

APPLICATIONS OF DIRECT OSMOSIS:
DESIGN CHARACTERISTICS FOR HYDRATION AND DEHYDRATION

by

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ABSTRACT

In direct (normal, forward) osmosis water automatically flows through a semipermeable membrane from a "source" solution of low concentration to a "driving" solution with higher solute content. The process requires a membrane which is impermeable to the solutes; hydrostatic pressure differences are not directly involved and can be set equal to zero.

In principle, direct osmosis is a low-technology, low-power consumption method for reducing the water volume of industrial effluents or liquid agricultural products, and for reclaiming brackish irrigation water. In the latter application the driving solution may utilize fertilizer as a solute; the source solution is drainage that contains harmful salt components. This type of operation has been experimentally demonstrated.

This paper summarizes basic physical principles and introduces some quantitative design factors which must be understood on both a fundamental and on an applications level.

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

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removing solvent. Standard methods are available. They include evaporation/recondensation, freeze drying 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, 1975, which will be referred to as MK; Moody and Kessler 1971; 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, and Loeb and Block 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.

The free energy of solution depends only weakly on solute species. Since the basis of the proposed method is the substitution of one solute for another it does not require the expenditure of work of separation. Given appropriate "driving" solutes and semipermeable membranes, the process is automatic. It does not require heat, pressure vessels or complex controls; the only active mechanical devices are the pumps and valves required for maintaining appropriate flow rates. In the fertilizer case, one may view the method as recovery of a part of the energy utilized in manufacturing the fertilizer. Energy of solution that is normally lost when the material is spread on the ground is used instead for reclaiming irrigation water. If naturally concentrated solutions, such as salt brines are available, dehydration requires no energy supply at all.

OSMOSIS

Consider two compartments, A and B in Fig. 1, containing solutions of a and b, respectively. They are separated by a membrane impermeable to a and b, but permeable to solvent. In principle, the compartments A and B can be pressurized. The free energy of the solution in terms of the water potential (Noble, 1974) is

$$\psi_i = p_i - \pi_i, \quad (1)$$

where p_i is the hydrostatic pressure and the subscript i refers to either a or b. The osmotic pressure is given by

$$\pi_i \approx \alpha_i c_i RT, \quad (2)$$

where c_i is the concentration of dissolved i -type ions or molecules and the factor α_i , which corrects for the activity, is the only factor depending on the particular solute in question.

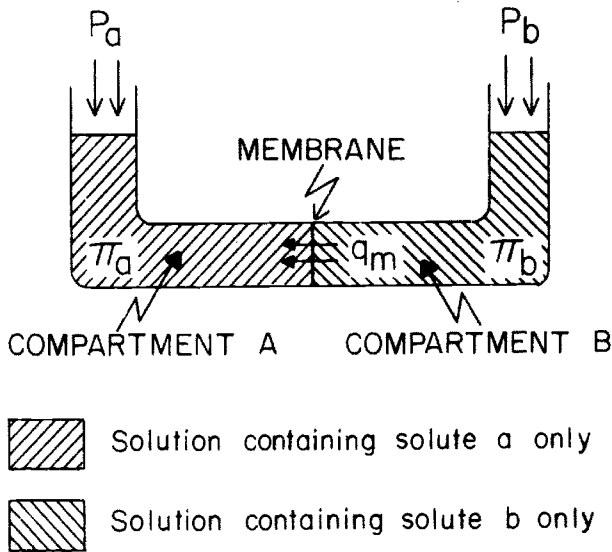


Fig. 1 Schematic of U-Tube apparatus for demonstrating osmosis. Assuming the concentration of solute a is greater than that of solute b, the osmotic pressure $\pi_a > \pi_b$. q_m indicates pure water flux through the semipermeable membrane when $p_a = p_b$ (forward osmosis), or when $p_b = \pi_b = p_a = \pi_a$ (reverse osmosis).

