# OPTIMIZATION OF SOLUTION CONCENTRATION BY ELECTRODIALYSIS

# APPLICATION TO ZINC SULFATE SOLUTIONS

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Abstract—Electrodialysis is used here for concentrating dilute solutions of zinc sulfate. Product concentration is limited by salt flux and water transport, i.e. hydration water, and osmotic, electroosmotic fluxes. Then, the variation in concentration of the concentrate solution can be expressed by a relation of the form:

 $\Delta C_b = C_b^0 (k_{1x} + k_{2x}x) / (k_{3x} + k_{4x}x)$ 

where the variable x is either the surface, or the number of elementary compartments. It can also be the time, or the current density. Optimization with respect to time shows that high concentration factors are obtained with an apparatus for which the product of the exchange area to the inverse of the channel width is high. Experimental results agree with this analysis in the case of ZnSO<sub>4</sub> aqueous solutions.

#### 1. INTRODUCTION

For almost a quarter of a century, ion-exchange membranes have been used for producing fresh water from salt water[1], or for concentrating sea-water, as in Japan [2]. Otherwise, electrodialysis is used for the purification by demineralization, of solutions of widely varying natures encountered in food[3], in chemical[4] or pharmaceutical[5] industries.

These last few years, electrodialysis has been chosen for treatment of industrial effluents[6] or of waste solutions from certain surface treatment works, particularly those involving galvanizing baths [7, 8].

In another sector, hydrometallurgical processes are being more and more widely developed for the treatment of minerals. These often generate electrolyte solutions too dilute in metal ions to be recycled as they are, but too rich to be disposed of as waste [9].

#### 2. POSSIBILITIES OF ELECTRODIALYSIS

Electrodialysis, a separation process based on the migration of ions in solutions under the influence of an electric field in the presence of permselective membranes, makes it possible to treat these solutions. Generally, electrodialysis units are formed by stacking together membranes which are alternately anionexchange and cation-exchange separated by frames. In the two types of compartments thus enclosed, circulate firstly the solution undergoing dilution (the diluate), and secondly the solution being concentrated (the concentrate); these flow either as a sheet of liquid, or follow a tortuous path (fig. 1).

The potential difference  $\Delta U$  applied across the stack is such that the current density *i* remains less than the limiting density, determined by one of the methods already described [10].

It is important to define the goal to reach, either:

(1) To lower the concentration of a dilute solution sufficiently for it to be able to be discharged into the surrounding environment, or else, to be re-used, for instance as rinse water.

(2) To concentrate the solution, in order to recycle it to the production circuit.

If both of these goals are to be reached in one operation, a process with at least two stages must be used; however particular situations, such as those encountered in galvanizing works, make it possible to use the diluate and the concentrate at two different points in the treatment process [7, 8].

#### 3. LIMITING FACTORS IN THE ELECTRODIALYTIC REACTION

(1) Whether or not a sufficiently dilute solution can be obtained, depends mainly on the final concentration desired. In order to allow the electric current to pass, it is essential that the metal ion concentration should be sufficiently great. If the diluate conductivity falls too low, the resistance of the module increases, and the energy available for separation is reduced.

(2) In the stationary state, the final concentration of the concentrated solution is:

$$C_b = n_b / V_b. \tag{1}$$

The number of moles  $n_b$  of salt, for example Zn SO<sub>4</sub>, at the outlet of the concentrating circuit of the electrodialysis stack, is equal to the number of moles at the inlet, to which is added the quantity transferred from the



Fig. 1. Principle of electrodialysis. a, anionic membrane; c, cationic membrane; +, anode; -, cathode.

diluate to the concentrate:

$$\Delta n = J_{\text{SALT}} S.N. \Delta \theta. \tag{2}$$

(S exchange area, N number of basic elements,  $\Delta \theta$  residence time).

The electrolyte flux  $J_{SALT}$  depends on the applied current density and on the efficiency, but also on the influence of the concentration difference  $\Delta C$  between neighbouring diluate and concentrate compartments, for the back diffusion (2):

$$J_{\text{SALT}} = \frac{\eta}{z} \frac{i}{F} - K_s \,\Delta C \tag{3}$$

F being the Faraday constant.

