

## List of symbols

$nm$	number of electrodes	$\partial\Omega_i^m$	frontier of an electrode $\Omega_i^m$
$V_i$	fixed potential of an electrode $i$	$\partial\Omega^e$	frontier of the electrolyte $\Omega^e$
$\underline{E}$	electrical field (V/m)	$\Gamma_{iN}^m$	part of $\partial\Omega_i^m$ in contact with an insulator
$\underline{i}$	electrical current vector	$\Gamma_{iN}^m(V_i)$	part of $\partial\Omega_i^m$ at a fixed potential $V_i$
$i$	electrical current (A)	$\Gamma_{iBV}$	part of $\partial\Omega_i^m$ (or $\partial\Omega^e$ ) at an interface electrolyte-electrode
$u_i^m$	electrical potential of the electrode $i$ (V)	$\Gamma_N^e$	part of $\partial\Omega^e$ in contact with an insulator
$u^e$	electrical potential of the electrolyte (V)	$\partial_t$	time derivative
$a_{ij}$	elements of the matrix $A$	$\sigma$	electrical conductivity ( $\Omega^{-1}mm^{-1}$ )
$u_i^i$	potential value in the electrode $i$	$\sigma^m$	electrical conductivity of the metal (electrode) ( $\Omega^{-1}mm^{-1}$ )
$u_i^m$	potential value in the electrode $i$	$\sigma_i^m$	electrical conductivity of electrode $i$ ( $\Omega^{-1}mm^{-1}$ )
$A_i^m$	stiffness matrix	$\sigma^e$	electrical conductivity of the electrolyte ( $\Omega^{-1}mm^{-1}$ )
$A$	stiffness matrix	$\Phi$	electrical potential (V)
$\underline{B}$	'Butler-Volmer' vector	$\Phi_i^m$	electrical potential of the electrode $i$ (V)
$x_i$	potential at the node $i$	$\Phi^e$	electrical potential of the electrolyte (V)
$I$	unit matrix	$\underline{\Phi}^m$	vector of nodes values of the approximation of $\Phi_i^m$
$P$	total power (W)	$\underline{\Phi}^e$	vector of nodes values of the approximation of $\Phi^e$
Gb	dimensionless geometric bypass	$\underline{\nu}$	unit normal vector to the frontier
Bn	dimensionless bipolar number	$\varphi$	generalized Butler-Volmer function
$\Omega$	bounded domain of $\mathbb{R}^2$ or $\mathbb{R}^3$	$H^1(\Omega)$	set of functions
$\Omega^e$	domain occupied by the electrolyte	$\Psi$	current by-pass
$\Omega^m$	domain occupied by the electrodes	$\psi$	function
$\Omega_i^m$	domain occupied by the electrode $i$	$\mu$	half distance between two interface nodes (mm)
$\bar{\Omega}$	bounded domain with the border	$\lambda$	parameter ( $> 0$ )

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**Abstract.** A new industrial process for the electrolytic regeneration of  $Mn_2(SO_4)_3$  is presented in which:

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- a new industrial electrochemical reactor is developed for an economical electrogeneration of  $Mn_2(SO_4)_3$ .

## 1. Introduction

Benzaldehyde and its derivatives are important organic intermediates in the production of dyes, pharmaceuticals, perfumeries, and pesticides.

There are currently three commercial routes for the production of substituted benzaldehyde [1]:

*i)* vapor phase oxidation of substituted toluene by air over a catalyst ( $V_2O_5$ ) at high temperature (500°); *ii)* side-chain

halogenation of substituted toluene followed by hydrolysis; *iii)* liquid-phase oxidation of substituted toluene with pyrolusite (natural  $MnO_2$ ).

For a chlorine-free product (required for the production of pharmaceuticals and fragrance ingredients) liquid-phase oxidation with pyrolusite by the batch process is suitable. The main problem in this process is the formation of large amounts of wastewater containing  $H_2SO_4$ ,  $MnSO_4$ , organics, and other impurities (initially present in the pyrolusite) which must be treated before disposal.

