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Modeling the process of convective mass transfer in a tubular electrochemical reactor

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Abstract. The model, describing a processes of convective masstransfering in a tubular electrolytic cell with the much distinguishing sizes of electrodes is proposed suitable for practical calculations.

The electrochemical reactor permitting to clearing of water with the help of chemical reactions in bulk of a solution at participation of electrogenerated reagent is created.

Key words: modeling, tubular electrolytic cell, convective masstransfering, electrolysis of water, convection flow, convection in the vertical cylinder, modeling in Ansys Fluent.

Introduction

Electrochemical methods of water purification [1], the use of which is considered to be promising [2], are of particular interest in the water treatment areas of power generating objects [3]. Their advantage is the absence of secondary contamination of the treated water with ballast ions, the ability to carry out due to the electrolysis products decarbonization and disinfection of water, as well as the simplicity of hardware design and the possibility of automating the process through the use of Programmable Logic Controller.

For the electrolysis of water is usually used diaphragm (or membrane) electrolysis (DE), allowing for the separation of interelectrode spaces to carry out a variety of processes at the cathode and anode, adjust the pH in the cathode and anode chamber. DE can be operated in continuous operation for a relatively short time, then the diaphragm (membrane) is clogged with poorly soluble electrolysis products (hydroxyl compounds of multicharged ions). This leads to additional energy costs and causes the process to stop.



In addition, non-diaphragm electrolyzers – electrocoagulators (EC) are used to pre-purify water, in which dissolution of the anode takes place, followed by the formation of poorly soluble products with good coagulating ability. EC, working in a continuous mode, require special preparation of incoming water (preliminary pH change). In this regard, the task arises to develop an adequate model of the electrolyzer, which can combine the advantages of DE and EC, but does not have the above disadvantages.

The search for ways to intensify and improve the energy efficiency of the process of electrolysis of aqueous solutions involves the use of hidden possibilities. One of the approaches that can significantly change the ratio and parameters of the cathode and anode processes is the manipulation of the current density value. This approach can be implemented by using a geometric factor.

Let us consider the case of a tubular coaxial, diaphragmless electrochemical reactor with a significant (by 2-3 orders of value) difference in the area of the electrodes. The central thin cathode electrode is made of stainless steel wire grade 95X18, the outer electrode of larger area is a cylinder made of aluminum grade A95. The choice of such cell design is due to the axial symmetry of the electric field. At the same time, due to the significant difference in areas, the current density at the electrodes is also significantly different. Therefore, the process speed at the central electrode – cathode, will be much greater than the process speed at the external electrode – anode. In all further considerations, we assume that the reactor has a vertical orientation and a tubular shape, while the length (height) of the cell is much larger than its diameter.

The electrolytic cell is filled with a background electrolyte; the current of the electrolysis is close to the limit currents (i_{LIM}) of mass transfer [4]. In the presence of a background electrolyte, ions of which are present in excess compared to substances involved in electrode reactions, their migration in the electric field can be neglected. It is obvious that in this case mass transfer will be determined primarily by convective diffusion.

After switching on the electric current, at the initial stage of the process (time $\tau < 10$ s), the change in concentration determines the diffusion to the cathode. During the electrolysis, the gradient of the charge carrier concentration decreases and the diffusion current decreases. At the same time, the thermal convection caused by the heating of the solution near the central electrode is enhanced. The thermal convection flows, pushing the OH^- ions away from the cathode, are directed from the center to the periphery. At some point in time, the diffusion and convective flows have the same order, and then the convection process prevails. According to the published data [4-6], after a certain period of time, in the cell a stationary regime with a constant current intensity is established. The concentration of the reactant at the outer boundary of the diffusion layer is equal to the concentration inside the electrolyte ($C = C_0$) and is constantly maintained by convection currents that exist even in an unmixable liquid. After establishing a stationary mode of supplying the reactant to the electrode, the current does not change in time, but is determined only by the applied voltage. The entire volume of the fluid can be divided into two areas: a small area along the central electrode, inside which there is a rapid change in the concentration of the electrolysis products (the boundary diffusion layer of Levich) and the rest of the volume of the apparatus – the area of constant concentration (the Prandtl hydrodynamic layer).