The expressions for the efficiency  $\eta$  and for the diffusion coefficient K, are simplified when the dialysis coefficient for the electrolyte through the anion-exchange<sup>(a)</sup> and the cation-exchange<sup>(c)</sup> membranes are zero. Under these conditions, for example:

$$\eta = z(\bar{t}_c^+ - \bar{t}_a^+) \text{ and } K_s = 0$$
 (4) (5)

 $\bar{t}_c^+$  and  $\bar{t}_a^+$  being the transport numbers for the cation in membranes c and a.

Consequently, the number of moles  $n_b$  of a z : z salt at the outlet of the electrodialyzer is:

$$n_{b} = n_{b}^{0} + \frac{\eta}{z} \frac{i}{F} SN \Delta \theta.$$
 (6)

The volume  $V_b$  of the concentrate at the outlet of the concentrating circuit of the electrodialysis unit is equal to the volume at the inlet  $V_b^0$  adjusted to account for the volume  $\Delta V_b$  transferred from the diluate to the concentrate and the variation in volume caused by the change in concentration of the concentrate:

$$V_b = \pi \cdot V_b^{\ 0} + \Delta V_b \tag{7}$$

—the volume transfer  $\Delta V_b$  results from the mass transfer of the salt and water:

$$\Delta V_b = \Delta V_{\text{SALT}} + \Delta V_{\text{WATER}} \tag{8}$$

• the first is a function of the flux of each ionic species j, i.e. it is proportional to the current density i:

$$\Delta V_{\text{SALT}} = \frac{i.N}{F} \sum_{f} (\bar{t}_{jc} - \bar{t}_{ja}) . \bar{V}_{j} . S. \Delta \theta \qquad (9)$$

• the second is more complex:

$$\Delta V_{\text{WATER}} = J_{\text{WATER}} \cdot \bar{V}_{w} \cdot S \cdot N \cdot \Delta \theta \tag{10}$$

 $\overline{V}_{b}$ ,  $\overline{V}_{w}$  being the molar volume of the ionic species j and of water, w.

It is known from experimental observations[11], that during transfer, each mole of salt carries with it a certain quantity of water. This apparent molar flux of water  $J_{\text{WATER}}$  results from the transport of water of hydration bound to the ions  $J_{\text{HYD}}$  and from the osmotic and electroosmotic fluxes  $J_{\text{ECO}}$ :

$$J_{\text{WATER}} = J_{\text{HYD}} + J_{\text{EOO}} \tag{11}$$

• the first flux is directly proportional to the salt flux  $J_{SALT}$  and so, is proportional to the current density *i*. The hydration numbers of the ions have been determined by measurement of the ultrasonic vibration potential at 220 KHz[12]. In the range of concentration considered, the hydration number *h* is essentially constant for the salt:

$$J_{\rm HYD} = J_{\rm SALT} \,.\, h \tag{12}$$

• the osmotic and electroosmotic fluxes arise when charged species travel along pores of a greater size than the Stern-Chapman double layer. In the framework of non-equilibrium thermodynamics, the fluxes are related to the forces: in the present case, the forces involved are the gradients of potential, concentration, pressure and temperature across the membrane:

$$J_{EOO} = L_{\phi} \cdot \Delta \phi + \Sigma L_{ak} \cdot R \cdot T \cdot \Delta \ln a_k + L_p \cdot \Delta p + L_T \cdot \Delta T.$$
(13)

For an electrodialysis unit of the filter press type, containing N basic elements, the effective potential drop  $\Delta\phi$ per cell pair is equal to the potential difference  $\Delta U/N$  per basic element, from which is subtracted the potential drop  $\Delta\phi_{memb}$  due to the concentration difference of the solutions in contact with the membrane, i.e.:

$$\Delta \phi = \frac{\Delta U}{N} - \Delta \phi_{\text{memb}} \tag{14}$$

For a perfectly dissociated z:z electrolyte, the transmembrane potential may be expressed in terms of activities  $a_d$  and  $a_b$  of the diluate <sup>(d)</sup> and the concentrate<sup>(b)</sup>, together with  $\xi$  the clearance factor of the diluate:

$$\xi = \frac{\Delta C_d}{C_d} = \frac{i}{i_{\rm him}} \tag{15}$$

where  $i_{\rm lim}$  is the limiting current density.

