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Packed-bed reactor with continuous recirculation of electrolyte

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A comparison of calculated and experimental parameters for the packed-bed reactor working with recirculation of the electrolyte is given. A simple mathematical model was applied and the applicability of the relation

$$c = c^0 \exp(-k_1 At/V) \text{ for } V_c \ll V_R$$

was tested. For the investigated reactor a dimensionless relation has been established from experimental I–E curves for the single pass mode

$$(Sh) = 0{\cdot}5(Re)^{0{\cdot}7}(Sc)^{0{\cdot}33}.$$

For pure practical engineering requirements these two equations together give us a satisfactory way of predicting the concentration–time dependence.

Symbols

a_0	specific area of material of given geometry (cm^{-1})
A	electrode area (cm^2)
A_s	specific area of electrode bed (cm^{-1})
c^0	initial concentration in the bulk (mol cm^{-3})
c_i	inlet concentration (mol cm^{-3})
c_o	outlet concentration (mol cm^{-3})
c^t	concentration in the bulk after a given electrolysis time (mol cm^{-3})
d_e	equivalent diameter (cm)
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
I_l	limiting current (A)
k_l	mass transfer coefficient, $I_l/zFAc^0$ (cm s^{-1})
L	height of electrode bed (cm)
R^1	degree of conversion in single pass, I_l/zFc^0Q
R_f	final degree of conversion, corresponding to the final concentration in bulk of solution
(Re)	Reynolds Number, vd_e/ν
(Sc)	Schmidt Number, ν/D
(Sh)	Sherwood Number, $k_l d_e/D$
t	time (s)
T	weight (g)
Q	volumetric flow rate ($\text{cm}^3 \text{s}^{-1}$)
v	linear flow velocity (cm s^{-1})
V_c	cell volume (cm^3)
V_R	reservoir volume (cm^3)
V	total electrolyte volume (cm^3)
ϵ	porosity
ν	kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$)

Introduction

There has been considerable attention given recently to the improvement of electrochemical reactors [1] and possibilities for increasing their productivity. Some of these attempts relate to the comparison of the performance of reactors with a single pass of electrolyte to those with a continuously recirculating electrolyte. Studies of cells with recirculation [2–8] have led to a theoretical treatment, which relates the change of reactant concentration with: (a) flow rate of electrolyte, (b) electrode area, and (c) cell and electrolyte volumes. This paper will describe experimental results for a system with recirculation and the theoretical assumptions of the mathematical model for recirculation will be verified. A tube reactor with a fixed porous electrode, similar to Sioda's reactor configuration [9–11] was used for investigations. The working characteristics of this type of reactor have been, from the engineering point of view, successfully described for the system with a single pass of electrolyte [11–14].

2. Mathematical model of a reactor with recirculating electrolyte

The assumptions of so-called 'plug flow' in the reactor and 'ideal stirring' in the reservoir form the basis of the mathematical model. Both inlet and outlet concentrations are changed with electrolysis time so that two equations are necessary to describe the concentration variation. The outlet concentration from the reactor depends on its efficiency and the inlet concentration. It can be expressed in the form of the material balance

$$Qc_\mathrm{i} = Qc_\mathrm{o} + V_\mathrm{c}(\mathrm{d}c_\mathrm{o}/\mathrm{d}t) + k_1Ac_\mathrm{o}. \qquad (1)$$

The inlet concentration is dependent on the outlet concentration from the reactor and the stirring efficiency in the reservoir

$$Qc_\mathrm{o} = Qc_\mathrm{i} + V_\mathrm{R}(\mathrm{d}c_\mathrm{i}/\mathrm{d}t). \qquad (2)$$

The solution of these relations, given by Pickett [2] and Walker and Wragg [3], represents a form whose exact solution cannot be easily achieved. However, for given conditions, it is possible to offer a solution in a simpler form [8], this being more practical [4–7]

$$-(\mathrm{d}c/\mathrm{d}t) = k_1Ac/V \quad \text{for } V_\mathrm{c} \ll V_\mathrm{R}. \qquad (3)$$

Under the condition that $V_\mathrm{c} \ll V_\mathrm{R}$ the reactor can be considered as a part of the reservoir, i.e. it is possible to identify the reservoir as a reactor of large volume but with a very small electrode area.

