

# Application of metallic foams in electrochemical reactors of the filter-press type:

## Part II Mass transfer performance

A. MONTILLET, J. COMITI, J. LEGRAND

*Laboratoire de Génie des Procédés, Institut Universitaire de Technologie, Heinlex—BP 420 44606 Saint-Nazaire Cedex, France*

Received 15 December 1992; revised 13 September 1993

This paper focuses on mass transfer characteristics of classical filter-press electrochemical reactors without membranes. In the tested configuration, the working electrode consists of a plane plate with a sheet of foam and the counter-electrode consists of a plane plate with a turbulence promoter. The global mass transfer coefficients of the two electrodes have the same order of magnitude. Moreover, a comparison with literature data shows that their values remain in the range of those previously presented. Due to the high specific surface area of the foam used ( $A_{ve} = 6400 \text{ m}^{-1}$ ), the ratio of the surface area of the working electrode to that of the counter electrode is 15. The electroreduction of ferricyanide has been carried out to test the performance of this configuration. The value of the final conversion has been compared to that calculated from mass transfer coefficients and surface areas of the electrodes.

### List of symbols

$A_{ve}$	dynamic specific surface area of the foam: surface area per volume of material ( $\text{m}^{-1}$ )	$Q_v$	volumetric flow rate in the channel ( $\text{m}^3 \text{ s}^{-1}$ )
$A'_{ve}$	dynamic specific surface area of the electrode consisting of a plate and a sheet of foam: surface area per volume of electrode ( $\text{m}^{-1}$ )	$Re$	Reynolds number, $Re = U_0 d_h \nu^{-1}$
$A_{vs}$	static specific surface area ( $\text{m}^{-1}$ )	$S$	active surface area of the electrode ( $\text{m}^2$ )
$C_{in}$	ferricyanide concentration at the inlet of the cell ( $\text{mol m}^{-3}$ )	$S_a$	surface area of the anode ( $\text{m}^2$ )
$C_{out}$	ferricyanide concentration at the outlet of the cell ( $\text{mol m}^{-3}$ )	$S_c$	surface area of the cathode ( $\text{m}^2$ )
$\mathcal{D}$	diffusion coefficient ( $\text{m}^2 \text{ s}^{-1}$ )	$Sc$	Schmidt number, $Sc = \nu \mathcal{D}^{-1}$
$d_h$	equivalent hydraulic diameter, $d_h = 2lh / (l + h)$ (m)	$Sh$	Sherwood number, $Sh = k_d D_h / \mathcal{D}$
$\mathcal{F}$	Faraday number ( $\text{C mol}^{-1}$ )	$U_0$	superficial velocity ( $\text{m s}^{-1}$ )
$h$	channel thickness (m)	$V$	volume offered to fluid flow in the volumic electrode ( $\text{m}^3$ )
$I$	limiting diffusion current (A)	$V'$	volume of one tank reactor in the cascade ( $\text{m}^3$ )
$I_{ca}$	final limiting diffusion current intensity at the anode (A)	$X$	conversion
$I_{cf}$	final limiting diffusion current intensity at the cathode (A)	$X_f$	final conversion
$k_a$	mass transfer coefficient at the anode ( $\text{m s}^{-1}$ )	<i>Greek letters</i>	
$k_c$	mass transfer coefficient at the cathode ( $\text{m s}^{-1}$ )	$\epsilon$	porosity
$k_d$	mass transfer coefficient ( $\text{m s}^{-1}$ )	$\nu$	kinematic viscosity ( $\text{m}^2 \text{ s}^{-1}$ )
$l$	channel width (m)	$\rho$	density ( $\text{kg s}^{-1}$ )
$n$	number of electrons in the electrochemical reaction	$\tau$	residence time in a continuous stirred tank reactor $\tau = V' \epsilon / Q_v$ (s)
		<i>Subscripts</i>	
		e	electroconversion experiment
		mt	mass transfer experiment

### 1. Introduction

The first part of this contribution [1] was devoted to the characterization of flow through an ElectroSyn-Cell [2] with or without metallic foam in the flow

channels. The introduction of metallic foam was shown to induce a slight modification of the hydrodynamics in the electrolyser. Moreover, modelling of the flow in the reaction zone has shown that dispersion is greater with a sheet of foam than with the

commonly used turbulence promoters. Nevertheless, the increase in the surface area may largely compensate for the change in the hydrodynamic behaviour.