The electrolytic oxidation of substituted toluene to the corresponding benzaldehyde is one alternative that should be considered. Since direct electrooxidation of substituted toluene is not capable of giving the aldehyde with good productivity, the indirect two-stage electrochemical process ('ex-cell' process) becomes the method of choice [2-4]. In the 'ex-cell' process, a carrier ( $M^{n+}$ ) is oxidized in the electrochemical reactor [ $M^{(n+m)+}$ ] and then

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allowed to react with the substituted toluene in a chemical reactor. When the reaction is complete, a separation of the product takes place, and the spent liquor is returned to the electrochemical reactor where the carrier is generated (Fig. 1).

The 'ex-cell' process and its advantages have been described in a number of publications, but its application on industrial scale is limited, essentially for the following reasons:

- the industrial electrochemical reactor for an economical electrogeneration of the carrier is not developed,
- the current efficiency for the electrogeneration of the carrier is much lower than that of fresh electrolyte.

In this paper, the weakness of the indirect 'ex-cell' process is discussed, and a new technology for the industrial production of *p*-(*tert*-butyl)benzaldehyde (TBB) using *p*-(*tert*-butyl)toluene (TBT) as starting material is presented [5][6].

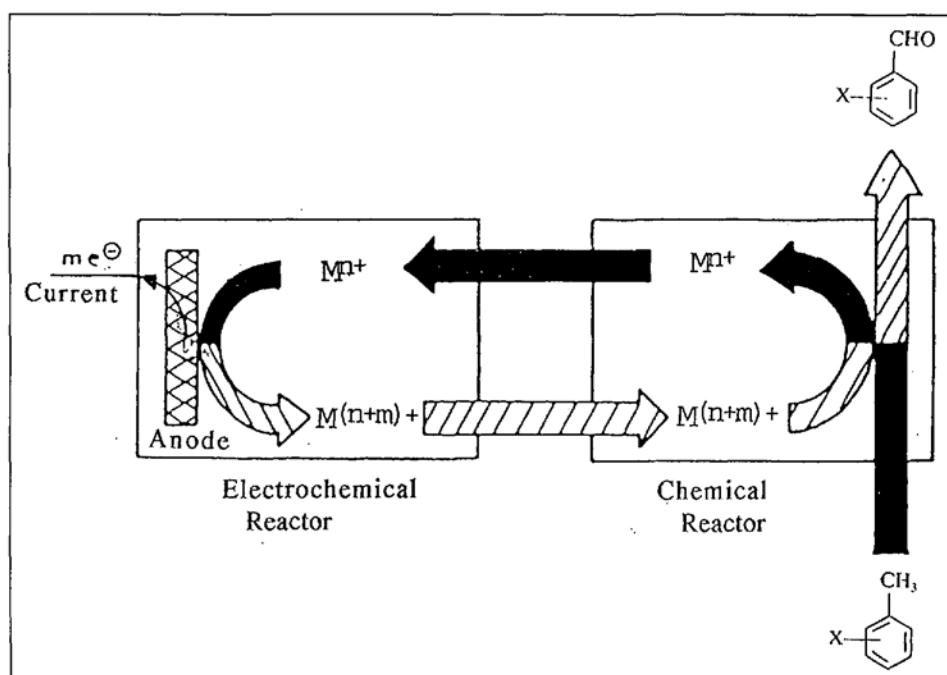
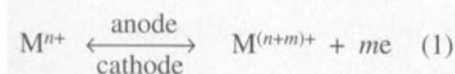


Fig. 1. Schematic presentation of the indirect two-stage electrochemical process ('ex-cell' process) for the oxidation of substituted toluene to the corresponding benzaldehyde.  $M^{n+}$ : reduced form of the carrier;  $M^{(n+m)+}$ : oxidized form of the carrier.