When $\psi_a = \psi_b$ no water flows through the membrane. When $\psi_a < \psi_b$ water flows ^a to the ^b left in Fig. 1, and conversely for $\psi_a > \psi_b$. If $\psi_a = 0$ one must apply a pressure $p_b \geq \pi_b$ in order to obtain a waterflow from right to left. This is reverse osmosis. If $p_b < \pi_b$, ψ_b is negative, $\psi_b < \psi_a = 0$, and water will flow from left to right by "forward" or "direct" osmosis. If $p_b \approx p_a \approx 0$ and $0 < \pi_b < \pi_a$, then also $\psi_a < \psi_b$ and water will flow from right to left, again by forward osmosis.

This last case is the basis of the procedures discussed in this paper, where some relatively concentrated "driving" solution in A is to be augmented by the automatic osmotic flow through a membrane from a more dilute

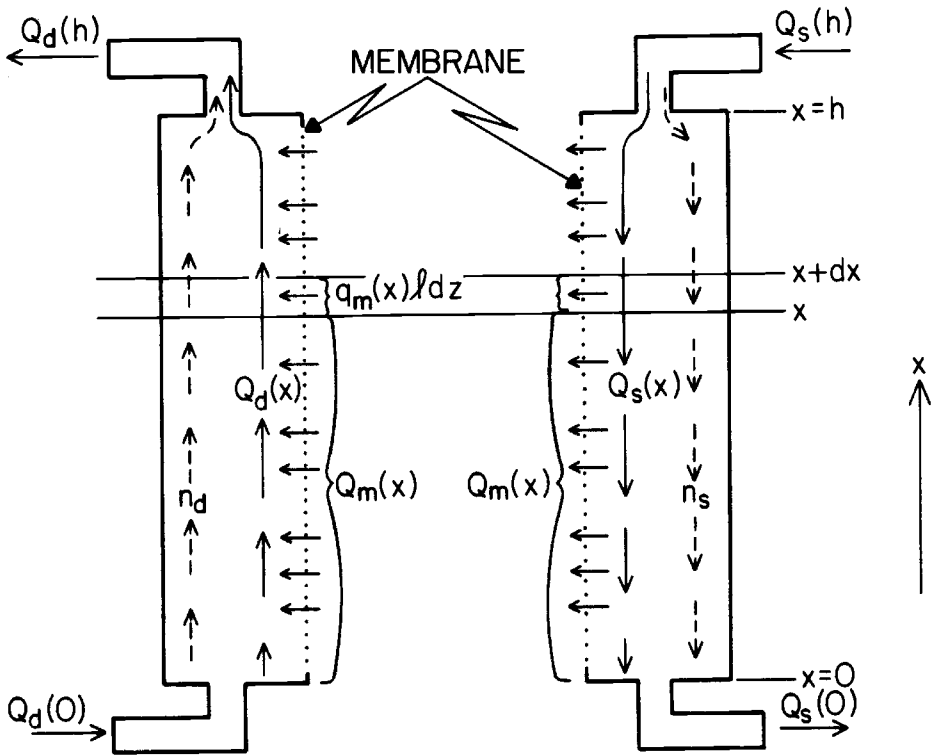


Fig. 2. Schematic exploded view of the countercurrent extractor, illustrating the conservation of solute current (dashed arrows) and the change of solvent current (solid arrows) due to the addition and subtraction of the membrane solvent current Q_m . The width of the extractor and membrane (into the 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 membrane, site of the schematic separation of the two halves of the extractor, is indicated by dots.

"source" solution in B. The magnitude of the effect can be illustrated by considering seawater. The concentration of salts is about 3.5 weight %; the corresponding osmotic pressure $\pi \approx 25$ atmospheres. This is the least hydrostatic pressure which would have to be applied to seawater to initiate reverse osmosis solvent flow through a membrane. The same effect can also be obtained by merely placing 6.5 weight % solution of $(\text{NH}_4)_2\text{SO}_4$ fertilizer in contact with the "other" side of the membrane, with no hydrostatic pressure difference.

THEORY

The flow of solvent through the semipermeable membrane may be approximated by

$$q_m = L(\psi_s - \psi_d), \quad (3)$$

where ψ_s and ψ_d are the water potentials of the source and driving solutions, L is the membrane conductance and q_m is the membrane flux. See the Appendix for units. When $p_s \approx p_d \approx 0$,

$$q_m = L(\pi_d - \pi_s). \quad (4)$$

The linearity of these equations depends on the assumptions that the compartments containing the solutions are perfectly mixed and that boundary layer effects are negligible. Experiments show that these assumptions are very nearly valid for low viscosity solutions and low membrane flux.