Integration of Equation 3 leads to

$$c = c^0\exp(-k_1At/V). \qquad (4)$$

If the dependence of k_1 on the other parameters is known, it can be introduced into Equation 4 to yield a relation that may be used to describe the performance of the reactor with electrolyte recirculation in the steady-state condition.

3. Experimental and discussion

3.1. *Single electrolyte pass*

Experiments have been carried out with the tube reactor with a fixed porous electrode (Fig. 1) to define and describe the performance of the reactor operating in the single pass mode as a function of basic construction and operational parameters (Table 1). These were carried out by measuring the steady-state *I–E* relations at various flow rates for the reduction of ferricyanide ion (Fig. 2).

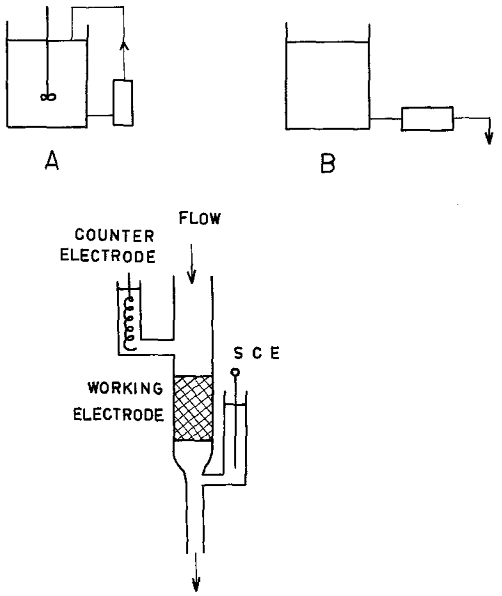

Fig. 1. Tube reactor with fixed porous electrode.

The construction of the reactor and operating factors were adjusted according to the requirement that the whole electrode should work at the limit-

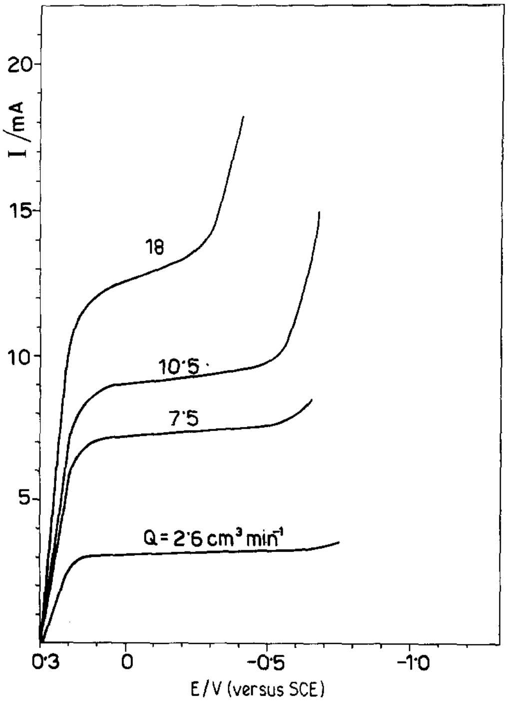

Fig. 2. *I–E* relations for different flow rates of electrolyte.

Table 1. Basic construction and operation parameters

Electrode	*Reactor*	*Solution*
Pt-rolled grid	$\phi_{\text{column}} = 0{\cdot}5$ cm	$c^0 = 1 \times 10^{-3}$ M $K_3Fe(CN)_6$/1 N KC
$L = 1{\cdot}85$ cm	$P_{\text{column}} = 0{\cdot}1963$ cm^2	$\rho = 1{\cdot}084$ g cm^{-3}
$T = 1{\cdot}8222$ g	empty column volume $= 0{\cdot}363$ cm^3	$\mu = 0{\cdot}968$ cP
$\phi_{\text{meshes}} = 0{\cdot}37$ mm	net-occupied volume $= 1{\cdot}8222/21{\cdot}45 = 0{\cdot}085$ cm^3	$\nu = 0{\cdot}941 \times 10^{-2}$ cm^2 s^{-1}
$\phi_{\text{wire}} = 0{\cdot}09$ mm	free volume $= 0{\cdot}363 - 0{\cdot}085 = 0{\cdot}278$ cm^3	$D_{\text{ferri}} = 0{\cdot}763 \times 10^{-5}$ cm^2 s^{-1}
$\rho_{\text{Pt}} = 21{\cdot}45$ g cm^{-3}	porosity $\epsilon = 0{\cdot}278/0{\cdot}363 = 0{\cdot}766$	$(Sc) = 1233$
	$a_{\text{o, cylinder}} = 444$ cm^{-1}	
	$A_s = P_{\text{electr}}/\text{emp. col. vol.} = 37{\cdot}7/0{\cdot}363 = 103{\cdot}9$ cm^{-1}	
	$= a_{\text{o, cyl}}(1 - \epsilon) = 444 \times 0{\cdot}234 = 103{\cdot}9$ cm^{-1}	
	$P_{\text{electr}} = 444 \times 0{\cdot}085 = 37{\cdot}7$ cm^2	
	$P_{\text{free}} = 0{\cdot}1963 \times 0{\cdot}766 = 0{\cdot}1504$ cm^2	
	$d_e = 4\epsilon/A_s(1 - \epsilon) = 0{\cdot}126$ cm	