## 2. Choice of the Carrier ( $M^{n+}$ )

For an economical electrogeneration of the carrier, an undivided electrochemical reactor is needed. The main advantages are: simple construction and elimination of the costly and often troublesome diaphragm or membrane. The use of this simple electrochemical reactor is only possible when the loss in current efficiency due to the reduction of the oxidized form of the carrier [ $M^{(n+m)+}$ ] is negligible.

Consider the electrogeneration of a carrier in the form of a slurry in  $H_2SO_4$  solution.



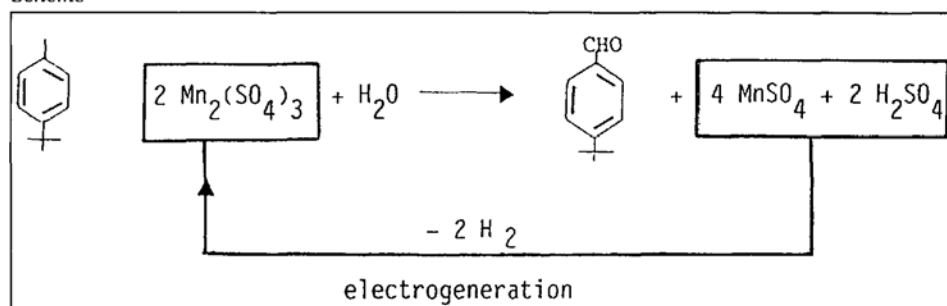
Considering that mass transport is a rate-determining step, and that the concentration (dissolved) of both reduced and oxidized form of the carrier are constants during electrolysis, the loss in current efficiency (LCE) due to the reduction of  $M^{(n+m)+}$  at the cathode is given by:

$$\% \text{ LCE} = \frac{k_c [M^{(n+m)+}]}{k_c [M^{(n+m)+}] S_c + k_a [M^{n+}] S_a} \times 100 \quad (2)$$

where

- $k_a, k_c$ : mass transfer coefficient at the anode and cathode
- $S_a, S_c$ : anode and cathode surface area
- $[M^{n+}]$ : solubility of the reduced form of the carrier in the electrolyte
- $[M^{(n+m)+}]$ : solubility of the oxidized form of the carrier in the electrolyte

Scheme



For geometrically identical anode and cathode ( $S_a = S_c$ ) and uniform stirring rates ( $k_a = k_c$ ) Eqn. 2 becomes

$$\% \text{ LCE} = \frac{k_c [M^{(n+m)+}] S_c}{[M^{(n+m)+}] + [M^{n+}]} \times 100 \quad (3)$$

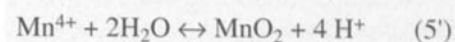
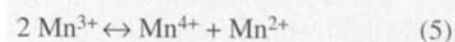
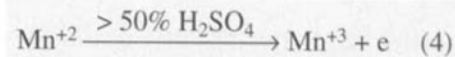
The  $Mn^{2+}/Mn^{3+}$  system has the advantage over the other carriers usually used ( $Ce^{3+}/Ce^{4+}$ ,  $Co^{2+}/Co^{3+}$  ...) that, in conc.  $H_2SO_4$  (55%) at  $85^\circ$ , the solubility (dis-

solved) of  $Mn^{2+}$  (155 mmol/l) is much higher than the solubility of  $Mn^{3+}$  (19 mmol/l); thus, in undivided electrochemical reactor, the current efficiency loss during the electrochemical oxidation of a  $MnSO_4$  slurry (1.8 mol/kg) in 55%  $H_2SO_4$  is acceptable (LCE ~ 10% for 90% conversion of the  $MnSO_4$  slurry).

## 3. Electrochemistry and Chemistry of the Process

### 3.1. Anodic Oxidation of $Mn^{2+}$ to $Mn^{3+}$ (Fresh Electrolyte)

The anodic oxidation of  $Mn^{2+}$  to  $Mn^{3+}$  (Eqn. 4) can be performed with high current efficiency (C.E.), only if the  $H_2SO_4$  concentration in the electrolyte is greater than 50% (weight). At lower  $H_2SO_4$  concentration, the C.E. of Eqn. 4 drops due to the deposition of  $MnO_2$  at the anode surface (Eqns. 5 and 5').