In the present paper, one of the applications suggested in Part I is tested. This application consists in working with a single hydraulic circuit (undivided mode). Its principle is based on the imbalance between the surface area of the working electrode (plane plate with a sheet of foam) and that of the counter-electrode (plane plate with a turbulence promoter). This kind of application may be of interest in order to solve industrial problems such as regeneration of mediators in organic electrosynthesis or the treatment of chromium waste electrolyte.

## 2. Mass transfer

### 2.1. Introduction

Experiments were carried out with a single representative unit cell (r.u.c.) consisting of an anode and a cathode. A sketch of the r.u.c. is given in Fig. 1(a). Part I of this contribution has described the flow behaviour in this configuration.

Mass transfer to the auxiliary electrode has been studied [3] in the same reactor. However, the tested r.u.c. was different: it consisted of two plane plates with turbulence promoters, Fig. 1(b). No membrane was used. In Part I, quasi plug-flow behaviour was shown to exist. No study of mass transfer to a working electrode consisting of a plane plate and an adjacent metallic foam has been performed in the ElectroSynCell.

### 2.2. Experimental details

Plane nickel plates from [2], and 2.5 mm thick (60 pores per inch) nickel foams from [4], were used for the electrodes. The foam thickness was identical to the apparent thickness of the plastic net (2.5 mm) acting as turbulence promoter on the

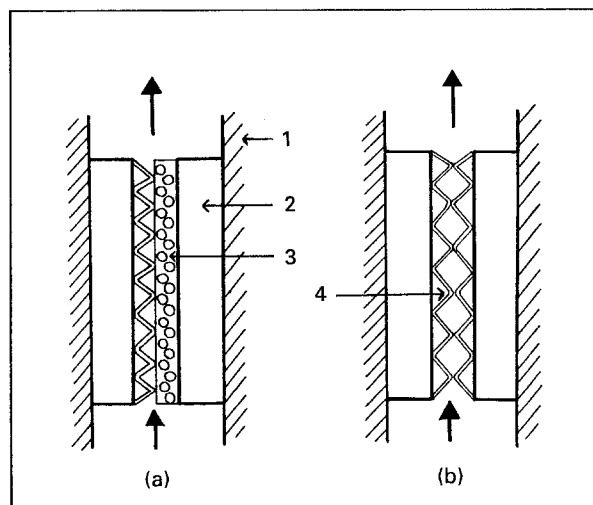


Fig. 1. (a) Sketch of the r.u.c. studied in this work; (b) sketch of the r.u.c. studied in [3]. (1) Frame of the electrolyser, (2) plane plate, (3) sheet of foam, (4) plastic net (turbulence promoter).

Table 1. Physical properties of the solution at 30° C

Kinematic viscosity, $\nu/\text{m}^2\text{s}^{-1}$	$8.89 \times 10^{-7}$
Density, $\rho/\text{kg m}^{-3}$	1039
Diffusion coefficient of ferricyanide, $\mathcal{D}/\text{m}^2\text{s}^{-1}$	$6.74 \times 10^{-10}$
Schmidt number, $Sc$	1320

counter-electrode (Fig. 1). To ensure good electrical contact between the plane plate of the working electrode and the foam, the latter was bonded to the plate with a conductive cyanolite, at a few points.

Net from [4] was used as turbulence promoter on the auxiliary electrode. Characteristics of this polymeric material are as follows: internal dimension of short mesh diagonal = 8 mm; internal dimension of long mesh diagonal = 9.5 mm; orientation of short mesh diagonal parallel to the main direction of flow; and overall porosity = 0.89.

In the reaction zone, the cross-sectional area for the electrolyte flow was limited to  $5 \times 140 \text{ mm}^2$ .

The mass transfer coefficient between the liquid and the electrode was obtained using the cathodic reduction of ferricyanide ions. The limiting diffusion current,  $I$ , was measured as a function of the flow rate,  $Q_v$ . Experiments were carried out as follows:

- (i) The electrodes were cleaned *in situ* with a 0.1 M solution of  $\text{H}_2\text{SO}_4$ .
- (ii) The working electrode was cathodically activated in a 0.5 M solution of NaOH (5 A for 1 h).
- (iii) The electrolyte (a mixture of  $10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  and 0.1 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in 0.5 M NaOH) was admitted in the cell and continuously recirculated at 30° C. The physical properties of the mixture are given in Table 1.