The theory of operation of a forward osmosis counterflow extractor will now be presented. The geometry is indicated in Fig. 2 and also Fig. 1 of MK. The solvent currents Q_d and Q_s are assumed vertical, respectively on the left and right of the membrane. The membrane current Q_m augments Q_d and subtracts from Q_s . It is assumed that all quantities depend only on the one space variable x . It is further assumed that the membrane is completely impermeable to the solutes used; the solute currents are therefore conserved on each side of the extractor:

$$n_i = \frac{Q_i(x) c_i(x)}{1000} = \frac{Q_i(h) c_i(h)}{1000} = \frac{Q_i(0) c_i(0)}{1000} = \text{const.} \quad (5)$$

Considering a segment of the extractor ($x, x + dx$), and ignoring the very small changes in partial molal volume of solvent, the conservation of solvent yields

$$\ell q_m(x)dx = Q_d(x + dx) - Q_d(x) = Q_s(x + dx) - Q_s(x), \quad (6)$$

where Q_d is taken positive upwards and Q_s is positive downwards. Then

$$\ell q_m = \frac{dQ_d}{dx} = \frac{dQ_s}{dx}, \quad (7)$$

where ℓ is the width of the membrane. Integrating Eqs. 7,

$$Q_m(x) \equiv \ell \int_0^x q_m dx = Q_d(x) - Q_d(0) = Q_s(x) - Q_s(0), \quad (8)$$

$Q_m(x)$ being the total membrane current between $x = 0$ and $x = x$. The last equality in Eq. 8 is the integral of the second of Eqs. 7:

$$Q_d(x) - Q_s(x) = Q_d(0) - Q_s(0) = K^*Q_d(0), \quad (9)$$

where $K^*Q_d(0)$ is the chosen form of the integration constant. Combining Eqs. 2, 4 and 5,

$$\frac{dQ_d}{dx} = 1000 \ell RT \left(\frac{n_d^{\alpha_d}}{Q_d} - \frac{n_s^{\alpha_s}}{Q_s} \right). \quad (10)$$

Defining $Q_m^*(x) \equiv Q_m(x)/Q_d(0)$, and making use of Eqs. 9 and 8 (which states that $dQ_m/dx = dQ_d/dx$), one obtains

$$\frac{dQ_m^*}{dx} = \frac{1000 \ell RT}{Q_d(0)^2} \left(\frac{n_d^{\alpha_d}}{Q_m^* + 1} - \frac{n_s^{\alpha_s}}{Q_m^* + 1 - K^*} \right). \quad (11)$$

The solution of Eq. 11, integrated over the whole extractor, is

$$\frac{1000 \ell RT (n_d^{\alpha_d} - n_s^{\alpha_s})}{Q_d(0)^2} = \frac{K^{*2}}{\beta^2} \left[(\beta + 1) \ln \left(1 - \frac{Q_m^*(h)}{\frac{K^*}{\beta} - 1} \right) \right] + \left(1 + K^* + \frac{K^*}{\beta} \right) Q_m^*(h) + \frac{Q_m^*(h)^2}{2}, \quad (12)$$

