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Mathematical Modeling in Chemical Engineering: A Tool to Analyse Complex Systems

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1. Introduction

The essence of engineering modeling is to capture the fundamental aspects of the problem which the model is intended to describe and to understand what the model's limitations as a result of the simplifications are.

Engineering models are therefore not judged by whether they are "true" or "false", but by how well they are suitable to describe the situation in question. It may therefore often be possible to devise several different models of the same physical reality and one can choose among these depending on the desired model accuracy and on their ease of analysis.

Even though in engineering applications the choice of the model can be done among the following :

1. Physical models: small-scale replica of the system or its parts (pilot plant, scale models of buildings, ships models);
2. Analog models (electronic, electric and mechanical devices);
3. Drawing and maps;
4. Mathematical models,

over the past decade there has been an increasing demand for suitable material in the area of mathematical modeling, because they represent a more convenient and economic tool to understand the factors that influence the performance of a system.

Developments in computer technology and numerical solver have provided the necessary tools to increase power and sophistication which have significant implications for the use and role of mathematical modeling.

The conceptual representation of a real physical system can be translated in mathematical terms adopting the usual types of models and their combinations:

- Deterministic models: the relationships between different quantities of different engineering system are given via the continuum equations describing the conservation of mass, momentum and energy and the relevant constitutive equations. The appropriate differential equations are solved for a set or system of process variables and parameters;
- Statistical-Stochastic models: the principle of uncertainty is introduced instead of the possibility of assigning defined values to each dependant variable for a set of values of independent ones. Being the input-output relationships and the structure of elements not precisely known, the use of statistical tools is implemented;

- Empirical models: they are directly connected to the functional relationships between variables and parameters by fitting empirical data, without assigning any physical meaning and consequently any cause to their relationships. Examples of empirical models are those based on polynomials used to fit empirical data by the “least square” method,

or using more recent tools such as neural network and fuzzy logic techniques or fractal theory.

Mathematical models are of great importance in chemical engineering because they can provide information about the variations in the measurable macroscopic properties of a physical system using output from microscopic equations which cannot usually be measured in a laboratory. On the other hand, mathematical models can lead to wrong conclusions or decisions about the system under investigation if they are not validated with experimental tests. Therefore, a complete study of a physical system should integrate modeling, simulation and experimental work.

Computer aided modeling, simulation and optimization permit a better understanding of the chemical process behaviour, saves the time and money by providing the fewer configuration of the experimental work. In addition, computer simulation and optimization can help to improve the performance and the quality of a process and represent a more flexible and cost effective approach in design and operation.

This chapter presents two different examples of developing a mathematical model relevant to two different complex chemical systems. The complexity of the system is related to the structure heterogeneity in the first case study and to the various physical-chemical phenomena involved in the process in the second one.

Specific task is demonstrating how, through the use of information coming from experimental investigations and simulation, it is possible checking the validity of the assumptions made and fine tuning the predictive mathematical model capability.

The possibility of analysing and quantifying the role played by each step of the process is examined in order to define the relevant mathematical expressions. The latter allows getting useful indications about the impact of different operating conditions on the role of each step discussing the improvements in operation (efficiency of the process) brought about by simulation.

Next step focuses on the estimation of the significant parameters of the process. In complex systems the determination “a priori” of some parameters is not always feasible and they are therefore determined as a comparison of experimental and simulation data.

The final result is therefore the availability of a tool, the verified and validated (V&V) mathematical model, that can be used for simulation, process analysis, process control, optimization, design.

2. How to build a mathematical model

The general strategy of analysis of real systems consists of the following steps:

Problem definition

Preliminary we must pick up the essential information related to the case study/project; establish the objectives and related priority; state what is given and what is required. Then, we must analyse the entire process and the system in which it develops to fix the independent and dependent variables. When the process and/or the system is so complex that it is difficult either understand and describe it as a whole, we can break it down into

subsystems. They do not necessarily have to correspond to any physical parts of the real process; they can be hypothetical elements which are isolated for detailed considerations. After the process has been split up into the elements and each part has been analysed, relationships existing among the subsystems have to be defined and assembled in order to describe the entire process. Through the analysis of the variables and their relationships, it is possible to define a simple and consistent set which is satisfactory for the scope. While doing this, we can simplify the problem by introducing some assumptions so that the mathematical model can be easy to manipulate. These simplifications had to be later evaluated to have assurance of representing the real process with reasonable degree of confidence.

Model development

Defined the problem, we must translate it into mathematical terms.

Models based on transport phenomena principles, the first category of mathematical models mentioned in Introduction, are the common type models used in chemical engineering. The various mathematical levels (molecular, microscopic, multiple gradient, maximum gradient and macroscopic) used to represent the real processes are chosen according to the complexity of the internal detail included in the process description. For engineering purposes, molecular representation is not of much direct use. Microscopic and multiple-gradient models, give a detailed description of processes but they are often excessively complex for practical applications. Maximum-gradient model level may be considered a multiple-gradient model in which the dispersion terms are deleted and only the largest component of the gradient of the dependent variable is considered in each balance. These models are more easy to deal with and generally satisfactory for describing chemical systems. Then, macroscopic scale is used to represent a process ignoring spatial variations and considering properties and variables homogeneous throughout the entire system. In this way no spatial gradients are involved in equations and time remains the only differential independent variable in the balances. Mathematical description results greatly simplified, but there is a significant loss of information regarding the behaviour of the systems.

The development of a mathematical model requires not only to formulate the differential or algebraic equations but as well to select appropriate initial and/or boundary conditions. In order to determine the value of the constants which are introduced in the solution of differential equations, it is necessary to fix a set of n boundary conditions for each n th order derivative with respect to the space variable or with respect to time. In particular, boundary conditions can influence the selection of a coordinate system used to formulate the equations in microscopic and multiple-gradient models.

After setting up the model, we must evaluate the model parameters. In the microscopic models, the required parameters are transport properties. Various methods of estimating values for pure components and for mixtures are available in literature. The "effective" parameters, introduced in mathematical models to describe transport phenomena in homogeneous or multiphase systems, are clearly empirical and must be determined for the particular system of interest. In literature predicting relationships only for traditional systems may be available.

If deterministic models cannot be satisfactory applied in developing a model, stochastic or empirical models can be used. These model-building techniques have more limited applications as a consequence of that a lot of the limitations of deterministic models apply also to stochastic and empirical ones. Moreover, the empirical models show additional

limitations due to the fact that they are valid only for the process for which data were collected.

Whatever is the model-building technique adopted, as more complex is the mathematical description of the process, as more difficult is its solution. Therefore the process description shall be a compromise among the required details, the available information on model parameters and the limitations of the available mathematical tools.

Model solving

The goal of this step is to obtain the analytical solution (if this is possible) and/or, failing that, the numerical solution of the model equations, which may include algebraic equations, differential equations and inequalities. For many complex chemical processes the model result is set of nonlinear equation requiring numerical solution. The most common way to deal with this is to use modelling software such as gPROMS , COMSOL, Aspen Custom Builder or other software such as Matlab.

Model verification and validation (V&V)

These actions are essential part of the model building process.

Verification concerns with building the model right. In this step a comparison between the chosen conceptual representation and the outcome of the model is carried out to evaluate its suitability to describe the conception. Verification is achieved through tests performed to ensure that the model has been implemented properly and that the input parameters and logical structure of the model have been correctly represented.

Validation concerns with building the right model. This step grants that the model is in line with the intended requirements with reference to the methods adopted and outcome. Validation is achieved through an interactive process of comparing prediction data to experimental ones and using discrepancies between the values and information coming from comparison to improve the model. This procedure is repeated as many times as desired model accuracy is achieved.

3. Development of a mathematical model to analyze the behavior of a prototype electrochemical reactor

The availability of mathematical modeling is of paramount importance in the development of new equipments to evaluate their performances at operating conditions variations.

On the other hand, referring to systems characterized by either complex structure and/or processes which involve several steps or phases, the settlement of a reliable simulation model leads to the availability of experimental data allowing to check the assumptions taken in the model and to estimate the model parameters. Therefore it is the combination of equipments availability and the development of a specific mathematical model that allows to achieve a good level of process simulation.

