

MATHEMATICAL MODELLING OF A FORWARD OSMOSIS EXTRACTOR

by

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ABSTRACT

Osmosis occurs when two solutions of differing osmolar concentrations are separated by a membrane permeable to the solvent but not (or nearly not) to the solutes. This paper derives the relationship between the kinetics and design parameters of systems designed for the purpose of applying this process to problems such as agricultural water reclamation, dehydration of solutions and the production of potable nutrient solutions from sea water. Three mathematical models that include increasingly complex fundamental process assumptions are presented. In all cases the fundamental mechanical device is assumed to be a continuous flow extractor that incorporates a semipermeable membrane.

INTRODUCTION

The free energy of a solution is lower than the combined free energies of its pure constituents. Formation of solutions is therefore spontaneous, whereas a definite minimum amount of work is required for partial or complete separation of solvents and solutes (Pratt, 1967; Sourirajan, 1970, Ch. 3). The usual motives for such separations are recovery of solvent, or reduction of the volume of a solution (increase of its concentration by removing solvent). Standard methods are available. They include evaporation/recondensation, separation by freezing and reverse osmosis. All require expenditure of at least the minimum energy of separation and also relatively sophisticated equipment.

In this paper another method is suggested (see also Moody and Kessler, 1971, 1975; Kessler and Moody, 1975, 1976; Murray, 1968; Muller, 1974; Osterle and Feng, 1974), and some of its design aspects are discussed. This method depends on forward, or direct, osmosis. It may be employed in situations which do not require the separation of pure solvent. One application is the concentration of a solution, "dehydration" in the aqueous case, where the fate of the solvent is irrelevant (Sourirajan, 1970, p. 389; Loeb and Bloch, 1973, consider forward osmosis as an aid to reverse osmosis; also D. Wang, 1975). Another type of situation occurs in irrigation where water containing salt solutes deleterious to plants may be readily available. The forward osmosis method can be used to transfer water from such a brackish source solution to a harmless or useful one -- containing fertilizer, for instance -- thereby reclaiming a resource that would otherwise be lost (MK 1975).

One of the most interesting situations where forward osmosis may be applied is in the derivation of emergency potable water supplies for humans in small ocean vessels such as lifeboats. In that case the process may be used to transfer water from the sea into a concentrated nutrient solution (Kravath and Davis, 1975; Kessler and Moody, 1976).

The principal advantages of the proposed process over other purification processes currently available are:

- (1) The only energy required is in the initial construction, in maintenance and, sometimes, in the pumping of fluids. This feature is important in remote installations, such as lifeboats or primitive agriculture, or where the energy costs are unusually high.
- (2) The elimination of hydrostatic pressure differences results in advantages over the popular reverse osmosis method.
 - (a) There is no membrane compaction problem.
 - (b) For extracting water from an infinite source (e.g. seawater), it is not necessary to increase the concentration of the source solution. This advantage both minimizes the work required to extract the water and reduces the pretreatment requirements.
 - (c) The mechanical construction may utilize lightweight plastics which would be inexpensive and not subject to corrosion.
 - (d) There is no need for expensive and potentially dangerous high pressure pumping systems which require extensive operator training and maintenance checks.

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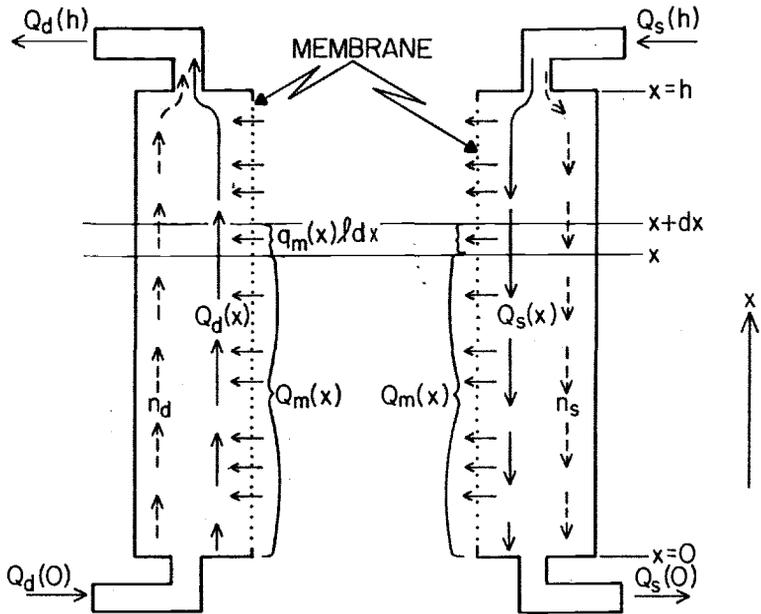


Fig. 1. Schematic exploded view of the countercurrent extractor, illustrating the conservation of solute current (dashed arrows) and the change of solvent current (solid arrows of changing length) due to the addition and subtraction of the membrane solvent current Q_m . The width of the extractor and membrane (into the paper) is ℓ . The height is h , the height dimension being specified by $0 \leq x \leq h$. The differential membrane current in the increment Δx is $q_m \ell \Delta x$, where q_m is the membrane flux. The subscripts d and s stand for "driving" and "source", respectively. The dots indicate the membrane halves in this "exploded" diagram.