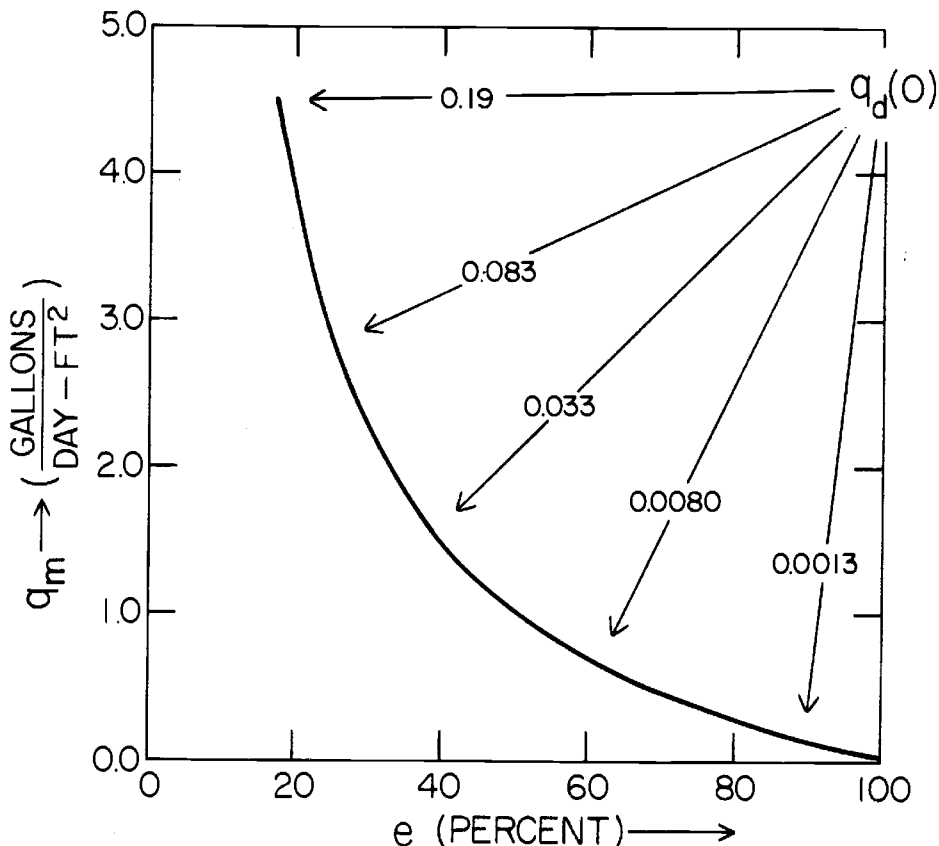


Fig. 3. Plot of calculated average membrane flux \bar{q}_m vs. e , the absolute water reclamation efficiency per driving solute. The input flux of driving solution, $q_d(0)$, is indicated in the same units as \bar{q}_m ; $q_d(0)$ is a parameter contained in \bar{q}_m and e , as well as in their ratio. The other parameters implicitly included are: $RT = 24.5 \text{ l-atm-mol}^{-1}$, $\alpha = 1.86$, $\beta = 2.30$, $c_s(h) = 0.0513 \text{ molal}$, $c_s(0) = 0.6 \text{ molal}$, $c_d(0) = 5.75 \text{ molal}$, $L = 10^{-5} \text{ cm-sec}^{-1}\text{-atm}^{-1}$. To convert from U.S. gal-day⁻¹-ft² to cm-sec⁻¹ divide by 2.12×10^4 .

where $\beta = (n_s \alpha_s - n_d \alpha_d) / n_d \alpha_d$.

The average membrane flux for the whole counterflow extractor, $\bar{q}_m = Q_m(h) / \ell h = Q_m^*(h) Q_d(0) / \ell h$, may be calculated from Eq. 12. It is the required measure of water volume recovery rate for a given apparatus size, and for given input solution currents and concentrations.

A determination of the applicability of the method also requires information on the quantity of driving solute (fertilizer, here) required to recover a given amount of water. It can be shown from Eqs. 5 and 8 that the output concentration is

$$c_d(h) = \frac{c_d(0) Q_d(0)}{Q_m(h) + Q_d(0)} \quad (13)$$

One may now define an efficiency η of water reclamation as the volume of water added to the driving solution by the membrane flow, per mole of driving solute. Thus $\eta \equiv 10^{-3} Q_m(h) / n_d \text{ l-mol}^{-1}$; again using Eq. 5,

$$\eta = \frac{1}{c_d(h)} - \frac{1}{c_d(0)} \quad (14)$$

With Eq. 13, Eq. 14 becomes

$$\eta = \frac{Q_m(h)}{Q_d(0) c_d(0)} \quad (15)$$

The maximum value of η occurs when $c_d(h)$ is a minimum, i.e. when $\pi_d(h) = \pi_s(h)$. One may then define an absolute efficiency $e \equiv \eta / \eta_{\max}$ which varies from 0 to 1.0. One may easily show that

$$e(h) = \frac{Q_m(h)}{Q_d(0)} \left(\frac{\pi_s(h)}{\pi_d(0) - \pi_s(h)} \right) \quad (16)$$