The channel electrolyte superficial velocity,  $U_0$ , in the reactive zone was varied between 0.028 and  $0.21 \text{ m s}^{-1}$ . Thus the Reynolds number,  $Re$ , based on the equivalent hydraulic diameter of the channel,  $d_h$ , lay between 300 and 2300.

### 2.3. Calculation of the mass transfer coefficient $k_d$

**2.3.1. Mass transfer coefficient at the working electrode.** The electrode is three dimensional. The dynamic specific surface area of 60 p.p.i. nickel foam,  $A_{ve}$ , has been found to be  $6400 \text{ m}^{-1}$  [5]. The specific surface area measured by gas adsorption  $A_{vs}$  (BET method) is approximately five times as large as  $A_{ve}$  [6]. The difference between  $A_{ve}$  and  $A_{vs}$  is due to the sensitivity of the methods used: the gas adsorption method can probe surface irregularities and pore interiors even at the atomic level, which is not the case with permeametry [7].  $A_{ve}$  is of particular interest for engineering applications, as its magnitude is that of the specific surface area where momentum, heat or mass transfer occur during fluid flow. Therefore,  $A_{ve}$  will be used in the following

Table 2. Experimental variations of  $k_d$  against  $U_0$  obtained respectively with expressions 4 and 6

Plane plate	$k_d = 7.3 \times 10^{-5} U_0^{0.61} \text{ m s}^{-1}$
+	
Sheet of foam	(cascade of six CSTR)
Plane plate	$k_d = 1.1 \times 10^{-4} U_0^{0.57} \text{ m s}^{-1}$

calculations as the effective mass transfer surface area of the foam.

The flow rate in each channel is considered to be equal to half the total flow rate, as previously shown in the pressure drop study [1].

In part one of this series [1], the flow in the channel of the working electrode was described as a cascade of six continuous stirred tank reactors (CSTR) of identical volume. Under limiting diffusion current conditions, the cathodic reduction of ferricyanide ions is a first order reaction:

$$rV = -\frac{I}{\mathcal{F}} = -k_d SC(t) \quad (1)$$

then

$$r = -k_d \frac{C(t)S}{V} = -k_d A'_{ve} \epsilon^{-1} C(t) \quad (2)$$

where  $V$  is the volume occupied by the fluid in the volumic electrode and  $\epsilon$  the porosity of the foam, i.e. 0.975.  $A'_{ve}$  is the specific surface area of the three-dimensional electrode consisting of a plate and a sheet of foam. For a cascade of six CSTRs the conversion is

$$X = 1 - \frac{C_{out}}{C_{in}} = 1 - [1 + k_d A'_{ve} \epsilon^{-1} \tau]^{-6} \quad (3)$$

The following expression can be deduced:

$$k_d = \frac{(1 - X)^{-1/6} - 1}{A'_{ve} \tau} \epsilon \quad (4)$$

with

$$X = \frac{I}{n\mathcal{F}Q_v C_{in}} \quad (5)$$

$X$  is the fractional conversion of ferricyanide ions per pass assuming a faradic yield of one. Its experimental value lies between 20 and 40%.

The experimental variation of  $k_d$  with  $U_0$  is given in Table 2 and plotted in Fig. 2.

2.3.2. *Mass transfer at the counter-electrode.* In contributions dealing with the study of mass transfer coefficient to plane plates,  $k_d$  is calculated using the

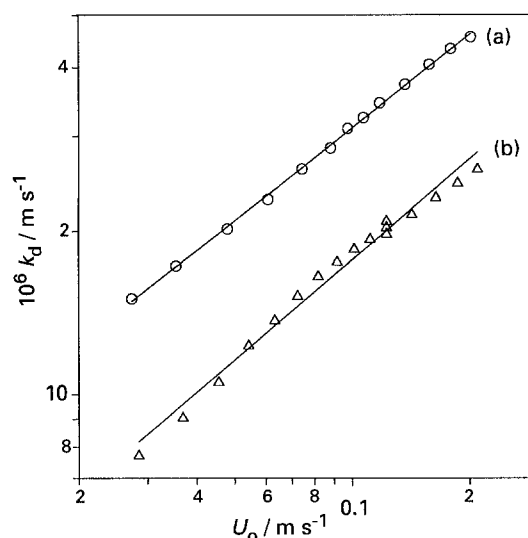


Fig. 2. Experimental data and correlations expressed as  $k_d$  against  $U_0$ . (a) Mass transfer to a plane plate, (b) mass transfer to a plane plate with a sheet of foam.

