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Application of metallic foams in electrochemical reactors of filter-press type
Part I: Flow characterization

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The aim of the present paper is to investigate the application of nickel foam electrodes in classical filter-press type electrochemical cells. For this purpose the ElectroSynCell®, commercialized by Electrocell AB, has been used. The interest of using metallic foams linked to a classical plane plate is to improve the performance of the electrochemical cell by increasing the electrode surface area. Moreover, for some industrial applications it is possible to use the cell without a membrane. In the proposed configuration, the working electrodes consist of metallic foam linked to a plane plate and the auxiliary electrode is simply a plane plate. The imbalance between the surface areas of working and auxiliary electrodes allows operation with a single hydraulic circuit. This paper, focuses on the study of residence time distribution and pressure drop in order to compare the flow behaviour with that in a classical configuration. A model for the reactive zone of the cell is also given.

Notation

D_{ax}	axial dispersion coefficient ($m^2 s^{-1}$)
ER	root mean square error
$F(s)$	transfer function in Laplace domain
I	number of continuous stirred tank reactors in the first cascade (model of the two cascades)
J	number of continuous stirred tank reactors in the second cascade (model of the two cascades)
L	length of the path in the reactor (m)
ΔP	pressure drop (Pa)
Pe_r	Peclet number of reactor
Q_v	volumic flow rate ($m^3 s^{-1}$)
$\bar{t}_s$	mean residence time (s)
u	interstitial velocity ($m s^{-1}$)
U_0	mean superficial velocity ($m s^{-1}$)
$X(t)$	experimental signal at the inlet of the reactor
$Y(t)$	experimental signal at the outlet of the reactor
$Y_{cal}(t)$	calculated signal at the outlet of the reactor
Greek letters	
ϵ	porosity of the duct in the reactor
σ	standard deviation
τ_1	mean residence time in the first cascade (s)
τ_2	mean residence time in the second cascade (s)

1. Introduction

Among the large number of porous materials available for the constitution of three-dimensional electrodes, metallic foams are particularly interesting. Like polyurethane foams, they are characterized by a reticulated structure and porosities close to unity. Previous work has outlined a few intrinsic properties of this material such as a high dynamic specific surface area, a tortuosity close to unity, a relative isotropy and low dispersion [1–4]. Diffusion-convection mass transfer and potential distribution during flow-through and flow-by nickel foams have also been studied in [5–7].

The aim of the present work is to study the possibility of using metallic foams in filter-press type electrochemical reactors. The principle of the proposed application is based on the increased surface area of the electrodes. For this purpose, a commercially available filter-press type cell was used: the ElectroSynCell® of Electrocell AB [8, 9].

The classical use of the ElectroSynCell® consists in stacking representative unit cells (r.u.c.). These consist of a plane plate, the electrode, which is covered by two plastic nets acting as turbulence promoters. The r.u.c.'s have alternating anolyte and catholyte compartments separated by membranes (Fig. 1). In this configuration, the replacement of turbulence promoters by sheets of nickel foam is expected to induce a significant increase in the surface area of the electrodes. In a filter-press type cell, interest in using a reticulated medium to increase the active surface area of the electrode has been demonstrated for mediated electrosynthesis [10]. However, the active surface area of the reticulated titanium used was not known and no characterization of the flow and mass transfer was attempted.

Depending on the type of reactions performed in the cell, a second mode of use of the ElectroSynCell® is available. It consists in working without a membrane, i.e. with a single hydraulic circuit. To