ing current. The reactor had a relatively large specific electrode area of $A_s \approx 100\ \text{cm}^{-1}$, with an electrode height of $L = 1{\cdot}85$ cm. The flow range was varied from 2·6–18 cm^3 min^{-1}. At higher flow rates and greater electrode heights, a considerable *IR*-drop occurs.

From the *I–E* relations obtained, the performance of the reactor has been defined in the form of a dimensionless relation, (Table 2, Fig. 3)

$$(Sh) = 0{\cdot}5(Re)^{0{\cdot}7}(Sc)^{0{\cdot}33}. \tag{5}$$

The reactor was working with a degree of conversion from 75–40%, dependent on the flow rate (Fig. 4).

3.2. *Recirculation of electrolyte*

If k_l based on Equation 5 is introduced into Equation 4 an expression is obtained which can be used for predicting the concentration variation for the recirculation operating mode, in steady-state conditions

$$c^t = c^0 \exp[-0{\cdot}5(Re)^{0{\cdot}7}(Sc)^{0{\cdot}33} DAt/Vd_e]. \tag{6}$$

Investigations were performed by recording the current fall with time under potentiostatic control at the potential of the plateau of limiting current. Recirculation and mixing in the reservoir were realised by a centrifugal pump (Verder MD-15). Results of these investigations are given in Figs. 5 and 6, and data obtained by calculation according to Equation 6 have been included in the same figures.

Also included in the plots are the points for the single pass mode under conditions where the concentration decrease is the same as when the total batch was passed through the reactor several times. For the sake of comparison the point for the decrease of concentration at the smallest flow rate ($Q = 2{\cdot}6$ cm^3 min^{-1}) in the single pass mode was also included in the figures.

In both modes the volume of electrolyte and the flow rate through the cell were the same.

The application of Equation 4 contains the condition $V_c \ll V_R$ which is fulfilled in this case as $V/V_c > 1500$. Present day trends in the development of reactors (fixed-bed, fluidized-bed, etc.) show that the continual electrochemical production will probably fulfill the condition $V_c \ll V_R$.

Agreement between experimental values and values calculated according to Equation 6 is obtained within 5%. Therefore, from the practical

Table 2

Q (cm^3 min^{-1})	v (cm s^{-1})	$I(\times 10^3)$ (A)	$k_l(\times 10^3)$ (cm s^{-1})	(Sh)	(Re)	R^1 (%)
2·6	0·289	3·1	0·852	14·06	3·87	74·2
7·5	0·833	7·2	1·979	32·65	11·62	59·7
10·5	1·166	8·8	2·418	39·90	15·62	52·1
18·0	2·0	11·9	3·271	53·97	26·80	41·1