Thus, under isothermal conditions, the osmotic and electroosmotic fluxes may be written as follows:

$$J_{EOO} = L_{11}\Delta p + L_{12} \cdot \ln \frac{a_b}{a_d} + L_{13}[\Delta U + \rho(1-\xi)]$$
(16)

where the coefficient  $\rho$  has the value:

$$\frac{\mathbf{N}\cdot\mathbf{R}\cdot\mathbf{T}}{2F}\sum_{j}(\bar{t}_{jc}-\bar{t}_{ja})$$

In this expression, for  $J_{EOO}$  only  $\Delta U$  is the function of the current density *i*. So the osmotic and electroosmotic

fluxes may be written in the form:

necessary to have:

$$J_{\rm EOO} = \alpha_{\rm W} + i \cdot \beta_{\rm W}$$

where the parameter  $\beta_w$  is the customary electroosmotic transport coefficient.

As a result, the apparent molar water flux, and consequently the contribution of the water to the volume change, may be arranged into the form of a linear function of the current density i. Since the salt contribution is proportional to i, the volume change of the concentrate is also a linear function of i:

$$\Delta V_b = (A + B \cdot i) SN \Delta \theta. \tag{17}$$

Taking into account all the assumptions made so far, the final concentration is as follows:

$$C_{b} = \frac{n_{b}^{0} + \frac{n}{z} \cdot \frac{i}{F} \cdot S \cdot N \cdot \Delta\theta}{\pi \cdot V_{b}^{0} + (A + B \cdot i) \cdot S \cdot N \cdot \Delta\theta}$$
(18)

and as a result, the concentration difference is:

$$\Delta C_b = C_b^{o} \frac{(1-\pi) + [(R^o - B^o)i - A^o]S \cdot N \cdot \Delta \theta}{\pi + (A^0 + B^0 \cdot i) \cdot S \cdot N \cdot \Delta \theta}$$
(19)

where

$$A^{0} = A(V_{b}^{0})^{-1} \quad B^{0} = B(V_{b}^{0})^{-1} \quad R^{0} = \eta(zn_{b}^{0}F)^{-1}.$$
(20)

For solutions of zinc sulfate, measurements of density at 25°C indicate that the contraction coefficient  $\pi$  may be taken equal to unity, since  $\pi = 1 - 13,24 \ 10^{-3} \ m^{1/2}$  in the range 0 to 200 g Zn/liter, i.e. for the molality *m* in the range to 3,15 mol/kg of water. Consequently, the change in concentration  $\Delta C_b$  for the concentrate may be written in the form:

$$\Delta C_{b} = C_{b}^{0} \frac{k_{1x} + k_{2x} \cdot x}{k_{3x} + k_{4x} \cdot x}$$
(21)

where x is one among the variables S, N,  $\Delta \theta$  or i, and  $k_{1x}$ ,  $k_{2x}$ ,  $k_{3x}$ ,  $k_{4x}$  are constants depending on the variable x.

#### 4. OPTIMIZATION OF THE OPERATING CONDITIONS

It is now possible to look for the best operating conditions for obtaining the highest possible concentration difference  $\Delta C_b$ . As far as the variables S, N, and  $\Delta \theta$  are concerned,  $k_{1x} = 0$ , and the following inequality must be satisfied for optimizing the final concentration:

$$\frac{\eta}{z.F.A.} - \frac{B}{A} \cdot C_b^{o} > \frac{C_b^{o}}{i}.$$
 (22)

Optimizing with respect to the variable *i* shows that it is

$$\frac{\eta}{z.F.B.}\left(1+\frac{A}{V_b^0}\cdot S.N.\Delta\theta\right) > C_b^0.$$
(23)

These two inequalities are satisfied if  $\eta$ , S, N and  $\Delta \theta$  are large. Also, B and  $C_b^{0/i}$  must be small, i.e. in the last case, the current density must be as high as possible.

As far as the parameter A is concerned, a close examination of the various relationships and inequalities shows that A must be as small as possible, or, better still, negative.

When the variable x is the time  $(x = \Delta \theta)$ , it is possible to linearize the variations for  $\Delta C_b$  and to write it in the form:

$$\frac{C_b^0}{\Delta C_b} = \frac{\alpha}{a - \alpha} + \frac{1}{a - \alpha} \frac{1}{\Delta \theta}$$
(24)

 $a = \frac{\eta}{z} \frac{i}{F} \frac{SN}{n_b^0}$ (25)

and

with

$$\alpha = (A + Bi)SN(Vb^{\circ})^{-1}.$$
 (26)