The chief disadvantage of the proposed process may be size. This factor becomes important if the fluid output rate must be large and the difference in the osmotic pressure between the two solutions must be minimized. It should be remembered, however that a one-molar concentration difference corresponds to approximately 20 atmospheres of hydrostatic pressure so that the size becomes excessive (or solvent transfer rate too slow) only near the equilibrium concentrations.

An ultimate objective assessment of the utility of the proposed process (for example à la Tribus, 1970) will depend on theoretical results such as those given in this paper, experimental results in the field, the availability of new membranes which may be designed especially for this process, and/or an assignment of utilities to the various advantages cited or as yet unknown.

OBJECTIVE

The objective of this paper is to establish a mathematical framework that can be used in determining design criteria which will maximize water transfer rate, minimize solute transfer, optimize the utilization of driving solute, minimize the physical size of the extractor and optimize any other pertinent factors.

PHYSICAL MODEL

A forward osmosis continuous flow extractor in countercurrent mode is shown schematically in Fig. 1. $\pi_d(x)$ is greater than $\pi_s(x)$, and solvent flows through the membrane from right to left from the source solution into the driving solution. If the membrane is also permeable to either solute, then there are also solute flows across the membrane (not shown in the schematic).

The feed rates, $Q_d(0)$ and $Q_s(h)$, can be varied in order to achieve different degrees of hydration of the driving solution and different degrees of dehydration of the source solution.

MATHEMATICAL MODELS

In Model 1 the membrane is assumed completely impermeable to the solutes, and the concentration polarization at the membrane is neglected. The one differential equation is solved analytically. In Model 2 the membrane is assumed permeable to the solutes and solvent. The membrane solute and water flows are assumed independent of each other; concentration polarization at the membrane is neglected, and the source solution concentration is assumed constant. The three differential equations which describe the membrane solute and water flows may be solved by numerical integration. Model 3 presents the same situation as Model 2 but in addition the concentration polarization on both sides of the membrane is taken into account in order to approximate the effect of countercurrent fluid dynamics on the membrane transfer rates.

MODEL 1

The simplest mathematical description of the forward osmosis countercurrent extractor is based on the assumptions listed below. Assumptions 1 and 2 may represent serious oversimplifications of the physical system.

- (1) The membrane is completely impermeable to all solutes.
- (2) Perfect mixing exists perpendicular to the counterflows so that at a given location x , the solution is homogeneous on each side of the membrane (i.e., neglect concentration polarizations at the membrane).
- (3) There exists no convective or diffusive mixing in the direction of the counterflows.
- (4) The temperature and the osmotic coefficients α_d and α_s , are constant.

The differential equation for the extractor is

$$(1-1) \quad \frac{dQ_m(x)}{\lambda dx} = q_m(x) = L(\pi_d(x) - \pi_s(x)),$$

where λ is the width of the membrane and is assumed constant. $q_m(x)$ is the local membrane flux in $\text{cm}^3/(\text{cm}^2\text{-sec}) = \text{cm}/\text{sec}$, and $Q_m(x)$ in (cm^3/sec) is the total flow through the membrane in the interval $(0,x)$. The osmotic pressures appearing on the right hand side of Eq. 1 are determined by

$$(1-2) \quad \pi_i(x) = \alpha_i RT C_i(x) \quad \text{and}$$

$$(1-3) \quad C_i(x) = 1000 n_i / Q_i(x)$$

By assumption 1, the solute currents on each side of the membrane are conserved so that n_i is constant. Solvent conservation is described by

$$(1-4) \quad \frac{dQ_d(x)}{dx} = \frac{dQ_s(x)}{dx} = \frac{dQ_m(x)}{dx}$$

Integration of Eqs. 1 and 4 indicates that $Q_d(x)$ and $Q_s(x)$ differ by a constant:

$$Q_m(x) = \int_0^x q_m(x) dx = Q_d(x) - Q_d(0) = Q_s(x) - Q_s(0),$$

and therefore

$$(1-5) \quad Q_d(x) - Q_s(x) = Q_d(0) - Q_s(0) \equiv K^* Q_d(0).$$

$K^* Q_d(0)$ is the constant difference between $Q_d(x)$ and $Q_s(x)$, and K^* may be considered to be a matching coefficient for the solvent counterflows of the two solutions.

Combining Eqs. 1, 2, and 3 yields

$$(1-6) \quad \frac{dQ_m(x)}{dx} = 1000 LRT \left(\frac{\alpha_d n_d}{Q_d(x)} - \frac{\alpha_s n_s}{Q_s(x)} \right).$$

Introducing the dimensionless membrane flux, $Q_m^*(x)$,

$$(1-7) \quad Q_m^*(x) = \frac{Q_m(x)}{Q_d(0)} = \frac{Q_d(x) - Q_d(0)}{Q_d(0)},$$

and β , the matching coefficient for the osmolar counterflows of the solutes in the two solutions

$$(1-8) \quad \beta = \frac{\alpha_d n_d - \alpha_s n_s}{\alpha_d n_d},$$

Eq. 6 can be rewritten using Eqs. 5, 7 and 8:

$$(1-9) \quad \frac{dQ_m^*(x)}{dx} = \frac{L L \pi_d(0)}{Q_d(0)} \left[\frac{1}{Q_m^*(x)+1} - \frac{(1-\beta)}{Q_m^*(x)+1-K^*} \right].$$

