

Solar Pond Modeling

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ABSTRACT

The procedure by which an energy balance may be used to evaluate the evaporation rate of a brine is described and related to models of a single solar pond and a series of ponds. The method includes correlating seepage and evaporation rates with the pond concentration factor and required pumping rates. The phase chemistry may be described mathematically and used to predict mother liquor compositions and crystal components as a function of concentration factor. Correlations such as these are essential to control pond operations.

INTRODUCTION

As is well known, solar energy is not only a cheap source of energy but is an inexhaustible source. It is thought that after conventional fuels like oil, coal, gas and even nuclear have been exhausted there will still be solar energy to replace them. The technology to utilize solar energy still remains to be developed. However, one of the areas where the use of solar energy is simple and cheap is in solar evaporation for saline recovery. The utilization of solar energy for concentration of brines in salt production is such a logical application that it has been done profitably for thousands of years. Even nature has utilized it in the formation of some of the salt deposits.

The application of solar energy was first limited to simple systems where a salt could be recovered in relatively pure form, and where purity was not a requirement as it is at the present time. One of the earliest applications of solar evaporation has been in producing sodium chloride and recently for producing other products such as potash. The application of solar evaporation for recovery of salt from more complex systems requires the use of more advanced technology, including phase chemistry, computer modeling, optimization, etc. Such technology is

now available and solar energy can therefore be profitably used in saline recovery from many complex and multi-component systems.

In recent years the mathematical relationships involved in solar processing have been established and an energy balance theory in which evaporation rate is determined by net gain in radiant energy, air temperature, humidity, and wind has been developed (Bonython, 1965). In addition, the effect of the vertical diffusion of water vapor into the atmosphere was added to the energy balance during an extensive investigation of the energy balance of a solar pond by Keyes *et al* (Keyes, Gregory, Gunaji, and Lunsford, 1970; Keyes, Gunaji, Lunsford, and Seckler, 1970; Keyes, Winans, Morales, Pritchett, and Gregory, 1970). An unsteady state energy balance for a solar pond has been solved which included heat transfer into the pond floor (Pancharatnam, 1972).

Factors other than evaporation rate have a bearing on the performance of a solar pond. Examples are pond design (Garrett, 1965a), pond operating procedure (Garrett, 1965b), and leakage (Kallerud, 1969). By thoroughly understanding all of the factors governing the operation of a solar pond, a system of solar ponds may be used to accomplish a wide variety of separations and concentrations under diverse conditions.

This discussion will include a brief description of the pond energy balance and how it may be applied, a description of the material balance associated with a solar pond, a description of the material balance associated with a series of solar ponds, and a discussion of the associated phase chemistry.

THE ENERGY BALANCE

Over long periods the energy coming into a solar pond equals the energy leaving. Energy primarily reaches a so-

lar pond by solar radiation and in some cases of heat transfer from the atmosphere. Energy leaves primarily by evaporation of liquid, heat transfer to the atmosphere, and radiation. These energy terms are related by the following equation (Bonython, 1965):

$$q = \lambda k (P_w - P_a) + h (T_2 - T_a) (1 + r/h) \quad (1)$$

where:

- q = net incoming radiant energy
- λ = latent heat of vaporization
- k = mass transfer coefficient
- P_w = vapor pressure at water surface
- P_a = partial pressure in atmosphere
- h = heat transfer coefficient
- T = temperature
- r = an emission coefficient for black body radiation

The above is a steady stage equation and does not take into account the heat capacity of the brine in the solar pond.

The following relationship has been found to exist (Ferguson, 1952):

$$\frac{k\lambda}{h} = 2 \text{ (}^\circ\text{C/MM of Hg)} \quad (2)$$

Evaporation rate, E , is related to the quantity evaporated from the brine by

$$E\rho\lambda = \lambda k(P_w - P_a) \quad (3)$$

If it is desired to determine the evaporation rate of a brine and the evaporation rate of pure water is known, the following procedure may be used. The following equation may be written for pure water:

$$q = E'\rho'\lambda' + h'(T_w' - T_a) (1 + r'/h') \quad (4)$$

The primes in the above expression indicate pure water is present. If the evaporation rate for the pure water was found under identical conditions to those present in the brine, then