In this case study we intend to develop a model allowing to evaluate the performance of a prototype electrochemical reactor for electro-coagulation and electro-flotation processes treating slurry. The reactor is equipped with reciprocating sieve-plates as electrodes. The peculiar characteristic of this reactor means that the fluid-dynamics of the system from "plug flow reactor" to "perfectly mixed reactor" can be varied as a function of the agitation level induced (Buso et al. 1991).

The reactor is a flanged plexi-glass tube, with a diameter of 40 mm and a height of 1060 mm. The column is fitted with an agitation device, consisting of a group of 16 stainless steel plate electrodes, mounted on a central shaft and uniformly distributed, with a space span of 50

mm. Each 6-mm thick plate had a diameter of 400 mm and 106 holes, each 12 mm across. Reciprocating is provided by an electric motor coupled to a gear drive fitted with frequency control, allowing the reciprocating frequency to range from 60 to 120 rpm. A continuously variable eccentric cam regulates reciprocating amplitude up to maximum plate spacing. Slurry is fed through two horizontal jet injectors.

The RPC reactor is a non homogenous system with complex geometric features. The perforated plates, mounted on a central shaft, have a double function: to grant, thanks to their movement, the desired agitation level and, being electrodes, to allow the generation of the electrochemical process. The latter is characterized by having several steps which contribute to define the overall kinetics.

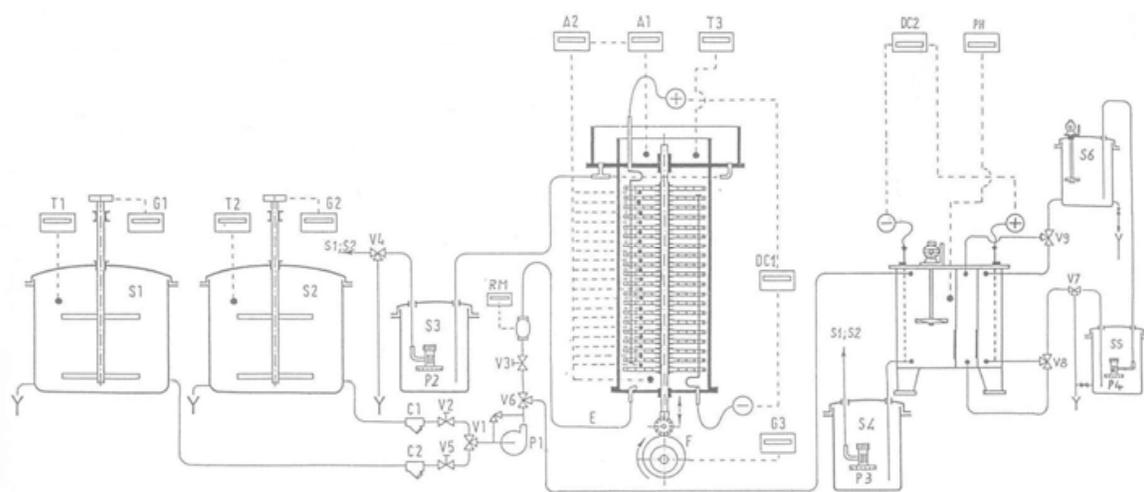


Fig. 1. Schematic representation of the pilot plant. A1,A2 conductivity cells; C1,C2 filters; DC1,DC2 D.C. power supply; E liquid injectors; F variable speed motor; G1÷G3 speed controls; P1÷P4 pumps; PH pH-meter; S1÷S6 storage tanks; T1,T3 thermometers; RM flow meters; V1÷V8 valves.

In this study the fluid-dynamic behaviour of the reactor is analysed by means of the time dependant input technique in the reactor itself, where the plates are not acting as electrodes. Experimental tests are carried out in the pilot plant shown in Fig. 1.

The two tanks, S1 and S2, contain the feed reactor and the relevant tracer which, by means of the 3-ways valve V1, is injected in the form of step input pulses.

The reactor is treated as system composed of two elements: the “feed zone” and the “reaction zone” comprising the 16 perforated reciprocating plates.

Various models to represent each subsystem can be used. In order to describe the whole system, we must define the relationships existing among the elements. In this case the input-forcing functions for the models proposed to represent the “reaction zone” are given by the outputs of the model adopted to describe the “feed zone”, when a STEP change in feed concentration is made.

The “feed zone” is considered to be either a CSTR or a tubular reactor. Its behaviour is represented mathematically in terms of the CSTR model and axial dispersed model, respectively, see Table 1.

The “reaction zone” is represented either by a tubular reactor or by a series of N backflow CSTR. Depending on the constructional features of the stack-plate, the literature suggests

different values for the number of stages N (Miyanami et al., 1973, Parthasarathy et al. 1984). With reference to the equipment studied, the space between two neighbouring plates can be considered an ideal mixer, that is $N = 16$. The N perfectly mixed cells have the same volume and constant net or bulk flow rate \dot{V} at all cross-sections and recirculation flow rate \dot{F} from each cell back to the preceding cell in the chain. The backflow ratio β is defined as $\beta = (\dot{F}/\dot{V})$. The mixing between the stages generates imperfection of the chain of several ideal mixers, so the parameter $\gamma = \beta/(1+\beta)$ is determined from the agitation level. Dotted cell (0) and $(N+1)$ are fictitious cells with negligible hold-up or volume, representing the inlet and outlet sections of the column. In the first case system behaviour is represented mathematically in terms of dispersed model, while a backflow cell model is used in the second one.

Moreover, only one model - dispersed or backflow cell - is used to describe the behaviour of the entire system, consisting of the "feed zone" and the "reaction zone".

The sets of equations proposed for each representation are then solved analytically or using numerical techniques if necessary. The breakthrough curves - (C/C_0) - for the suggested models vary progressively between two threshold conditions : from "plug flow reactor" to "perfectly mixed reactor", simply as a function of the characteristic parameters such as dispersion coefficient E and total flow ratio γ , see Table 1.

The experimental step input response curves are compared with the theoretical ones, obtained from the proposed models in order to determine the controlling parameters.

Parameters values are obtained by applying the methods of moments. (Himmelblau & Bishoff, 1968).

Models which simulate the "feed zone" as tubular reactor may describe the behaviour of different configurations of the "feed zone", as a function of induced mixing level and thus of dispersion coefficient, E . Moreover, the predictive capability can be improved estimating parameters E and γ for the sole "reaction zone".

Mathematical models simulating the whole system as a tubular reactor or a series of backflow CSTR take backmixing between the "feed zone" and the "reaction zone" into consideration, although the estimated parameters are less suitable for modelling reactor behaviour.

This analysis allows to select the most suitable model, according to the "feed zone" geometry and operating conditions range, that is, the agitation level adopted.

Experimental tests in the frequency range 60÷120 rpm and amplitude 0.1÷1.8 cm are carried out to evaluate the effects of the agitation level on fluid-dynamics parameters.

At zero agitation, the liquid velocity has a non-uniform radial profile and the dispersion coefficient is relatively high. As agitation ($A \cdot f$) is increased, when amplitude A is low, localised agitation improves radial mixing inducing a fluid-dynamic behaviour similar to that found in a plug flow-reactor. The dispersion coefficient decreases to a minimum. If agitation level is further increased, the mixing between the zones of reactor gave rise, until the behaviour of a perfectly mixed reactor is reached. The dispersion coefficient gradually increases.

The dispersion coefficient determined from experimental data is then compared with those estimated by correlations available in literature for single phase flow (Karr et al., 1987; Lounes & Thibault, 1996). Karr's correlation matches the experimental values satisfactory, although it is inadequate when low amplitude and high frequencies are used.

The second aspect that we have to investigate regards the effects of process kinetics on the system behaviour.

