

## A DIFFUSION MODEL OF DONNAN DIALYSIS UNDER FLOW CONDITIONS\*

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### Summary

A theoretical model for neutralization of alkaline waste waters, based on Donnan dialysis, is proposed. The alkaline water is flowed through a pipe made of a cation-exchange membrane. The outside of the pipe is rinsed with acid solution. Thus, laminar boundary layers form on both sides of the membrane. A neutralization reaction takes place in the vicinity of the inner boundary layer. This leads to ion transport across the membrane: the  $H^+$  ion goes into the pipe, while the basic ion goes out. The proposed theory allows optimization of the process.

### Introduction

Waste waters are very often polluted by acids or bases. Their neutralization can be achieved by reverse osmosis or electrodialysis. Both methods are, however, very sensitive toward even small amounts of colloidal particles and organic ions. A new method for neutralization of waste waters, based on Donnan dialysis, was proposed by Wisniewska and Winnicki [1,2] and Pozniak et al. [3]. In order to avoid lengthy explanations, we will consider below only the case of alkaline waste waters. The essence of the new method is the following. An alkaline polluted water is flowed through a pipe made out of cation-exchange membrane. The outer surface of the pipe is rinsed continuously with acid solution (Fig. 1). If the flows inside and outside the pipe are turbulent, laminar boundary layers of thicknesses  $\delta_1$  and  $\delta_3$  will form on the inner and outer pipe surfaces [4,5]. The thicknesses  $\delta_1$  and  $\delta_3$  can be estimated from the respective Reynolds numbers by means of well known formulae. As the cation-exchange membrane has negative bulk charge, the hydrogen ions and the cat-

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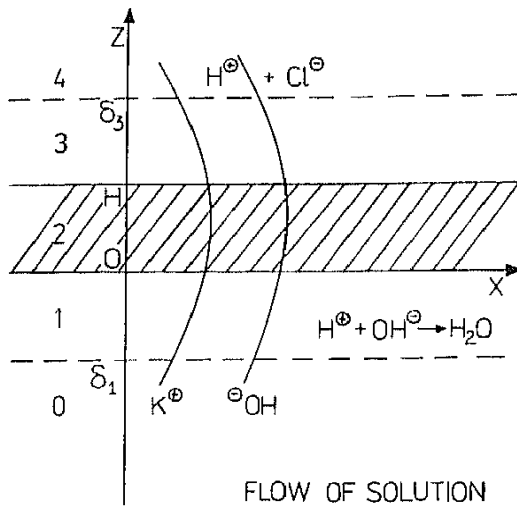


Fig. 1. A schematic representation of the system under consideration. (Not to scale).

ions from the base can penetrate it. Thus, concentration gradients appear. These lead to ion transport in the following directions:  $H^+$  through the membrane into the alkaline solution, while the base cation goes through the membrane into the acid solution. In the vicinity of the inner pipe surface the neutralization reaction takes place:



The ion transport will stop when the base in the pipe is totally neutralized. By exchanging the places of the acid and base solutions, and by using anion-exchange membrane, purification of acid polluted water can be performed. The new method has several advantages: (i) it does not require pretreatment of the waste waters; (ii) the equipment is simpler than that for electrodialysis; (iii) it is energetically more favorable; (iv) the ion fluxes are automatically controlled by the pH difference on both sides of the membrane.

Our purpose now is to develop a theory, which can be used for optimization of the technological process.

## Theory

We consider the following system: inside a pipe made of cation exchange membrane with bulk charge density  $\rho$ , a potassium hydroxide (KOH) solution is flowing. The flow velocity is  $V$ , and the base concentration at the pipe entrance is  $C_{en}$ . The outer surface of the membrane is rinsed continuously with hydrochloric acid (HCl) with concentration  $m$ . We are looking for a solution, connecting the flow velocity  $V$ , the concentrations  $C_{en}$  and  $m$ , the membrane charge density  $\rho$ , the membrane thickness  $H$ , the pipe radius  $R_p$ , and the pipe length  $L$ , necessary for complete neutralization.

The theoretical approach, we will be using, is similar to the one from Ref.

[4,5]. Thus, we divide the system into zones which are numbered as shown in Fig. 1. The  $z$ -axis is perpendicular to the membrane surface. As  $\delta_1 \ll R_p$  and  $\delta_3 \ll R_p$ , the pipe surface is assumed flat.