Longitudinal convection

To create an adequate picture of the ongoing process, the diffusion model is taken as a basis. We

assume that the flow structure is described by an expression similar to the equation of molecular diffusion [5,6]. The parameter of the model is the coefficient of longitudinal mixing D_A .

When considering convective processes, it can be excluded from consideration the upward flow, adjacent to the central electrode and due to the heating of the electrode [7,8] and the bubbling effect due to the release of hydrogen. In our case, convection and diffusion are directed in one direction and the equation for the concentration C in the longitudinal direction, along the z axis (1):

$$\frac{\partial}{\partial t} C(z, \tau) = D_A \frac{\partial^2}{\partial z^2} C(z, \tau) + V_C \frac{\partial}{\partial z} C(z, \tau), \quad (1)$$

where: D_A – coefficient of longitudinal (axial) mixing; V_C – velocity of convective flow, τ – time.

Set the initial and boundary conditions. At the initial time, the concentration of the reaction product (OH^- -ions) at the central electrode 10^{-7} mol/l, so that $C(z, 0) = 10^{-7}$. The first boundary condition is the ratio $C(\infty, \tau) = 10^{-7}$ mol/l. Both of these values are very small, so with a good approximation we can assume that $C(z, 0) = C(\infty, \tau) = 0$.

The second boundary condition is the dynamics of concentration change on the surface of the «solution-air» section ($z = 0$; z axis is oriented along the electrodes axis) in accordance with the equation (2):

$$C(0, \tau) = C_0 (1 - \exp(-k\tau)), \quad (2)$$

where: k – the rate constant of the electrode reaction, depending on the time τ .

Applying the Laplace transform to the equation (2) with the above initial condition, we obtain its solution (3):

$$C(z, \tau) = C_0 \cdot e^{\left(-\frac{V_C}{D_A} z\right)} \left(1 - e^{(-k\tau)}\right). \quad (3)$$

Radial convection

Equation (3), presented above, describes only the longitudinal component of the reaction product movement along the tubular reactor. In this case, it is advisable to consider its radial movement near the external electrode. Due to the complexity of the equation solution, taking into account the cylindrical geometry, we are content with a simplified case.

To describe the radial change in concentration, we make the following assumptions. Let us distinguish in a cylindrical volume of small height (the concentration change in height Δh in the first approximation is not taken into account) an area in the form of a thin parallelepiped between the axial and peripheral electrodes, to reduce the problem to the one-dimensional case. From the general equation of convective diffusion we obtain the following equation for the plane case (4):

$$v \frac{dc}{dr} = D \frac{d^2c}{dr^2}. \quad (4)$$

In order to simplify, the exact solution can be replaced by an approximate one, if one considers that, according to the conditions of the problem, $100 \cdot r_0 < R$, where r_0 is the diameter of the cathode wire, R is the diameter of the cylindrical anode (5):

$$c = c_0 \left(1 - e^{\frac{v}{D}(r-R)} \right). \quad (5)$$

We take into account the following assumptions in order to simplify: the fluid is incompressible and stationary (the Peclet number proportional to the velocity of the fluid is small ($Pe \ll 1$) or equal to zero).

Under the condition $v / D > 5 / r$, the exact solution differs from the approximate (5) by not more than 1%. We calculate the average concentration of the reaction product by volume (6):

$$\bar{C} = \frac{\int_0^R (2\pi r) \cdot c \cdot dr}{\pi R^2}, \quad (6)$$

where c – the concentration calculated by the formula (5). As a result of integration, we obtain an expression for the average concentration by volume (7):

$$\bar{C} = c_0 \left(1 - \frac{2D}{vR} + \frac{2D^2}{v^2 R^2} - \frac{2D^2}{v^2 R^2} e^{-vR/D} \right). \quad (7)$$

Consider the dependence of C on v , taking into account the restrictions introduced in the derivation of formula (5) and assuming that v is numerically greater than D . It follows from (7) that the dependence is a monotonically increasing function and for large values ($v/D > 10$) the concentration is $\rightarrow 1$. Obviously, even an insignificant increase in the convection velocity will help fill the volume of the cell with the product of the electrochemical reaction occurring on the central electrode, as confirmed by experiment [2].