$$h \approx h' \quad (5)$$

or the heat transfer coefficient for heat transfer from the water equals that for heat transfer from the brine. Of course, this is an approximation in any case since waves and other such phenomena will differ in brine and pure water resulting in somewhat different coefficients. By combining equations 1, 2, 4, and 5,

$$T_2 = \frac{E'\rho'\lambda/h - 2(P_w - P_a)}{(1 + r/h)} - T_w' \quad (6)$$

where

$$T_w' = f(P_w') \quad (7)$$

By rewriting Equation 3 for pure water

$$E'\rho'\lambda = 2h (P_w' - P_a) \quad (8)$$

or

$$P_w' = P_a + E'\rho'\lambda/2h \quad (9)$$

Also,

$$T_w = f(P_w + \Delta P_w) \quad (10)$$

Where ΔP_w is the vapor pressure lowering due to the dissolved salts in the brine. Equations 6, 7, 9, and 10 may now be solved simultaneously for T_w , P_w , T_w' , and P_w' if the evaporation rate for pure water, E' , the heat transfer coefficients, h and r , the air temperature and moisture and the vapor pressure lowering are known. Then,

$$E = 2h (P_w - P_a)/\lambda\rho \quad (11)$$

In other words, if the vapor pressure lowering is known for the brine and the evaporation rate for pure water in the solar pond is known, then the evaporation rate for the brine in the solar pond can be determined.

The proceeding procedure for determining evaporation rate based on that of pure water is preferred to solving Equation 1 directly by measuring radiation, etc. since these measurements are difficult to make. A still more exact procedure for determining evaporation rates for brines in solar ponds is to measure the evaporation rates at various brine concentrations by using the method described by Kallerud (1969). Figure 1 is an example of a curve obtained in this manner. Data such as Figure 1 is essential to the design of complex solar evaporation schemes.

The success of a solar pond operation depends on the net evaporation rate more than any other factor. The net evaporation rate is defined as evaporation rate less rainfall. A map of the Western United States, Figure 2, has been prepared which indicates net evaporation rate (Ridley, 1970).

In summary, the evaporation rate of a brine is an essential parameter for the modeling of solar ponds. The evaporation rate of pure water may be crudely estimated from a map such as Figure 2. The evaporation rate of a brine (Figure 1 for example) may be estimated from energy and weather data by use of equations 1 and 3; it may be measured for pure water and estimated from vapor pressure lowering data; or it may be measured for actual brines using the method of Kallerud (1969).

THE SINGLE STAGE SOLAR POND

A material balance may be written for a solar pond if the following are known: (1) evaporation rate as a function of concentration and time of year, (2) leakage rate, (3) salt precipitation rate as a function of evaporation rate, and (4)

the entrainment of brine in the precipitated salts. This material balance is diagrammed in Figure 3 and may be written as:

$$A\rho_B \frac{dD}{dt} = Q_I\rho_{BI} - Q_O\rho_{BO} - \Delta V\rho_B \quad (12)$$

where

D = pond depth

Q = inlet or outlet pumping rate

ΔV = material lost due to evaporation, leakage, precipitation, and entrainment in the precipitate

The material lost may be written as,

$$\Delta V = \Delta V_E + \Delta V_S + \Delta V_{ES} + \Delta V_L \quad (13)$$

where the subscript E refers to evaporation, S to precipitated salt, ES to entrainment in the salt, and L to leakage. These terms are related to evaporation and leakage rates as follows:

$$\Delta V_E = AE \quad (14)$$

$$\Delta V_L = A\beta \quad (15)$$

$$\Delta V_S \approx \frac{\Delta V_E (1 - X_w)\rho_w}{X_w \rho_s} \quad (16)$$

$$\Delta V_{ES} = \frac{\Delta V_S \epsilon}{(1 - \epsilon)} \quad (17)$$

where

A = pond area

E = evaporation rate

β = leakage rate

X_w = weight fraction water in the brine

ϵ = porosity of precipitated salts

Of course, the terms for precipitation and entrainment in the precipitate exist only in saturated brines.