We adopt the following notations for the concentrations:

$$[K^+] = C_+; [Cl^-] = C_-; [H^+] = m_+; [OH^-] = m_-$$

These notations will be used with superscript  $i=0,1,2,3,4$  denoting the zone number.

We will use the following main assumptions:

- (a) in zone 0 no  $H^+$  ions are present;
- (b) neither  $Cl^-$  nor  $OH^-$  ions can penetrate into the membrane;
- (c) there are no  $Cl^-$  ions in zones 0 and 1, nor  $OH^-$  ions in zones 3 and 4. This statement follows directly from assumption (b);
- (d) the variation of base concentration along the pipe is slow, so that only the dependence of the system variables on the transversal coordinate  $z$  must be accounted for in the transport equations;
- (e) the electroneutrality condition is fulfilled locally in every zone;
- (f) since there are not net free charges, the diffusion fluxes of all ions must remain constant (i.e. independent of  $z$ ) across each zone;
- (g) reaction (1) is considered as being irreversible and instantaneous. This implies assuming that all  $H^+$  that have crossed the membrane and reached the inner pipe surface react immediately, so that in region 1, where the solution is alkaline,  $m_{1+} \ll m_{1-}$ . For simplicity we assume  $m_{1+} = 0$ ;
- (h) the following simplifications are assumed, regarding the diffusion coefficients:  
 $D_0 = D_1 = D_3 = D$  for  $K^+$  and  $Cl^-$  in the respective zones,  $d_0 = d_1 = d_3 = d$  for  $H^+$  and  $OH^-$  in the respective zones,  $D_2 = D_m$  (for  $K^+$ );  $d_2 = d_m$  (for  $H^+$ ) in the membrane;
- (i) there are no specific interactions between the ions and the membrane, so that their distribution is determined solely by electrostatic interactions.

The range of validity of some of these assumptions is discussed at the end of the paper.

The ion fluxes are denoted by  $j_{iK}$  and  $j_{iCl}$  for  $K^+$  and  $Cl^-$  respectively, and by  $j_{iH}$  and  $j_{iOH}$  for  $H^+$  and  $OH^-$  ( $i=1,2,3$ ). Following the method of Ref. [5], we will eliminate the electric potentials  $\phi_i$  ( $i=1,2,3,4$ ) from the system of transport equations to obtain in this way the concentration profiles. The potentials,  $\phi_i$  ( $i=1,2,3$ ), are expressed in  $RT/F$  units,  $R$  being the gas constant,  $T$  temperature and  $F$  faraday.

### Zone 0

The ion concentrations in this zone are assumed to be independent of  $z$ . (This can be achieved by leading the process under turbulent regime, or by

installing convenient turbulizers in the pipe). Then the mass balance of the ions  $K^+$  or  $OH^-$  for  $z = -\delta_1$  reads:

$$\pi R_p^2 V \frac{dC_{0+}}{dx} = -2\pi R_p j_{iK} \quad \text{or} \quad \frac{dC_{0+}}{dx} = -\frac{2j_{iK}}{VR_p} \quad (2)$$

where  $x$  is the longitudinal coordinate. We note that in this zone  $C_{0+} = m_{0-}$ , so that the same equation is valid for the  $OH^-$  ions.

At the entrance of the pipe we have the following boundary condition:

$$C_{0+} = C_{en}, \text{ at } x=0 \quad (3)$$

while at the pipe exit no  $K^+$  (or  $OH^-$ ) ions should be present, thus:

$$C_{0+} = 0, \text{ at } x=L \quad (4)$$

If the dependence  $j_{iK}(C_{0+})$  is known, eqn. (2) can be integrated to yield:

$$\int_0^{C_{en}} \frac{dC_{0+}}{j_{iK}(C_{0+})} = -\frac{2L}{VR_p} \quad (5)$$

and we can easily obtain the length  $L$ , necessary for complete neutralization if the velocity  $V$  is given:

$$L = \frac{VR_p}{2} \left[ \int_0^{C_{en}} \frac{dC_{0+}}{j_{iK}(C_{0+})} \right] \quad (6)$$

If the flux  $j_{iK}$  does not depend on  $C_{0+}$  we obtain:

$$L = \frac{VR_p C_{en}}{2j_{iK}} \quad (7)$$

Equation (7) determines the pipe length  $L$ , necessary for complete neutralization for given velocity or vice versa. So, the problem is reduced to the determination of the quantity  $j_{iK}$ .