The solution of Eq. 9 over the extractor of length h is

$$(1-10) \quad \frac{L h L \pi_d(0)}{Q_d(0)} = \frac{1}{\beta} \left[\frac{Q_m^*(h)^2}{2} + (1-K^*+K^*) Q_m^*(h) + \left(\frac{K^*}{\beta}\right) (1-\beta) \ln \left(1 + \frac{Q_m^*(h)}{1-K^*/\beta} \right) \right].$$

The control variables for an extractor of this design and operating mode are the concentrations of the feed solutions, $c_d(0)$ and $c_s(h)$, the solvent feed rates, $Q_d(0)$ and $Q_s(h)$, the membrane area, Lh , the membrane water permeability constant, L , and the extractor temperature, T . These variables control the values of the output concentrations, $c_d(h)$ and $c_s(0)$, and the total membrane water flux, $Q_m(h)$.

In many applications one may assume that the output concentrations and the total membrane flux are specified first (with the restriction $\alpha_d c_d(x) > \alpha_s c_s(x)$ which implies a lower chemical potential of water on the driving side of the extractor at every point on the membrane), and the control variables are adjusted to meet these specifications. Some of the control variables are not easily varied. For example, $c_d(0)$ is at most the solubility of the driving solute at the given temperature. $c_s(h)$ is the concentration of the available source solution. L is determined by the state of the art in membrane technology. If we consider that for a given application $c_d(0)$, $c_s(h)$, L and T are fixed, then $Q_d(0)$, $Q_s(h)$ and Lh are the only remaining control variables which can be adjusted in order to produce the desired output concentrations and total membrane flow.

K^* , β and $Q_m^*(h)$ can be written in terms of the given concentrations, $c_d(0)$ and $c_s(h)$, and specified product concentrations, $c_d(h)$ and $c_s(0)$. The matching coefficient for the solvent counterflows is

$$(1-11) \quad K^* = \left(1 - \frac{c_d(0)}{c_d(h)} \frac{c_s(h)}{c_s(0)} \right) / \left(1 - \frac{c_s(h)}{c_s(0)} \right).$$

K^* ranges from $-\infty$ for constant source concentration (only hydration of the driving solution occurs) to $+1.0$ for constant driving solution concentration (only dehydration of the source solution occurs). $K^* = 0$ when the two solvent flows are matched, i.e., when $Q_s(x) = Q_d(x)$.

The matching coefficient for the two countercurrent osmolar flows is

$$(1-12) \quad \beta = 1 - \frac{\alpha_s c_s(h)(c_d(0)/c_d(h) - 1)}{\alpha_d c_d(0)(1 - c_s(h)/c_s(0))}$$

β ranges from $-\infty$ for constant source solution concentration to $+1.0$ for constant driving solution concentration. $\beta = 0$ when the two osmolar flows are matched, e.g., when $\alpha_s c_s(h) \cdot Q_s(h) = \alpha_d c_d(0) \cdot Q_d(0)$.

The dimensionless total membrane water flux, $Q_m^*(h)$, is

$$(1-13) \quad Q_m^*(h) = \frac{c_d(0)}{c_d(h)} - 1$$

One may calculate the value of $Q_d(0)/lh$ required to produce the specified product concentrations, $c_s(0)$ and $c_d(h)$, from Eq. 10:

$$(1-14) \quad \frac{Q_d(0)}{lh} = \frac{L \pi_d(0) \beta}{Q_m^*(h)^2/2 + (1 - K^* + K^*/\beta) Q_m^*(h) + (K^*/\beta)^2 (1 - \beta) \ln \left[1 - \frac{Q_m^*(h)}{1 - K^*/\beta} \right]}$$

$Q_d(0)/lh$ is a function of $c_d(0)$, $c_s(h)$, L , T , $c_d(h)$ and $c_s(0)$ where the values for K^* , β and $Q_m^*(h)$ are given by Eqs. 11, 12 and 13.

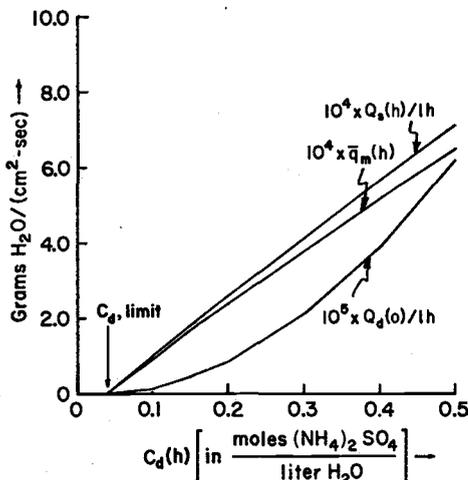
The average membrane flux per unit area is

$$(1-15) \quad \bar{q}_m(h) = \frac{Q_d(0)}{lh} \left(\frac{c_d(0)}{c_d(h)} - 1 \right)$$