equation:

$$k_d = \frac{I}{n\mathcal{F}CS} \quad (6)$$

assuming a constant value of the bulk concentration  $C$ . This equation is applicable if the conversion,  $X$ , is small (Equation 5). This model was used to calculate mass transfer coefficients to the counter-electrode. The correlation of  $k_d$  against  $U_0$  is given in Table 2 and plotted in Fig. 2.

2.3.3. *Discussion.* Data have been gathered for mass transfer to a sheet of nickel foam [9] and to a nickel plate covered with a turbulence promoter [3, 8, 10]; all these data were obtained in the undivided mode. Details of the cells used and their geometry are given in Table 3. Correlations are expressed in the following form:

$$Sh Sc^{1/3} = a Re^b \quad (7)$$

and are plotted in Fig. 3; the values of the coefficients  $a$  and  $b$  are given in Table 4.

(a) *Mass transfer to a plate covered with a turbulence promoter*

Our correlation is to be compared with that previously obtained in the ElectroSynCell [3]. Mass transfer is surprisingly much lower in our r.u.c. A single geometric dimension was different in our work: the width of the channel was smaller (Table 3). However, the mass transfer rate has the same order of magnitude

Table 3. Geometrical data of the cells used in [3, 8, 9, 10] and in the present work

Reference	Reactor	Thickness of the channel/mm	Reaction area width/m	$d_h/m$
[3]	ElectroSynCell	9.0	0.154	$1.7 \times 10^{-2}$
[8, 9]	Laboratory cell	2.5	0.070	$4.83 \times 10^{-3}$
[10]	FM01-LC (ICI)	5.5	0.040	$9.7 \times 10^{-3}$
Present work	ElectroSynCell	5.0	0.140	$9.66 \times 10^{-3}$

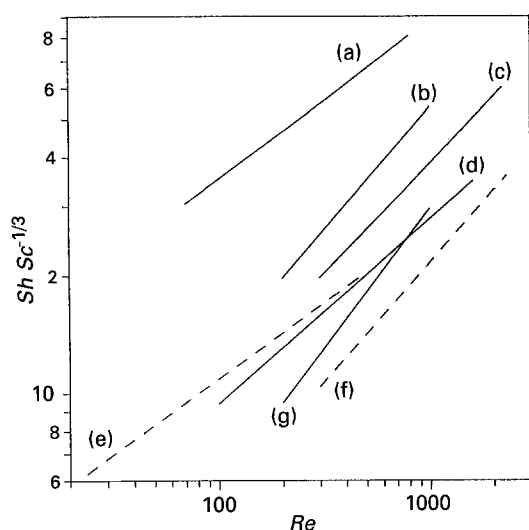


Fig. 3. Comparison of the data of the present work with respect to the literature. Mass transfer to a plane plate with a turbulence promoter: (a) [3], (b) [10], (c) present work, (d) [8], (e) mass transfer to a sheet of foam G60 [9], (f) mass transfer to a plate with a sheet of foam G60 p.p.i. (present work), (g) mass transfer to a plate alone [10].

as that measured in a laboratory cell [8] and in the FM01-LC of ICI [10]. The surprisingly high mass transfer obtained in [3] was already emphasized in [8].

#### (b) Mass transfer to the plate with metallic foam

Mass transfer is lower in term of Sherwood number than that obtained with a single sheet of foam [6] but has the same order of magnitude. This result is due to the difference in flow configuration and hydrodynamic conditions.

In our r.u.c., the ratio of mass transfer coefficients at the working electrode and the counter electrode is between 0.52 and 0.60. As the surface area of the working electrode is 15 times larger than that of the

counter electrode, the performances of this r.u.c., in terms of conversion, should be increased.

A comparison can be made with results of Brown *et al.* [10] for a plate and a plate with a turbulence promoter. The ratio of mass transfer coefficients to these electrodes is also about 0.5. In [1], the flow in an empty channel and that in a sheet of foam were shown to be the same from the dispersion point of view.