The depth of brine in the pond may be found by solving Equation 13,

$$D = D_{\text{initial}} + \int_{t_0}^t \left[\frac{Q_I\rho_{BI} - Q_O\rho_{BO} - \Delta\rho_B}{A\rho_B} \right] dt \quad (18)$$

The thickness of the deposited salts may be found from

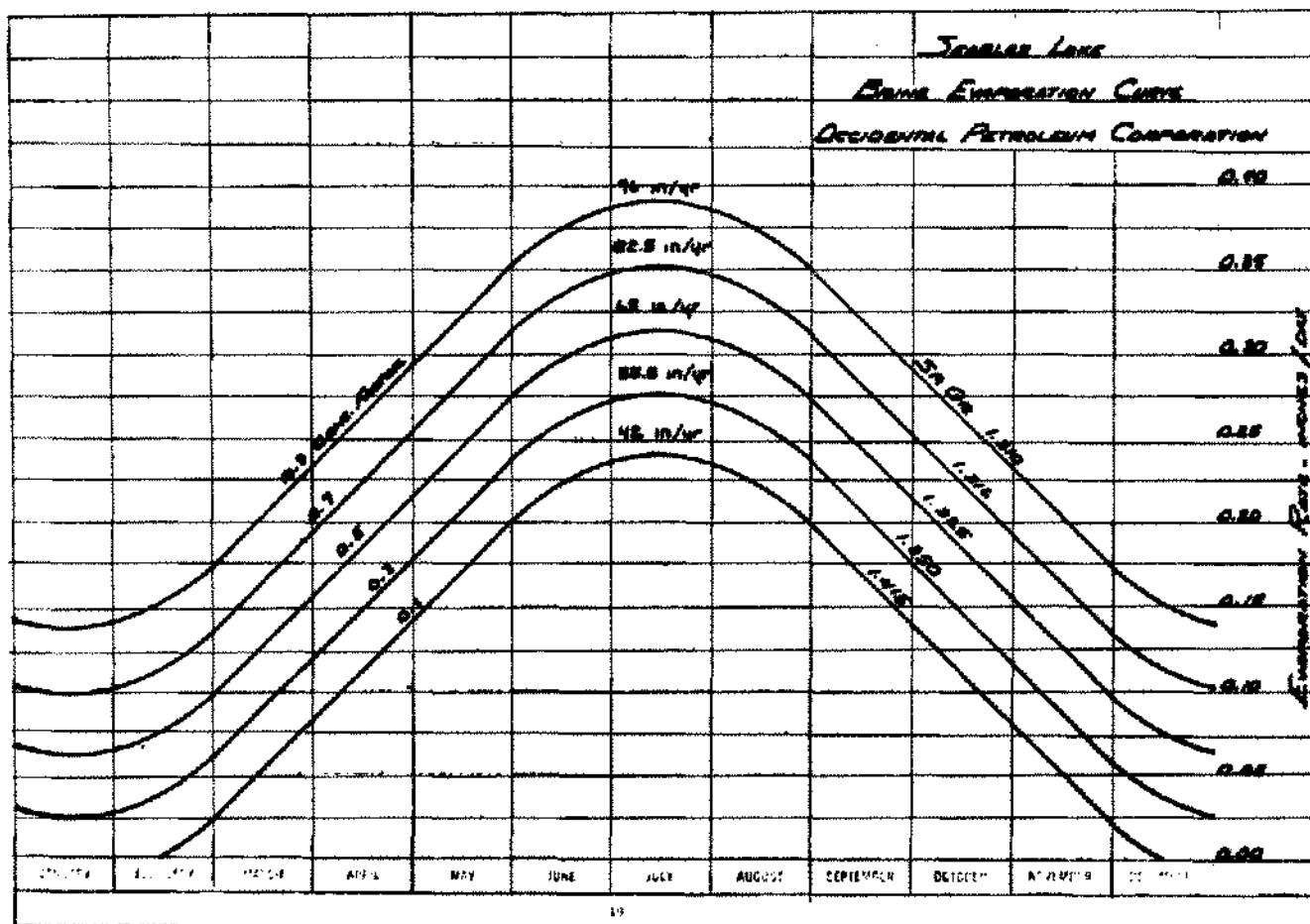


Figure 1. Typical Evaporation Rate Data Required to Model a Solar Pond, (m/yr).



