved with COMSOL Multiphysics 5.1.

2.6 Mesh
A triangular mesh is used (see figure 2) with a particular refinement at the interfaces between the electrodes and the electrolyte and at the top surface of the electrolyte where the liquid velocity is expected to be significant. In the bubbly flow model, the effect of the mesh refinement in these areas is assessed.
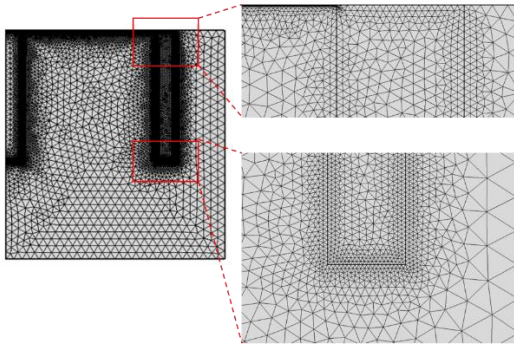

Figure 2. Meshing framework of the cell.

3. Results

3.1 Electrical Model

Figure 3 shows a current density mapping at the surface of the electrodes, for a given ACD value. At the anode, it can be seen that the inner part of the electrode (facing the cathode) is working at a higher current density than the outer part, due to ohmic drops. At the cathode, strong edge effects are observed at the bottom edge of the electrode.
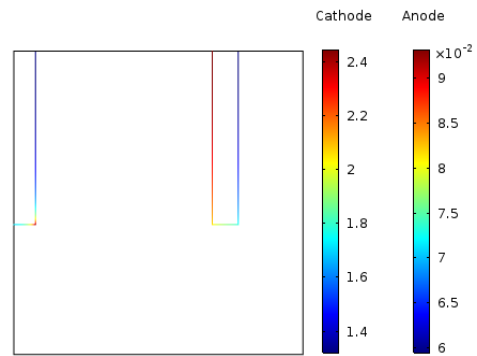

Figure 3. Current density (A.cm^{-2}) simulated at the electrode surface.

The variation of the current density along both electrodes' edges in the 2D-model are presented in figure 4 as a function of the anode-cathode distance. At the anode, the current is maximum at the top of the edge facing the cathode and decreases significantly when going down towards the bottom and then up along the opposite edge. The variation of current along the anode edges is more substantial for the shortest ACD values. For a higher ACD (75% higher), the average current density is significantly reduced at the anode, due to the larger surface area developed by the electrode in this configuration. At the cathode, as previously mentioned, the current distribution reveals a strong current peak located at the bottom edge. This edge effect is to be ascribed to the fast kinetics of the cathodic process associated with the metal deposition. For this electrode, however, the current profile is not influenced by the ACD value.
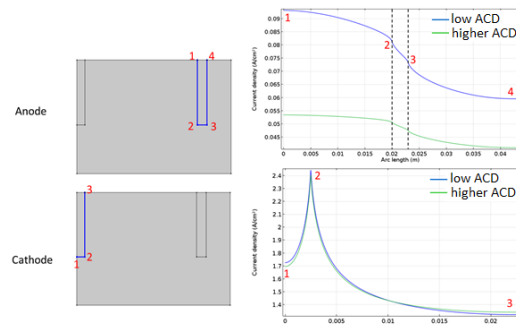

Figure 4. Current density variation along the electrodes, as a function of the anode-cathode distance.

3.2. Bubbly flow model

The influence of the size of the mesh elements located at the electrodes surface and at the surface of the electrolyte on the simulated liquid velocity arising from the anodic gas evolution was first assessed. Figure 5 shows the electrolyte velocity field u_l simulated under quasi-steady state conditions (t = 100 s) for three different mesh refinements. Even if the flow pattern remains the same in the three configurations, it can be observed that the local value of the electrolyte velocity varies significantly with the mesh element size. The use of smaller elements decreases the simulated velocity (see extremal values). When further refining the mesh, the velocity field remains stable. Hence, to avoid any numerical error, the influence of ACD as well as the bubble diameter was assessed using a significantly refined mesh as the one on the right-hand side of figure 5.
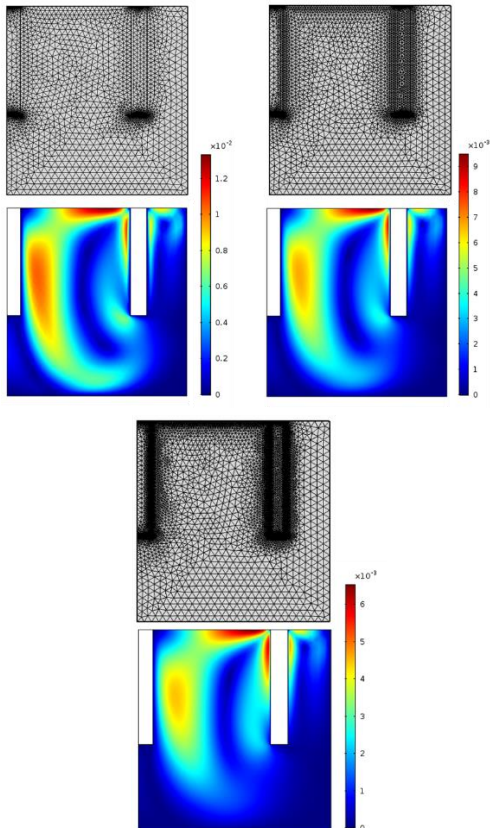

