

A Mass Transfer Study with Electrolytic Gas Production

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1. Introduction

In general, tall vertical electrolyzers are used industrially to produce only gases like chlorine, hydrogen and oxygen, or gases and products such as soda and chlorine. Moreover, these electrolyzers usually have a very short cathode-anode distance and often operate under forced convection. For many electrochemical processes mass transfer in electrolytic cells, in particular to electrodes, must be optimized to operate economically. Many electrochemical reactions involve a gaseous component and a great deal of research has been devoted to the study of the specific features of these reactions. Three main areas have been investigated such as: the bubble formation (Chirkov & Psenichnikov, 1986), the mass transfer and hydrodynamic instabilities at gas-evolving surfaces (Kreysa & Kuhn, 1985), and the behavior of gas in porous electrodes in fuel cells (White & Twardoch, 1988). Many works were developed up to the present about gas-evolving electrodes (St-Pierre & Wragg, 1993a, 1993b; Vogt, 1979, 1984a, 1984b, 1984c, 1989a, 1989b, 1992, 1994, 1997; Czarnetzki & Janssen, 1989; Boissonneau & Byrne, 2000; Ellis et al., 1992; Janssen et al. 1984; Lastochkin & Favelukis, 1998; Wongsuchoto et al., 2002; Buwa & Ranade, 2002; Gabrielli et al., 2002; Correia & Machado, 1998; Lasia, 1998; Iwasaki et al., 1998; Fahidy & Abdo, 1982; Lasia, 1998, 1997; Barber et al., 1998; Eigeldinger & Vogt, 2000; Solheim et al., 1989; Elsner & Coeuret, 1985; Dykstra et al., 1989; Khun & Kreysa, 1989; Lubetkin, 1989; Martin & Wragg, 1989; Lantelme & Alexopoulos, 1989; Gijsbers & Janssen, 1989; Chen, 2001; Lasia & Rami, 1990; Kienzlen et al., 1994; Saleh, 1999; Janssen, 1978) but, few data on mass transfer with different cathode geometries under flow-by or flow-through electrolyte conditions with gas-evolving have been studied (Fouad & Sedahmed, 1974; Rousar et al., 1975;; Janssen & Barendrecht, 1979, Mohanta & Fahidy, 1977; Sedahmed, 1978; Sedahmed & Shemilt, 1981; Elsner & Marchiano, 1982; Albuquerque et. al., 2009). This chapter does not intend to explore in detail the mechanism during the bubbles formed electrolytically but only show an comparative study about the effect of hydrodynamic condition over mass transfer gas-electrodes for two cathodes geometries, during the hydrogen production at chlor-alkali cell by diaphragm process in laboratory scale.

2. Mass transfer

In general, it is necessary to consider three basic mechanism to the mass transfer in electrochemical systems, : migration, convection, diffusion and reaction.

Migration is the movement of charged species through the electrolyte due to a potential gradient; the current of electrons through the external circuit must be balanced by the passage of ions through the solution between the electrodes (both cations to the cathode and anions to the anode). It is, however, not necessarily an important form of mass transport for the electroactive species, even if it is charged. The forces leading to migration are purely electrostatic and, hence, do not discriminate between types of ions. As a result, if the electrolysis is carried out with a large excess of an inert electrolyte in the solution, this carries most of the charge, and little of the electroactive species O_x (oxidized specie) is transported by migration, i.e. the transport number (Bockris & Reddy, 1977) O_x is low.

Convection is the movement of a species due to fluid dynamic forces. In practice, these forces can be induced by stirring or agitating the electrolyte solution or by flowing it through the electrochemical cell. Sometimes the electrode can be moved (e.g., rotating disk electrodes). When such forms of forced convection are present, they are normally the predominant mode of mass transport. By the other hand, natural convection can arise from small differences in density, temperature or gases caused by the chemical change at the electrode surface. The treatment of mass transport, highlights the differences between laboratory experiments and industrial-scale electrolyzers. As is pointed out by (Pletcher & Walsh, 1993), the need in an industrial cell is only to promote the desired effect within technical and economic restraints and this permits the use of a much wider range of mass transport conditions. In particular, a diverse range of electrode-electrolyte geometry and relative movement are possible.