### Zone 1

According to assumption (g) above, in this zone  $m_{1+} = 0$ . Hence, the electroneutrality condition is:

$$C_{i+} = m_{i-} \quad (8)$$

Since no electric current is present, the ion diffusion fluxes must be equal:

$$j_{iK} = j_{i-H} \quad (9)$$

For the ion fluxes we have the Nernst-Planck equations (cf. also (9)):

$$j_{1K} = -D \left[ \frac{dC_{1+}}{dz} + C_{1+} \frac{d\phi_1}{dz} \right] \quad (10)$$

$$j_{OH} = j_{1K} = -d \left[ \frac{dm_{1-}}{dz} - m_{1-} \frac{d\phi_1}{dz} \right] \quad (11)$$

The summation of (10) and (11), along with (8), allows eliminating  $d\phi_1/dz$ , thus leading to:

$$\frac{dC_{1+}}{dz} = \frac{dm_{1-}}{dz} = -\frac{j_{1K}}{2} \left( \frac{1}{d} + \frac{1}{D} \right) \quad (12)$$

Using the boundary condition  $C_{1+} = m_{1+} = m_{0-}$  at  $z = -\delta_1$  (see Fig. 1) we obtain the solution of eqn. (10):

$$C_{1+}(z) = m_{1-}(z) = -\frac{j_{1K}}{\mathcal{D}_1} (z + \delta_1) + m_{0-} \quad (13)$$

where

$$\frac{1}{\mathcal{D}_1} = \frac{1}{2} \left( \frac{1}{d} + \frac{1}{D} \right) \quad (14)$$

### Zone 2

The electroneutrality condition reads:

$$C_{2+} + m_{2+} - \rho = 0 \quad (15)$$

The absence of electric current requires:

$$j_{2K} + j_{2H} = 0 \quad (16)$$

Since the  $K^+$  ion flux must be conserved throughout all zones and remain equal to  $j_{1K}$  one thus obtains:

$$j_{1K} = j_{2K} = -j_{2H} \quad (17)$$

The diffusion fluxes are:

$$j_{2K} = -D_m \left[ \frac{dC_{2+}}{dz} + C_{2+} \frac{d\phi_2}{dz} \right] \quad (18)$$

$$j_{2H} = -d_m \left[ \frac{dm_{2+}}{dz} + m_{2+} \frac{d\phi_2}{dz} \right] \quad (19)$$

The ion distribution on both sides of the inner membrane surface ( $z=0$ ) is determined by the difference of the electric potentials in the respective phases (see assumption (i)):

$$\frac{C_{2+}}{C_{1+}} = e^{-(\phi_2 - \phi_1)}, \quad \frac{m_{2+}}{m_{1+}} = e^{-(\phi_2 - \phi_1)}, \quad \text{at } z=0$$

These conditions are in fact equivalent to the well known ion exchange equilibrium constant at the boundary between zones 1 and 2:

$$K_e = \frac{C_{2+} m_{1+}}{C_{1+} m_{2+}} = 1 \quad \text{at } z=0 \quad (20)$$

Equation (20) along with eqn. (8) and assumption (g) yields:

$$m_{2+} = m_{1+} C_{2+}/C_{1+} = C_{2+} m_{1+}/m_{1-} \ll C_{2+} \quad (21)$$

So, at the membrane surface eqn. (15) simplifies to:

$$C_{2+} = \rho \quad \text{at } z=0 \quad (22)$$

Substituting in eqn. (19)  $j_{2H}$  from eqn. (17) and  $m_{2+}$  from eqn. (15) one obtains:

$$j_{1K} = d_m \left[ -\frac{dC_{2+}}{dz} + (\rho - C_{2+}) \frac{d\phi_2}{dz} \right] \quad (23)$$

Equation (23) along with (17) and (18) allows obtaining an expression for  $d\phi_2/dz$ , which substituted back into eqn. (23) leads to the following differential equation for  $C_{2+}$ :

$$\frac{dC_{2+}}{dz} - C_{2+} \frac{2j_{1K}}{\rho \mathcal{D}_2} + \frac{j_{1K}}{D_m} = 0 \quad (24)$$