The source solvent feed rate is

$$(1-16) \quad \frac{Q_s(h)}{lh} = \frac{Q_d(0)}{lh} \left[\frac{\frac{c_d(0)}{c_d(h)} - 1}{1 - \frac{c_s(h)}{c_s(0)}} \right]$$

For the given assumptions of complete salt rejection by the membrane, given control variables: $c_d(0)$, $c_s(h)$, L and T , and specified product variables: $c_d(h)$, $c_s(0)$ and $Q_m(h)$, Eqs. 14, 15 and 16 calculate the operating solvent feed rates for the driving and source solutions and the average membrane flux. In Fig. 2, Eqs. 14, 15 and 16 are used to plot $Q_d(0)/lh$, $Q_s(h)/lh$ and $\bar{q}_m(h)$ versus $c_d(h)$ for the specific case of transferring fresh water from brackish water into a fertilizer solution.



(Fig. 2 caption -- see next page)

Fig. 2. Simulation by Model 1 of a forward osmosis extractor for the production of fertilizer water from brackish water. $c_d(h)$ is the product concentration of the ammonium sulfate fertilizer water; $c_d, \text{ limit} = (\alpha_c/\alpha_d) \cdot c_s(h)$; lh is the total membrane area in cm^2 ; $Q_d(0)$ is the fertilizer solvent feed rate in grams/sec; $Q_s(h)$ is the solvent feed rate of the brackish source solution; $q_m(h)$ is the average membrane water flux. Fixed parameters are: $L = 1.37 \times 10^{-5}$ grams $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{atm}^{-1}$; $c_d(0) = 5.75$ molal $(\text{NH}_4)_2\text{SO}_4$, $c_s(h) = 0.0513$ molal NaCl (3000 mg/liter), $c_s(0) = 0.6$ molal NaCl (35,000 mg/liter), $\alpha_d = 2.30$, $\alpha_s = 1.86$, $RT = 24.5$ liter $\cdot\text{atm}$ mole $^{-1}$. Model 1 assumes zero membrane solute flux and no concentration polarization.

For dehydration only or for hydration only, it is simpler to rewrite the differential equation Eq. 6 instead of evaluating Eqs. 14, 15 and 16 at the limits of K^* and β ($K^* = \beta = 1.0$ for dehydration; $K^* = \beta = -\infty$ for hydration). For dehydration only c_d is constant and Eq. 6 becomes

$$(1-17) \quad \frac{dQ_m(x)}{dx} = lL(\pi_d - 1000\alpha_s n_s RT/Q_s(x)).$$

Integrating Eq. 19 and rearranging the result yields the operating solvent feed rate of the source solution as a function of the given control variables: c_d , $c_s(h)$, L and T and the specified product concentration of the source solution, $c_s(0)$:

$$\frac{Q_s(h)}{lh} = \frac{L\pi_d}{1 - \frac{c_s(h)}{c_s(0)} + \frac{\pi_s(h)}{\pi_d} \ln\left(1 - \frac{1 - c_s(h)/c_s(0)}{1 - \pi_s(h)/\pi_d}\right)}.$$

Constant c_d requires that $Q_d(0)/lh \rightarrow +\infty$. The average membrane water flux is then

$$\bar{q}_m(h) = \frac{Q_s(h)}{lh} \left(1 - \frac{c_s(h)}{c_s(0)}\right).$$

For hydration only, c_s is constant and Eq. 6 becomes

$$(1-18) \quad \frac{dQ_m(x)}{dx} = lL(1000\alpha_d n_d RT/Q_d(x) - \pi_s).$$

Integrating Eq. 18 and rearranging the result yields the operating solvent feed rate of the driving solution as a function of the given control variables: c_s , $c_d(0)$, L and T and the specified $c_d(h)$.

$$(1-19) \quad \frac{Q_d(0)}{lh} = \frac{L\pi_s}{1 - \frac{c_d(0)}{c_d(h)} - \frac{\pi_d(0)}{\pi_s} \ln\left(1 - \frac{c_d(0)/c_d(h) - 1}{\pi_d(0)/\pi_s - 1}\right)}.$$

Constant c_s requires that $Q_s(h)/lh \rightarrow +\infty$. The average membrane water flux is

$$(1-20) \quad \bar{q}_m(h) = \frac{Q_d(0)}{lh} \left(\frac{c_d(0)}{c_d(h)} - 1\right).$$

For the specific case of transferring fresh water from seawater into a nutrient solution for humans, Eqs. 19 and 20 are used to plot $\bar{q}_m(h)$ and the fresh water obtained per mass of nutrient versus $lh/Q_d(0)$ in Fig. 3. FRESH is defined as kg. of water extracted per kg. of nutrient and is given by

$$\text{FRESH} = \frac{1000 \bar{q}_m(h) lh}{c_d(0) Q_d(0) \text{Molecular weight}_{\text{nutrient}}}$$

MODEL 2

Model 1 assumes that the membrane is solute impermeable and that concentration polarization is negligible. In this section the mathematical model includes the passage of solute through the membrane. Concentration polarization is still neglected. In addition, the source solution concentration is assumed constant so that only hydration of the driving solution occurs. This constant source solution concentration restriction is made for the purpose of using the extractor to transfer water from an unlimited seawater or brackish water source. The model can be expanded to describe the more