As the solubility of  $Mn^{2+}$  in concentrated  $H_2SO_4$  is low (155 mM in 55%  $H_2SO_4$  at  $85^\circ$ ), a  $MnSO_4$  slurry (1.8 mol/kg) in 55%  $H_2SO_4$  is used (Eqn. 6).

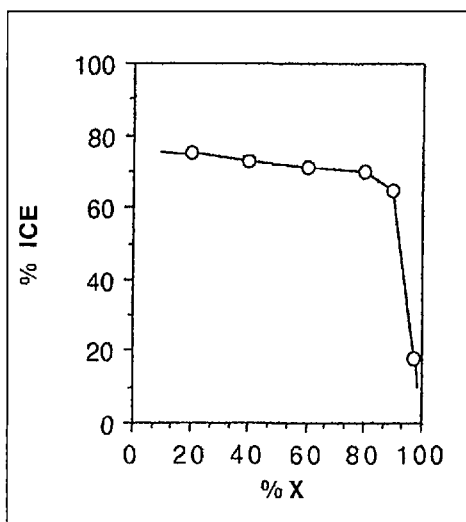


Fig. 2. Influence of conversion ( $X$ ) on the Instantaneous Current Efficiency (ICE) for the anodic oxidation of a  $MnSO_4$  slurry (1.8 mol/kg) in 55%  $H_2SO_4$ ,  $T = 85^\circ$ ,  $i = 4 \text{ kA/m}^2$ .

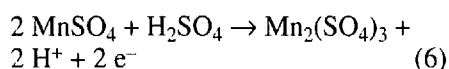


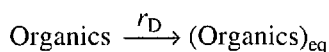
Fig. 2 shows the evolution of the Instantaneous Current Efficiency (ICE) during the anodic oxidation of the  $MnSO_4$  slurry in 55%  $H_2SO_4$ . The ICE remains almost constant until 90% conversion of the  $MnSO_4$  slurry, this is due to the fact that the concentration of  $Mn^{+2}$  (dissolved) remains constant during the anodic oxidation (zero order reaction for conversion lower than 90%).

### 3.2. Chemical Oxidation of Substituted Toluene with $Mn_2(SO_4)_3$ Slurry

This reaction is heterogeneous in nature in which three phases participate

- organic phase (substituted toluene)
- solid phase [ $Mn_2(SO_4)_3$ ]
- aqueous phase (55%  $H_2SO_4$  + 19 mM  $Mn^{+3}$ )

The experimental results have shown that the rate-determining step of the process is the dissolution of organics in the aqueous phase.



High dissolution rate of organics ( $r_D$ ) can be obtained by increasing the temperature (decrease of viscosity) and by increasing stirring rate.

### 3.3. Anodic Oxidation of $Mn^{+2}$ to $Mn^{+3}$ (Recycled Electrolyte)

It has been found that the current efficiency for the electrogeneration of  $Mn_2(SO_4)_3$  in the recycled electrolyte was much lower than that of fresh electrolyte. This decrease in current efficiency is due