Here:

$$\frac{1}{\mathcal{D}_2} = \frac{1}{2} \left( \frac{1}{D_m} - \frac{1}{d_m} \right) \quad (25)$$

The solution of eqn. (24), with the boundary condition (22) yields:

$$\frac{C_{2+}(z)}{\rho} = \left( 1 - \frac{\mathcal{D}_2}{2D_m} \right) \exp\left( \frac{2j_{1K}z}{\rho \mathcal{D}_2} \right) + \frac{\mathcal{D}_2}{2D_m} \quad (26)$$

### Zone 3

Before writing the transport equations for the ions, we remind that the ions  $\text{Cl}^-$  cannot penetrate into the membrane (assumption (b)), i.e. for their flux we have  $j_{3\text{Cl}} = 0$ . The flux of  $\text{K}^+$  ions remains constant again:

$$j_{3K} = j_{1K} \quad (27)$$

No electric current is present, so that:

$$j_{3K} + j_{3H} = 0 \quad \text{or} \quad j_{3K} = -j_{3H} = j_{1K} \quad (28)$$

The electroneutrality condition in this zone is:

$$C_{3+} + m_{3+} - C_{3-} = 0 \quad (29)$$

The fluxes of the ions  $K^+$ ,  $H^+$  and  $Cl^-$  can be written as follows:

$$j_{3K} = j_{1K} = -D \left[ \frac{dC_{3+}}{dz} + C_{3+} \frac{d\phi_3}{dz} \right] \quad (30)$$

$$-j_{3H} = j_{1K} = d \left[ \frac{dm_{3+}}{dz} + m_{3+} \frac{d\phi_3}{dz} \right] \quad (31)$$

$$j_{3Cl} = -D \left[ \frac{d(C_{3+} + m_{3+})}{dz} - (C_{3+} + m_{3+}) \frac{d\phi_3}{dz} \right] = 0 \quad (32)$$

The derivative  $d\phi_3/dz$  is eliminated in the same way as before and after short transformations we obtain:

$$\frac{j_{1K}}{D} = -\frac{dC_{3+}}{dz} + \frac{j_{1K}}{\mathcal{D}_3} \frac{C_{3+}}{(C_{3+} + m_{3+})} \quad (33)$$

$$\frac{j_{1K}}{d} = \frac{dm_{3+}}{dz} - \frac{j_{1K}}{\mathcal{D}_3} \frac{m_{3+}}{(C_{3+} + m_{3+})} \quad (34)$$

where:

$$\frac{1}{\mathcal{D}_3} = \frac{1}{2} \left( \frac{1}{D} - \frac{1}{d} \right) \quad (35)$$

By subtracting eqns. (33) and (34) and integrating the result over  $z$ , we find:

$$C_{3+} + m_{3+} = -\frac{j_{1K}}{\mathcal{D}_3} z + A_3 \quad (36)$$

The integration constant  $A_3$  can be determined by using the following boundary conditions:

$$C_{3+} = 0 \text{ and } m_{3+} = m_{4+} = m \text{ at } z = H + \delta_3 \quad (37)$$

where  $H$  is the membrane thickness. (The first eqn. (37) is the condition for immediate removal of the ions  $K^+$  once they have reached the outer boundary of zone 3.) Thus:

$$C_{3+}(z) = -m_{3+}(z) - \frac{j_{1K}}{\mathcal{D}_3} (z - H - \delta_3) + m \quad (38)$$

Now, we substitute  $C_{3+}$  from eqn. (38) in eqn. (34) and obtain an ordinary nonhomogeneous differential equation for  $m_{3+}$  whose solution is:

$$m_{3+}(z) = \frac{m + \frac{j_{1K}(z-H-\delta_3)}{d} \left[ 1 - \frac{j_{1K}(z-H-\delta_3)}{2\mathcal{D}_3 m} \right]}{1 - \frac{j_{1K}(z-H-\delta_3)}{\mathcal{D}_3 m}} \quad (39)$$

When deriving eqn. (39) we used the second boundary condition (37).