In the case of positive or zero values of A, the concentration  $C_b$  of the concentrate tends towards an asymptotic value with increasing time:

$$C_{\mathbf{b}} = \frac{1 + a\Delta\theta}{1 + \alpha\Delta\theta} C_{\mathbf{b}}^{\mathbf{o}} \to \frac{a}{\alpha} C_{\mathbf{b}}^{\mathbf{o}}$$
(27)

or in a developed form:

$$C_b \rightarrow \frac{\eta}{zF} \frac{i}{A+Bi} C_b^{\ 0} \text{ if } \Delta\theta \rightarrow \infty.$$
 (28)

However, it is possible to give an expression for "a" as a function of the geometric characteristics of the apparatus X, Y, Z, N, of the operating conditions  $V_b^0$ ,  $\eta$ ,  $\Delta\phi$  and of the nature of the solution by way of the equivalent conductivity  $\Lambda$ . Indeed, if the resistance of the cell pair is only dependent on the dilute solution concentration, and if the conductivity is supposed to be proportional to the concentration, it is easy to obtain an expression for "a", which we have previously indicated in the case of the electrodialysis of wine [13].

This expression may be derived from the results of Sonin *et al.*[14] with the previous hypothesis, and may be written in the form:

$$a = \frac{\Lambda}{zF} \frac{\eta \Delta \phi}{V_b^0} \frac{XZ}{Y} N.$$
 (25)

So, in the case of given operating conditions and for a known solution, the coefficient a is increased by a suitable modification of the geometric caracteristics of the apparatus. So, the ionic transfer can be increased by

increasing the exchange area XZ, or the number N of cell pairs, or by diminishing the thickness Y of the channel.

On the other hand, we should note the advantages of operating in such a way that the coefficient A is negative. This coefficient A brings together, in the water flux term given by eqn (17), all the effects not due to the passage of an electric current of density *i*. So, a negative value of A rapidly gives a high value for  $C_b$ .

### 5. EXPERIMENTAL

Starting from the previous basis, we have built two laboratory electrodialyzers for concentrating zinc sulfate solutions from 6g of metal per liter to 100g of Zn per liter. In the first apparatus, tortuous path separators are used (Fig. 2), while in the second, the separators are of the sheet flow type (Fig. 3). The liquid flow pattern is the



Fig. 2. Tortuous path separator.



b Fig. 3. Flow sheet separator.



Fig. 4. Liquid flows. b, concentrating solution; d, diluting solution; e, rince cathode solution; +, anode; -, cathode,  $\sigma_b$ ,  $\sigma_d$ , conductivities of concentrate, or diluate.

same in every case, as indicated on Fig. 4. The two stacks contain the same number N of cell pairs with 11 anion exchange membranes and 9 cation exchange membranes produced by the same manufacturer. In this work, two kinds of membranes were used, either ARP and CRP from the French company Rhône Poulenc, or AMV and CMV from the Japanese company Asahi Glass; both types show similar properties.

In each electrodialyzer are three flow streams: the first one, which flows past the two electrodes, is a solution of disodium sulfate 0,1 M, and the two others, the diluate and the concentrate, are solutions of zinc sulfate undergoing dilution or concentration. As would be required for an industrial application, the concentrate is continuously recycled until the desired value  $C^b$  for the concentration is reached. In some cases, the diluate was recycled, in others not.

The values of the concentrations are continuously controlled by measuring the conductivities of each solution, while the pH's of the three solutions are measured in order to make sure that the acidity of the solution is not decreasing. In fact, the solubility curves for zinc hydroxydes show that it is necessary to use values of pH as low as possible, in order to allow high zinc concentrations to be reached: for example, Zn  $(OH)_{2\varepsilon}$  begins to precipitate in solutions containing 100 g of Zn per liter, if the pH is not below 4.5[15].

In the case of the electrode solutions, the pH remains at a constant value if the anolyte and the catholyte are continuously mixed. The electrical circuit, as indicated on Fig. 5, contains a constant current source, with measurement of the difference in potential between:

- —the two electrodes  $\Delta U$ , and
- —the two outer membranes  $\Delta V$ ,

a measurement of the current I and the amount of electricity Q required during the time  $\Delta \theta$ . Each electrodialyzer operates in such a way, that the potential difference  $\Delta \phi$  between the cell pairs is very close to 2.5 volts, and that the current density i is always below  $250 \text{ A/m}^2$ .