Diffusion and reaction. Diffusion is the movement of a species down a concentration gradient and it occurs whenever there is an electrical charge exchange at a surface. An electrode reaction (generally fast reaction) converts starting material to product, e.g.;



where O_x and R_{ed} are the oxidized and reduced species respectively, hence close to the electrode surface there is a (concentration) boundary layer (up to 0.01mm thick) in which the concentration of O_x is lower at the surface than in the bulk solution while the opposite is the case for R_{ed} and, hence, O_x will diffuse towards and R_{ed} away from the electrode.

Fundamental mass transport studies in industrial electrolytic cells are dependent of the fluid dynamic or by the inertial and viscous forces. This ratio is given by the well-known Reynolds number Re , calculated from the Equation:

$$Re = \frac{\rho L v}{\mu} = \frac{L v}{\nu} \quad (2)$$

where ρ is the density of the solution, μ its dynamic viscosity, ν its kinematic viscosity, v a mean flow velocity and L a characteristic length (for example, the length of a flat plate electrode). At higher Reynolds number, the viscous damping is no longer predominant and turbulence increase, by the other hand, any obstacles to fluid flow, or roughness in the electrolytic cell will can cause the commencement of turbulence or micro-turbulence at lower Reynolds number. In a particularly case of electrolytic cell with gas production, the Reynolds number can be obtained by the following Equation:

$$Re^* = \frac{V_g \cdot d}{A \cdot \nu} \quad (3)$$

where d is the bubble detachment diameter (m), A the electrode area (m^2) and V_g is the volumetric flow rate of gas bubbles ($m^3.s^{-1}$), defined as;

$$V_g = RTj/nFP \quad (4)$$

where R ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$) is the gas constant, T the absolute temperature (K), j the current density of electrolysis ($A.m^{-2}$), n the estequiometric number of electrons, F the Faraday constant ($96,485 \text{ C.mol}^{-1}$) and P the pressure (atm).

Natural or forced turbulence in electrolytic cells is usually advantageous since the eddies both increase mass transport of the electroactive species to the electrode surface and promote the exchange of species between the bulk solution and the boundary layer, minimizing local pH and other concentration changes due to the electrode reaction. It is not uncommon to introduce insulating nets, bars or other structural features into the cell to act as turbulence promoters. By the other hand, the morphology of the electrode surface can act as turbulence auto-promoter (e.g. mesh, reticulated metal, particulate bed, fibrous material).

2.1 Sherwood number

The Sherwood number is a measure of the rate of mass transfer, k_d , which is usually calculated in electrolytic cells from the limiting current density j_L for several cells and electrodes configurations under specific hydrodynamic conditions, i.e., the potential of the electrode is held at a value where all the electroactive species reaching the surface undergo the electrode reaction. The Sherwood number can be obtained using the relationship:

$$Sh = \frac{k_d L}{D} = \frac{j_L L}{nFC^\infty D} = f \quad (5)$$

laminar or turbulent flow
 fluid properties
 temperature
 cell configuration
 structure and active area of the electrode

where L (m) is a characteristic dimension of the system, n the number of electrons involved in reaction, F the Faraday constant, C^∞ the bulk concentration (mol.m^{-3}) of the specie electrochemically active and D ($\text{m}^2.s^{-1}$) its diffusivity. In Equation (5) the hydrodynamic condition (laminar or turbulent flow) can be evaluated by the choice of the Equation (2) or (3) and the Schmidt number by Equation (6), where it represents the relationship between the resistivity of momentum and mass diffusivities.:

$$Sc = \frac{\mu}{\rho D} = \frac{\nu}{D} \quad (6)$$

In general, mass transport in electrolytic cells with flow may be expressed in terms of the following expression:

$$Sh = kRe^a Sc^b \quad (7)$$

In general, to Newtonian fluids, it is assumed 0.333 for the constant b . The constants “ k ” and “ a ” may be obtained from the logarithmic linearization of equation (7). The current limiting density, j_L is generally determined from the choice of a extremely fast reaction, for

example, the electroreduction of the ferricyanide-ion in alkaline solution providing a diffusional control under various flow rate conditions. A more detailed approach on obtaining experimental current density limit may be found in specialized publications (Coouret & Storck, 1984; Walsh, 1993; Bockris & Reddy, 1977).