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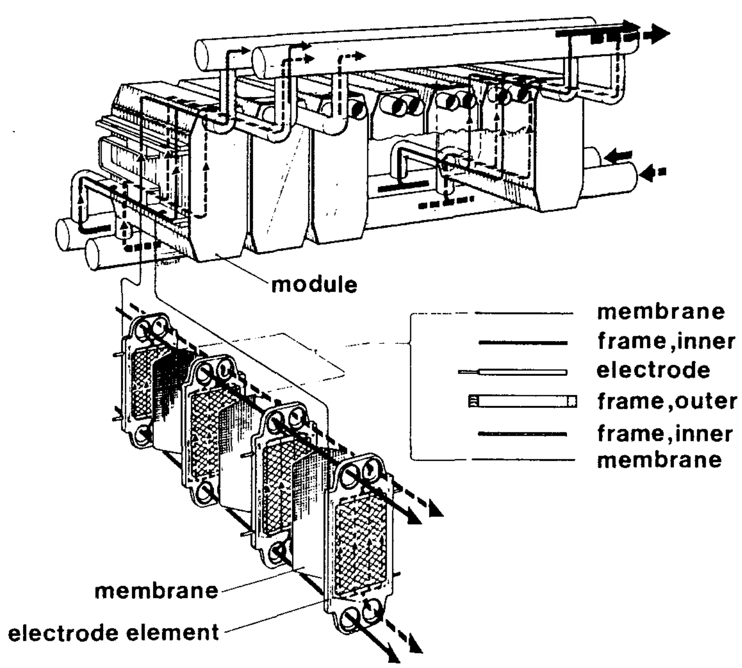

Fig. 1. The ElectroSynCell® system. Exploded view of a 7-module secton. (from [9]).

the authors′ knowledge, a filter-press type electrochemical cell with metallic foam working without a membrane is a new application which is based on the imbalance between the surface of the working electrode (plane plate covered with foam) and that of the auxiliary electrode (plane plate covered with turbulence promoters).

The present paper focuses on the study and modelling of the hydrodynamics in the ElectroSynCell® consisting of an r.u.c. according to the classical use and the new use (without membrane) (Fig. 2). For the classical use, the r.u.c. is successively made of: a plane plate covered with turbulence promoters (Fig. 2a); a plane plate with foams (Fig. 2b); and a plane plate alone (Fig. 2c). With the new suggested application, the r.u.c. consists of a plane plate covered with a turbulence promoter and another covered with a sheet of foam delimiting a single channel (Fig. 2d).

In each case, study of the residence time distribution (r.t.d.) is performed in the whole cell so as to describe its global behaviour. A model of the hydrodynamics in the reaction area of each r.u.c. is also proposed.

The present work allows an indication of modification of the hydrodynamics due to the foams. With industrial processes in view, a complementary experimental study has been performed in order to quantify the influence of foam introduction in the ElectroSynCell® on mechanical energy dissipation.

In a further paper [11], the new configuration will be tested by performing the electroconversion of ferricyanide to ferrocyanide ions. The paper will also include a study of mass transfer to the electrodes.

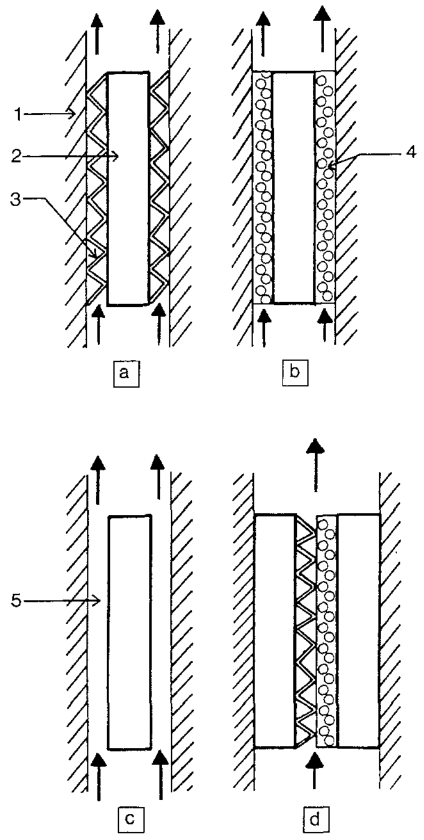

Fig. 2. The different representative unitary cells studied (r.u.c.). (1) Frame of the electrolyser, (2) plane plate, (3) turbulence promoter, (4) sheet of foam, (5) empty channel.