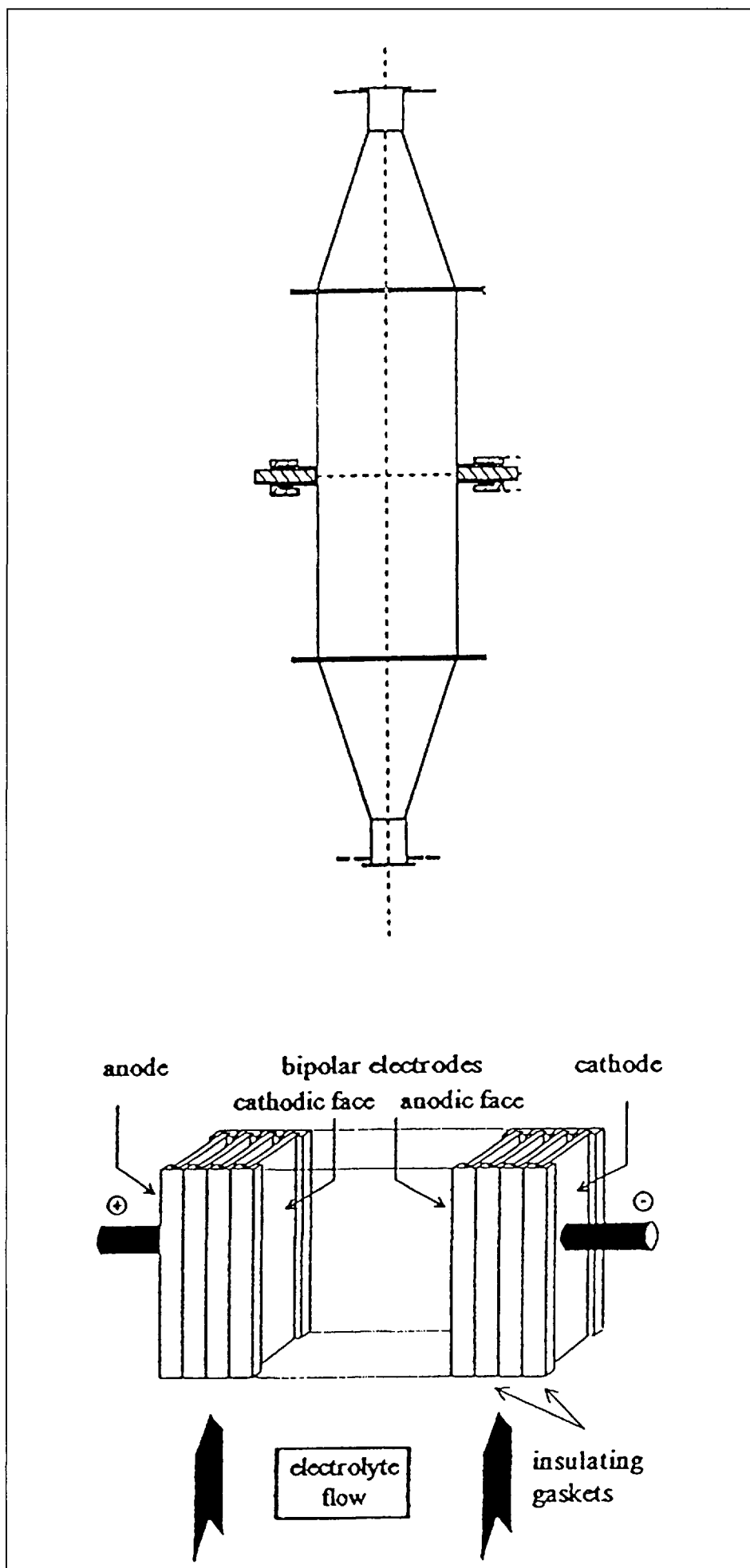


Fig. 3. Schematic representation of the electrochemical reactor (top) and the bipolar electrode stack (bottom)

to oxidizable organic material carried over with the electrolyte back to the electrochemical cell where it is oxidized to  $\text{CO}_2$ .

The 'carry-over' can be treated by equations for diffusion-controlled processes; thus, to estimate the current efficiency in the recycled electrolyte, the following relation can be derived [7]:

$$\frac{(\eta_c)_{\text{recycled}}}{(\eta_c)_{\text{fresh}}} = \frac{[\text{MnSO}_4] X}{[\text{MnSO}_4] X + Z/BM [\text{TOC}]} \quad (7)$$

where  $\eta_c$  is the current efficiency for  $\text{MnSO}_4$  oxidation,  $[\text{MnSO}_4]$  is the concentration of the manganous sulfate slurry,  $X$  is the conversion of  $\text{MnSO}_4$ , TOC is the amount of total organic carbon in the electrolyte (g/kg),  $B$  is the amount of carbon in the organic compound (expressed as a fraction),  $Z$  is the number of electrons involved in the oxidation of the organic compound to  $\text{CO}_2$ , and  $M$  is the molecular weight of the organic compound (substituted benzaldehyde).