2.2 The gas evolution mechanism

Gas evolution occurs on an electrode through several phenomena. The gas produced by electrochemical reactions on the electrode dissolves in the electrolyte and is transported by diffusion (boundary layer concentration) and convection towards the bulk of the solution. The mechanism of growth and detachment of bubbles from electrode surface can develop in two or three steps depending on the size and its configuration geometry- for example, perforated plate, meshes or expanded electrodes. As presented by (Gabrielli et al., 1989), the first correspond the transient step or the bubble's radius variation with time and it depends of the electrolyte density. During the bubble growth the second step can be limited by diffusion of the dissolved molecular gas in the solution or by the kinetics of the production of the gas. When the bubble is larger than the electrode, it is assumed that the gas produced in molecular form is all transformed to the gaseous form which increases the bubble size. The last stage of the bubble evolution, i.e. its detachment from the surface, occurs when the balance between the forces which tend to maintain it on the electrode and the forces which tend to release it is broken. These various forces include the weight of the bubble, the buoyancy, the superficial tension, the pressure, the inertia and the electrostatic forces.

2.3 Electrolytic gas production from chlorine-alkali cell

The Figure 1 has shown the well-known electrolytic diaphragm process to produce chlorine and soda products (Almeida Filho et al., 2010; Abdel-Aal & Hussein, 1993; Abdel-Aal et al., 1993). The saturated aqueous sodium chloride (saturated brine) feeds the anodic

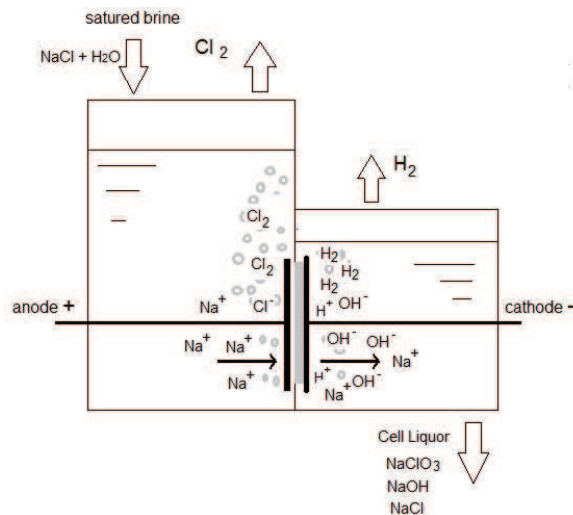


Fig. 1. Basic schematic of an electrolytic cell to produce chlorine and soda by the diaphragm process (Almeida Filho et.al, 2010)

compartment. The chlorine gas produced by the anodic reaction leaves the semi-cell, while the brine diffuses to the cathode compartment through the diaphragm due to the hydrostatic pressure drop between the two compartments. Hydrogen and hydroxyl ions are produced in the cathode compartment, which together with the sodium ions (Na^+) present in brine (anodic compartment) form sodium hydroxide (NaOH) at the same time that chlorine and hydrogen gas flow outside the cell. The part of the NaCl that did not react in the anodic compartment to produce chlorine gas diffuses into the cathode compartment through the diaphragm, joining the NaOH to form an aqueous solution of NaCl and NaOH called cell liquor.

The main reactions that occur in the process are as follows:



In the electrolytic production of chlorine-soda, high current density produces bubbles that can cover some parts of the electrode surfaces, causing an undesirable decrease in mass transfer. These limitations can be minimized through proper tuning of the cathode geometry and the electrolytic cell configuration (St-Pierre & Wragg, 1993). In industrial electrolytic operations that involve gas production, perforated plate or expanded electrodes are traditionally used to increase the reactive area per unit volume of the cell. However, the accumulation of generated bubbles on the surface of the cathode can block the electrochemically active area. This reduces efficiency by increasing ohmic drops in the layer of electrolyte adjacent to the electrode surface. Thus, the increase in the volume of bubbles adsorbed per unit area causes a decrease in mass transfer at the electrode surface (Vogt, 1984; Albuquerque, 2006, 2009). For these reasons, there has been increased interest in finding electrode geometries that promote the detachment of gas bubbles in order to increase mass transfer and ultimately efficiency.

