

# SIMULATION OF THE BEHAVIOUR OF ANODE SLIME DURING COPPER ELECTROLYSIS

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Using the CFD–software package FIRE®, the fluid flow in a copper refining cell is calculated three dimensionally. The simulation is based on density variations in the boundary layer at the electrode surface. A transport equation for the copper concentration is solved in addition using a density/concentration correlation. Moreover, a two–phase–flow approach is developed, based on the „Discrete Droplet Model“ to simulate the behaviour of anode slime during electrolysis. Position, velocity and diameter of each anode slime particle are described. The actual inhibitor concentration in the cell is calculated, too. Calculations and experimental measurements are in good correspondence.

## 1. Introduction

Amongst all metallurgical processes, the hydro–electrolytical unit operation is one having the lowest specific production rates. Thinking about an intensification of electrolytical processes, the fluid flow in the electrolytic cell has to be improved. In literature only few experimental work and some calculations on miniature scale can be found. The current paper will present only a small part of our investigations [4, 5] to calculate the fluid flow field in a copper refining cell.

## 2. Principles of fluid flow, mathematical model and numerical solution

In a copper refining electrolysis cell there are two different kinds of convection – a forced convection and a so called natural convection. In all copper refining electrolysis plants electrolyte is pumped through the cell. Forced convection: the amount of pumped electrolyte is described to be 20 – 30 l/min when being defined as volume per time, or three hours when being described as time for changing the entire electrolyte volume of a cell. The natural convection arises because near the electrode the diffusion is the dominating process of mass transport (migration and convection can be neglected). Changes of concentration ( $\text{Cu}^{2+}$ ) in front of the electrode are directly related to corresponding density changes of the electrolyte. Due to the dissolution of copper at the anodes, the concentration and density is increased, which results in the characteristic down flow at the anode surface. At the cathode an upcoming flow can be observed due to the density and concentration decrease. The velocity is zero at the electrode surface, increases until a maximum is reached, then decreases again. The comparatively small region, in which the upward or downward flow occurs primarily, is called the hydrodynamic boundary layer. Similarly, the diffusion layer is defined as the region where the concentration is significantly different from that in the bulk. Ibl [1]

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describes the thickness of the hydrodynamic boundary layer to be 0.05 to 0.5 mm depending on a variety of complex parameters like current density, electrode height, chemical composition, viscosity and density of the electrolyte.

The described model of a copper refining electrolysis takes the density changes near the electrodes into account. To simulate the characteristic down/upward flow at the electrodes, the density in a small volume layer at the cathodic surface is decreased and increased at the anode surface. Although data about density variations near electrodes are hardly to be found in literature, one can estimate as a first assumption [2], that the density at the cathode/anode deviates about the same value, positive or negative, from the average electrolyte density, depending on current density and electrode height.

In the following calculations an average electrolyte density of  $1300 \text{ kg/m}^3$  is taken. The density deviation in the volume layer at the electrode surface was assumed to be 3.8 or 7.6 %, which means  $\pm 50$  or  $100 \text{ kg/m}^3$ . The thickness of this layer (after extensive parametric studies [5]) was assumed to be 0.24 mm.

Using the  $k\text{-}\varepsilon$  turbulence model, which assumes local isotropic turbulence, the influence of turbulence on the fluid flow was investigated. In the volume layer at the electrode surface, changes of the diffusion coefficient, viscosity and density as a function of the electrode height are neglected due to simplification.

The flow field of a fluid with the density  $\rho$  and the laminar viscosity  $\mu_l$  is described by the following two partial differential equations:  
the continuity equation

$$\text{div}(\rho \bar{u}) = 0 \quad (1)$$

and the momentum equation

$$\frac{\delta}{\delta t}(\rho u) + \text{div}(\rho \bar{u}u) = -\text{grad}p + \text{div}(\mu \text{grad}u) + Q_x \quad (2)$$

Equation (2) is a specific case of the overall transport equation, where  $\bar{u}$  is the velocity vector,  $u$  the velocity component in  $x$ -direction,  $p$  the pressure and  $Q_x$  the source term. Due to the turbulent nature of the flow, a turbulent viscosity is added to the laminar viscosity according to the „eddy-viscosity“ concept, which is calculated by means of a turbulence model.