2. Residence time distribution

2.1. *Experimental details*

The study of the residence time distribution (r.t.d.) allows establishment of macroscopic characterization of the flow behaviour in a reactor [12, 13]. In the present work, r.t.d. of the whole ElectroSynCell® was investigated by means of a polarographic method with two-point measurement [14]. The reactor was

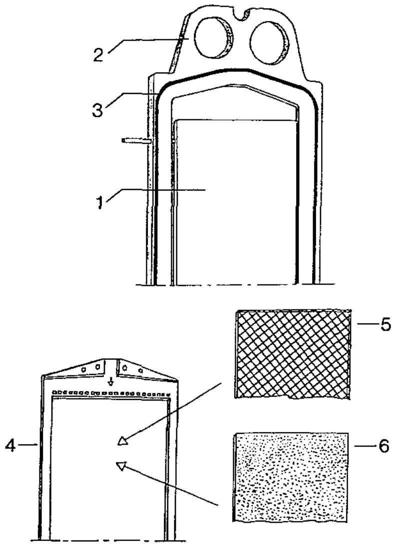

Fig. 3. Description of different components of the ElectroSynCell®: (1) plane plate, (2) 'outer' frame, (3) seal, (4) 'inner' frame, (5) plastic net of the 'inner' frame (turbulence promoter), (6) metallic foam (used instead of the plastic net).

provided with a single r.u.c. so as to compare the flow behaviour. The different configurations tested are shown in Fig. 2.

In the ElectroSynCell® (Fig. 3), each plane electrode is usually inserted into an 'outer' polymeric frame covered with two 'inner' frames. The 'inner' frames are composed of fluid distributors, located upstream and downstream of the reaction area, and of plastic nets acting as turbulence promoters in the reaction area. The plastic net is a lattice of triangular threads of polypropylene with 0.01 m × 0.008 m diamond shaped mesh; its porosity is 0.90.

For the purpose of experiments carried out in the configuration 'd' (Fig. 2d), some plastic nets were removed and replaced by a sheet of foam of the same thickness (2.5 mm). The sheets of foam were connected to the plane electrodes with conductive cyanolyte. In order to define an r.u.c., the electrolyte flowed in a single channel, i.e. between two plates, as shown in Fig. 2d. Then, in configuration 'd', the thickness of the channel was twice as large as those of configurations 'a', 'b', and 'c'. Both plane plates and the foam used in the experiments were made of nickel. The foam was grade 60, i.e. 60 pores per inch; the specific surface area offered to the fluid flow was 250 000 m^{-1} [2] (surface area per volume of solid) and the porosity was 0.975. A large grade range is commercially available; among the previously studied foams [3], those of grade 60 have been shown to present an interesting ratio between the surface area and the pressure drop.

A schematic view of the hydraulic circuit of the apparatus is given in Fig. 4. The tracer was injected upstream in the reactor and both responses at the inlet $X(t)$ and at the outlet $Y(t)$ of the reactor were recorded. The principles of the experimental method are given in [14]. The aqueous electrolyte contained 0.5 M NaOH, 10^{-3} M[$K_3(Fe(CN)_6)$] and 5×10^{-2} M[$K_4(Fe(CN)_6)$] at 30°C. At this temperature, the values of liquid density and dynamic viscosity were determined to be 1021 kg m^{-3} and 0.932×10^{-3} Pa s. The tracer was a saturated aqueous potassium ferricyanide solution. The variation of the concentration of ferricyanide ions was measured at two cathodic sensors working under limiting diffusion current conditions. The limiting diffusion current intensity measured at the cathodic sensors is directly proportional to the ferricyanide concentration. The cathodic sensors were small expanded nickel discs. Two counter-electrodes consisting of knitted nickel wire were located respectively upstream and downstream of the cathodic sensors. Their surface areas were greater in order to ensure that limiting diffusion current conditions were obtained at the cathodic sensors.

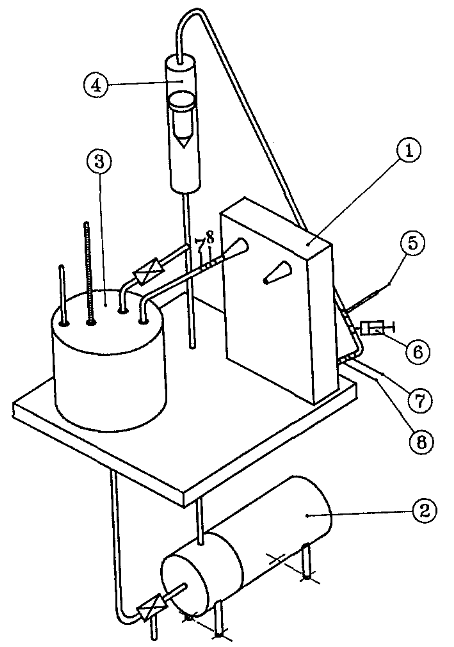

Fig. 4. Schematic view of the hydraulic circuit of the experimental apparatus: (1) ElectroSynCell®, (2) centrifugal pump, (3) thermoregulated tank, (4) flow meter, (5) reference electrode, (6) injection of tracer, (7) counter electrode, (8) working electrode (sensor).