Feed zone: CSTR + Reaction zone: Dispersed reactor	
Feed zone: Dispersed Reactor + Reaction zone: Dispersed reactor	
Feed zone: CSTR + Reaction zone: Series of backflow CSTR	
Feed zone: Dispersed Reactor + Reaction zone: Series of backflow CSTR	
Feed zone + Reaction zone: Dispersed Reactor	
Feed zone + Reaction zone: Series of backflow CSTR	

Table 1. Fluid-dynamics simulation. Schematic representations of the RPC reactor and concentration profiles for various values of dispersion coefficient, E , and total flow ratio, γ . C_1 dimensionless initial molar concentration; C_0 dimensionless inlet reaction zone molar concentration; C dimensionless exit molar concentration; τ_A mean residence time of CSTR; C_A dimensionless molar concentration in CSTR; L_1 length tubular reactor.

Electrochemical processes on the electrode involve the following steps: diffusion from the bulk toward the electrode surface, adsorption, electron exchange, de-adsorption and diffusion from the electrode to the bulk. These steps contribute to define the overall kinetics. Since in the waste water treatment dilute solutions are involved, the mass transport can be considered the limiting step. In these conditions the mass transport coefficient become the controlling parameter and the process kinetics are determined by the fluid-dynamics behaviour of the solution rather than the electrode characteristics.

In the limiting current conditions, when reactant concentrations fell to zero close to the electrode surface, the flux expression was reduced to (Prentice, 1991):

$$N_j = \frac{60 \mathfrak{I}_l}{n F} = K_m C_\infty \quad (1)$$

where:

- C_∞ - bulk ion molar concentration
- F - Faraday's constant
- \mathfrak{I}_l - limiting current density
- K_m - mass transport coefficient
- n - number of electrons involved in the reaction
- N_j - molar flux of the j -th species

provided that reactant migrations as consequence of the electric field is negligible.

In these conditions, the mass transport coefficient may be determined experimentally by measuring the concentration of solution, C_∞ , and the limiting current density, \mathfrak{I}_l , by means of the following:

$$K_m = \frac{60 \mathfrak{I}_l}{n F C_\infty} \quad (2)$$

In order to obtain accurate data relevant to the limiting current density, electrochemical characterization of an aqueous solution of potassium iodide, with an excess of sodium sulphate as supporting electrolyte, is carried out using the laboratory apparatus shown in Fig.2, equipped with stainless steel electrodes having the same thickness and distance as those used in the reactor.

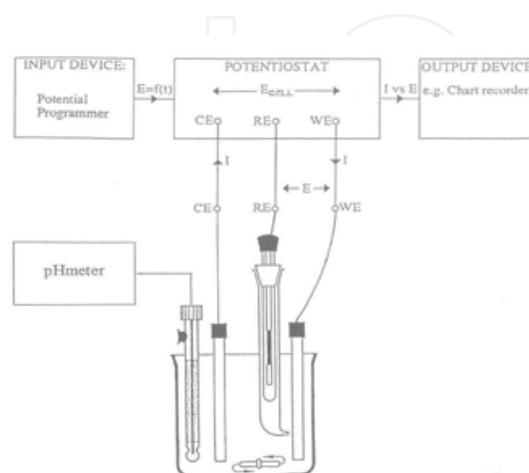


Fig. 2. Electrochemical laboratory apparatus. CE counter- electrode; Re reference electrode WE working electrode.

The main reaction at the anode are:



and/or



Current polarisation curves for the potassium iodide solution for various agitation levels are obtained. These curves are then compared with the polarisation curves of the supporting electrolyte solution obtained in the same operating conditions, in order to identify any noise phenomena as a result of undesirable oxidation.

Data obtained allow to define the operating conditions which are used in tests on the reactor where the plates are acting as electrodes.

The same aqueous solution of potassium iodide, with an excess of sodium sulphate as supporting electrolyte is used in batch runs, carried out first on a single cell then on an increasing number of cell, until the whole reactor became involved. In these conditions data collected may be compared with those of the laboratory apparatus results. For each run, polarisation curves are obtained by varying the agitation level within the range 60÷150 rpm. In this way information about the effect of the agitation level on current, in mass transfer controlled regions, can be obtained. In particular, when higher agitation levels are used, the limiting current values increase with the agitation level and the potential range in which the current assumes the limiting value decreases until mass transport become a non-controlling phenomenon (Buso et al., 1997).

In order to analyze the effect of agitation level on mass transport coefficient, K_m , the reactor is completely filled with the solution of potassium iodide and tests are carried out separately, varying the amplitude and frequency of the plate oscillation. The applied potentials are chosen according to the limiting current values previously obtained.

The mass transport coefficient may be evaluated using equation (2) where the limiting current density is expressed through limiting current, I_l , and total active electrode surface, S . It is therefore possible to estimate the values of the $(K_m S)$ group, simply by measuring limiting current, I_l , and concentration of solution, C_∞ . In this way the values of the $(K_m S)$ group are available in the same form used in the mathematical models which describe the behaviour of the electrochemical reactor.

The effect of geometric, fluid-dynamic and physical-chemical variables on the rate of mass transfer may be evaluated through the following controlling dimensionless number relationship:

$$\text{Sh} = \psi (\text{Re})^\kappa (\text{Sc})^\theta \quad (7)$$

where:

ψ, κ, θ - empirical constant

$(\text{Re}) = (A f)(d/s)(\rho/\mu)$ - dimensionless Reynolds number

$(Sc) = (\mu/\rho D)$ - dimensionless Schmidt number

$(Sh) = (K_m L/D)$ - dimensionless Sherwood number

A - stroke

d - hole diameter

D - diffusion coefficient

f - frequency

L - characteristic length

s - fractional free flow area

ρ - solution density

μ - solution viscosity.

In this case both the geometry and the solution properties are constant. Equation (7) may be rewritten as follows:

$$K_m S = \xi (Re)^\kappa \quad (8)$$

$$\xi (Re)^\kappa = \psi (Sc)^\theta \left(\frac{DS}{L} \right) \quad (9)$$

According to Reynolds number definition, equation (8) becomes:

$$K_m S = \zeta (A f)^\kappa \quad (10)$$

$$\zeta = \xi \left(\frac{\rho d}{s \mu} \right)^\kappa \quad (11)$$

The values of parameters κ and ζ may be obtained by fitting of experimental data.

In this way we have obtained a dimensionless numbers relationship which allows, according to the electrochemical process of interest, to evaluate the effects of agitation level on mass transfer rates.

Now, we have the information to develop a steady-state reactor model.

With reference to the electrochemical system studied, the reactor may be represented as $N/2$ perfectly mixed cells including cathodes, $N/2$ reactions cells including anodes, feed zone and the fictitious cells relevant to the inlet and the outlet sections of the reactor. Electrochemical process occurs only in cells with anodes, so that, in steady state conditions, the inlet concentration in the "feed zone" and in the "reaction zone" are the same. Therefore, the models proposed for the whole reactor become the more suitable to represent mathematically the system behaviour.

The dispersed model equations and relevant boundary conditions are:

$$0 = -v \frac{\partial c}{\partial z} + \frac{\partial^2 c}{\partial z^2} + \left(\frac{K_m S}{V} \right) \quad (12)$$

$$v c|_{z=0^+} - E \frac{\partial c}{\partial z} \Big|_{z=0^+} = v c|_{z=0^-} \quad (13)$$

$$\left. \frac{\partial c}{\partial z} \right|_{z=L} = 0 \quad (14)$$

where:

- c - ion concentration
- v - overall velocity
- z - length coordinate through reactor.

The backflow cell model equations are:

$$\begin{aligned}
 & \text{inlet cell } n = 1 \\
 & 0 = \dot{V}c_0 + \beta \dot{V}c_2 - \dot{V}(1+\beta)c_1 \\
 & \text{anodes } n = 2, 4, \dots, 16 \\
 & K_m S_a c_n = \dot{V}(1+\beta)c_{n-1} + \beta \dot{V}c_{n+1} - \dot{V}(1+2\beta)c_n \\
 & \text{cathodes } n = 3, 5, \dots, 17 \\
 & 0 = \dot{V}(1+\beta)c_{n-1} + \beta \dot{V}c_{n+1} - \dot{V}(1+2\beta)c_n \\
 & \text{outlet cell } n = 18 \\
 & 0 = \dot{V}(1+\beta)c_{17} + \dot{V}(1+\beta)c_{18}
 \end{aligned} \quad (15)$$

where:

- S_a - total active anode surface

The dispersed model solution was obtained analytically, while the backflow cell model was solved numerically using the Thomas algorithm.