The interaction of the fluid with the solid phase is taken into account by modified source terms in the transport equations. The simulation of anode slime particles is based on the Discrete Droplet Methodology, in which the slime particles, their position, velocity, mass and temperature are described by Lagrangian ordinary differential equations, expressing the conservation laws

$$\frac{dx_{iParticle}}{dt} = u_{iParticle} \quad (3)$$

$$\frac{du_{iParticle}}{dt} = \frac{3}{4} \cdot C_D \cdot \frac{\rho_{Gas}}{\rho_{Particle}} \cdot \frac{1}{D_{Particle}} \cdot (\bar{u}_i - u_{iParticle}) \cdot |\bar{u}_i - u_{iParticle}| + \left(1 - \frac{\rho_{Gas}}{\rho_{Particle}}\right) g_i + R_i \quad (4)$$

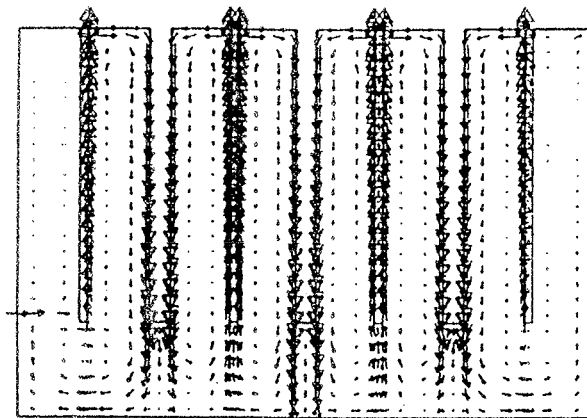
where  $x_{i\text{particle}}$ ,  $u_{i\text{particle}}$ ,  $u_i$ ,  $g_i$ ,  $R_i$  are particle position and velocity, gas velocity, body force and source vectors,  $\rho_{\text{Gas}}$  and  $\rho_{\text{Particle}}$  are densities,  $D_{\text{Particle}}$  is the diameter and  $c_D$  the drag coefficient. The source vectors containing terms like pressure gradient, Basset and Magnus forces, are ignored.

For the numerical solution of the particle equations a Lagrangian two-phase flow model is implemented in the general CFD-package FIRE®, developed by AVL LIST GmbH, Graz, Austria. For the calculations a geometric model of an electrolytic cell was chosen, from which the dimensions and qualitatively the fluid flow field were known from literature [3]. The dimensions were: cell: 0.35 x 0.21 x 0.25 m, 3 anodes: 0.19 x 0.19 x 0.012 m, 4 cathodes: 0.19 x 0.19 x 0.005 m. The interpolar distance was assumed to be 3.7 cm. The volume mesh which was used for the present calculations had around 30000 cells.

## 2. Results and Discussion

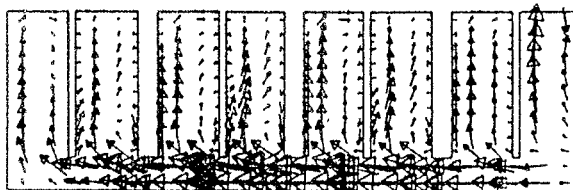
### 2.1. The fluid flow field in a copper refining electrolysis cell – transverse flow principle

In fig. 1 a vertical cut through the symmetric middle plane can be seen. As visible in fig. 1, the electrolyte at the anode surface having a higher specific density flows downwards, whereas electrolyte having a lower specific density at the cathode surface flows upwards. This describes the characteristic flow pattern of natural convection during electrolysis. The velocity near the electrodes is 2 – 3.5 cm/s, which is about 10 times higher than elsewhere in the cell.



*Fig. 1, Vertical cut through the middle of the cell; 0.3fold electrolyte circulation per hour;*

$$\rho_{\text{boundary layer}} = 1200/1400 \text{ kg/m}^3; \rho_{\text{electrolyte}} = 1300 \text{ kg/m}^3$$



*Fig. 2, Horizontal cut;  $v_{\text{max}} = 0.5 \text{ cm/s}$ ; 0.3fold electrolyte circulation per hour;*

$$\rho_{\text{boundary layer}} = 1200/1400 \text{ kg/m}^3; \rho_{\text{electrolyte}} = 1300 \text{ kg/m}^3$$