An effective method for increasing the rate of mass transfer is to induce electrolyte turbulence near the surface to prevent the accumulation of bubbles. The behavior of this type of system was studied with expanded metal electrodes in which the electrochemical reaction on the electrode surface is controlled by diffusion and detachment of gas bubbles. (Elsner, 1984) concluded that the mechanism that drives the resulting increase in mass transfer varies based on the type and orientation of the expanded metal electrode geometry and the volumetric flow direction of the electrolyte. In general, we can assume that forced convection and detachment of bubbles will improve mass transfer when the geometry of the electrode does not inhibit the release of the bubbles generated electrochemically. A strong correlation between the mass transfer coefficient and gas production has been shown in mass transfer studies. (Fouad & Sedahmed, 1973) studied this relationship for electrodes oriented vertically and horizontally, concluding that the average mass transfer coefficient is greater for horizontal electrodes. (Nishiki et al., 1987) found that generated gas bubbles decrease the conductivity between electrodes by increasing the resistance of the solution. This affected overall cell performance by increasing the potential (energy consumption of the cell). It is evident that appropriate choice of electrode material and geometry may help

to mitigate such problems. (Hine et al., 1984) studied perforated plate electrodes, concluding that variation in electrolyte resistance and overvoltage is a function of both the porosity and distance between the electrode/diaphragm interface. The porosity appears to be an important parameter for reducing the cell potential. (Jorne & Louvar, 1980) and (Jansen et al., 1984) concluded that expanded metal electrodes with a three-dimensional texture can help to prevent generated gas from accumulating on the electrode surface, thereby decreasing the ohmic drop.

3. Un example of experimental study of mass transfer with gas production

The relevance and main contribution of this study was to compare and analyze the influence of the flow perpendicular to two geometries of cathode used in electrochemical industry, on the mass transfer associated with the electrolytic production of hydrogen. The electrolytic cell used in this study is a prototype for laboratory-scale production of chlorine-soda via an electrolytic diaphragm process (see Fig. 1). The reactor has two compartments of plexiglas with 1.45 L and 0.316 L to the anode and cathode electrodes respectively, separated by an asbestos-coated diaphragm (deposited on the cathode) like shows the Fig. 2. The Fig. 3 shows the two geometric shapes to the cathode - perforated plate and mesh geometry both with 7.0 x 8.0 cm made from commercial SAE 1020 alloy. The reduction of potassium ferricyanide in alkaline medium was used for the mass transfer study with NaOH as the electrolyte support. A PAR (Princeton Applied Research)-VMP3 potentiostat, was utilized for this purpose. Table 3 lists the properties of the electrolyte solution to 27°C.

	$K_3Fe(CN)_6 = 0.005\text{ N}$
Composition	$K_4Fe(CN)_6 = 0.05\text{ N}$
	$NaOH = 1.0\text{ N}$
$v\text{ (m}^2\cdot\text{s}^{-1}\text{)}$	0.9648×10^{-6}
$D^a\text{ (m}^2\cdot\text{s}^{-1}\text{)}$	6.0×10^{-10}

^a The diffusion coefficient was calculated from the Stokes-Einstein equation: $D\mu/T=2,49\times 10^{-15}\text{ [kg}\cdot\text{m}\cdot\text{s}^{-2}\cdot\text{K}^{-1}\text{]}$

Table 3. Composition and properties of the electrolyte solution.

The reduction of potassium ferricyanide in alkaline medium was used for the mass transfer study with NaOH as the electrolyte support. A PAR (Princeton Applied Research)-VMP3 potentiostat, was utilized for this purpose. Table 3 lists the properties of the electrolyte solution to 27°C.