#### 6. EXPERIMENTAL RESULTS AND DISCUSSION

TPE. A first series of experiments was performed, using the electrodialyzer with tortuous path separators



Fig. 5. Tortuous path apparatus. Linearisation of the increase  $\Delta C_b$  (g Zn/1) of the concentration of brine as a function time t (h).  $\triangle$ ,  $C_b^0 = 6$ ,  $C_b^f = 55$ ,  $\blacksquare$ ,  $c_b^0 = 40$ ,  $C_b^f = 98$ .

(TPE), for which the width is X = 1 cm, the thickness Y = 3 mm, the length 7 times 6 cm. The concentration of the diluate and the concentrate at the beginning and at the end of each experiment are given in Tables 1 and 2.

The graph showing the variations in  $C_b^0/\Delta C_b$  as a function of  $1/\Delta\theta$  shows that a linear law is followed, whether (Table 1) or not (Table 2) the diluate is recycled.

From these graphs, of which Figs. 5 and 6 are examples, and where  $1/\Delta C_{b}$  is shown as a function of  $1/\Delta \theta$ , it is possible to determine the values of the coefficients *a* and  $\alpha$  of eqn (27), as indicated in Tables 1 and 2.

When the diluate is recycled, the values of a vary with  $C_b^0$ , the initial concentration of the concentrate. From these results, it seems that a is divided by a factor of 2

			Experiment					
			1	2	3	4		
Dilusta	сa	g Zn/l	6,0	6,0	6,0	6,0		
DIIUace	ca	g Zn/l	3,3	4,0	4,6	4,4		
Concentrate	C.	g 2n/1	47,8	51,9	52,0	96,3		
	сь	g Zn/l	77,1	82,1	92,4	106,9		
a		h <sup>-1</sup>	0,439	0,400	0,419	0,258		
α		h <sup>-1</sup>	0,239	0,213	0,198	0,220		
<u>a</u> 0		-	1,837	1,877	2,116	1,172		

Table 1. TPE apparatus; concentration of Zn SO<sub>4</sub> with recirculation

Table 2. TPE apparatus; concentration of Zn SO<sub>4</sub> without recirculation

			Experiment						
			5	6	7	8	9	10	
	cå	g Zn/l	3,5	6,0	6,0	6,0	6,0	6,0	
bildate	ca	g Zn/l	1,5	3,5	5,0	3,0	4,0	4,0	
Concentrate	с°р	g Zn/l	6,0	6,0	35,4	38,4	40,0	40,0	
	с <sub>ъ</sub>	g Zn/l	51,0	55,5	91,2	97,5	98,0	100,5	
a		h <sup>-1</sup>	3,298	2,652	0,248	0,506	0,433	0,535	
α		h <sup>-1</sup>	0,313	0,215	0,059	0,146	0,123	0,182	
a G		_	10,537	12,339	4,203	3,465	3,520	2,939	



Fig. 6. Tortuous path apparatus. Linearisation of the increase  $\Delta C_b$  (g Zn/1) of concentration of brine as a function of time t (h).  $\oplus$ ,  $C_b^0 = 96$ ,  $C_b^f = 107$ .

when the initial concentration is doubled. This is well predicted by eqn (25) for the case where the initial volume is kept constant: if  $C_b^{0}$  increases, so does  $n_b^{0}$ , so that a decreases. The values of  $\alpha$ , close to  $0.22 h^{-1}$ , show that the volume contributed by the diluate is not related to the operating conditions. This shows that it is necessary to operate rapidly in order to avoid dilution of the concentrate. As a result, the coefficient  $a/\alpha$  for the asymptotic value of  $C_b$  (eqn 27) is a function of  $C_b^{0}$ : its value is indicated in the last line of Table 1. It can be seen that it is possible to obtain a final solution of 100 g Zn per liter by means of three successive concentrations. This operation required an electrodialysis apparatus, for which we have already given a calculation in the case of sea water [16].

When the diluate is recycled during electrodialysis (Table 2), the final concentrations are higher than when the diluate is not recycled: the mean value of  $\alpha$  decreases, and the mean value of a increases. So, for the first concentration step, with  $C_b^0 = 6g$  Zn per liter, the asymptotic value of  $C_b$  is more than ten times  $C_b^0$ , and for the second step, that is  $C_b^0 = 40g$  Zn per liter, the asymptotic value is greater than  $3C_b^0$ . So, the number of units of the stack is reduced by one.