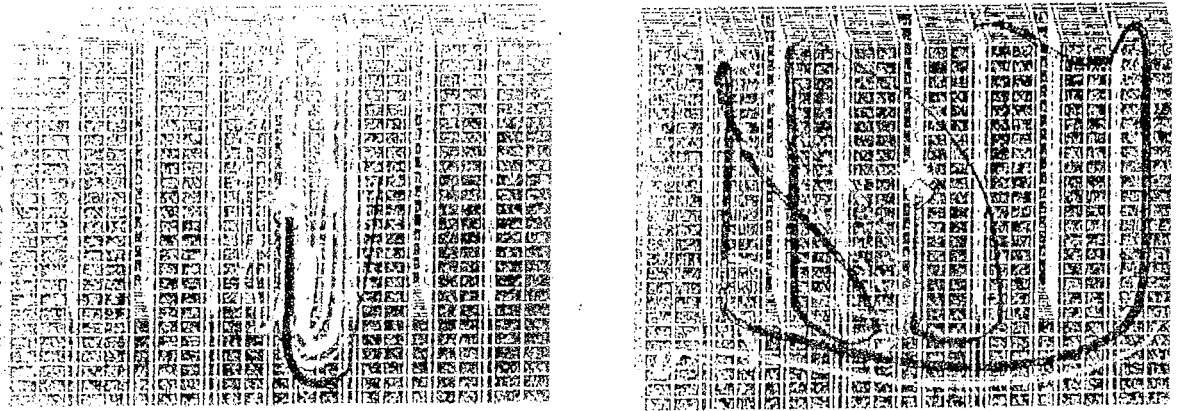
For this calculation the change of the electrolyte for the entire cell volume of a cell is achieved within three hours, which is common industrial practice. The natural convection dominates the general flow field, and the downwards flow at the anodes continues in the area below the electrodes. Because of the low velocity level ( $< 0.1$  mm/s) in this area, the collection of anode slime should be possible. As fig. 2 shows in a horizontal cut (16 cm above the cell bottom), the major part of incoming electrolyte directly flows along the side wall of the cell to the outlet. Due to the high velocities near the wall, the electrode space is supplied by fresh electrolyte.

A parametric study [5] reveals that beginning at two electrolyte circulations per hour the concentrated bottom layer of electrolyte is destroyed. Hein et al [3] found this behaviour at 2.2 electrolyte circulations per hour. From previous investigations it seems that a considerable decrease in thickness of the hydrodynamic boundary layer is hardly possible by increasing the flow rate of electrolyte. In order to get a significant increase of the limiting current density, the arrangement of the electrolyte in/outlet should eventually be changed.

## 2.2. Anode slime

The general fluid flow field in the cell determines the behaviour of anode slime, which is generated during the electrolytic process, to a great extent. Depending on the chemical anode quality, a particular portion of generated slime remains at the anode surface, another portion can be found at the cell bottom. Whereas coarse particles reach the cell bottom more easily, colloidal particles ( $< 1$   $\mu\text{m}$ ) can float towards the cathode. Afterwards, these particles mechanically or cataphoretically can be comprised into the cathodic copper deposit. A collection of the anode slime at the cell bottom – as practised industrially today – should give a high yield of precious metals, but should also prevent that anode slime particles reach the cathode surface. In the following section the way of slime particles having an infinite small mass are traced throughout the cell by integrating the fluid flow field according to  $v_i = dx/dt$ . Although this method only is a rough assumption, it shows the behaviour of anode slime during electrolysis in an illustrative way.

In fig. 3 tracing curves of three particles, generated at the half electrode height, are presented. For the calculations a conventional cell was chosen. The tracing curves at first are dominated by the down coming flow at the anode surface, thereafter they immediately turn into the electrode space. From this it can be seen how easily anode slime particles can float to the cathode surface and how they can be comprised into the metal deposit as impurities. Increasing the volume flow rate of the electrolyte, the flow – especially in the area below the electrodes – is enhanced, which can also be seen from the particle traces in fig. 3 right. At first the tracing curves follow the downcoming flow near the anode surface, afterwards the slime particles are raised and float through the entire cell.