2.2. *Modelling the fluid flow in the whole electrolyser*

As the experimental variation of the tracer concentration against time was registered only at the inlet and outlet of the cell, the flow in the cell is described by a simple dispersed plug flow model whose parameters are the mean residence time, $\bar{t}_s$ and the Peclet number Pe_r:

$$Pe_r = \frac{U_o L}{\epsilon D_{ax}} \tag{1}$$

The concentration, C, of a tracer uniformly injected over the cross section of a bed of non porous particles is given as a function of time, t, and axial position, z, by the equation:

$$\frac{\partial C}{\partial t} = D_{ax} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \tag{2}$$

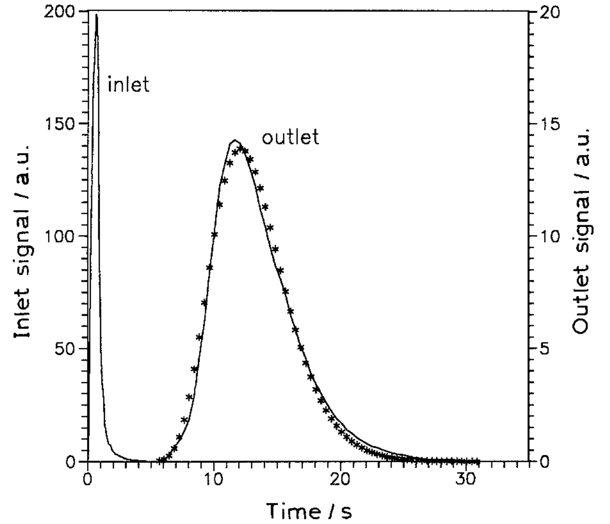

Fig. 5. An example of a $Y(t)$ curve (——) and the corresponding calculated $Y_{\mathrm{cal}}(t)$ curve (***) obtained with the configuration 'a' (Fig. 2). $Q_{\mathrm{v}} = 167 \mathrm{dm}^3\,\mathrm{h}^{-1}$, $Pe_{\mathrm{r}} = 33.7$, $\bar{t}_{\mathrm{s}} = 12.4\,\mathrm{s}$ and $ER = 7.0\%$.

Assuming that the dispersion is of the same order of magnitude upstream and downstream of the cathodic sensors, the transfer function in the Laplace domain is:

$$F(s) = \exp\left\{\frac{Pe_{\mathrm{r}}}{2}\left[1 - \left(1 + \frac{4}{Pe_{\mathrm{r}}}\bar{t}_{\mathrm{s}}s\right)^{1/2}\right]\right\} \tag{3}$$

Each pair of curves $X(t)$ and $Y(t)$ at the inlet and outlet of the reactor was analysed: the parameters Pe_{r} and $\bar{t}_{\mathrm{s}}$ were deduced from curve fitting in the time domain. The method, introduced by Wakao [15], is described in [4] and [14]. The optimization of the curve fitting is based on the minimization of a root mean square error ER:

$$ER = \frac{\int_0^{2\mathrm{T}} [Y(t) - Y_{\mathrm{cal}}(t)]^2\, dt}{\int_0^{2\mathrm{T}} [Y(t)]^2\, dt} \tag{4}$$

where $Y_{\mathrm{cal}}(t)$ is the calculated signal at the outlet of the reactor. The curves $Y(t)$ and $Y_{\mathrm{cal}}(t)$ are expressed, in time domain, in terms of Fourier series. Whatever the studied configuration, the value of the error, ER, is small, except in the case of the configuration 'a' (Fig. 2) using turbulence promoters for which the values of ER lie between 5 and 8%. An example of a $Y(t)$ curve obtained with the configuration 'a' and the corresponding calculated curve $Y_{\mathrm{cal}}(t)$ is given in Fig. 5. The comparison between $Y(t)$ and $Y_{\mathrm{cal}}(t)$ is made for one of the highest values of ER (7%), and so the dispersed plug flow model is appropriate.