The experimental procedure was performed at the following conditions: volumetric flow rate between 0.03 and $0.13\times 10^{-3}\text{ L/s}$. A procedure found in the literature (Elsner, 1984) was used to determine the average mass transfer coefficient with gas production. This procedure consisted of measuring the concentration variation of the reduced electroactive species ($Fe(CN)_6^{3-}$) with respect to time. The electro-reduction of ferricyanide ions in alkaline solution occurs under diffusional control. The electrochemically generated current intensity from controlled diffusion in the presence of hydrogen bubbles can then be determined from the following equation:

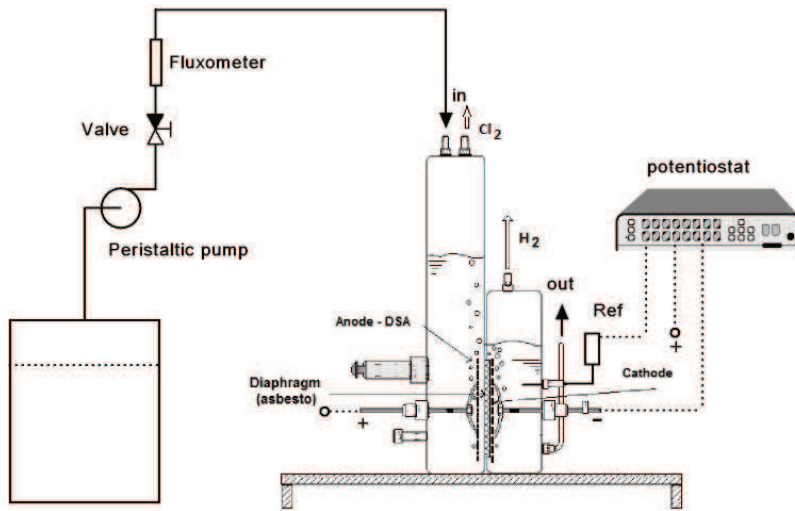


Fig. 2. Experimental set-up. Ref-reference electrode (Ni), out - soda produced (Albuquerque et. Al, 2009)

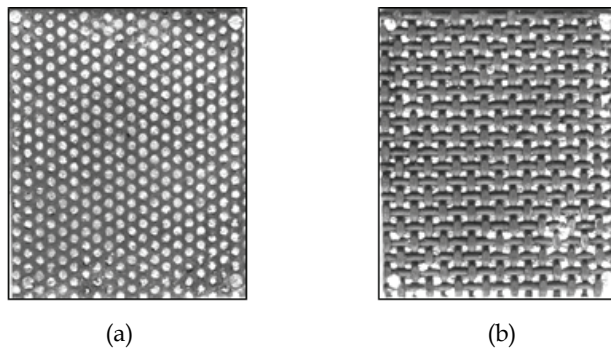


Fig. 3. Cathode geometries (a) perforated plate and (b) mesh geometry.

$$j_d^g = \frac{nFV_c \Delta C}{t} \tag{11}$$

Where j_d^g (A) is the current intensity from diffusion in the presence of bubbles produced electrochemically, ΔC (mol.m^{-3}) is the gradient concentration (ferricyanide ion concentration before and after electrolysis), V_c is the volume of the cathode compartment (m^3), n is the number of electrons involved in the and t is the time of electrolysis (s). From the electrolytic current intensity, the average mass transfer coefficient was determined from the following expression:

$$\bar{k}_d^* = \frac{j_d^g}{nFAC} \tag{12}$$

where $\overline{k_d^*}$ is the combined average mass transfer rate (m.s^{-1}), A the active area of the cathode (m^2) and \overline{C} is the average concentration of ferricyanide ions during electrolysis (mol.m^{-3}). The ferricyanide concentration was determined by amperometric titration (Vilar, 1996) using a cobalt chloride (0.0339M) solution like agent in a three-electrode cell setup consisting of a Hg/HgO reference electrode, a working rotatable platinum electrode (1,000.0 rpm, 2.0 mm diameter) controlled by CTV101 speed control unit, both - Radiometer analytical and 1x1cm sheet of platinum as counter electrode. The experimental setup was controlled by potentiodynamic technique using a PAR (Princeton Applied Research)-VMP3 Potentiostat.

3.1 Modeling

The following correlation was determined to best represent the chlorine-soda electrochemical reactor used in the present work (Zlokarnik, 2002):

$$\overline{Sh} = aRe^b Sc^{1/3} = \frac{\overline{k_d^* L}}{D} = a \left(\frac{vL}{v} \right)^b \left(\frac{v}{D} \right)^{1/3} \quad (13)$$

where L (the characteristic dimension) is given by the following relationship between the porosity of the electrode ε and the specific area A_s (m^{-1}):

$$L = \frac{\varepsilon}{A_s} \quad (14)$$

and

$$A_s = \frac{A_g}{V_s} \quad (15)$$

where ε is the porosity (0.51 and 0.75 to perforated plate and mesh geometry respectively) A_g is the geometric area ($57.0 \times 10^{-4} \text{m}^2$ both), and V_s the volume of solid electrode.