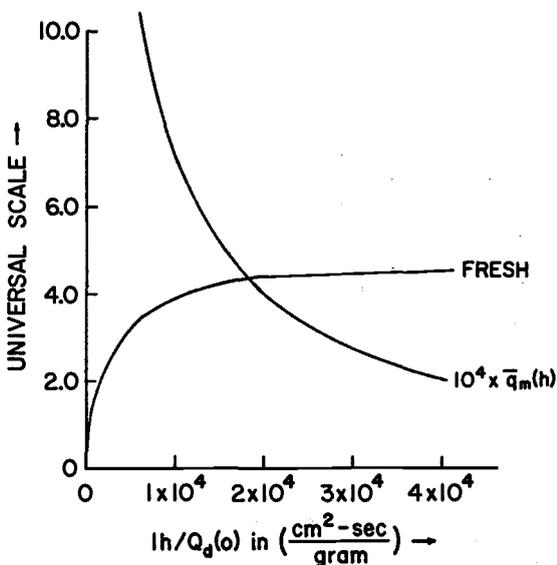


Fig. 3. Simulation by Model 1 of a forward osmosis extractor for the extraction of drinking water from seawater. Fresh is liters of water extracted per kg. of nutrients; $\bar{q}_m(h)$ is the average membrane water flux in grams - cm^{-2} - sec^{-1} ; λh is the membrane area in cm^2 ; $Q_d(0)$ is the nutrient solvent feed rate in grams/sec. Fixed parameters are: $L = 4.05 \times 10^{-5}$ grams - cm^{-2} - sec^{-1} - atm^{-1} , $c_d(0) = 10.0$ molal glucose-fructose, $c_s = 0.6$ molal NaCl, $\alpha_d = 1.04$, $\alpha_s = 1.88$, $RT = 24.5$ liter-atm mole $^{-1}$. Model 1 assumes zero membrane solute flux and no concentration polarization.

general hydration-dehydration operation of the forward osmosis extractor, but for brevity the additional equations are not included here.

The new assumptions are:

- (1) Solute rejection by the membrane is less than 100%.
- (2) Water and solute membrane flows are independent.
- (3) Concentration polarization at the membrane surfaces is neglected.
- (4) The source solution concentration, c_s , is constant. The change of π_s due to loss of source solute molecules and due to gain of driving solute molecules is neglected.
- (5) There exists no convective or diffusive back mixing in the direction of the counterflow.
- (6) The temperature and the osmotic coefficients, α_s and α_d , are constant.

There are three differential equations for the membrane flows of water and solutes. For membrane water flow into the driving solution,

$$(2-1) \quad \frac{dQ_d(x)}{dx} = q_m(x) = L (\pi_d(x) + \pi_{ds}(x) - \pi_s) \cdot$$

For loss of driving solute from the driving solution,

$$(2-2) \quad \frac{dn_d(x)}{dx} = - \frac{w_d c_d(x)}{1000} \cdot$$

For gain of source solute into the driving solution,

$$(2-3) \quad \frac{d n_{ds}(x)}{dx} = \frac{w_s (c_s - c_d(x))}{1000}.$$

The algebraic equations for the extractor are:

$$(2-4) \quad \pi_i = \alpha_i C_i(x) RT,$$

$$(2-5) \quad c_d(x) = 1000 n_d(x) / Q_d(x),$$

$$(2-6) \quad c_{ds}(x) = 1000 n_{ds}(x) / Q_d(x),$$

$$(2-7) \quad C_p(x) = \frac{w_s (c_s - c_d(x))}{\rho_m(x)},$$

$$(2-8) \quad Q_m(x) = Q_d(x) - Q_d(0).$$

The boundary conditions at $x = 0$ for Eqs. 2-1, 2-2 and 2-3 are:

$$n_d(0) = c_d(0) Q_d(0) / 1000;$$

$$n_{ds}(0) = c_{ds}(0) Q_d(0) / 1000 \quad (= 0.0 \text{ if the driving feed solution contains no source molecules});$$

$$Q_d(0) = \text{arbitrary constant} = 1.0 \text{ gram/sec for simplicity.}$$

The membrane transport coefficients (w_s , w_d and L) are related to each other by the state of the art in membrane technology. Manufacturers' attempts to decrease the solute permeability generally result in decreasing the water permeability. For example, Sourirajan (1970, p. 229) presents data for sodium chloride and water permeabilities of cellulose acetate membranes. For low pressure membranes, w_{NaCl} and L are related by the empirical equation, $L = 9.38 \times 10^{-4} (w_{NaCl})^{2.9}$. The additional information provided by such empirical equations between L , w_s and w_d can be used in conjunction with Model 2 in order to select the optimum membrane for a given application. The results of a simulation by Model 2 of a forward osmosis extractor for the extraction of drinking water from seawater are shown in Fig. 4.