For the oxidation of substituted toluene we can consider the following average values:  $B = 0.75$ ,  $Z = 35$ ,  $M = 130$ .

Using these average values, Eqn. 7 becomes

$$\frac{(\eta_c)_{\text{recycled}}}{(\eta_c)_{\text{fresh}}} = \frac{1.8}{1.8 + 0.36 [\text{TOC}]} \quad (8)$$

From this relation, the current efficiency for the electrogeneration of  $\text{Mn}_2(\text{SO}_4)_3$  in the recycled electrolyte can be estimated from the TOC analysis (g/kg) of the electrolyte.

These results show that purification of the electrolyte from organics before elec-

trogeneration of  $\text{Mn}^{+3}$  is necessary. The degree of purification of the electrolyte before electrogeneration must be optimized as the purification cost increases with the degree of purification contrary to electrolysis cost which decreases with purification.

Table. Characteristics and Operation Data of the Industrial Bipolar Electrochemical Reactor

Anodic surface/element:	1.11 m <sup>2</sup>
Number of elements:	18
Total anode surface:	20 m <sup>2</sup>
Current (max):	4 kA
Current density (max):	3.6 kA/m <sup>2</sup>
Potential (max):	75 V
Potential/element (max):	4.1 V
Power (max):	300 kW

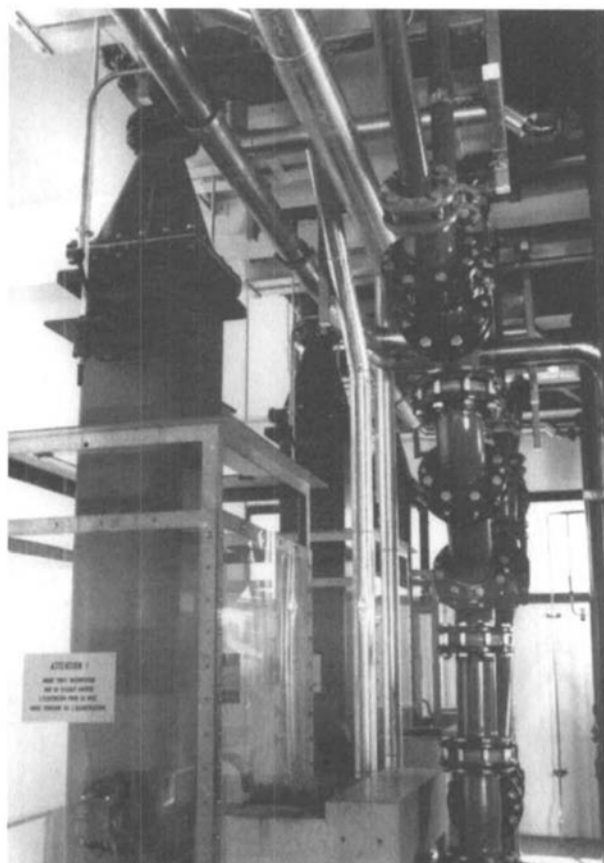


Fig. 5. Electrochemical reactors used for the electrogeneration of  $\text{Mn}_2(\text{SO}_4)_3$