Figure 2. Net Evaporation Rate Map for the Western U.S.A. (Ridley, 1970).

$$A \frac{d\tau}{dt} = \Delta V_S + \Delta V_{ES} \quad (19)$$

where τ = thickness of deposited salts. The pond surface elevation, H , is given by

$$H = D + \tau + H_0 \quad (20)$$

or by solving Equation 19 and combining with Equation 20.

$$H = H_0 + \int_{t_0}^t \left[\frac{Q_I \rho_{BI} - Q_D \rho_{BD} - \rho_B (\Delta V_E + \Delta V_2)}{A \rho_B} dt \right] \quad (21)$$

If evaporation and leakage rates are known as a function of time and concentration, Equation 18 may be easily solved numerically. However, the concentration must also be known as a function of time. Equation 21 was solved for an actual situation occurring in a solar pond at Searles Lake, California. During a period when no pumping occurred the calculated surface elevation closely matched the measured data as shown in Figure 4.

To determine the concentration factor in a pond during evaporation requires a material balance for a tracer. For a well mixed pond,

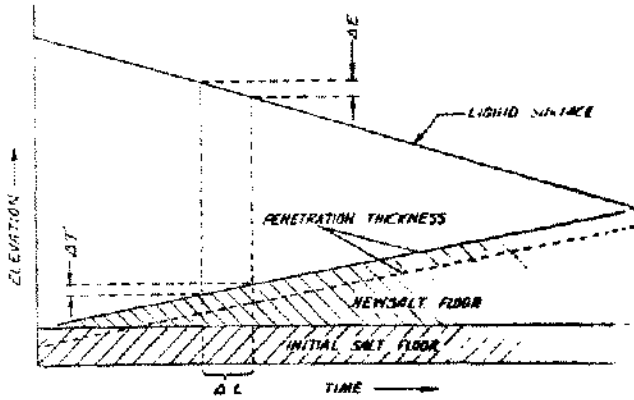


Figure 3. Diagram of Batch Pond Model.

$$\rho_B \frac{dCV}{dt} = \rho_{BI} Q_I C_I - \rho_{BO} Q_O C_O - \rho_B C (\Delta V_L + \Delta V_{ES}) \quad (22)$$

where C = tracer concentration
 V = pond volume

To solve this equation numerically, it may be rewritten in finite difference form,

$$\rho_B C_{j+1} V_{j+1} - \rho_B C_j V_j = \rho_{BI} Q_I C_I - \rho_{BO} Q_O C_O - \rho_B (\Delta V_L + \Delta V_{ES}) (C_{j+1} + C_j)/2 \quad (23)$$

where a time increment of one hour is implied. The subscript j is the number of the time increment. By solving for C_{j+1} in terms of C_j

$$C_{j+1} = \frac{C_j (V_j - Q_O \rho_{BO} / 2 \rho_B - \Delta V_L / 2 - \Delta V_{ES} / 2) + \rho_{BI} Q_I C_I / \rho_B}{V_{j+1} + \rho_{BO} Q_O / 2 \rho_B + \Delta V_L / 2 + \Delta V_{ES} / 2} \quad (24)$$

Equation 24 may be solved for C at any time simultaneously when Equation 18 of evaporation and leakage rates are known. This has been done for the case illustrated in Figure 4 using potassium ion as a tracer (this ion does not precipitate at these concentrations). The results are shown in Figure 5.

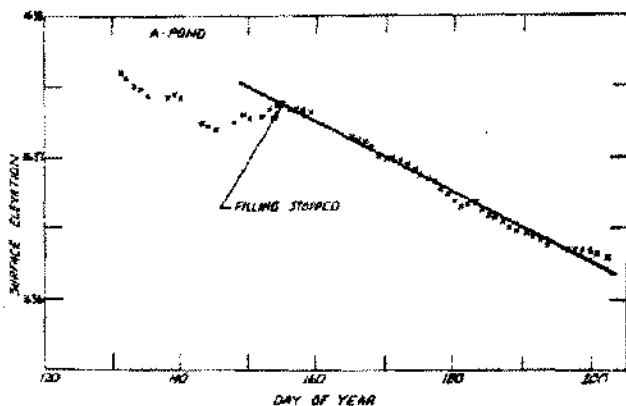


Figure 4. Pond Surface Elevation as Calculated From Equation 21.