3.2 Results and discussion

Figure 4 shows the effect of the percolation rate of electrolyte through the diaphragm on the average mass transfer coefficient. The percolation rate (m.s^{-1}) was calculated as the ratio between the feed flow and the open cathode area (0.00287m^2 for perforated plate and 0.0042m^2 for mesh geometry).

It can be observed in Figure 4 that for the perforated plate geometry, the combined average mass transfer coefficient decreases with increasing percolation rate of electrolyte. The opposite behavior is observed for the mesh geometry. There are also two distinct regions in both curves, highlighted by the inflection points. This is characteristic of areas of hydrodynamic transition phenomena, probably due to laminar flow with rippling. Figure 5 helps to describe this behavior. The geometric influences are illustrated by the vector velocity of percolation (black arrows) and the direction of micro-convection (white arrows) caused by the rise of the bubbles. For the perforated plate geometry, Figure 5 (A) and (B) illustrates the supposition that the layer of micro-convection caused by the rise bubbles is pushed away from electrode surface when the cross-percolation velocity of electrolyte is

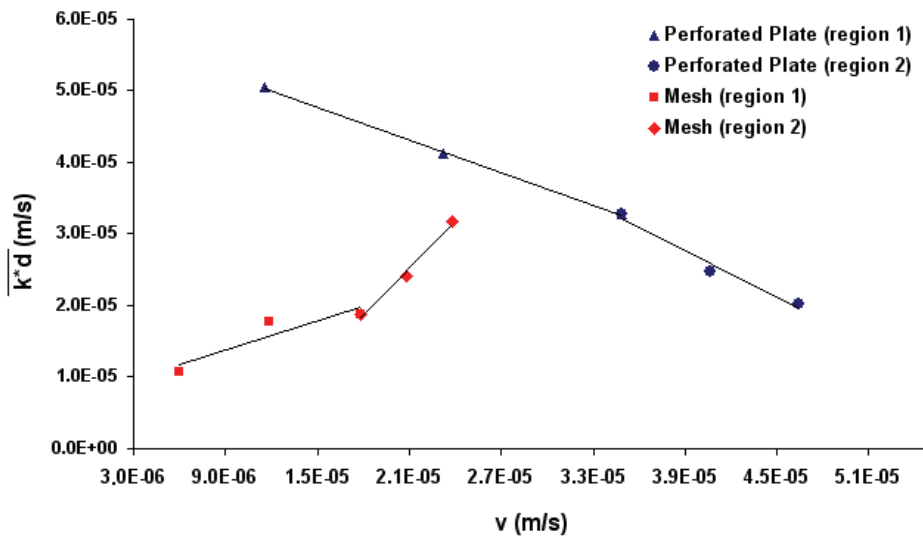


Fig. 4. Combined average mass transfer coefficient with respect to percolation rate of electrolyte.

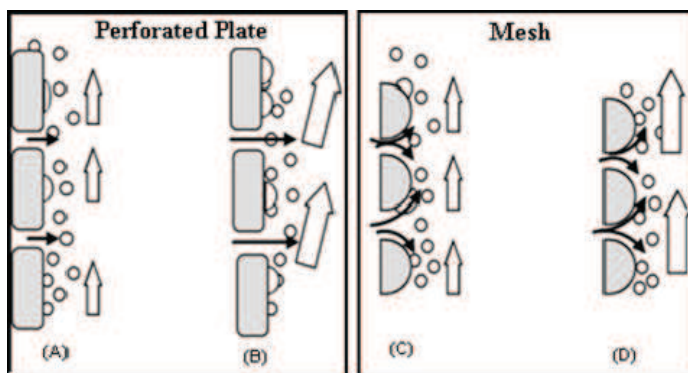


Fig. 5. Hypothesis of the situation between the change of cross-velocity percolation vectors with the rise of bubbles for; -Perforated plate, (A) -low and (B) - high velocities, -Mesh geometry, (C) -low and (D) - high velocities.

increased. This phenomena can hinder the detachment of the bubbles adhered to the cathode surface, causing a decrease in the rate of mass transfer with increasing percolation velocity. For the mesh geometry, a contrary phenomenon is illustrated. The Figure 5 (C) and (D) illustrates the same vector representation, but in this case the curved surface promotes increasing the velocity in the Prandtl hydrodynamic layer (Coeuret & Storck, 1984; Walsh, 1993), which enhances the detachment of gas bubbles. The increasing turbulence facilitates the detachment of the bubbles and the micro-convective movement reduces the Nernst boundary layer, and thereby increases the combined average mass transfer coefficient.