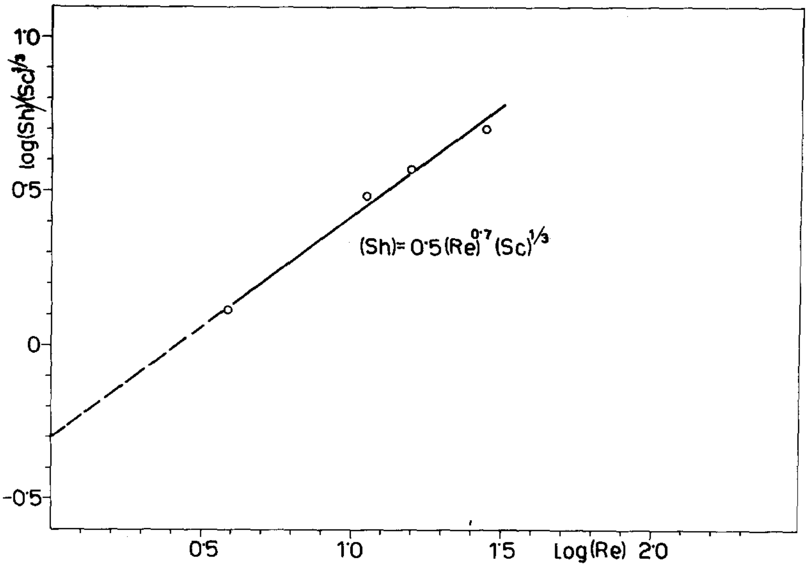

Fig. 3. Log $(Sh)/(Sc)^{1/3}$ versus log (Re) dependence.

engineering point of view, the simpler form of the solution is satisfactory i.e., the form of Equation 4. The exact mathematical treatment of the conversion in reactors with recycling has been discussed by Pickett [2]. A comparison of the exact values with those obtained from Equation 4 using his data shows an error which does not amount to more than the experimental one, or which is significant in chemical engineering.

Interesting observations and conclusions are reached when the two operating modes are compared on the basis of experimental results. If the electrolysis time is taken as a basis for comparison, it is only possible within a certain time range defined by the discontinuous process of electrolysis at a single electrolyte pass.

Sioda [8] made a mathematical analysis for the comparison of both models and came to the conclusion that a shorter time was required for the same final degree of conversion with recirculation if $R^1 \ll R_f$ was satisfied. This requirement is, however, too extreme as shown experimentally by us. For the sake of obtaining a more exact explanation, the comparison of both models should be made by tackling the problem rigorously. Thus from the standpoint of the electrolysis time required for the same final conversion, the following conclusions are reached:

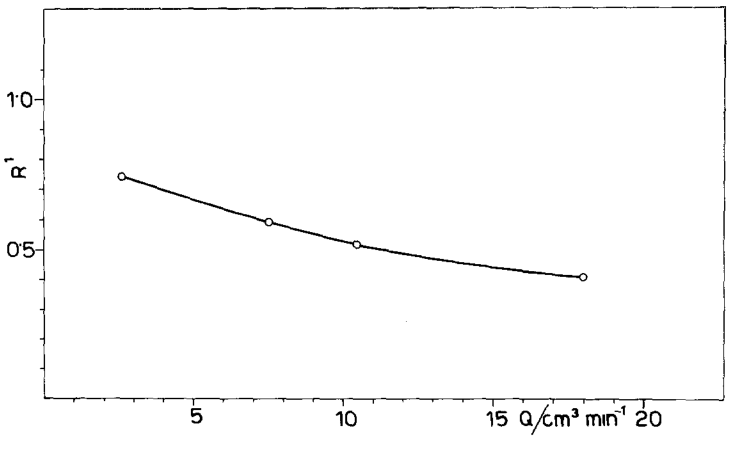

Fig. 4. Conversion degree, dependent on flow rate, at a single pass.