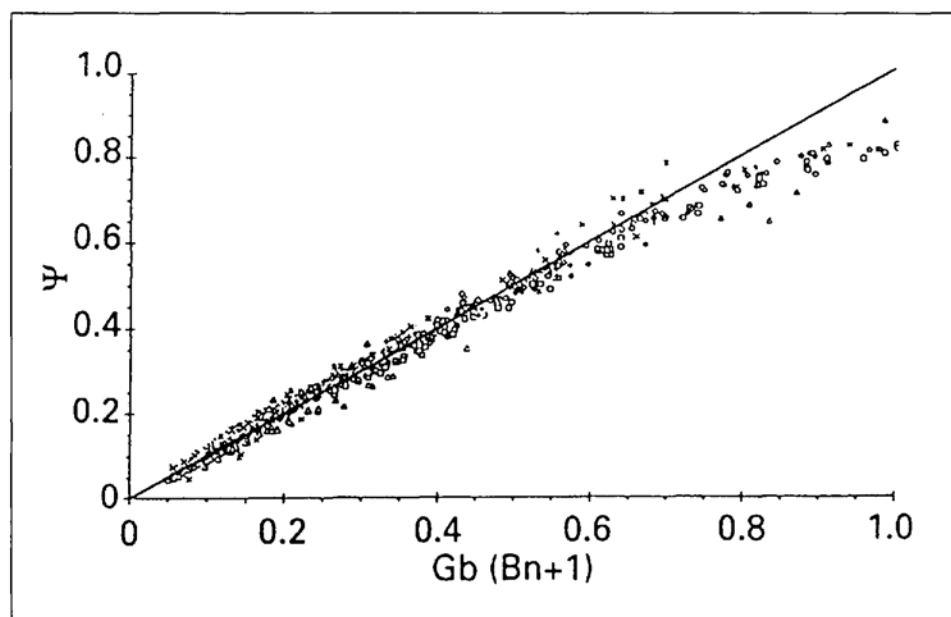


Fig. 4. Experimental current bypass ( $\psi$ ) plotted against the calculated values using Eqn. 9

#### 4. Development of the Industrial Electrochemical Reactor

The majority of available industrial electrochemical reactors are of the filter press type. This type of reactor is expensive, complex in operation, and cannot be used if the electrolyte is a slurry. The industrial electrochemical reactor presented in this paper is a bipolar undivided electrochemical reactor with flat parallel electrodes [8]. Its design is very simple, it consists of a bipolar stack of 5–40 electrodes and two base plates acting as current feeder (Fig. 3). The effective electrode area of such reactor can be varied from 1 to 40 m<sup>2</sup>.

Two major attractions of the bipolar reactor are the saving in floor space that a compact design allows, and the lower cost of the electrical equipment. No busbars