MODEL 3

Model 3 approximates the effect which the fluid dynamics of the counterflows has on the membrane transfer rate by assuming the existence at the membrane of two unstirred films or concentration boundary layers of thicknesses δ_d and δ_s . The concentrations are assumed to equal the bulk solution concentrations, $c_d(x)$ and c_s , at the distances δ_d and δ_s from the membrane. As in Model 2 the concentration of the source solution far from the membrane is taken to be constant, i.e., the extractor is assumed to operate in the hydration mode with an infinite source supply. Again the model can be expanded to describe the more general hydration-dehydration operation of a counterflow forward osmosis extractor. This step has not been taken here because the ensuing complications obscure the main points, and also because the present model is adequate for dealing with the hydration application of the succeeding paper (KM 1976).

The assumptions for Model 3 are:

- (1) Solute rejection by the membrane is less than 100% and greater than 90%.
- (2) The concentration boundary layer thickness, δ_s and δ_d are not functions of x or local changes of concentration and flow rate.
- (3) Assumptions 2, 4, 5 and 6 of Model 2.

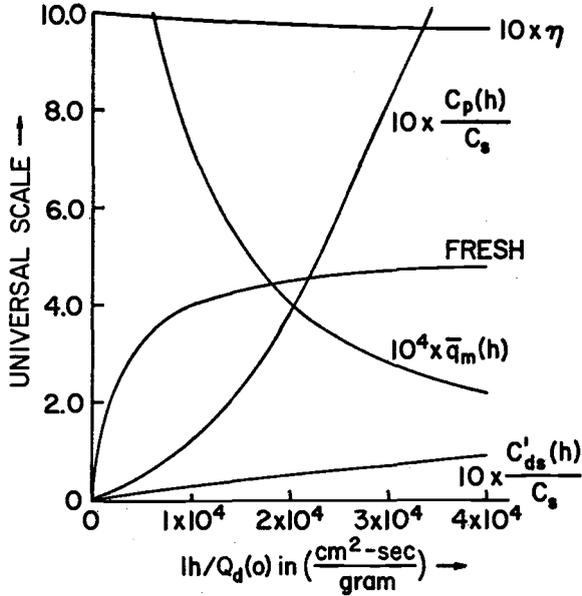


Fig. 4. Simulation by Model 2 of a forward osmosis extractor for the extraction of drinking water from seawater. $c_p(h)$ and $c_{ds}'(h)$ are the local and total salt concs. of the membrane flux; FRESH is liters of water extracted per kg. nutrient; lh is the membrane area in cm^2 ; $q_m(h)$ is the average membrane water flux in $grams - cm^{-2} - sec^{-1}$; $Q_d(0)$ is the nutrient solvent feed rate in $grams/sec$; η is the nutrient fraction conserved. The membrane properties are: $L = 4.05 \times 10^{-5} \text{ grams} - cm^{-2} - sec^{-1} - atm^{-1}$, $w_{NaCl} = 2.02 \times 10^{-5} \text{ cm/sec}$, $w_d = 7.13 \times 10^{-6} \text{ cm/sec}$. The operating parameters are: $c_d(0) = 10.0 \text{ molal glucose-fructose}$, $c_s = 0.6 \text{ molal NaCl}$, $\alpha_d = 1.04$, $\alpha_s = 1.86$, $RT = 24.5 \text{ liter-atm-mole}^{-1}$. Model 2 neglects concentration polarization.

In response to water flowing through the membrane, the concentration of the source solute increases near the membrane surface on the source side of the extractor, and the concentration of the driving solute decreases near the membrane surface on the driving side of the extractor. In order to calculate the water and solute fluxes through the membrane, it is necessary to know the solute concentrations at the membrane surfaces.

For a binary system the mole flux of the solute A relative to stationary coordinates is (Geankoplis, 1972)

$$(3-1) \quad N_{Ay} = -C^* D_{AB} \frac{dx_A}{dy} + C_A^* U$$

where: y is the direction normal to the membrane;

C^* is the total number of moles per cm^3 of solution;

C_A^* is the number of moles of solute A per cm^3 of solution;

D_{AB} is the diffusion coefficient of solute A in solvent B;

x_A is the mole fraction of solute A;

U is the mole average velocity relative to stationary coordinates.

Inserting into Eq. 3-1 the equation for U , $U = (N_{Ay} + N_{By})/C^*$, yields

$$N_{Ay} = -C^* D_{AB} \frac{dx_A}{dy} + x_A (N_{Ay} + N_{By})$$

Rearranging terms,

$$(3-2) \quad dy = \frac{c^* D_{AB} dx_A}{-N_{Ay} + x_A (N_{Ay} + N_{By})}$$

In addition, c^* is a function of x_A .

$$c^* = \frac{1}{x_A V_A + x_B V_B} = \frac{1}{V_B (1 + x_A (n-1))}$$

where V_A, V_B are the partial mole volumes of A and B, and $n \equiv V_A/V_B$.

Defining $\epsilon = N_{Ay}/N_{By}$, and inserting the above equation for c^* into Eq. 3-2,

$$(3-3) \quad dy = \frac{D_{AB} dx_A}{q_m (-\epsilon + x_A (1 - \epsilon(n-2)) + x_A^2 (n-1)(1+\epsilon))}$$

where $q_m = V_B N_{By}$.