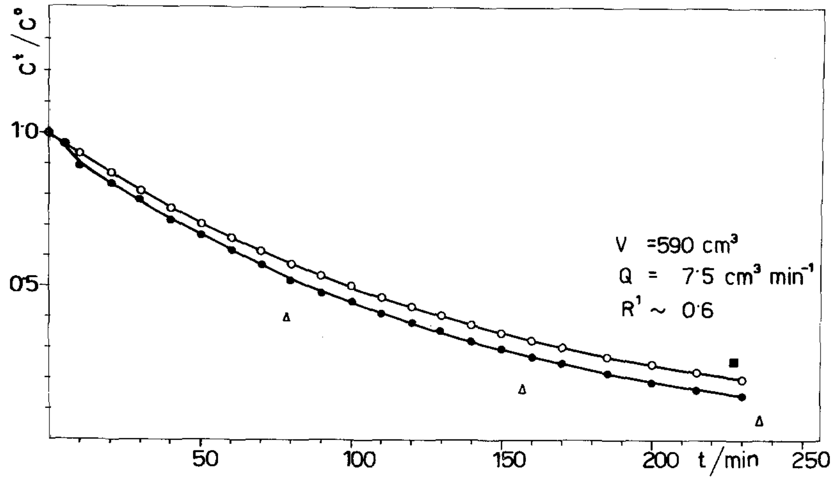

Fig. 5. Experimental data and data obtained by calculation for recirculation at $Q = 7{\cdot}5$ cm^3 min^{-1}. ● experimentally; ○ by calculation; △ single pass, $Q = 7{\cdot}5$ cm^3 min^{-1}; ■ single pass, $Q = 2{\cdot}6$ cm^3 min^{-1}.

(a) The recirculation mode leads to a shorter electrolysis time only if comparison is made between a reactor which works in the single pass mode with high conversion efficiency ($R \to 1$) and a reactor which works with lower conversion efficiency (based exclusively on different construction parameters) and which works with recirculation. Moreover, increase in the flow rate leads to a further shortening of the electrolysis time.

(b) However, a comparison of both models operating with equal conversions (equal Q and R^1) shows that the single pass mode requires a shorter time at the same flow rate. This can be easily understood from the definition of the degree of conversion, and it has been experimentally established that reactor efficiency does not depend on inlet concentration [15] (under the condition of limiting current all over the electrode). As in recirculation the concentration at the inlet of the reactor is lower, so conversion will always be relatively smaller.

(c) Complete conversion of reagents ($R = 1$) can be achieved by varying construction parameters, at a single pass of electrolyte only. This, however requires the matching of operational factors (Q and c) with construction parameters of

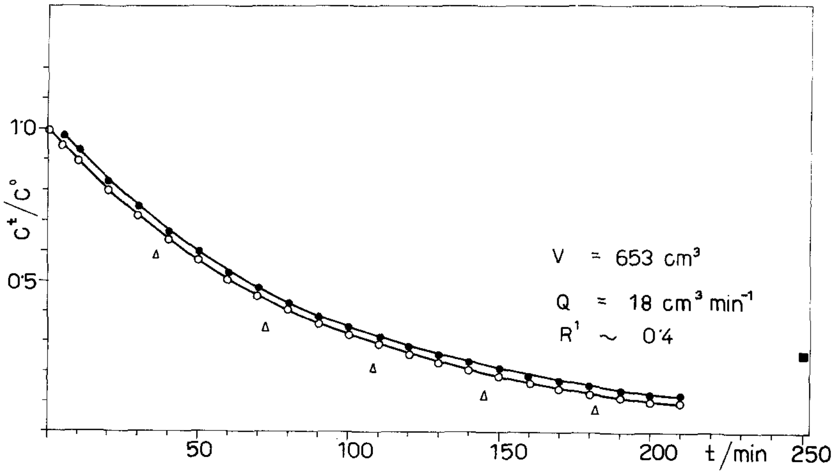

Fig. 6. Experimental data and data obtained by calculation for recirculation at $Q = 18$ cm^3 min^{-1}. ● experimentally; ○ by calculation; △ single pass, $Q = 18$ cm^3 min^{-1}; ■ single pass, $Q = 2{\cdot}6$ cm^3 min^{-1}.

the reactor (ϵ and L). If the IR-drop is overcome, parts of electrode can become practically inactive or they can reach a potential higher than that of the limiting current plateau where undesirable processes (decomposition of supporting electrolyte) may take place. Therefore the application of the reactor with a fixed-bed electrode is currently limited to work with low concentrations [16–21]. A certain improvement can be achieved by varying the construction of the reactor [22, 23].

4. Conclusion

From these preliminary investigations it can be concluded that it is sensible to recirculate the electrolyte at increased flow rates with a tube reactor at lower inlet concentrations. The increase of flow rate results in the shortening of electrolysis time, but it is limited by an increase of the IR-drop.

Often processes in the electrochemical industries (e.g. Cl_2) operate with recirculation of the electrolyte. The reactant is continuously replenished to maintain the inlet concentration to the reactor and the products may be extracted onstream.

From purely practical engineering requirements it is possible to apply the simpler form of Equation 6, which within limitations enables a prediction of concentration–time relationship.

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