To validate the proposed models, experimental tests are carried out in the pilot plant, especially modified to operate in steady-state conditions. Samples are taken at the inlet, outlet and at various sections of the reactors.

The characteristic parameters of the two models, (E, K_m) and (γ, K_m) , are adjusted to give the best fit to the experimental concentration profiles relevant to different operating conditions. Their values are then compared with the output of fluid-dynamic study and electrochemical characterization developed separately, together with those estimated in literature.

A typical comparison of the model outputs and the experimental value are shown in Fig. 3.

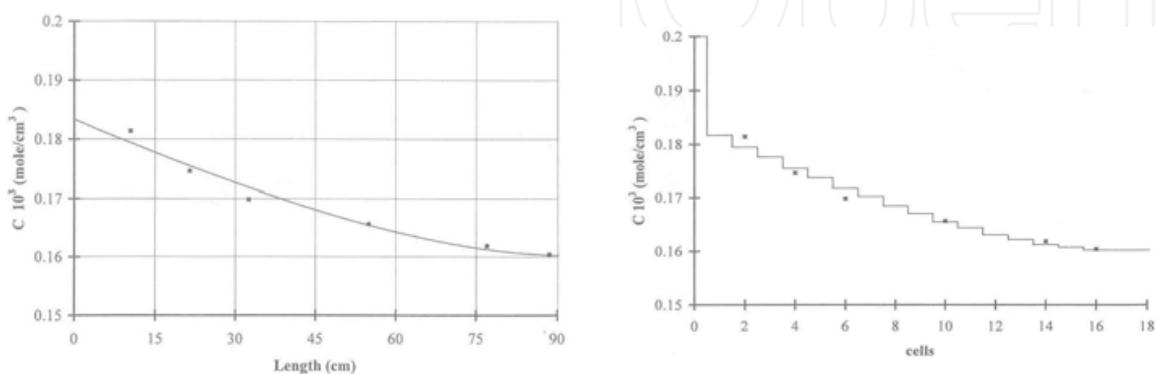


Fig. 3. Concentration profile in the RPC reactor. Comparison of experimental data and predictive profile obtained with dispersed model and backflow cell model.

The good match among the data confirms the predictive capacity of the proposed models. Moreover, it is possible to verify the results of the effects of agitation level on the fluid-dynamic kinetic parameters.

The response solutions of the continuous diffusion and backflow cell models, obtained with the same value of the kinetic parameter ($K_m S$), are then compared using the Crank method (Roemer & Durbin, 1967). The good match between the characteristic parameters:

$$Pe = \frac{v L}{E} = 2.34 \quad (12)$$

$$\Phi = \frac{2N(1-\gamma)}{1+\gamma} = 2.13 \quad (13)$$

determined using E and γ estimated from experimental data, confirms that the diffusion model response approaches that of the backflow cell model.

The methodology proposed provides, for the process of interest, tools to define operating conditions which improve both reduction rates and energy consumption.

4. Development of a mathematical model to analyze the electro-generation of hydrogen peroxide using an oxygen-reducing gas-diffusion electrode

Hydrogen peroxide is a powerful oxidising agent. It finds applications in a wide variety of chemical processes (Brillas et al, 2000; Drogui et al., 2001; González-García et al., 2007). Due to the low solubility of the oxygen in aqueous solution, in the electrosynthesis of hydrogen peroxide, electrochemical devices with high specific surface area are required. Gas-diffusion electrodes (GDE) are devices suitable to supply commercially reasonable current densities for practical implementation of this process (Alcaide et al., 2002; Da Pozzo et al., 2005; Lobyntseva et al., 2007).

The availability of mathematical models for optimal design and process control strategy, can improve the use of these devices.

In this case study we intend to develop a model which allows to evaluate the contributions of the transport and reaction steps to the overall electrosynthesis process.

The process of interest occurs at the cathode. In the dilute acidic solution it can be described by the following reaction (Alcaide et al., 2002, 2004, Kolyagin&Kornienko, 2003):



When a GDE is used as cathode, the process involves three phases: the gas phase (O_2), the liquid phase (a dilute acidic solution) and, in the middle, the porous electrode.

The pore space of the electrode is filled partly with liquid and partly with gas. The gaseous component (O_2) must overcome the mass transport resistances in the external gas film and the gas-filled pore volume before it can be absorbed in the liquid phase. Then oxygen diffuses through the flooded part of the pore and is reduced on the electrode surface, forming hydrogen peroxide. This product is transported from the reaction zone through the flooded layer out of the pore and into the liquid bulk.

Due to process complexity, some assumptions shall be taken to develop a model which has to be sufficiently representative and easy to use. Moreover determining "a priori" some parameters will not be an easy task, and therefore it might be necessary to obtain them

through a comparison between experimental data and simulation values. The availability of experimental equipments allows to check the assumptions taken, to determine the parameters and finally to validate the proposed model.

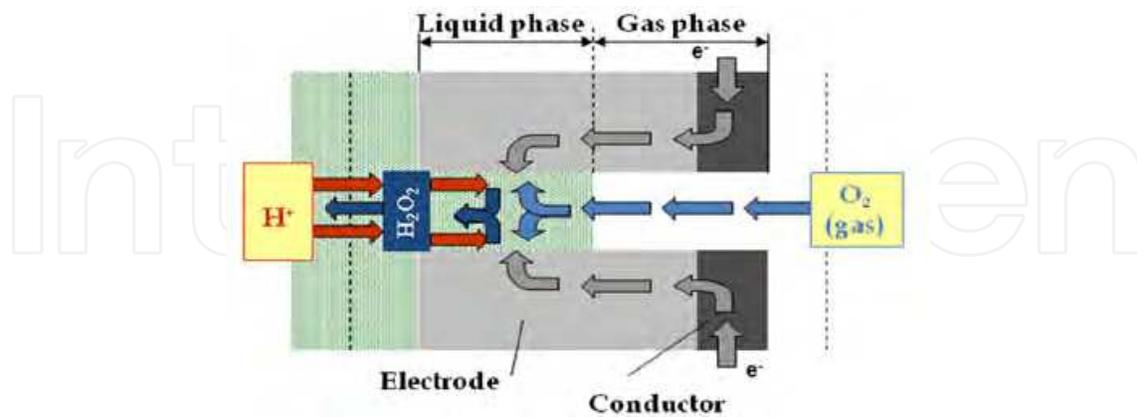


Fig. 4. Gas Diffusion Electrode: schematic representation of the three-phase process.

In this case study, either laboratory equipment and pilot plant are used. In particular, the scheme of the pilot plant is shown in Fig. 5.

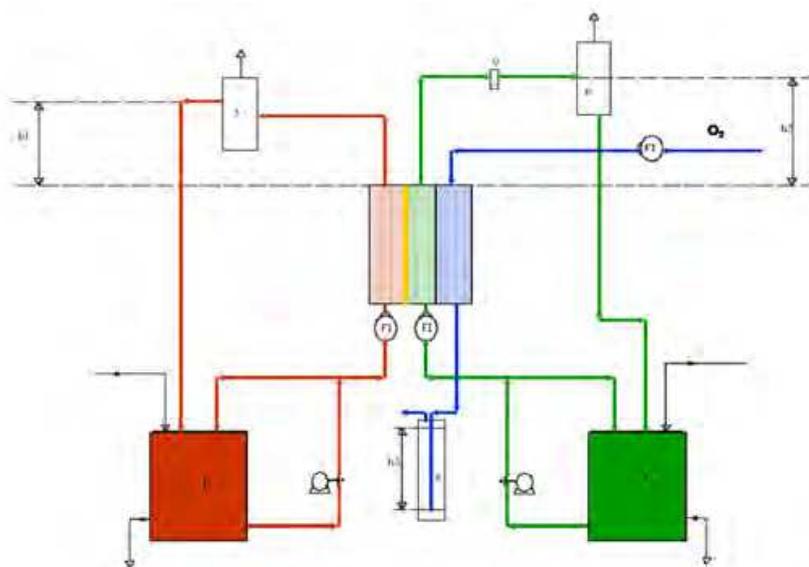


Fig. 5. Schematic diagram of pilot plant. (1) analyte reservoir; (2) anodic compartment; (3) cathodic compartment; (4) gas chamber; (5) and (6) liquid holders; (7) catholyte reservoir; (8) drechsel; (9) tank for the reference electrode; (h_1) anodic circuit head; (h_2) cathodic circuit head; (h_3) gas circuit head.