Combining Eq. 16 with the definition of \bar{q}_m one finally obtains

$$\bar{q}_m(h) = \frac{Q_d(0)}{\ell h} \left(\frac{\pi_d(0)}{\pi_s(h)} - 1 \right) e(h) \quad (17)$$

This relation is plotted in Fig. 3. The curve is the result of using Eq. 12 to compute \bar{q}_m and e for different values of $Q_d(0)$, while holding all the other parameters constant. Some individual values of $q_d(0) \equiv Q_d(0) / \ell h$ are indicated.

The particular choice of parameters made in computing Fig. 3 was based on the available membrane, and the environmental constraints imposed by the Wellton-Mohawk irrigation district example discussed in MK. The driving solute was taken as $(\text{NH}_4)_2\text{SO}_4$, the source solute as NaCl. The output concentration of the source solution was taken to equal seawater salt concentration. The results would not change materially if one desired a more concentrated solution for disposal in local brine pools. Fig. 3 is to be compared in the Fig. 2 of MK.

DISCUSSION AND SUMMARY

This paper has derived approximate mathematical expressions governing one possible embodiment of a direct osmosis hydration/dehydration scheme. Other designs are of course possible; they may be matched to particular tasks and boundary conditions. Although experiment and theory have been shown to correspond reasonably well for solutions of NaCl and $(\text{NH}_4)_2\text{SO}_4$, the correspondence has not been as good for the case of more viscous solutions. In that case, details of the membrane boundary layer mixing and other fluid dynamic effects will have to be examined. Furthermore, it may be appropriate to develop special membranes, since the readily available membranes used in the experiments are thick enough to support many atmospheres of reverse osmosis hydrostatic pressure, an entirely unnecessary feature. The extra thickness brings about boundary layer problems.

The following paper (MK) gives experimental results and demonstrates the utility of the method in an irrigation water reclamation context. The ultimate utility remains to be determined. It will depend on capital and energy costs relative to existing processes, on the environmental determinants and possibly on the development of improved membrane materials.

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APPENDIX - Symbols and Units

- a,b - general solution subscripts
 A,B - compartment labels
 c(x) - concentration ($\text{mol}\cdot\text{l}^{-1}$ of solvent) at x
 c(x) - molal concentration ($\text{mol}\cdot\text{kg}^{-1}$ of solvent)
 (the above are used interchangeably, for water)
 d - subscript for driving solution
 h - height, long dimension of membrane (cm)
 i - subscript, general case
 l - width of membrane (cm)
 L - membrane conductance ($\text{cm}\cdot\text{sec}^{-1}\cdot\text{atm}^{-1}$)
 K* - integration constant (Eq. 9)
 MK - paper by Moody and Kessler, 1975
 m - subscript, membrane
 n - solute current ($\text{mol}\cdot\text{sec}^{-1}$)
 p - hydrostatic pressure (atm)
 q(x) - solvent flux at x ($\text{cm}^3\cdot\text{cm}^{-2}\cdot\text{sec}^{-1} = \text{cm}\cdot\text{sec}^{-1}$)
 Q(x) - solvent current at x ($\text{cm}^3\cdot\text{sec}^{-1}$)
 Q*(x) - Q(x)/Q(0)
 \bar{q}_m - average membrane flux $Q_m(h)/\ell h$ ($\text{cm}\cdot\text{sec}^{-1}$)
 RT - thermal energy ($1\cdot\text{atm}\cdot\text{mol}^{-1}$)
 s - subscript for source solution
 x - coordinate system variable (cm)
- α - osmolality conversion factor
 β - solute parameter - see Eq. 12.
 η - efficiency ($1\cdot\text{mol}^{-1}$)
 $\pi(x)$ - osmotic pressure (atm) at x
 ψ - water potential (atm)
- 1000 - conversion factor ($\text{cm}^3\cdot\text{l}^{-1}$)