The Figure 5 can be explained by the supposition that turbulence can be more pronounced at the surface of the mesh electrodes than the surface of the perforated plate electrodes. For the mesh geometry, this mechanism is more significant at high percolation rates (see region 2 of Figure 4). Furthermore, this result indicates that for low percolation rates, the turbulence caused by micro-convection is not strong enough to detach the bubbles trapped in the mesh holes. This is probably due to greater bubble surface adhesion in this geometry. With respect to dimensionless correlation, the constants *a* and *b* were determined from logarithm function applied to Equation (13). The results are shown in Figure 6 and the Table 4 list all the correlations and Reynolds numbers domains studied in this study.

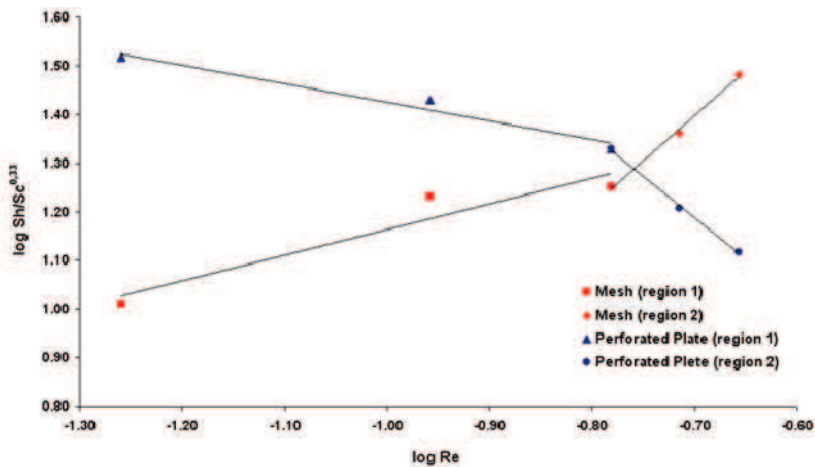


Fig. 6. The relationship between $\log (Sh/Sc^{1/3})$ and $\log Re$ for mesh and perforated plate cathode geometries.

	Mesh	Perforated Plate	Reynolds
Region			
1	$\bar{Sh} = 11.01 Re^{0.38} .Sc^{1/3}$	$\bar{Sh} = 49.11 Re^{0.53} .Sc^{1/3}$	$0.055 < Re < 0.165$
2	$\bar{Sh} = 486.41 Re^{1.84} .Sc^{1/3}$	$\bar{Sh} = 1.01 Re^{-1.70} .Sc^{1/3}$	$0.165 < Re < 0.220$

Table 4. Empirical correlations for both geometries and Reynolds number domains studied.

These correlations were compared with those found in the literature. (Stephan & Vogt, 1974) proposed a model expressed by Equation (17), which correlates the mass transfer in various systems with gas evolution. This model was evaluated for 32 experiments, as shown in Figure 7.

$$\text{Sh} = \frac{\overline{k_d^* \cdot d}}{D} = \frac{3.385}{C_\phi^{0.33}} (\text{Re}^* \text{Sc})^{0.487} (1 - \theta)^{0.5} \quad (17)$$

where d is the bubble detachment diameter ($d = 40 \mu\text{m}$ for bubbles of hydrogen in alkaline solution), θ is the fraction of area covered ($\theta = 0.2$ for semi-spherical bubbles and 0.3 for spherical bubbles) and C_ϕ is the sphere diameter ($C_\phi = 8$ for bubble and 4 semi-spherical bubbles). The Reynolds number Re^* was determined by Equations (3) and (4) and the combined average mass transfer rate, $\overline{k_d^*}$ by Equation (12). The results of the present study were compared with the experimental data compiled by (Stephan & Vogt, 1974) as shows by the Figure 7. These data were obtained from acidic or alkaline solutions using various electrode materials such as platinum, copper and graphite. The data are valid for the following domain: $0^\circ \text{C} < T < 80^\circ \text{C}$; $3 \text{ A.m}^{-2} < j < 10^5 \text{ A.m}^{-2}$; $160.00 < \text{Sc} < 23,000.00$ and $3.0 \cdot 10^{-6} < \text{Re}^* < 9.0 \cdot 10^{-1}$