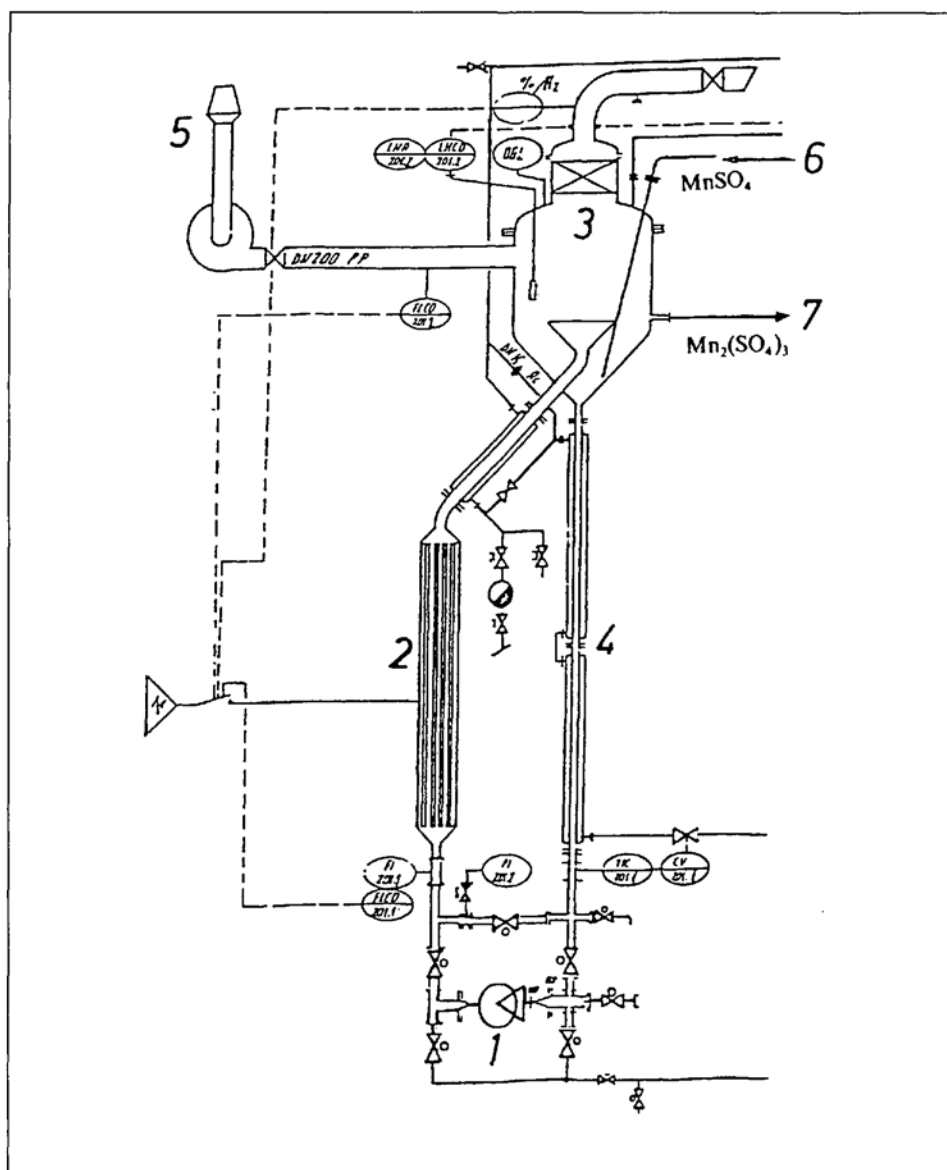


Fig. 6. Schematic presentation of the equipment used for the electrogeneration of  $Mn_2(SO_4)_3$ : 1) circulating pump; 2) bipolar reactor; 3) gas-liquid separator; 4) heat exchanger; 5) ventilator; 6) electrolyte inlet; 7) electrolyte outlet

are required inside the electrode stack and the reactor operates at much lower current and higher voltage than its monopolar analog.

The main disadvantage of the bipolar electrochemical reactor is the presence of parasitic electrical currents, or current bypass [8]. For the scale-up, a relation between the current bypass ( $\psi$ ) and two dimensionless numbers ( $G_b$  and  $B_n$ ) has been derived [8].

$$\psi = G_b (B_n + 1) \quad (9)$$

The bipolar number  $B_n$  depends on the electrochemical system used ( $Mn^{2+}/Mn^{3+}$ ) and on the process parameters (electrolyte conductivity, current density) in contrast to the geometric number  $G_b$ , which depends only on the geometry of the bipolar reactor.

Comparison of experimental results for four different reactor configurations

(5, 10, 15, and 21 electrodes in the bipolar stack) with those predicted using Eqn. 9 demonstrates the validity of the scale-up relation for  $\psi \leq 0.68$  (Fig. 4). Much more details concerning the scale-up of the bipolar electrode stack are given elsewhere [8].

## 5. Industrial Plant

Since March 1992, Givaudan-Roure, Vernier Genève, has been operating an industrial plant for the production of *p*-(*tert*-butyl)benzaldehyde (TBB) using *p*-(*tert*-butyl)toluene (TBT) as starting material, according to the global reaction (Scheme).

The electrogeneration of  $Mn_2(SO_4)_3$  has been carried out using four bipolar electrochemical reactors (Fig. 5).

Fig. 6 shows a schematic presentation of the industrial installation used for one

bipolar electrochemical reactor, and in the Table are given the characteristics and the operating data for each bipolar reactor.

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