SFE. In the light of the expression of a in relation 29, experiments were performed with an apparatus (SFE) where the liquid flow channel contained a sheet of plastic netting. In this case, X = 4 cm, Y = 0.8 mm and Z = 12.5 cm. The concentration of the concentrate and the diluate at the beginning and at the end of the experiment are shown on Tables 3 and 4.

The graph showing the variation of  $C^0/\Delta C_b$  as a function of  $1/\Delta\theta$  shows that the linear law is once again followed, either when the diluate is recycled (Table 3), or not (Table 4). From these curves, of which Fig. 7 and 8 are examples, and where  $1/\Delta C_b$  is plotted as a function of  $1/\Delta\theta$ , it is possible to calculate the coefficients *a* and  $\alpha$ indicated in Tables 3 and 4.

When the diluate is not recycled, the SFE apparatus gives an outlet concentration for  $C_b$  of 40 g of Zn per liter if the initial concentration is about 6g of Zn per liter. The mean value of a is 0,849 h<sup>-1</sup>, and for  $\alpha$  it is about 0,041. The volume contributed by the diluate is greatly reduced in comparison with the two kinds of experiments performed with the TPE apparatus. The asymptotic value of  $C_b$  is now greater than 20  $C_b^{0}$ , that is approximately twice the value of the TPE apparatus.

Once again, in some cases, the coefficient  $\alpha$  is nega-

			Experiment						
			11	12	13	14	15	16	
	сå	g/1	5,3	5,0	5,25	6,3	6,4	6,25	
5110200	сa	g/1	4,8	4,75	4,4	4,7	6,0	3,2	
Concentrate	сŝ	g/1	5,6	5,6	5,25	6,3	6,4	6,25	
	сь	g/1	16,0	17,5	20,0	25,5	35,0	42,5	
a h <sup>-1</sup>		1,147	0,656	0,712	0,170	0,433	1,983		
a		h <sup>-1</sup>	0,231	-0,016	-0,078	-0,085	0,007	0,185	
<u>.</u> α		-	4,965	-	-	_	61,8	10,7	

Table 3. SFE apparatus; concentration of ZN SO4 with recirculation

			Experiments					
			17	18	19	20	21	22
Dilucto	c.	g Zn/l	5,75	6,30	6,8	5,25	42,0	44,5
Diidate	cd	g Zn/l	3,1	1,25	6,7	2,2	27,5 38	38,0
Concentrate •	с <sub>в</sub>	g Zn/l	10,0	6,1	6,7	5,9	42,0	43,5
	съ	g Zn/l	47,5	53,7	58,0	52,7	67,5	119,0
a		h <sup>-1</sup>	0,547	1,841	1,540	0,324	0,160	0,204
α		h <sup>-1</sup>	0,010	0,072	0,094	-0,170	-0,089	-0,013
<u>a</u> ū		-	54,70	25,6	16,4	_	_	-

Table 4. SFE apparatus; concentration of Zn SO<sub>4</sub> without recirculation



Fig. 7. Sheet flow apparatus. Linearisation of the increase  $\Delta C_b$  (g Zn/1) of the concentration of brine as a function of time t(h).  $\blacksquare$ ,  $C_b^0 = 6$ ,  $C_b^f = 42$ ;  $\blacktriangle$ ,  $C_b^0 = 6$ ,  $C_b^f = 58$ .



Fig. 8. Sheet flow apparatus. Linearisation of the increase  $\Delta C_b$  (g Zn/1) of the concentration of brine as a function of time t(h).  $\Phi$ ,  $C_b^{\ 0} = 43$ ,  $C_b^{\ f} = 120$ .

tive; negative values of  $\alpha$  are most advantageous, and are due to the change in sign of A appearing in relation 26; they promote high values for the final concentration  $C_b$ .

The same effect is encountered when the diluate is not recycled. Table 4 shows that for the SFE apparatus,  $\alpha$  increases for the first step ( $C_b^0 = 6$  g Zn per liter), while

the mean value of  $\alpha$  decreases when the operation is performed without recycling. So, the asymptotic value of  $C_b$  is very high. However, this high value is caused by negative values of  $\alpha$ . It can be seen that in this case, the notion of asymptote disappears, since the expression for  $\Delta C_b$  shows that  $\Delta \theta$  cannot be greater than  $1/\alpha$ .