The connection between the ion concentrations on both sides of the outer membrane surface is again determined by the ion exchange equilibrium constant  $K_e$  (see eqn. (20)). In this case it yields:

$$\frac{m_{2+}}{C_{2+}} = \frac{m_{3+}}{C_{3+}} \quad \text{at } z=H \quad (40)$$

Expressions for the above concentrations are obtained by setting  $z=H$  in eqns. (15), (26), (38) and (39). By substituting them into eqn. (40) one obtains a transcendental equation for the only unknown quantity  $j_{1K}$ :

$$e^Q = 1 + \frac{1 - \frac{\mathcal{D}_3}{d} U \left( 1 + \frac{U}{2} \right)}{\lambda (1 + U)^2} \quad (41)$$

where

$$Q = \frac{2Hj_{1K}}{\rho\mathcal{D}_2}, \quad U = \frac{\delta_3 j_{1K}}{\mathcal{D}_3 m}, \quad \lambda = \frac{\mathcal{D}_2}{2D_m} - 1 \quad (42)$$

The numerical solution of eqn. (41), for suitable values for the parameters (see below) is shown in Fig. 2. One sees that depending on the acid concentration

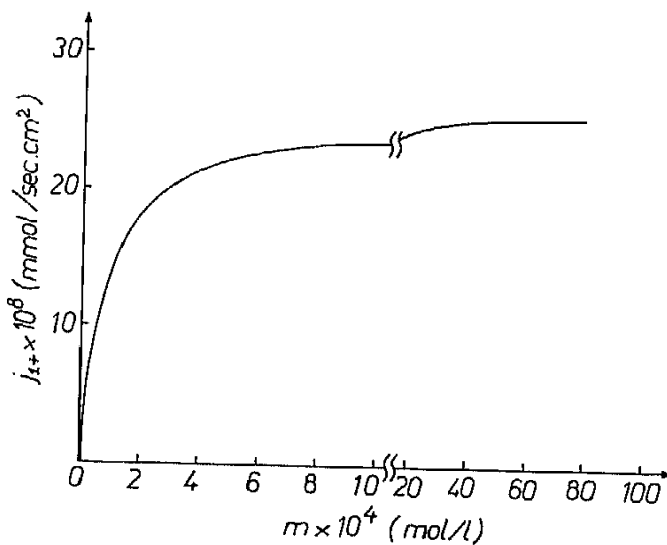


Fig. 2. The dependence of the flux  $j_{1K}$  on the outer concentration  $m$ .



$m$ , one can distinguish two regimes: (i) initial steady increases of the flux  $j_{1K}$  with  $m$ , and (ii) a plateau region, where the flux  $j_{1K}$  is independent of  $m$ . This shape of the curve follows also from physical considerations. At low acid concentrations  $m$ , the flux  $j_{1K}$  should be proportional to  $m$ , so that in the limit  $m \rightarrow 0$ , one must have  $j_{1+} \rightarrow 0$  and  $Q \rightarrow 0$ , while  $U$  will remain finite. Then by setting  $Q=0$  in eqn. (41) and solving the ensuing algebraic equation for  $U$ ,

$$U^2 + 2U - \frac{2d}{\mathcal{D}_3} = 0 \quad (43)$$

one obtains (cf. eqns. (25), (35) and (42) for notation):

$$j_{1K} = \frac{Dd}{\delta_3(d-D)} \left( \sqrt{d/D} - 1 \right) m \quad (44)$$

Thus the pipe length, necessary for complete neutralization is (cf. eqn. (7)):

$$L = \frac{VR_p \delta_3 C_{en} (d-D)}{2dD (\sqrt{d/D} - 1) m} \quad (45)$$

This limiting case corresponds to the initial (rising) portion of the curve in Fig. 1. Note that neither  $j_{1K}$ , nor  $L$  depend on the membrane properties. One sees also that increasing the acid concentration  $m$  will allow using a shorter pipe. The role of the other parameters on the occurrence of the process is also clear from eqns. (44) and (45).