The anodic solution (0.5 M H_2SO_4) is circulated through the reactor by a centrifugal pump. During the experiments, the feed fluid is partially recycled back to the tank to mix the stored solution. A liquid holder allows to purge the gas generated in working conditions at the anode, according to the following reaction: $\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$. A similar flow circuit is arranged to feed the reactor with catholyte (0.07 M NaCl solution). In this case, purging removes the gases generated from hydrogen peroxide degradation or those passing through the cathode into the solution. Liquid holders are placed to ensure the right pressure values

in the anodic and cathodic compartments. Pure O₂ is supplied to the gas chamber in contact with the cathode. A drechsel maintains the correct pressure in the gas chamber.

The electrochemical cell is composed of three separate elements: the side-units act as the anodic and gas compartments, respectively. The anodic solution is fed from the bottom, whereas the gas flows in from the top. In the central unit the electrodes are placed. The anode is made of platinum-coated titanium net and the cathode is a O₂-diffusion electrode. The latter consists of a silver-plated nickel web, covered with layers of VULCAN XC-72 Carbon catalyst on both sides of the assembly and a coating of SAB (Shawinigan Acetylene Black) on the gas-side. This hydrophobic barrier prevents flooding of the electrode. The inter-electrode compartment has lower inlet and upper outlet tubes for catholyte circulation. The cathode compartment is separated from the anode compartment by a cation-exchange membrane.

The process analysis starts with the study of the process kinetic aspects.

Electrochemical processes are generally described by reaction path including several reactions, but often it is possible to choose a single reaction as the one which is controlling the process. In this case we assume that the process can be described only by the reaction (14) while the side reactions (Alcaide et al., 2002; Agladze et al., 2007; Kolyagin & Kornienko, 2003):



can be considered negligible.

Reaction rate expression, R_{O_2} , is formulated as a first-order equation with reference to oxygen (Brillas&Casado, 2002):

$$R_{\text{O}_2} = K c_{\text{O}_2} \quad (17)$$

In Eq. (4), c_{O_2} is the oxygen molar concentration in the liquid phase. Since the surface overpotential is a large negative value during the process, the exponential term of the anodic portion of reaction (14) in the Butler-Volmer equation can be neglected. In dilute solution, at constant pH value, rate coefficient K is given as:

$$K = \frac{j_0 a}{n F c_{\text{O}_2}^*} \exp \left[-\alpha n \frac{F}{RT} (U - U_0) \right] \quad (18)$$

where :

- a - specific electrode surface
- $c_{\text{O}_2}^*$ - oxygen equilibrium concentration
- F - Faraday constant
- j_0 - exchange current density
- n - number of electrons involved in the reaction (14)
- R - gas law constant
- T - temperature
- U - potential
- U_0 - open circuit potential
- α - cathodic transfer coefficient.

Pilot plant behaviour is studied in a batch recycle mode of operation.

The model analysis is restricted to the cathodic section, where oxygen reduction for hydrogen peroxide generation occurs. Experimental data, available in literature (Kolyagin & Kornienko, 2003), shown that the pH of the catholyte remains almost constant during electrolysis, indicating that H^+ ion transport from the anodic compartment (through the proton-exchange membrane) is not a limiting step for the process.

The cathodic section is treated as system composed of two elements: the liquid phase reservoir and the cathodic semi-cell, containing the GDE.

For the reservoir, the mixing conditions achieved by partial recirculation of the feed solution allow to consider it a perfectly mixed vessel. Therefore to simulate its behaviour in a batch recycle mode of operation, an unsteady-state perfectly mixed model is used.

In order to analyse the role played by each step of the process, the cathodic semi-cell can be divided into two subsystems: the porous electrode and the cathodic compartment, as shown in Fig.6.

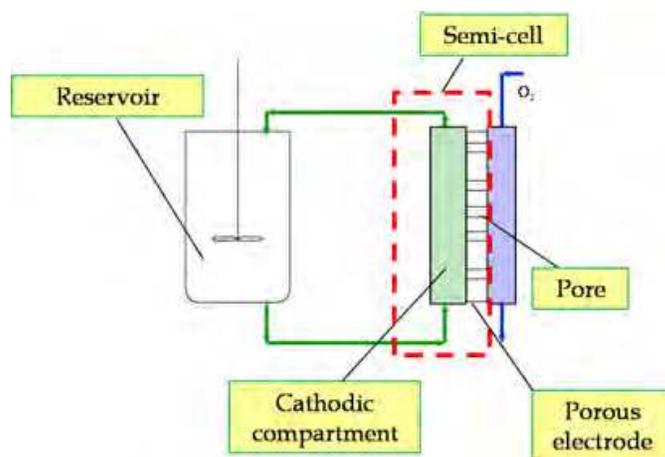


Fig. 6. Schematic representation of the cathodic section.

Porous electrode: considering that the front face of the GDE is in contact with the catholyte and the other face with the gas compartment, each pore of electrode can be represented as a sum of two elements: the gas-filled pore volume and the flooded layer. As a consequence of hydrophobicity of the electrode material, the penetration depth of the liquid phase is assumed to be 50% of the electrode thickness.

In the experimental tests pure oxygen is used. We can assume that no transport limitations in the gas phase occur. Therefore, only the gas-liquid interface condition is considered. At the interface oxygen dissolves in the liquid phase and this process is assumed to be in equilibrium.

In the flooded layer oxygen diffuses and is reduced on the electrode surface, forming hydrogen peroxide. This product moves from the reaction through the flooded layer until the end of the pore. Then it is transported into the liquid bulk.

In order to represent the oxygen and hydrogen peroxide behaviour in the flooded layer, no radial transport limitations are assumed.

Unsteady-state models are developed as a consequence of the fact that experimental runs were carried out in a batch recycle mode of operation.

Water is not taken into account, as it is the excess component in the liquid phase and has no significant influence on the overall process.

Cathodic compartment: this subsystem can be represented as a non homogeneous reactor in which the hydrogen peroxide production occurs on the wall in front of electrode. Its

behaviour may be described using models which keep into account, in different way, the role played by fluid-dynamic conditions on the hydrogen peroxide production.

Two ideal flow models, the CSTR model and the plug flow reactor model, are considered first. They represent two limiting cases of flow patterns: perfect mixing assumes complete uniformity of composition throughout the reactor. At the other extreme, plug flow occurs when fluid velocity is uniform over the entire cross-section of the reactor and there is no intermixing of fluid elements entering the vessel later. The flow patterns found in actual reactors fall between these two extremes. Many models have been suggested (Fahim & Wakao, 1982; Vakao & Kagueti, 1982) to represent non-ideal flow conditions, of which one-dimensional dispersion seems to be the most widely used (Trinidad et al., 2006). Therefore, the dispersed model is also applied to represent the chatodic compartment, considering dispersion in the axial direction, characterised by a dispersion coefficient independent of position.

To simulate chatodic compartment behaviour in a batch recycle mode of operation, unsteady-state models are used.

When the whole cathodic section is considered, the dead time of the feed liquid line, due to feed pipes, fittings and flow meter, is added to the mean residence time of the storage tank.

The model of the cathodic section consists of the unsteady-state material balance equations for oxygen and hydrogen peroxide in liquid phase, carried out over the reservoir and the semi-cell. It contains the constitutive equations for the physical-chemical properties of the species involved in the process and the kinetic expression for the reaction as presented above. Moreover it includes the relationships existing among the selected subsystems and the appropriate initial and boundary conditions.