Table 1. Mean value of Pe_r and corresponding values of the standard deviation σ.

Tested configuration	*Mean Peclet number ± standard deviation*
Plane plates with two promoters	34.5 ± 2.0
Plane plate with two sheets of foam	17.5 ± 3.0
Plane plate alone	17.4 ± 2.3
Two plane plates, a sheet of foam and a promoter	19.9 ± 1.6

Experimental values of Pe_{r} are plotted in Fig. 6 against the volumetric flow rate Q_{v}. The range of values of Q_{v} largely covers the hydrodynamic domain advised by the manufacturer. The flow behaviour depends on the tested configuration: in particular, axial dispersion is less significant when the frames contain turbulence promoters than when they contain sheets of nickel foam G60. For each configuration, the variation of the Peclet number, Pe_{r}, against the volumetric flow rate is small. The mean values of Pe_{r} and the corresponding standard deviation σ are given in Table 1. Neglecting the variation of Pe_{r} with the flow rate, the flow behaviour is the same whether the frames contain nickel foams or are empty. Filling channels in the ElectroSynCell® with sheets of foam does not introduce a major modification of the flow behaviour, whereas using turbulence promoters induces approximately plug flow.

In the particular case of the configuration 'd' (Fig. 2) corresponding to an asymmetric system, the flow behaviour is intermediate, but closer to that observed with frames containing nickel foam only.

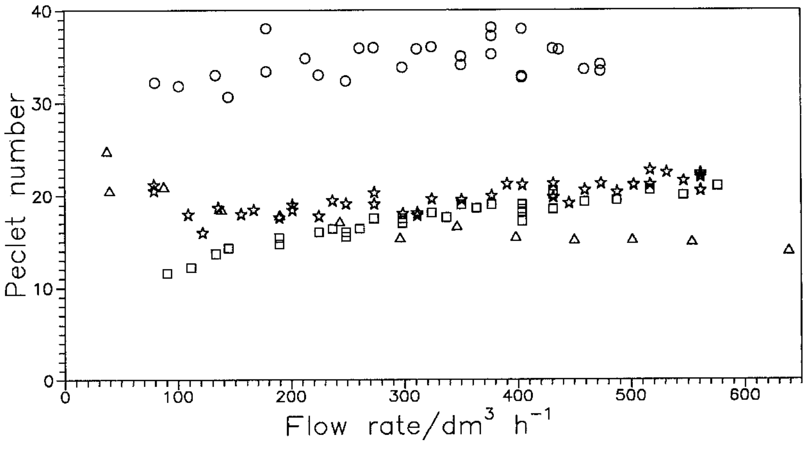

Fig. 6. Representation of the Peclet criterion Pe_{r} against the volumetric flow rate Q_{v}. Key: (○) turbulence promoters 'a'; (△) empty channels 'c'; (□) nickel foam G60 'b'; (☆) foam plus turbulence promoter 'd'.

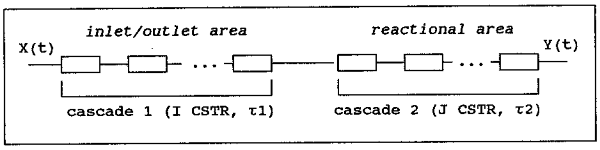

Fig. 7. Sketch of the model of the cascades.

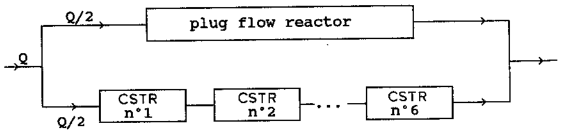

Fig. 8. Sketch of the modelling of configuration 'd' with a plug flow reactor and a cascade of 6 CSTR.

2.3. *Modelling the fluid flow in the reaction area*

In order to attempt a characterization of the flow behaviour in the reaction area, which may be interesting for potential applications, the experiments are analysed using a second model. This model differentiates the flow in the electrochemically active area from the flow in the non-working area: inlet and outlet zones including the flow distributors of the frames. It consists of two cascades of continuous stirred tank reactors (CSTR) of identical volume:

(i) the first cascade of CSTR corresponds to the flow in the non working area and is characterized by a mean residence time τ_1 and a number of reactors I.