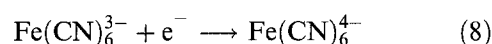
### 3. Electroconversion of ferricyanide

In membrane separated compartments, generation of Ce(IV) with reticulated titanium was attempted in the MicroProdCell of Electrocell AB [11]. With a high starting concentration of Ce(III), 0.42 M, interesting results were obtained; in particular the highest current densities ever reported for generation of an anodic mediator. More recently, Pletcher *et al.* [12] tested reticulated vitreous carbon cathodes, still in the divided mode, in order to remove Cu(II) with a single pass reactor. With low initial concentration (10 p.p.m.), high fractional conversions were measured (99%).

In the present work, the cathodic conversion of ferricyanide (intermediate concentration) was tested in an undivided configuration and with solution recycle.

#### 3.1. Theoretical aspects

The reaction consists in the cathodic reduction of potassium ferricyanide to potassium ferrocyanide:



Under limiting diffusion current conditions at the cathode, the reaction is first order. Initially, the electrolyte is composed of NaOH and  $\text{K}_3\text{Fe}(\text{CN})_6$ . At

Table 4. Values of the coefficients of the correlations expressed as  $Sh$  against  $Re$  and data of the experimental conditions

Reference	Tested electrode	$Sc$	$10^{10} \mathcal{Q} / \text{m}^2 \text{ s}^{-1}$	$Re$ range	$Sh = a Sc^{1/3} Re^b$
[3]	plane plate + turbulence promoter	1572	6.8	70–800	$a = 5.57$ $b = 0.40$
[8]	plane plate + turbulence promoter	1060	8.8	100–1600	$a = 1.09$ $b = 0.47$
[9]	sheet of foam 60 p.p.i.	1570	6.4	24–480	$a = 1.81$ $b = 0.39$
[10]	plane plate + turbulence promoter	1562	9.67	200–1000	$a = 0.74$ $b = 0.62$
[10]	plane plate	1562	6.2	200–1000	$a = 0.22$ $b = 0.71$
Present work	plane plate + turbulence promoter	1320	6.7	300–2200	$a = 0.77$ $b = 0.57$
Present work	plane plate + sheet of foam 60 p.p.i.	1320	6.7	300–2300	$a = 0.32$ $b = 0.61$

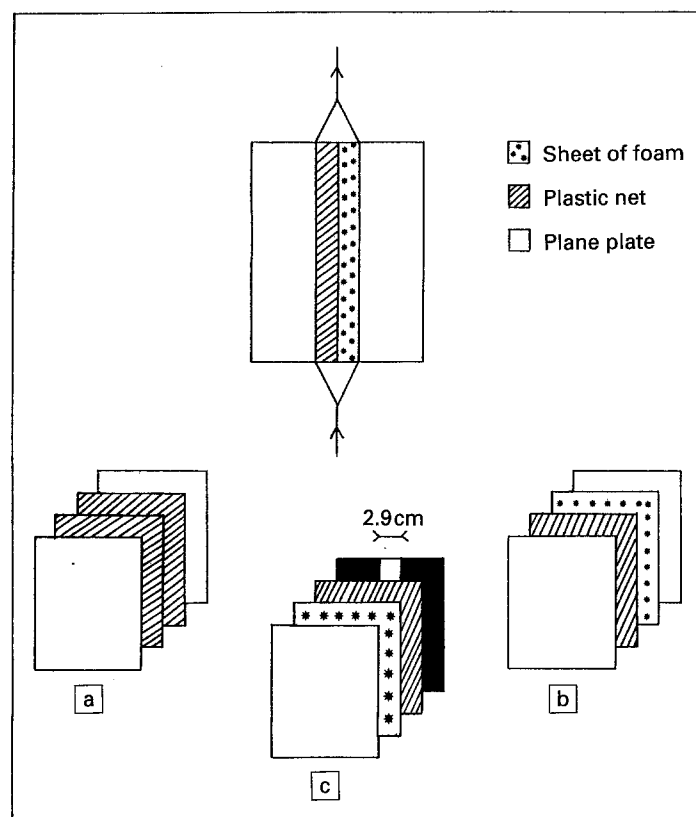


Fig. 4. Representation of the configurations tested with the electroconversion of ferricyanide.