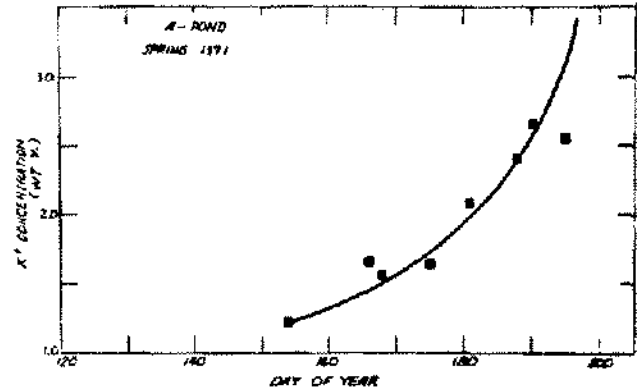


Figure 5. Potassium Ion Concentration Calculated From Equation 24.

As shown in Figure 3, mixing may occur between pond brine and entrained salts. Thus the effective depth of the pond for concentration calculations may in some cases be slightly greater than the actual pond depth.

PONDS IN SERIES

The model for a single solar pond may be extended to a series of ponds. The example presented here incorporated two assumptions which greatly simplify the mathematics: the ponds are to be operated at constant depth and each pond is well mixed. Therefore, a balance of material volumes may be written

$$Q_I - Q_O \sum_{i=1}^n \Delta V_i \quad (25)$$

where i = the number of the pond as in Figure 6
 n = the total number of ponds in the series

In the last pond,

$$Q_O C_O \rho_{BO} + \Delta V_{L,n} C_O \rho_{BO} = (\Delta V_n + Q_O) C_{n-1} \rho_{B,n-1} \quad (26)$$

or

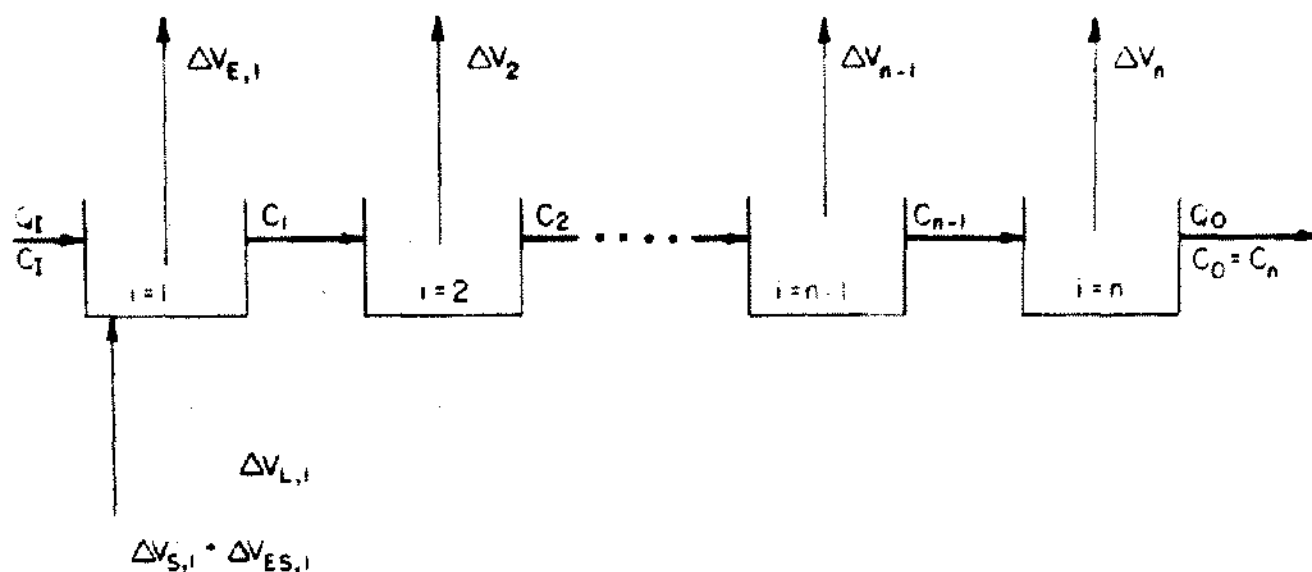
$$Q_O = \frac{\Delta V_{L,n} C_O \rho_{BO} - \Delta V_n C_{n-1} \rho_{B,n-1}}{\rho_{B,n-1} C_{n-1} - \rho_{BO} C_n} \quad (27)$$