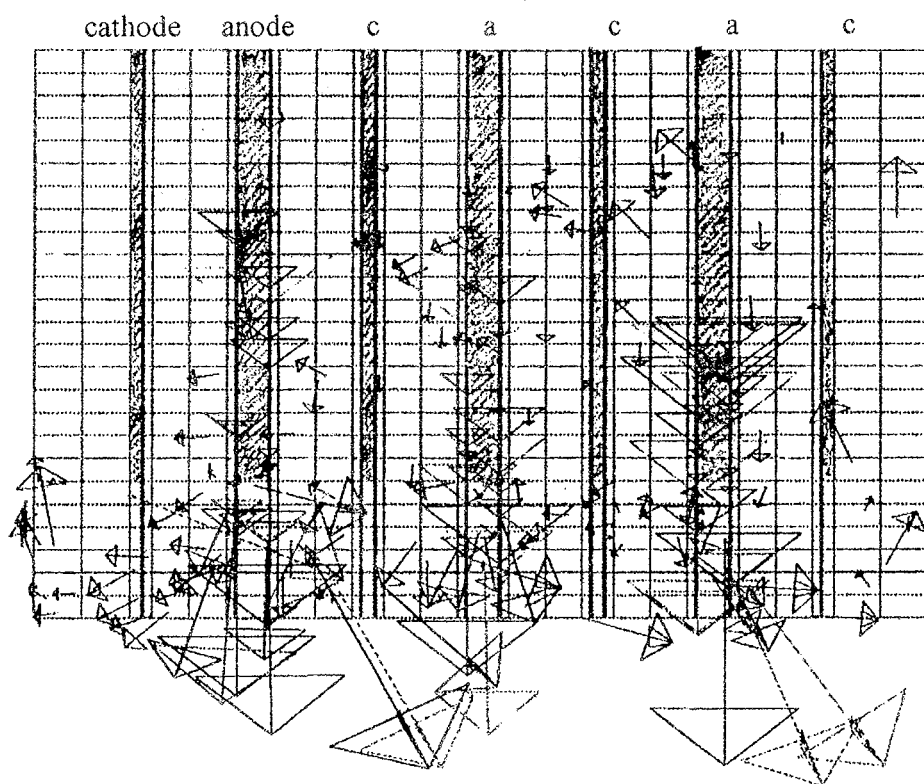


*Fig. 3, Particle traces of anode slime particles, left: cell type having 0.3 electrolyte circulation per hour, right: 10 electrolyte circulation per hour*

As a first example of the two-phase-flow calculations, where the anode slime is included as solid particles, particle vectors of the anode slime are presented. For these calculations the following simplified assumptions were applied:

- A Gaussian normalised particle distribution of anode slime between 0.5 and 70  $\mu\text{m}$  was used; the average particle diameter was 35  $\mu\text{m}$ .
- The slime particles were generated accidentally over the whole anodic surface.
- The amount of generated slime was set to 1% of the anode weight assuming an anode life time of 22 days.
- The density of the particles was fixed to 5600  $\text{kg}/\text{m}^3$ .

Fig. 4 represents a conventional cell type having an electrolyte circulation rate of 0.3 per hour (fluid flow of electrolyse, see fig. 1). Looking at the velocity vectors of the anode slime particles it can be seen, that small colloidal particles ( $< 3 \text{ mm}$ ), having velocities of 0.1 – 0.2  $\text{mm}/\text{s}$ , are floated towards the cathodic surface and can easily be comprised as impurities in the cathode copper. Bigger slime particles – e.g. agglomerates  $> 40 \mu\text{m}$  – settle down at the cell bottom where they can be collected. Only a few particles are carried out of the cell through the electrolyte outlet.



*Fig. 4, Velocity vectors of anode slime particles in a conventional cell;  
0.3 electrolyte circulation per hour;  $v_{max} = 0.05$  cm/s*

### 3. References

- [1] N. Ibl: Die Rolle des elektrolytischen Stoff- und Ladungstransportes in der Elektrometallurgie. *Erzmetall*, Vol. 22 (added issue), 1969, p. 87–98
- [2] F. Alavyoon: Unsteady Natural Convection and Mass Transfer in Copper Electrolysis with a Supporting Electrolyte. *Electrochimica Acta*, Vol. 37, 1992, p. 333–344
- [3] K. Hein, H. Starszinzky, D. Schab: Strömungsbedingungen in Elektrolysezellen für die elektrolytische Kupferraffination. *Neue Hütte*, Vol. 18, 1973, p. 346–352
- [4] A. Lackner, G. Schmidt, P. Paschen: Strömungssimulation in einer Elektrolysezelle. *Metall*, Vol. 49, 1995, p. 788–794
- [5] A. Lackner, K. Pachler, P. Paschen, K. Hein: CFD–Simulation of Copper Electrolysis – a Way to a New Cell Design. *Proc. of the Symp. on CFD and Heat/Mass Transfer Modelling in the Metallurgical Industry*, Montreal, Canada, 25.–29.8.1996, ed.: Argyropoulos, S., CIM, Canada, p. 293–304