the beginning of the reaction, the major fraction of the anodic current corresponds to oxygen generation; the remaining current corresponds to the conversion of ferrocyanide into ferricyanide. The concentration of ferricyanide gradually decreases to an equilibrium characterized by a constant current. At equilibrium, both electrodes are working under diffusion conditions, then the final limiting current intensities at the cathode and the anode,  $I_{c_f}$  and  $I_{a_f}$ , are given by

$$I_{c_f} = n\mathcal{F}k_c S_c [\text{Fe}(\text{CN})_6^{3-}]_f \quad (9)$$

$$I_{a_f} = n\mathcal{F}k_a S_a [\text{Fe}(\text{CN})_6^{4-}]_f \quad (10)$$

The definition of the final conversion  $X_f$  is

$$X_f = 1 - \frac{[\text{Fe}(\text{CN})_6^{3-}]_f}{[\text{Fe}(\text{CN})_6^{3-}]_i} \quad (11)$$

where  $[\text{Fe}(\text{CN})_6^{3-}]_i$  is the initial concentration of ferricyanide.

Then, as  $I_{c_f} = I_{a_f}$ ,  $X_f$  can be expressed as

$$X_f = 1 - \left(1 + \frac{k_c S_c}{k_a S_a}\right)^{-1} \quad (12)$$

### 3.2. Experimental details

The ElectroSynCell was provided with a single representative unit cell (r.u.c.). Three different r.u.c.'s (Fig. 4) were successively tested.

The first cell, (a), was a reference: both working electrode and the counter electrode consisted of a plate covered with a turbulence promoter (Fig. 4(a)).

In the second cell, (b), the working electrode consisted of a plate covered with a sheet of foam (G60)

whose thickness was identical to that of the classical plastic net (2.5 mm). The counter electrode was a plane plate covered with a turbulence promoter (Fig. 4(b)).

With the third r.u.c., (c), there was an increase in the ratio of the surface areas of the electrodes. The working electrode still consisted of a plate covered with a sheet of foam, whereas the active surface area of the counter-electrode (plate) was reduced (Fig. 4(c)).

In each case, both plate and foam were made of nickel. The surface areas of the electrodes used in each r.u.c. as well as their ratio, are given in Table 5. The value of the active surface area of the sheet of foam was calculated from the dynamic specific surface area. Experiments were carried out with total recirculation of the fluid, according to the following procedure:

(i) the electrodes were cleaned *in situ* with a 0.1 M solution of  $\text{H}_2\text{SO}_4$  and activated with a cathodic reduction of a 0.5 solution of NaOH.

Table 5. Surface area of the couple of electrodes used in the tested configurations

Configuration	(a)	(b)	(c)
Surface area of the working electrode /m <sup>2</sup>	$44.1 \times 10^{-3}$	$669 \times 10^{-3}$	$669 \times 10^{-3}$
Surface area of the counter electrode /m <sup>2</sup>	$44.1 \times 10^{-3}$	$44.1 \times 10^{-3}$	$10.7 \times 10^{-3}$
Ratio $S_c/S_a$	1	15.2	62.5
Final conversion, $X_f$	0.470	0.951	0.983

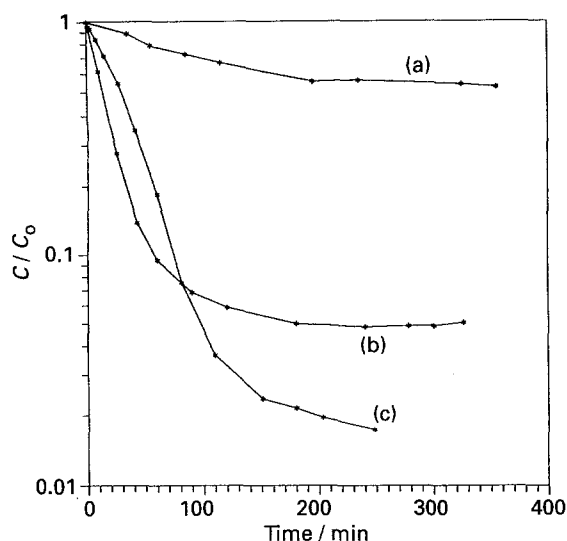


Fig. 5. Variation of the ratio  $C/C_0$  against time obtained with the tested configurations. X: (a) 47.0%, (b) 95.1% and (c) 98.3%.