The equations developed to represent mathematically the cathodic section behaviour are the following:

Reservoir

Oxygen

$$V_S \frac{d c_{O_2}^S}{dt} = \dot{V} (c_{O_2}^R - c_{O_2}^S) \quad (19)$$

To define the initial condition we assume that only liquid in the flooded layer can achieve saturation before current supply starts. Therefore:

$$c_{O_2}^S(0) = 0 \quad (20)$$

In equation (19) :

- $c_{O_2}^S$ - molar concentration of oxygen in catholyte reservoir
- $c_{O_2}^R$ - molar concentration of oxygen in cathodic compartment of cell
- V_S - volume of chatolyte in the tank
- \dot{V} - volumetric flow rate of catholyte
- t - time

Hydrogen Peroxide

$$V_S \frac{d c_{H_2O_2}^S}{dt} = \dot{V} (c_{H_2O_2}^R - c_{H_2O_2}^S) \quad (21)$$

To define the initial condition we assume that no hydrogen peroxide is present in the catholyte at the beginning of the process. Therefore:

$$c_{\text{H}_2\text{O}_2}^{\text{S}}(0) = 0 \quad (22)$$

where:

- $c_{\text{H}_2\text{O}_2}^{\text{S}}$ - molar concentration of hydrogen peroxide in catholyte reservoir
 $c_{\text{H}_2\text{O}_2}^{\text{R}}$ - molar concentration of hydrogen peroxide in cathodic compartment of cell

Cathodic semi-cell

Porous electrode

Flooded layer

Oxygen

$$\frac{\partial c_{\text{O}_2}^{\text{P}}}{\partial t} = D_{\text{eff O}_2} \frac{\partial^2 c_{\text{O}_2}^{\text{P}}}{\partial z^2} - R_{\text{O}_2} \quad (23)$$

Hydrogen Peroxide

$$\frac{\partial c_{\text{H}_2\text{O}_2}^{\text{P}}}{\partial t} = D_{\text{eff H}_2\text{O}_2} \frac{\partial^2 c_{\text{H}_2\text{O}_2}^{\text{P}}}{\partial z^2} - R_{\text{H}_2\text{O}_2} \quad (24)$$

In equations (23) and (24):

- $c_{\text{O}_2}^{\text{P}}$ - molar concentration of oxygen in flooded layer of electrode
 $c_{\text{H}_2\text{O}_2}^{\text{P}}$ - molar concentration of hydrogen peroxide in flooded layer of electrode
 z - length coordinate through pore.

The rate of consumption of O_2 , R_{O_2} , is expressed by equation (17). The rate of production of H_2O_2 , $R_{\text{H}_2\text{O}_2}$, is:

$$R_{\text{H}_2\text{O}_2} = -R_{\text{O}_2} \quad (25)$$

directly derived from the stoichiometry of reaction.

For each components i , the pore diffusion coefficient is related to the molecular diffusion coefficient by the relationship:

$$D_{\text{eff } i} = \chi D_i \quad (26)$$

where:

- χ - tortuosity factor .

To define the initial condition we assume that a flow of oxygen is first established through the cathode up to saturation of the stagnant solution in the flooded layer; then, at time zero, current supply starts and the cathodic solution is circulated through the reactor. The hydrogen peroxide is assumed not to evaporate during the process and the continuity of molar fluxes at the pore exit is accounted for (Varma & Morbidelli,1997).

Oxygen

$$c_{\text{O}_2}^{\text{P}}(z,0) = c_{\text{O}_2}^{\text{sat}} \quad (27)$$

$$c_{O_2}^P(0,t) = c_{O_2}^{sat} \quad (28)$$

$$-D_{eff O_2} \left(\frac{\partial c_{O_2}^P}{\partial z} \right)_{L,t} = K_{mO_2} \left[(c_{O_2}^P)_{L,t} - c_{O_2}^R \right] \quad (29)$$

where

K_{mO_2} - oxygen mass transfer coefficient

L - thickness of flooded layer.

Hydrogen Peroxide

$$c_{H_2O_2}^P(z,0) = 0 \quad (30)$$

$$\left(\frac{\partial c_{H_2O_2}^P}{\partial z} \right)_{0,t} = 0 \quad (31)$$

$$-D_{eff H_2O_2} \left(\frac{\partial c_{H_2O_2}^P}{\partial z} \right)_{L,t} = K_{mH_2O_2} \left[(c_{H_2O_2}^P)_{L,t} - c_{H_2O_2}^R \right] \quad (32)$$

where:

$K_{mH_2O_2}$ - hydrogen peroxide mass transfer coefficient.

The oxygen concentration in the liquid phase, $c_{O_2}^{sat}$, is related to the partial pressure in the gas phase, P_{O_2} , by Henry's law:

$$P_{O_2} = H_{O_2} c_{O_2}^{sat} \quad (33)$$

where H_{O_2} is the Henry constant. This equation represents the relationship existing among the considered elements: the gas-filled pore volume and the flooded layer.

Cathodic compartment

- *CSTR model*

Oxygen

$$V_R \frac{d c_{O_2}^R}{dt} = \dot{V} (c_{O_2}^S - c_{O_2}^R) + n_{O_2} \quad (34)$$

where:

V_R - volume of catholyte in cathodic compartment.

The molar flow rate of oxygen in liquid film, n_{O_2} , is expressed the linear transport law:

$$n_{O_2} = A \varepsilon K_{mO_2} \left[(c_{O_2}^P)_{L,t} - c_{O_2}^R \right] \quad (35)$$

where:

A - electrode surface

ε - total porosity of electrode.

To define the initial condition we assume that only liquid in the flooded layer can achieve saturation before current supply is started. Therefore:

$$c_{O_2}^R(0) = 0 \quad (36)$$

Equation (35) represents the relationship existing among the considered elements: flooded layer and cathodic compartment.

Hydrogen Peroxide

$$V_R \frac{d c_{H_2O_2}^R}{dt} = \dot{V} (c_{H_2O_2}^S - c_{H_2O_2}^R) + n_{H_2O_2} \quad (37)$$

The molar flow rate of hydrogen peroxide in liquid film, $n_{H_2O_2}$, is expressed the linear transport law:

$$n_{H_2O_2} = A \varepsilon K_{mH_2O_2} \left[(c_{H_2O_2}^P)_{L,t} - c_{H_2O_2}^R \right] \quad (38)$$

To define the initial condition we assume that no hydrogen peroxide is present in the catholyte at the beginning of the process. Therefore:

$$c_{H_2O_2}^R(0) = 0 \quad (39)$$

Equation (38) represents the relationship existing among the considered elements: flooded layer and cathodic compartment.

- *Plug-flow reactor model*

Oxygen

$$\frac{\partial c_{O_2}^R}{\partial t} = -v \frac{\partial c_{O_2}^R}{\partial y} + \frac{A \varepsilon}{V_R} K_{mO_2} \left[(c_{O_2}^P)_{L,t} - c_{O_2}^R \right] \quad (40)$$

where:

v - velocity

y - length coordinate through cathodic compartment.

According to the above said assumptions, the initial and boundary condition are expressed by the following expressions:

$$c_{O_2}^R(y,0) = 0 \quad (41)$$

$$c_{O_2}^R(0,t) = c_{O_2}^S \quad (42)$$

Hydrogen Peroxide

$$\begin{aligned} \frac{\partial c_{H_2O_2}^R}{\partial t} = & -v \frac{\partial c_{H_2O_2}^R}{\partial y} \\ & + \frac{A \varepsilon}{V_R} K_{mH_2O_2} \left[(c_{H_2O_2}^P)_{L,t} - c_{H_2O_2}^R \right] \end{aligned} \quad (43)$$

According to the above said assumptions, the initial and boundary condition are expressed by the following expressions:

$$c_{\text{H}_2\text{O}_2}^{\text{R}}(y,0) = 0 \quad (44)$$

$$c_{\text{H}_2\text{O}_2}^{\text{R}}(0,t) = c_{\text{H}_2\text{O}_2}^{\text{S}} \quad (45)$$

- *Dispersed model*
Oxygen

$$\begin{aligned} \frac{\partial c_{\text{O}_2}^{\text{R}}}{\partial t} = & -v \frac{\partial c_{\text{O}_2}^{\text{R}}}{\partial y} + E_{\text{O}_2} \frac{\partial^2 c_{\text{O}_2}^{\text{R}}}{\partial y^2} \\ & + \frac{A \varepsilon}{V_{\text{R}}} K_{\text{mO}_2} \left[(c_{\text{O}_2}^{\text{P}})_{\text{L,t}} - c_{\text{O}_2}^{\text{R}} \right] \end{aligned} \quad (46)$$

The initial and boundary condition are expressed by the following expressions:

$$c_{\text{O}_2}^{\text{R}}(y,0) = 0 \quad (47)$$

$$v c_{\text{O}_2}^{\text{R}} \Big|_{y=0} - E_{\text{O}_2} \frac{\partial c_{\text{O}_2}^{\text{R}}}{\partial y} \Big|_{y=0} = v c_{\text{O}_2}^{\text{S}} \quad (48)$$

$$\frac{\partial c_{\text{O}_2}^{\text{R}}}{\partial y} \Big|_{y=h} = 0 \quad (49)$$

where:

h - height of the cathodic compartment of the cell.