For constant D_{AB}, q_m, ϵ and n , Eq. 3-3 can be integrated with the boundary conditions: at $y = 0, x_A = x_{Aw}$ and at $y = \delta, x_A = x_{A\infty}$.

$$(3-4) \quad \frac{q_m (1+\epsilon) \delta}{D_{AB}} = \ln \left[\frac{((1+\epsilon)x_{A\infty} - \epsilon)(n-1)x_{Aw} + 1}{((1+\epsilon)x_{Aw} - \epsilon)(n-1)x_{A\infty} + 1} \right]$$

The membrane is chosen and the extractor is operated so that $\epsilon \ll (x_{Aw}$ and $x_A)$. If $(n-1)x_{Aw}$ and $(n-1)x_{A\infty} \ll 1$, then Eq. 3-4 can be approximated by

$$\frac{q_m \delta}{D_{AB}} \approx \ln \frac{x_{A\infty}}{x_{Aw}}$$

The mole fraction of solute A at the membrane surface is

$$x_{Aw} = x_{A\infty} e^{-q_m \delta / D_{AB}}$$

Making the approximation, $\frac{c_{Aw}}{c_{A\infty}} = \frac{x_{Aw}}{x_{A\infty}}$, yields

$$c_{Aw} = c_{A\infty} e^{-q_m \delta / D_{AB}}$$

For non-negative q_m, δ_s and δ_d , the molal concentrations at the membrane surfaces are:

$$(3-5) \quad c_{dw} = c_d e^{-q_m \delta_d / D_d};$$

$$(3-6) \quad c_{sw} = c_s e^{q_m \delta_s / D_s}$$

The membrane water flux into the driving solution is

$$(3-7) \quad q_m(x) = L (\pi_{dw}(x) + \pi_{ds}(x) - \pi_{sw}(x))$$

Inserting Eqs. 2-4, 2-7, 3-5 and 3-6 into Eq. 3-7 yields

$$(3-8) \quad q_m(x) = L \left(\pi_d(x) e^{-q_m(x) \delta_d / \bar{D}_d(x)} + \pi_{ds} - \pi_s e^{q_m(x) \delta_s / D_s} \right)$$

$\bar{D}_d(x)$ is the diffusion coefficient of the driving solution averaged in the y direction and is defined by:

$$(3-9) \quad \bar{D}_d(x) \equiv \frac{c_{dw}(x) \int_{c_{dw}(x)}^{c_d(x)} D_d(c_d) dc_d}{\int_{c_{dw}(x)}^{c_d(x)} dc_d}$$

Because Eq. 3-8 cannot be solved directly for $q_m(x)$, the authors took the derivative of Eq. 3-8 with respect to ldx ($dq_m(x)/ldx$). The resulting Eq. 3-10 although more complicated than Eq. 3-8 yields a linear equation for $dq_m(x)/ldx$. The first order differential equation for $dq_m(x)/ldx$ can be numerically integrated to obtain $q_m(x)$, and then $q_m(x)$ can be numerically integrated to yield $Q_d(x)$.

For Model 3, the six coupled differential equations are: (Although not so noted, c_d , c_{ds} , c_{dw} , \bar{D}_d , Q_d , q_m and π_d are functions of the location x)

$$(3-10) \frac{dq_m}{ldx} = \frac{\left(\frac{c_d \delta_d q_m}{\bar{D}_d^2} \left(\frac{\partial \bar{D}_d}{\partial c_d} \frac{dc_d}{ldx} + \frac{\partial \bar{D}_d}{\partial c_{dw}} \frac{dc_{dw}}{\partial c_{ds}} \frac{dc_{ds}}{ldx} \right) + \frac{dc_d}{ldx} \right) \alpha_d RT e^{-q_m \delta_d / \bar{D}_d} + \alpha_s RT \frac{dc_{ds}}{ldx}}{\frac{1}{L} + \alpha_d RT \frac{\delta_d}{\bar{D}_d} \left(1 - \frac{q_m}{\bar{D}_d} \frac{\partial \bar{D}_d}{\partial c_{dw}} \frac{\partial c_{dw}}{\partial q_m} \right) e^{-q_m \delta_d / \bar{D}_d} + \alpha_s RT c_s \frac{\delta_s}{D_s} e^{q_m \delta_s / D_s}}$$

$$(3-11) \frac{dQ_d}{ldx} = q_m ;$$

$$(3-12) \frac{dc_d}{ldx} = -\frac{w_d}{Q_d} c_d e^{-q_m \delta_d / \bar{D}_d} - \frac{c_d}{Q_d} q_m ;$$

$$(3-13) \frac{dc_{dw}}{ldx} = \frac{\partial c_{dw}}{\partial q_m} \frac{dq_m}{ldx} + \frac{\partial c_{dw}}{\partial c_{ds}} \frac{dc_{ds}}{ldx} ;$$

$$(3-14) \frac{d\bar{D}_d}{ldx} = \frac{\partial \bar{D}_d}{\partial c_d} \frac{dc_d}{ldx} + \frac{\partial \bar{D}_d}{\partial c_{dw}} \frac{dc_{dw}}{ldx} ;$$

$$(3-15) \frac{dc_{ds}}{ldx} = \frac{w_s}{Q_d} (c_s e^{q_m \delta_s / D_s} - c_{ds}) - \frac{q_m}{Q_d} c_{ds} ;$$