(ii) an aqueous solution containing 0.01 M potassium ferricyanide was introduced. The working flow rate was  $244 \text{ dm}^3 \text{ h}^{-1}$ , and the temperature  $30^\circ \text{C}$ .

(iii) a suitable potential was imposed between the electrodes so that experiments finished under limiting diffusion current conditions at the cathode. Then, the concentration of ferricyanide was measured until equilibrium was reached, i.e. the current became constant.

### 3.3. Analysis of experimental results

For each experiment, the variation of the ratio  $C/C_0$  with the operating time is given in Fig. 5.  $C$  is the ferricyanide concentration at any time, whereas  $C_0$  is the initial concentration. The mean residence time in the cell is approximately 10 to 15 times shorter than the operating time. The experimental results show that the value of the conversion depends on the ratio of the surface area of the electrodes. Nevertheless, the optimization of the final conversion, due to the reduction in the counter electrode surface area, should be coupled with a study of the potential distribution.

It is interesting to calculate the final ratio  $S_c k_c / S_a k_a$ , for the configuration (b), to compare its value with that obtained from the mass transfer study. From the electroconversion and Equation 12,  $(S_c k_c / S_a k_a)_e = 20$ . With mass transfer experiments (Section 2.3.3.), the ratio  $(S_c k_c / S_a k_a)_{mt}$  for the same flowrate is 9 ( $k_c$  is calculated from Equation 4 and  $k_a$  from Equation 6). During the ferricyanide reduction experiments the generation of oxygen, and to a

lesser extent hydrogen, modifies the flow behaviour previously studied with mass transfer experiments. From the electrochemical point of view, oxygen generation probably gives rise to a reduction of the active surface area of the electrodes. Then, the difference in values of  $(S_c k_c / S_a k_a)_e$  and  $(S_c k_c / S_a k_a)_{mt}$  is not surprising.

The ferricyanide reduction experiments give encouraging results and show that the compactness of an electrochemical reactor of filter-press type can be increased through a simple technical modification.

## 4. Conclusion

The study of mass transfer to the two electrodes of the tested configuration shows that the mass transfer coefficients measured at a plane plate covered with a classical turbulence promoter is about twice as large as that measured at a plane plate covered with a sheet of 60 p.p.i. foam. With the tested configuration, data for the reduction of ferricyanide ions show that this reticulated medium in a filter-press type cell is promising, since high values of conversion are reached without use of a membrane.

Introducing metallic foams in filter-press type cells, instead of ordinary turbulence promoters, is a simple way of increasing the compactness of these reactors.

## Acknowledgement

The authors thank the Direction des Etudes et Recherches d'Electricité de France for the supply of the ElectroSynCell.

## References

- [1] A. Montillet, J. Comiti and J. Legrand, *J. Appl. Electrochem.* **23** (1993) 1045.
- [2] Electrocell AB, PO Box 34, S 18400 Akersberga, Sweden.
- [3] L. Carlsson, B. Sandegren, D. Simonsson and M. Rihovsky, *J. Electrochem. Soc.* **130** (1983) 342.
- [4] SORAPEC, 192 rue Carnot, 94129 Fontenay sous Bois, France.
- [5] A. Montillet, J. Comiti and J. Legrand, *J. Mat. Sci.* **27** (1992) 4460.
- [6] S. Langlois and F. Coeuret, *J. Appl. Electrochem.* **19** (1989) 43.
- [7] S. Lowell and J. E. Shields, 'Powder Surface Area and Porosity', Chapman and Hall, London (1984).
- [8] M. M. Letord-Quemere, F. Coeuret and J. Legrand, *J. Electrochem. Soc.* **135** (1988) 3063.
- [9] S. Langlois and F. Coeuret, *J. Appl. Electrochem.* **19** (1989) 51.
- [10] C. J. Brown, D. Pletcher, F. C. Walsh, J. K. Hammond and D. Robinson, *ibid.* **23** (1993) 38.
- [11] R. M. Spotnitz, R. P. Kreh, T. J. Lundquist and P. J. Millington, *ibid.* **20** (1990) 209.
- [12] D. Pletcher, I. Whyte, F. C. Walsh and J. P. Millington, *ibid.* **23** (1993) 82.