Figure 5. Influence of refining the mesh on the simulated electrolyte velocity field (values in m.s^{-1}). D_b = 1 mm.

The influence of the anode-cathode distance on the electrolyte velocity profile was then assessed, considering an average bubble diameter of 1 mm. Figure 6 shows the velocity field for two different values of ACD. Clearly, a small ACD favours the convective motions between anode and cathode where the electrolyte flows at a higher velocity. This is a result of both a confinement effect and the fact that the gas bubbles are released to a higher rate in the case of a small ACD due to a larger value of anodic current density j_A (see figure 4).
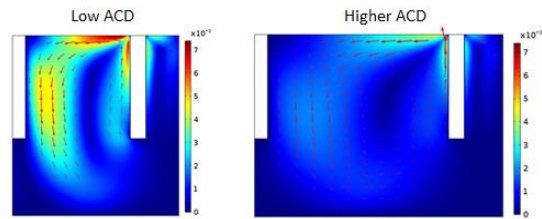

Figure 6. Electrolyte velocity field (m.s^{-1}) as a function of the anode-cathode distance. Average bubble diameter: 1 mm.

Finally, the effect of the average diameter of the bubbles released at the anode on the electrolyte velocity profile can be analysed in figure 7. The bubbles diameter ranges from 0.7 mm to 2 mm while the anode-cathode distance was kept constant. When larger bubbles are released, the average electrolyte velocity decreases significantly in the area between the electrodes, even if larger bubbles are expected to move faster towards the surface. When increasing Db, the volume fraction of gas is also decreased towards the electrodes and the number density are bubbles in the electrode vicinity is lower as compared to smaller bubbles. Therefore, even if the upward velocity of small bubbles is lower, their "dragging" effect on the surrounding liquid seems to be more efficient, leading to a higher overall velocity of the liquid phase.
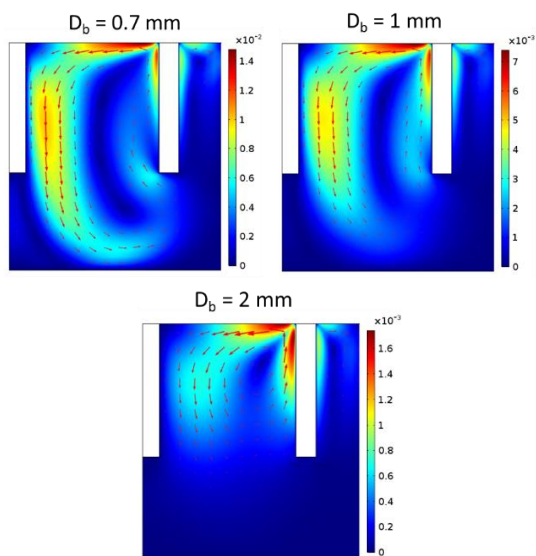
Figure 7. Simulated Electrolyte velocity field (m.s^{-1}) as a function of the average bubble diameter D_b.

4. Conclusion

In this paper, a lab-scale molten-salt electrolysis cell for the recovery of metals is studied with Comsol Multiphysics. Two physical aspects of the cell are investigated: charge transfer and fluid dynamics.

With a first electrical model, the current density distribution at the electrode surface is simulated as a function of the anode-cathode distance (ACD). It is found that the distribution varies significantly at the anode while it remains stable at the cathode, the latter being associated with strong edge effect.

In a second model, the electrolyte motions due to the anodic gas evolution is computed with a laminar bubbly flow approach, using the anodic reaction rate distribution calculated with the electrical model as gas inflow source. The bubbly flow model requires a fine meshing of the electrode and the electrolyte surface to avoid numerical error. The influence of both ACD and the average bubble diameter (D_b) on the dynamics behaviour of the electrolyte is assessed. It is found that the electrolyte convective motions between anode and cathode are favoured by small values of ACD and D_b. In practical applications, significant convection in the cell will be preferable for improving mass transport and avoiding transport limitation issues.

5. References

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6. Acknowledgements