In the other extreme case, very high acid concentration  $m$ , the ion transport is controlled by the diffusivity of the ions  $K^+$  and  $H^+$  in the membrane. Therefore,  $j_{1K}$  should reach saturation (constant value, independent of  $m$ ),  $Q$  should remain also constant, whereas  $U$  should become small. If  $U \ll 1$ , we can neglect all terms, proportional to  $U$  in the right hand side of eqn. (41) to obtain:

$$e^Q = 1 + (1/\lambda) \quad (46)$$

or (cf. eqns. (25) and (42)):

$$j_{1K} = \frac{\rho D_m d_m}{H(d_m - D_m)} \ln \left( \frac{d_m}{D_m} \right) \quad (47)$$

The necessary pipe length in this case is given by the equation (substitute  $j_{1K}$  from (47) in (7)):

$$L = \frac{VR_p C_{en} H (d_m - D_m)}{2\rho D_m d_m \ln(d_m/D_m)} \quad (48)$$

This regime corresponds to the plateau in Fig. 2. The acid concentration  $m^*$ , at which the transition between the two regimes will take place can be estimated by equating the fluxes from eqns. (44) and (47):

$$m^* = \frac{\rho D_m d_m (d - D) \delta_3 \ln(d_m / D_m)}{D d (d_m - D_m) H (\sqrt{(d/D)} - 1)} \quad (49)$$

One sees that the lower the ion diffusivities  $D_m$  and  $d_m$  in the membrane, the lower the acid concentration at which the transition between the two regimes will take place. It is noteworthy that  $m^*$  depends mainly on the membrane and ion properties but not on the base concentration  $C_{en}$ . It is also clear that when the membrane charge density  $\rho$  becomes higher the values of  $m^*$  and the flux  $j_{1K}$  in the plateau region (cf. eqn. (47)) will increase, which will result in more intensive neutralization and hence smaller pipe length. The permeability of the membrane affects  $D_m$  and  $d_m$  and in the limit  $D_m = d_m = 0$ , one has from eqn. (47)  $j_{1K} = 0$ , i.e. no neutralization is possible. It is obvious that from technological viewpoint it is meaningless to increase  $m$  above  $m^*$ .

For the sake of illustration we have taken the following specific values for the system parameters:  $\rho = 10^{-2}$  mol/L,  $D = 10^{-6}$  cm<sup>2</sup>/sec,  $d = 10^{-4}$  cm<sup>2</sup>/sec,  $D_m = 10^{-7}$  cm<sup>2</sup>/sec,  $d_m = 10^{-6}$  cm<sup>2</sup>/sec,  $H = 10^{-1}$  cm,  $\delta_3 = 10^{-1}$  cm,  $V = 40$  cm/sec,  $R_p = 5 \times 10^{-1}$ ,  $C_{en} = 10^{-4}$  mol/L. With these values  $m^* = 1.06 \times 10^{-4}$  mol/L and eqns. (44) and (45) become:

$$j_{1K} = 2.40 \times 10^{-4} \times m \quad (50)$$

$$L = 4.16/m \quad (51)$$

The pipe length for  $m = m^*$  turns out to be around 400 m.

We will discuss in conclusion some limitations of our theory. Strictly speaking our assumption (e) for electroneutrality will not be valid when diffuse electric layers are present. It will hold if the boundary layers  $\delta_1$  and  $\delta_3$  and the membrane  $H$  are much thicker than the diffuse layers. Since, even at  $10^{-6}$  mol/L electrolyte the latter is ca.  $0.3 \mu\text{m}$ , this condition seems to be always fulfilled. The requirement  $m_{1+} \ll m_{1-}$  (see assumption (g)) will not be fulfilled at  $\text{pH} < 8$ . This may happen only at the pipe exit, if complete neutralization is achieved.

We estimated the applicability of assumption (b) *a posteriori*, by using our final equations. The relative rejection of the ions  $\text{Cl}^-$  at the phase boundary  $z = H$  is determined by the equation:

$$\frac{C_{2-}}{C_{3-}} = \frac{m_{3+}}{m_{2+}} \text{ at } z = H \quad (52)$$

The values of  $m_{3+}$  and  $m_{2+}$  were calculated by means of eqns. (15), (26) and (39) with  $z = H$ . We used two membrane charge densities:  $\rho = 10^{-2}$  mol/L and  $10^{-1}$  mol/L. The respective values of  $m^*$  from eqn. (48) are  $10^{-4}$  mol/L and  $10^{-3}$  mol/L respectively. Since  $m^* \sim \rho$ , both  $Q$  and  $U$  in eqn. (42) will depend only on the ratio  $j_{1K}/\rho$ , i.e. the value of this ratio, determined from eqn. (41), will not depend on  $\rho$ . Indeed, in both cases the numerical solutions of (41)