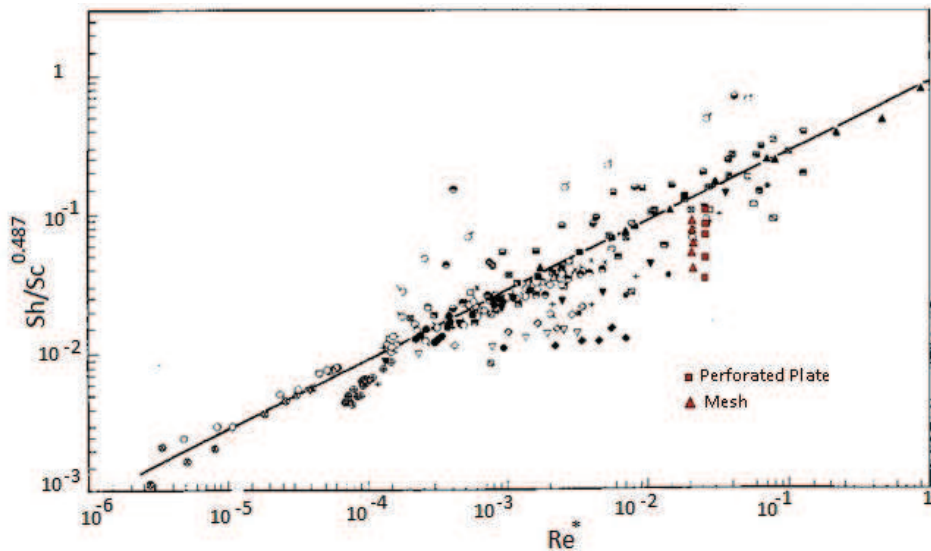


Fig. 7. Comparison of the experimental data of mass transfer with gas production (Stephan & Vogt, 1974) and the experimental data from this study.

According to Equations (3) and (4), the value of the Reynolds number is related to both the bubble velocity and the current density. For the purpose of comparison, only current density was used in this work so there is only one value of the Reynolds number.

4. Conclusions

It was shown that the mechanism controlling the average combined mass transfer coefficient during hydrogen production in electrochemical processes is dependent on the electrode geometry. The perforated plate geometry with deposited asbestos showed a slight advantage, compared with the mesh geometry, due to the detachment of bubbles from the active surface at low percolation velocities. Furthermore, increasing the percolation velocity resulted in a decrease of the average mass transfer coefficient, due to displacement of the micro-convective layer away from the electrode surface. For the mesh geometry, increasing the percolation velocity leads to an increase in the average mass transfer due to combined micro-convective effects. Specifically, rising bubbles associated with increased flow velocity over the curved wire surface, contribute to the displacement of bubbles blocked by adhesion. Finally for the chlorine-soda diaphragm process, a particularly operational industrial condition utilizing a percolation rate between $5.32 \cdot 10^{-6}$ and $6.16 \cdot 10^{-6}$ m.s⁻¹, the present study showed that the perforated plate geometry is plus advantageous.

To improve the electrochemical cells with electrolytic gas production it is very important for the mass transfer researches with new electrodes materials and geometries for cathodes and/or anodes. Thus it may be possible to achieve low energy consumption in a high efficiency process and low residues production.

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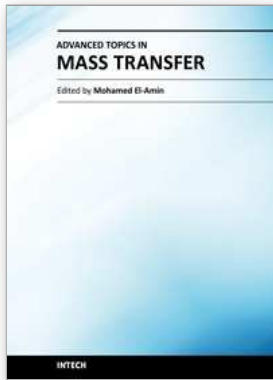
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