(ii) the second cascade of CSTR corresponds to the flow in the reaction area and is characterized by a mean residence time τ_2 and a number of reactors J.

The model is sketched in Fig. 7. Its transfer function in the Laplace domain is:

$$F(s) = \left(1 + \frac{s\tau_1}{I}\right)^{-J}\left(1 + \frac{s\tau_2}{J}\right)^{-I} \quad (5)$$

As the volume of the reactional area is known, τ_2 can be calculated. τ_1 cannot be accurately measured because of volume of gas remained in the inlet and outlet pipes of the cell during the experiments. Three parameters are optimized: τ_1, I and J. The optimization is based on the minimization of ER. The mean calculated numbers of I and J, as well as the corresponding standard variation, are given in Table 2.

Depending on the tested configuration, the mean value of I is slightly different, whereas the non working area of configurations 'a', 'b' and 'c' is the same. Nevertheless, the model is too approximate for the result to be considered significant.

By contrast, the mean value of J strongly depends on the configuration. In the classical use of the ElectroSynCell® (configuration 'a'), the mean number of reactors representing the flow in the reaction area is large enough to consider that plug flow occurs. In the new proposed application (configuration 'd'), the mean number of reactors, J, is much lower, but significantly different from that obtained with the configurations 'b' and 'c'. When the frames are empty or filled with sheets of foam (configurations 'c' and 'b'), the mean number of reactors representing the reaction area is six, which means that the flow is more dispersed.

Table 2. Mean values of I and J and their corresponding standard deviations

Tested configuration	$\bar{I} \pm \sigma$	$\bar{J} \pm \sigma$
With promoters	5.9 ± 0.3	$\bar{J} > 100$
With foams	4.0 ± 0.7	5.8 ± 0.7
Plate alone	3.2 ± 0.2	6.1 ± 2.0
Foam/promoter	4.8 ± 0.7	35 ± 16

Considering the results obtained with configuration 'a' and 'b', i.e. a plug flow reactor for configuration 'a' and a cascade of 6 CSTR for configuration 'b', it is of interest to see if a cascade of 6 CSTR placed in parallel with a plug flow reactor (Fig. 8) correctly predicts the flow in configuration 'd'. For a pulse input, this model is equivalent to a cascade of 20 CSTR, whereas a cascade of 35 CSTR was shown to correctly fit the experimental r.t.d. curves obtained in configuration 'd'. These two numbers are similar because the behaviour of two cascades of, respectively, 20 and 35 CSTR of identical volume is very close. The difference can be explained by the fact that no membrane is used in configuration 'd'. In the single channel constituted by the foam and the turbulence promoter, the velocity profile is different from that in the narrower channels of configuration 'a' or 'b'. Moreover, the absence of a membrane allows flow exchanges between the areas of the foam and the turbulence promoter. This mixing does not occur with the model sketched in Fig. 8.

The study of the residence time distribution in four different configurations underscores the particular ability of turbulence promoters to create plug flow in the reaction area, Moreover, it has been shown that the use of sheets of foam induces a flow which is equivalent, from a r.t.d. point of view, to that observed with empty channels. Nevertheless, the enhancement of the surface area of the electrodes by a factor of 15 should largely compensate for the modification of the flow pattern due to the use of nickel foam G60 instead of plastic nets as turbulence promoters.

3. Overall pressure drop measurements in the ElectroSynCell®

The dissipation of mechanical energy associated with the flow through a reactor is an important criterion for industrial application. As well as the modification of the flow pattern, the use of a porous material such as metallic foams in the ElectroSynCell® may introduce additional pressure losses. Therefore, global pressure drops were measured in the previously studied range of flow rates. The ElectroSynCell® successively consisted of one of the first three r.u.c. described in Fig. 2 (configurations 'a', 'b' and 'c'). The pressure drops are plotted in Fig. 9 against the electrolyte flow rate.