yielded  $j_{1K}/m^* = 1.44 \times 10^{-4}$  cm/sec. This in turns means that the relative rejection  $C_{2-}/C_{3-}$  at  $z=H$  and  $m=m^*$ , which also depends on  $j_{1K}/\rho$ , will be independent of the charge density  $\rho$ . We obtained, for the relative rejection, the value 2.7%, which confirms the validity of our hypothesis for the regime (i), i.e. for  $m \leq m^*$ . At  $m \gg m^*$ , the presence of a large quantity of positive ions in the membrane will effectively decrease its negative charge and will facilitate the penetration of the negative ions. Indeed, for  $m=10m^* = 10^{-3}$  mol/L and  $\rho = 10^{-2}$  mol/L we obtained  $C_{2-}/C_{3-} = 11\%$  at  $z=H$ . This is, however, immaterial for our theory, because  $m \gg m^*$  corresponds to regime (ii), which is far from being optimal from technological viewpoint (see above).

We obtained similar results for the ions  $\text{OH}^-$  at  $z=0$ : with  $\rho = 10^{-2}$  mol/L and  $C_{\text{en}} = 10^{-4}$  mol/L we found  $m_{2-}/m_{1-} < 1\%$ .

## Conclusion

We have formulated a theory for the neutralization of alkaline or acid solutions by Donnan dialysis through an ion exchange pipe. The main assumptions used in the theory are the electroneutrality of all phases and absence of electric currents. The ion flux expressions are used to eliminate the electric potentials and to obtain in this way the ion distribution. The final eqn. (41) relates the hydrogen ion concentrations  $m$  in the outer rinsing solution, the potassium ion flux  $j_{1K}$  and the other system parameters. The process has two regimes: (i) at low acid concentration  $m$  the ion flux is proportional to the acid concentration and (ii) at high acid concentration  $m$  a saturation is reached and the ion flux does not depend on  $m$ . Equations (45) and (48) allow calculating the pipe length  $L$ , necessary for complete neutralization for the two regimes respectively. In regime (i)  $L$  decreases with increasing  $m$ . The transition between the two regimes occurs at a concentration  $m^*$ , defined by eqn. (49). The increase of  $m$  above  $m^*$  does not improve the efficiency of the neutralization process. Equations (44) and (47) can be used to optimize the process with respect to the other system parameters.

## Acknowledgements

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## List of symbols

$A_3$	integration constant
$C_{\text{en}}$	concentration of the solution at the pipe entrance
$C_{i+}$	concentration of ions $\text{K}^+$ ( $i=0,1,2,3,4$ )
$C_{i-}$	concentration of ions $\text{Cl}^-$ ( $i=0,1,2,3,4$ )

$D$	diffusion coefficient of $K^+$ in the solution
$d$	diffusion coefficient of $H^+$ in the solution
$D_m$	diffusion coefficient of $K^+$ in the membrane
$d_m$	diffusion coefficient of $H^+$ in the membrane
$\mathcal{D}_1$	see eqn. (14)
$\mathcal{D}_2$	see eqn. (25)
$\mathcal{D}_3$	see eqn. (35)
$H$	membrane thickness
$j_{iK}$	flux of ions $K^+$ ( $i=1,2,3$ )
$j_{iCl}$	flux of ions $Cl^-$ ( $i=1,2,3$ )
$j_{iH}$	flux of ions $H^+$ ( $i=1,2,3$ )
$j_{iOH}$	flux of ions $OH^-$ ( $i=1,2,3$ )
$K_e$	ion exchange equilibrium constant
$L$	pipe length
$m_{i+}$	concentration of ions $H^+$ ( $i=0,1,2,3,4$ )
$m_{i-}$	concentration of ions $OH^-$ ( $i=0,1,2,3,4$ )
$m$	outer concentration of acid
$m^*$	optimal outer concentration of acid
$Q$	$\frac{2Hj_{i+}}{\rho\mathcal{D}_2}$
$R_p$	pipe radius
$U$	$\frac{\delta_3 j_{i+}}{\mathcal{D}_3 m}$
$V$	flow velocity
$x$	longitudinal coordinate
$z$	transversal coordinate

### Greek letters

$\delta_i$	laminar boundary layers near the membrane surface ( $i=1,3$ )
$\lambda$	$\frac{\mathcal{D}_2}{2D_m} - 1$
$\rho$	membrane charge density
$\phi_i$	electric potentials expressed in $RT/F$ units ( $i=1,2,3$ )

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