These negative values for  $\alpha$  are also encountered for the second step ( $C_b^0 = 40$  g Zn per liter), and make it easy to reach concentrations greater than 100 g Zn per liter

### 7. CONCLUSION

The expression for the final concentration obtained in the concentrating solution of an electrodialyzer shows that it is possible to reach high values only if the water flux is not too high. However, the limiting value for  $C_b$  is related to the operating conditions, to the geometric characteristics of the apparatus, and to the nature of the solution: so it can be optimized in accordance with them. As to the time of treatment, the increase in concentration can be linearized with respect to the reciprocity of time. This relation is verified in the case of two kinds of apparatuses, one of the tortuous path type, the second of the flow sheet type. So, it is possible to reach high concentrations more rapidly, and to concentrate a zinc sulphate solution 20 times.

## NOTATION

	NOTATION	
а	coefficient, $s^{-1}$ or (hour <sup>-1</sup> )	
$a_b, a_d$	activities of salt in b, in d	
a <sub>k</sub>	activity of species k, ion or not	
<b>A</b> , A <sup>o</sup>	coefficients for volume change m s <sup>-1</sup>	
_	and $m^{-2}s^{-1}$	
<b>B</b> , <b>B</b> <sup>0</sup>	coefficients for volume change,	
	$m^{3}s^{-1}A^{-1}$ and $A^{-1}s^{-1}$	
С, Сь,	concentration of salt in $b$ , in $d$ ,	
	$mol m^{-3}$ or $(kg m^{-3})$	
F	Faraday constant A s equiv.	
h	hydration number mol water. mol	
_	salt <sup>-</sup>	51
I	current ampere	
1	current density A m	
$J_{EOO}, J_{HYD}$	flux density, mol m s	
JSALT, JWATER	flux density, mol m <sup>-2</sup> s <sup>-1</sup>	
$k_{1x}, k_{2x}, k_{3x}, k_{4x}$	constants	
K <sub>s</sub>	diffusion coefficient, in s	
In	metality moleling of water <sup>-1</sup>	
<i>m</i>	molality, mol. kg of watch	
$n, n_b, n_b$	number of call poirs	
יינ ת	number of cen pairs	
P O	quantity of electricity coulomb	
Q R	constant of gases joule $\operatorname{mol}^{-1}$	
n	kelvin <sup>-1</sup>	
R <sup>0</sup>	coefficient for volume change.	S
ĸ	$A^{-1}s^{-1}$	
S	area, m <sup>2</sup>	
$\tilde{T}$	temperature kelvin	
$\overline{t}_c^+, \overline{t}_a^+$	transport number of cation in $c$ , in a	
$\Delta U, \Delta V$	potential volt	
$V_b, V_b^0,$	volume of $b$ , of salt, of water, $m^3$	1
VSALT, VWATER		
$ar{V}_{i}, ar{V}_{w}$	molar volume of j, of w, $m^3 mol^{-1}$	[
X, Y, Z	width, thickness, length of channel,	ſ
	m	

variable r

- ionic valence, equiv. mol<sup>-1</sup> z. z+
  - phenomenological coefficient, L.  $mol m^{-2} s^{-1} V^{-1}$
- phenomenological coefficient, Lak  $mol m^{-2} s^{-1} J^{-1}$
- $L_p$ phenomenological coefficient,  $mol m^{-2} s^{-1} Pa^{-1}$
- LT phenomenological coefficient,  $mol m^{-2} s^{-1} K$
- L<sub>11</sub> phenomenological coefficient,  $mol m^{-2} s^{-1} Pa^{-1}$
- phenomenological coefficient,  $L_{12}$  $mol m^{-2} s^{-1}$
- phenomenological coefficient, mol  $m^{-2} s^{-1} V^{-1}$  $L_{13}$

# Greek symbols

- coefficient,  $s^{-1}$  or (hour<sup>-1</sup>) α
- coefficient for asmotic flux  $\alpha$  $mol m^{-2} s^{-1}$
- coefficient for electroosmotic flux, β.,  $mol s^{-1} A^{-}$ 
  - $\xi$  clearance factor,
- faradic yield η
- A time, s or (hour)
- equivalent conductivity, m<sup>2</sup> ohm<sup>-1</sup> ٨ equiv.
- contraction coefficient  $\pi$
- coefficient volt
- effective potential drop volt  $\Delta \phi$

### ubscripts

- for activity of species ka۲
- anion a
- Ь concentrate
- cation c
- d diluate
- all ionic species f
- ion i
- k ion or water
- lim limit
- water w
- for potential ø

uperscript

#### initial 0

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