FEM modeling in ANSYS

To obtain an analytical expression for convective heat and mass transfer, it is necessary to integrate the Navier-Stokes equations system, describing fluid hydrodynamics and heat transfer in it. Even with significant assumptions, this is possible only in a few simple cases. Therefore, for numerical solution of the problem of velocity distribution and convection visualization, one can use the finite element method (FEM) simulation in ANSYS.

There are two solvers for hydrodynamics problems – ANSYS CFX and ANSYS FLUENT. The main differences are in the way of integrating the equations of fluid flow and in strategies for solving equations. The ANSYS CFX solver uses a finite element grid (numerical values at grid nodes), similar to those used in strength analysis, to sample the area. Unlike ANSYS CFD, the ANSYS FLUENT solver uses a finite volume grid (numerical values at the centers of the grid cells). ANSYS FLUENT offers several approaches to the solution (density-based method, split pressure-based method, conjugate pressure-based method). In ANSYS CFX, special emphasis is placed on solving the basic equations of motion (conjugate algebraic grid).

In our case, the geometric model is created in AutoCAD and then imported into ANSYS-19.

We define the boundary conditions for the case of free convection. In the menu, select the adhesion condition "No Slip", the slip condition "Specified Shear", set the heat flux "Heat Flux " on the respective sides. In the "Reference Value" menu, the initial values of some parameters are set: density, viscosity, temperature.

Figure 1 shows the simulation result of velocity distribution of convective flow (vertical arrangement of the reactor, an aqueous solution of electrolyte, the steady-state mode).

When interpreting the results, it should be taken into account that in the case of an increase in the intensity of the process, the real flow studied in the experiment can lose axisymmetry, but in two-dimensional calculations we are based on the axisymmetric condition.

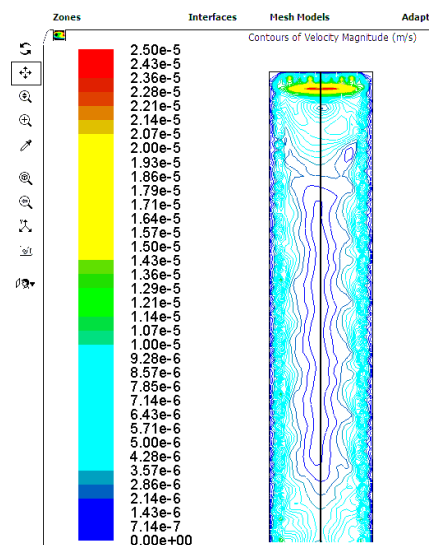


Figure 1. Simulation in ANSYS of velocity distribution of convective flows

It can be assumed that the flow rates are numerically equal to the mass transfer coefficient, with the dimension $\text{m/s} = (\text{mol/s})/(\text{m}^2 \cdot \text{mol/m}^3)$, where mol/s is the mass transfer rate, m^2 is the mass transfer area, m^3/mol is the molar concentration.

From figure 1 it can be seen that due to the convective mixing in a diaphragm-free cell, the

electrolysis products almost completely fill the volume of the apparatus, which increases the efficiency of the apparatus. This distinguishes this scheme from traditional electrolyzers with the same area electrodes separated by a semipermeable membrane, where this effect is not observed due to carrier recombination and the presence of a diaphragm.

Summary

The above model was used by us in substantiating the efficiency of using a tubular coaxial membrane-free electrolysis cell for the electrolysis of water in order to purify it and explanation of occurring processes. When passing through the electrolyzer of the initial solution, we obtain a solution enriched with hydroxyl or hydrogen ions generated on the internal electrode. This is due to the fact that the solution enriched with the reaction products on the internal electrode and occupying almost the full volume of the cell, will be in turbulent motion and easily removed, and the solution saturated with the reaction products on the external electrode forms a laminar layer, which has an extremely low velocity (it is practically immovable and remains at the surface and in the irregularities of the external electrode).

Thus, the proposed approach makes it possible to purify water with the help of chemical reactions in the entire volume of the solution with the participation of an electrogenerated reagent, which is possible due to the hydrodynamic regime realized primarily due to the geometric configuration of the electrodes and the absence of a diaphragm.

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