Hydrogen Peroxide

$$\begin{aligned} \frac{\partial c_{\text{H}_2\text{O}_2}^{\text{R}}}{\partial t} = & -v \frac{\partial c_{\text{H}_2\text{O}_2}^{\text{R}}}{\partial y} + E_{\text{H}_2\text{O}_2} \frac{\partial^2 c_{\text{H}_2\text{O}_2}^{\text{R}}}{\partial y^2} \\ & + \frac{A \varepsilon}{V_{\text{R}}} K_{\text{mH}_2\text{O}_2} \left[(c_{\text{H}_2\text{O}_2}^{\text{P}})_{\text{L,t}} - c_{\text{H}_2\text{O}_2}^{\text{R}} \right] \end{aligned} \quad (50)$$

The initial and boundary condition are expressed by the following expressions:

$$c_{\text{H}_2\text{O}_2}^{\text{R}}(y,0) = 0 \quad (51)$$

$$v c_{\text{H}_2\text{O}_2}^{\text{R}} \Big|_{y=0} - E_{\text{H}_2\text{O}_2} \frac{\partial c_{\text{H}_2\text{O}_2}^{\text{R}}}{\partial y} \Big|_{y=0} = v c_{\text{H}_2\text{O}_2}^{\text{S}} \quad (52)$$

$$\frac{\partial c_{\text{H}_2\text{O}_2}^{\text{R}}}{\partial y} \Big|_{y=h} = 0 \quad (53)$$

The availability in literature of suitable data and empirical correlations concerning mass transport in this kind of systems allows to evaluate model parameters, such as physical-chemical properties of the species involved in the process, Henry constant, porosity and tortuosity factor of the electrode and external mass transfer coefficients. The kinetic coefficient, K , can be determined using the equation (18). In order to obtain the required data, experimental runs were carried out in an electrochemical laboratory apparatus. The evaluation of the dispersion coefficient requests the availability of data relevant to the effects of fluid-dynamics on the system behaviour. Normally, for complex systems, these information are obtained by carrying out the work in equipments, where the time dependent input technique is used. Lack of information about the fluid flow within the cathodic compartment, leads to assign to this parameter various values in order to analyse the role that these fluid-dynamics aspects have on the whole system performance.

The model's equations can be solved numerically by g-PROMS software.

In order to validate the model, electrolyses are carried out in the pilot plant above described. The amount of hydrogen peroxide generated is monitored during the experiments.

With reference to the working conditions of experimental tests, the concentration profiles from various proposed models are obtained.

To verify the models, tests are performed varying the dispersion coefficient value in the dispersed model. Results confirm that, increasing the dispersion coefficient, it is possible to change from the behaviour of a "plug flow reactor" to a "perfectly mixed reactor", described by the relevant models.

The comparison between the concentration of hydrogen peroxide at the exit section of the electrochemical cell at the threshold conditions typical of the "plug flow reactor" and "perfectly mixed reactor", allows to define the range in which dispersion coefficient affects the behaviour of the system. At the beginning of electrolysis, the effects of non-ideal flow patterns in the hydrogen peroxide concentration profiles inside the cathodic compartment are striking, as Fig. 7 clearly shows.

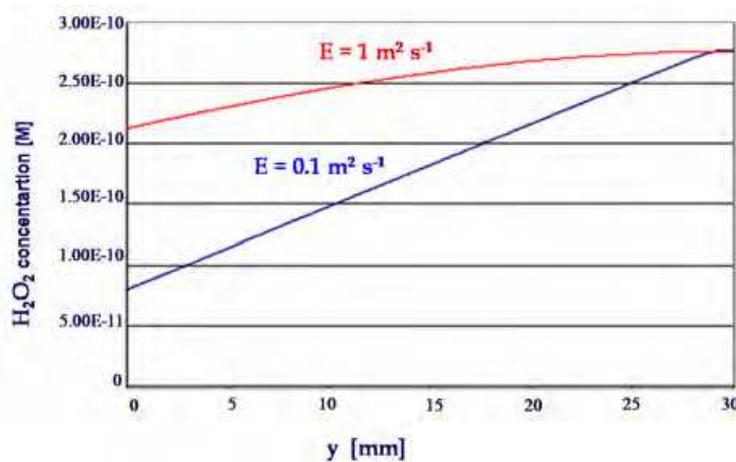


Fig. 7. Simulated hydrogen peroxide concentration profile inside the cathodic compartment . Effect of dispersion.

With increasing time, the effects become more blurred because of recirculation. In these conditions, the system is poorly sensitive to variations in the dispersion coefficient.

The shape of hydrogen peroxide concentration profiles in the flooded layer inside the pore, at various times is a combination of the resistances of the electrochemical reaction and the

diffusion of both components in the liquid phase. In the given working conditions, results of simulation, shown in Fig. 8, highlight that at longer times, more hydrogen peroxide accumulates within the pore. This may become a limiting factor when the contribution of the peroxide decomposition reaction to the overall process is considered.

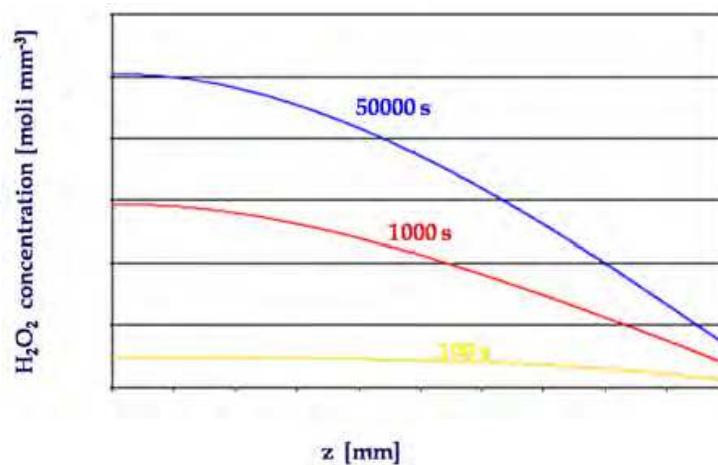


Fig. 8. Simulated hydrogen peroxide concentration profile inside the flooded layer at different times.

Lastly, validation is achieved comparing predictions based on equations (6)÷(40) with the experimental data obtained in the pilot plant (Giomo et al., 2008). Fig.9 shows the results with reference to simulated values obtained from CSTR model.

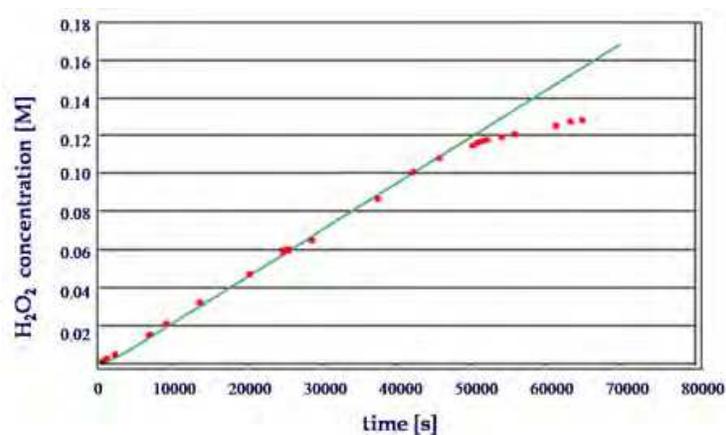


Fig. 9. Hydrogen peroxide electro-generation in the catholyte during the electrolysis. Comparison of experimental data and simulation values obtained from CSTR model.