The pressure drops measured with turbulence promoters and those measured with nickel foams

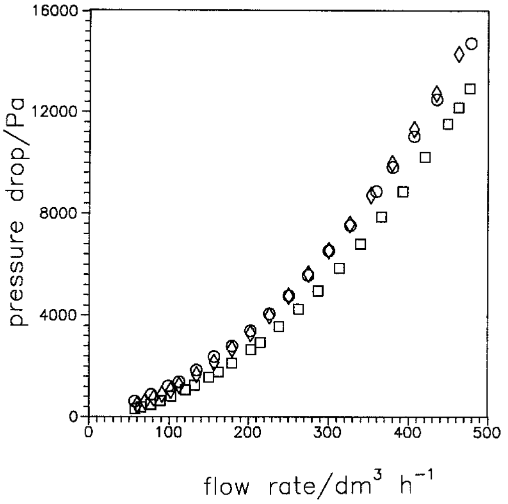

Fig. 9. Representation of the measured pressure drops ΔP against the volumetric flow rate Q_V. Key: (□) empty channels; (○) nickel foam G60; (◇) turbulence promoters.

G60 have the same order of magnitude. The pressure drop is expressed as:

$$\Delta P = A\ Q_V + B\ Q_V^2 \qquad (6)$$

where $A\ Q_V$ is the global viscous-resistance term and $B\ Q_V^2$ is the global inertial-resistance term. The experimental pressure drops are expressed as given in Equation 6 in Table 3.

In the range of flow rates 60–200 $\mathrm{dm^3\,h^{-1}}$, the dissipation of mechanical energy is greater with nickel foams as their high specific surface area gives rise to a larger viscous-resistance component of the pressure drop; the maximum deviation of pressure drop is 23%.

In the range of high flow rates 350–500 $\mathrm{dm^3\,h^{-1}}$, the kinetic energy losses are larger with the turbulence promoters, because of their particular structure. The pressure drops are slightly smaller with nickel foam (maximum deviation: 6%). Between these two ranges, the deviation of pressure drops is negligible.

Pressure drop measurement shows that the use of nickel foams G60 leads to a mechanical dissipation which is similar to that measured with the turbulence promoters. In a potential industrial application, the mechanical energy cost would not be increased.

As far as the new suggested application is concerned (Fig. 2, configuration 'd') the flow may be considered to be equally divided in the channels. These channels consist of a sheet of foam and of a plastic net respectively placed in parallel. This hypothesis can be supported by the fact that r.t.d. curves obtained with configuration 'd' have a quasi-gaussian shape.

Table 3. Expression of the pressure drops according to Relation 6.

Configuration	*Promoters*	*Foam G60*	*Empty channels*
$Q_V/\mathrm{m^3\,s^{-1}}$	1.66×10^{-5} to 12.8×10^{-5}	$1.5 \times 10^{-5}$to 13.2×10^{-5}	1.5×10^{-5} to 13.2×10^{-5}
$\Delta P/Q_V = f(Q_V)$ $/\mathrm{kg\,m^{-4}\,s^{-1}}$	$16.6 \times 10^6 + 7.4 \times 10^{11}\ Q_V$	$26.3 \times 10^6 + 6.3 \times 10^{11}\ Q_V$	$9.2 \times 10^6 + 6.7 \times 10^{11}\ Q_V$

4. Conclusion

Depending on the reactions performed in electrochemical reactors of the filter-press type, it is possible to replace commonly used turbulence promoters with metallic foams, to increase the surface area of the electrodes and, therefore, the compactness of the reactor. The use of metallic foams also allows this kind of electrolyser to work without membranes and, consequently, with a single hydraulic circuit. In this paper, the hydrodynamic behaviour of nickel foams has been tested in the ElectroSynCell®. To establish a comparison, the hydrodynamic behaviour corresponding to the classical use of this reactor was also studied. The plug flow model with axial dispersion correctly describes the flow in the reactor in both cases. A second modelling of the flow has been proposed in order to characterize the hydrodynamics in the reaction area, which is useful for a potential industrial application. The hydrodynamics in the electrolyser have been shown to be modified slightly, due to the presence of the foams; in the reaction area, the flow is no longer of the plug type. Nevertheless, the increase in the surface area of the electrode should largely compensate for the modification of the flow behaviour in the cell.

It has also been shown that the mechanical dissipation of energy due to flow has the same order of magnitude when nickel foam G60 replaces the turbulence promoters.

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