The algebraic equations for the partial derivatives are:

$$(3-16) \frac{\partial c_{dw}}{\partial q_m} = \left(\frac{1}{L} + \alpha_s RT \frac{\delta_s}{D_s} c_s e^{q_m \delta_s / D_s} \right) / \alpha_d RT$$

$$(3-16a) \frac{\partial c_{dw}}{\partial c_{ds}} = -\alpha_s RT / \alpha_d RT$$

(3-17) $\frac{\partial \bar{D}_d}{\partial c_d}$ and (3-18) $\frac{\partial \bar{D}_d}{\partial c_{dw}}$ require an empirical equation for the diffusion coefficient, D_d , as a function of the molal concentration, c_d .

The values of q_m , Q_d , c_d , c_{dw} , \bar{D}_d and c_{ds} at $x = 0$ are:

$$Q_d(0) = 1.0 \text{ grams/sec;}$$

$$c_d(0) = \text{Feed concentration of the driving solution;}$$

$$c_{ds}(0) = 0.0 \text{ (} c_{ds}(0) \text{ is non-zero only if the driving feed solution contains source molecules);}$$

$q_m(0)$, $c_{dw}(0)$ and $\bar{D}_d(0)$ can be obtained by successive approximations with the first two terms of the Taylor Series expansion for $q_m(0)$ where $q_m(0)$ is defined by Eq. 3-8; $\bar{D}_d(0)$ is defined by Eq. 3-9; and $c_{dw}(0)$ is obtained from Eq. 3-19.

$$(3-19) \quad C_{dw}(0) = \frac{1}{\alpha_d RT} \left[\frac{q_m(0)}{L} + \alpha_s RT (c_s e^{q_m(0) \delta_s / D_s} - c_{ds}(0)) \right]$$

Eqs. 3-8 through 3-19 require estimates of the concentration boundary layer thicknesses, δ_s and δ_d . In the succeeding paper (Kessler and Moody, 1976) δ_s and δ_d for a laboratory forward osmosis extractor are estimated by minimizing the sum of squares deviation of the experimental results and the results predicted by Model 3.

SUMMARY

Three mathematical models for the forward osmosis extractor have been presented. For the ideal case where there exists no membrane solute flow and no concentration polarization at the membrane surfaces, Model 1 describes the extractor. The analytic solution of the governing differential equation for membrane water flow can be used without recourse to a computer. For the more general case where the membrane is slightly permeable to the solutes and with the assumption that no concentration polarization exists at the membrane surfaces, Model 2 describes the extractor's potential for a given membrane. Model 3 contains the complete design characteristics for the forward osmosis extractor based on the membrane transport properties, the diffusion coefficients of the two solutions and average values of the thicknesses of the concentration boundary layers.

SYMBOLS

c_i	--	concentration of solute i in moles/liter H_2O .
c^*	--	total mole concentration in moles/ $m^3 = C_A + C_B$.
C_A, C_B	--	concentration of the solute and solvent respectively in moles/cm.
$c_p =$	--	source solute concentration of the membrane permeate. $c_p = \frac{1000 j_s}{q_m}$. moles/liter H_2O
D_i	--	diffusion coefficient for solute i in water in cm^2/sec .
j_s	--	mole flux of source solute through the membrane in moles/ cm^2 -sec.
K^*	--	dimensionless matching coefficient for the solvent counterflow on the driving side and the source side of the forward osmosis extractor.
L_p	--	membrane water permeability coefficient in $\frac{cm}{sec/atm}$.
N_A, N_B	--	mole flux relative to a fixed point of solute and solvent respectively in moles/ cm^2 -sec.
n_i	--	solute counterflow for solute i in moles/sec.
q_m	--	local membrane flux in cm/sec.
\bar{q}_m	--	average membrane water flux is cm/sec ($\bar{q}_m = Q_m/\text{Membrane Area}$).
Q_m	--	membrane water flow in $cm^3/sec = L \int_0^x q_m(x') dx'$.
Q_i	--	solvent counterflow for solution i in cm^3/sec .
Q_m^*	--	dimensionless membrane water flow.
R	--	universal gas constant = $.0821 \frac{\text{liter-atm}}{\text{mole-degree}}$.
T	--	temperature in degrees Kelvin.
w_i	--	membrane permeability coeff. for solute i in cm/sec.

- V_A, V_B -- partial mole volume of components A and B in solution (cm^3/mole),
 x_A, x_B -- mole fraction of the solute and solvent respectively,
 α_i -- osmotic coefficient of solute i (= 1.86 for NaCl),
 β -- dimensionless matching coefficient for the countercurrent osmolar flows of the driving solution and the source solution.
 δ_i -- boundary layer thickness of the concentration polarization on side i of the membrane in cm.
 π_i -- osmotic pressure of solute i in atm.

SUBSCRIPTS

- d -- driving solution,
ds -- source solute which has passed through the membrane into the driving solution.
dw -- driving solute property at the membrane surface.
i -- refers to either source or driving solute.
s -- source solution.
sw -- source solute property at the membrane surface.

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