A good match between simulated and experimental values is observed at the beginning of electrolysis, in accordance with the literature (Da Pozzo et al., 2005). At longer times, the model overestimates hydrogen peroxide production, perhaps due to several factors, e.g., higher rate of side reactions (15) and (16) (Da Pozzo et al., 2005), electrode flooding (Pasaogullari & Wang, 2004), or existence of considerable local overpotential or OH⁻ concentration values on the cathode surface, followed by H₂O₂ decomposition and H₂O production (Alcaide et al., 2002; Agladze et al., 2007; Kolyagin & Kornienko, 2003), not represented by the first-order kinetic equation used in this first model approach.

5. Conclusion

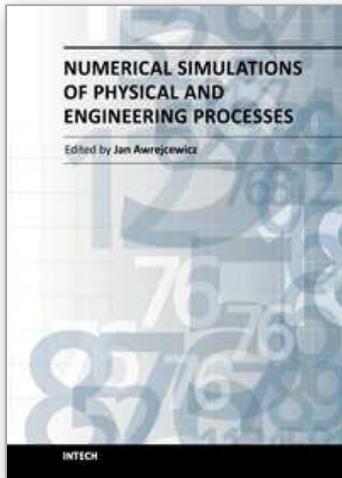
The two applications presented are basic examples of:

- simulations of the same system by using different models so as to compare their predictive capacity and the limitations of the solution techniques required to solve them;
- splitting the process into the main steps to define the subsystems which allow to analyse those particular attributes of the process that are of interest;
- development of mathematical models for each subsystems which allow to highlight the role played by the single step of the process and the parameters which are controlling its behaviour. The purpose is to obtain a representation of the whole process based on fairly simple representations for the parts;
- design of several laboratory apparatus or pilot plants to analyse the behaviour of subsystems, to obtain information about the essential features of the process and to evaluate the parameters in the model;
- comparison between calculated values and experimental data to evaluate how well the model represents the real process and to check the validity of assumptions made.

6. References

- Agladze, G.R. ; Tsursumia, G.S.; Jung, B.I.; Kim, J.S. & Gorelishvili, G. (2007). Comparative study of hydrogen peroxide electro-generation on gas-diffusion electrodes in undivided and membrane cells. *Journal of Applied Electrochemistry*, Vol. 37 , No. 3, pp. 375-383, ISSN 1572-8838
- Alcaide, F.; Brillas, E. & Cabot, P.L. (2002). Impedance study of the evolution of a HO₂-generating hydrophobic gas diffusion electrode. *Electrochemistry Communications*, Vol. 4, No. 10, pp. 838-843, ISSN1388-2481
- Brillas, E.; Calpe, J.C. & Casado J. (2000). Mineralization of 2,4-D by advanced electrochemical oxidation processes. *Water Research*, Vol. 34, No.8, pp. 2253-2262, ISSN 0043-1354
- Buso, A. ; Giomo, M. & Paratella, A. (1991). Multistage Vibrating-Disk Column with concurrent gas-liquid flow. Fluidynamic simulation. *Chemical and Biochemical Engineering Quarterly*, Vol. 5, No. 1-2, pp. 23-33
- Buso, A. ; Giomo, M.; Boaretto, L.; Sandonà, G. & Paratella, A. (1997). New electrochemical reactor for waste water treatment: electrochemical characterisation. *Chemical Engineering and Processing*, Vol. 36, No. 4, pp.255-260, ISSN0255-2701
- Da Pozzo , A; Di Palma , L.; Merli, C.; Petrucci, E. (2005) An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide, *Journal of Applied Electrochemistry*, Vol. 35, No. 4, pp. 413-419, ISSN 1572-8838
- Drogui, P.; Elmaleh, S. ; Rumeau, M. & Rambau A. ; (2001) Hydrogen peroxide production by water electrolysis: Application to disinfection, *Journal of Applied Electrochemistry*, Vol. 31 , p. 877-887, ISSN 1572-8838
- Fahim, M.A. & Wakao N. (1982) *Chemical Engineering Journal*, Vol. 25, p. 1, ISSN....
- Giomo, M.; Buso, A.; Fier, P.; Sandonà, G.; Boye, B. & Farnia G. (2008) A small-scale pilot plant using an oxygen-reducing gas-diffusion electrode for hydrogen peroxide electrosynthesis, *Electrochimica Acta*, Vol. 54, No. 2, pp. 808-815, ISSN0013-4686

- González-García, J.; Bank, C.E.; Sljukic, B. & Compton, R.G. (2007). Electrosynthesis of hydrogen peroxide via the reduction of oxygen assisted by power ultrasound. *Ultrasonics Sonochemistry*, Vol. 14, No.4, pp.405-412, ISSN1350-1477
- Himmelblau, D.H., Bishoff, K.B. (1968) *Process Analysis and Simulation*, J. Wiley& Sons, USA
- Karr , A. E.; Ramanujam, S; Lo, T. C.; Baird, M.H.I. (1987) Axial mixing and scale-up of reciprocating plate column. *Canadian Journal Chem. Eng.*,Vol. 65, No.3, pp. 373-381, ISSN1939-019X
- Kolyagin, G.A. &Kornienko,V.L. (2003). Kinetics of hydrogen peroxide accumulation in electrosynthesis from oxygen in gas diffusion electrode in acid and alkaline solutions. *Russian Journal Applied Chem.*, Vol. 76, No.7, pp. 1070-1075, ISSN1608-3296
- Lobyntseva , E.; Kallio, T.; Alexeyeva, N.; Tammeveski, K. & Konturri, K. (2007). Electrochemical synthesis of hydrogen peroxide: Rotating disk electrode and fuel cell studies. *Electrochimica Acta*, Vol. 52,No.25, pp. 7262-7269, ISSN0013-4686
- Lounes, M. & Thibault, J. (1996). Axial dispersion in a reciprocating plate column. *Canadian Journal Chem. Eng. ,* Vol.74, No.2 , pp.187-194, ISSN1939-019X
- Miyunami, K.; Tojo, K. & Yano, T.J. (1973). Liquid-phase mixing in a multistage vibrating-disk column with concurrent gas-liquid flow. *Chemical Engineering Japan*, Vol. 6, No.6, p.518-522
- Parthasarathy, P.; Sriniketan, G.; Srinivas, N.S. & Varma, Y.B.G. (1984). Axial mixing of continuous phase in reciprocating plate columns. *Chemical Engineering Science*, Vol. 39, No. 6, pp.987-995, ISSN0009-2509
- Pasaogullari U. & Wang, C.Y (2004). Liquid water transport in gas diffusion layer of polymer electrolyte fuel cells. *Journal of Electrochemistry society*, Vol. 151 ,No. 3, pp. A399-406, ISSN1945-7111
- Prentice, G. (1991) *Electrochemical engineering principles*, Ed. Prentice-Hall , New Jersey USA
- Roemer, M. H. & Durbin L.D. (1967). Transient response and moments analysis of backflow cell model for flow systems with longitudinal mixing. *Industrial and Engineering Chemistry Fundamentals*,Vol. 6, pp. 120-129, ISSN0196-4313
- Trinidad , P.; Ponce de León , C. & Walsh, F.C. (2006). The application of flow dispersion model to the FM01-LC laboratory filterpress reactor. *Electrochimica Acta*, Vol. 52, No. 2,pp. 604-613, ISSN0013-4686
- Vakao, N. & Kaguei S. (1982) *Heat Transfer in Packed Beds*, Gordon and Breach Science, New York USA
- Varma , A. & Morbidelli M. (1997) *Mathematical Methods in Chemical Engineering*, Oxford University Press, Oxford, MA, USA



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