As in the case of the single pond, a material balance may be written for a tracer concentration,

$$\rho_{BI} V_i \left[\frac{dC_i}{dt} \right] = \rho_{B,i-1} (Q_O + \sum_{i=1}^n \Delta V_i) C_{i-1} - \left[\rho_{B,i} (Q_O + \sum_{i=1}^n V_i) C_i + \Delta V_{L,i} C_i \rho_{B,i} \right] \quad (28)$$

These equations have been solved using the finite difference techniques outlined for the single pond. The results for a specific case composed of four ponds are illustrated in Figures 7 and 8. Initially the outlet flow rate given by Equation 26 is zero since C_n was less than C_O . However,

MODEL OF SOLAR PONDS IN SERIES



DEPTH = CONSTANT IN EACH POND

EACH POND WELL MIXED

$$\Delta V_i = \Delta V_{E,i} + \Delta V_{L,i} + \Delta V_{S,i} + \Delta V_{ES,i}$$

Figure 6. Diagram of Solar Pond Series Model.

after C_n became sufficiently concentrated, C_n was held equal to C_o by pumping out according to Equation 27.

PHASE CHEMISTRY

The ultimate objective is always the separation of the product from the other components. The rate of evaporation will tell us the rate of loss of water. The rate of seepage will give us information on the loss of brine by seepage. However, it is the phase relationships that allow us to govern the operation so that we reach our goal following the selected path. Of course the selected path would be the most economical one.

Solar evaporation might be used for the purpose of brine concentration only, to minimize concentration costs or it may be used to precipitate the salts as pure components or mixtures which can be easily separated. In either case, reliable equilibria data at the operation conditions are required. Phase chemistry calculation procedures are well known. For purposes of pond modeling, especially for complex systems, a simple but flexible procedure should be used. The Jäneke type phase diagram is ideal for this purpose. It can be used to represent a four component system, including water. We can include a fifth component if the brine is always saturated with respect to this component. This is a common case. We could also include an-

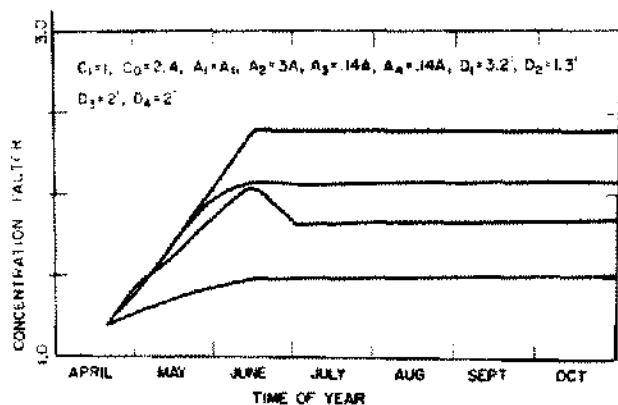


Figure 7. Typical Solution to Equations 25 and 27 for Four Ponds in Series.

other component, if it is contained in the brine at certain concentration level and it does not precipitate within the range of the pond operation. The effect of concentration of this component over the solubility of the key components would be taken into account. Similarly, by imposing some kind of restrictions we could include other components, as long as the solubility data is available.

Figure 9 shows a three dimensional Jäneka diagram for the system $\text{NaCl-H}_3\text{BO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 35°C . We have selected this system for simplicity. Any point inside the figure corresponds to the composition of solution saturated with respect to at least one of the three salts. The nomenclature used is included in the figure. It is obvious that the points: $x = 1$, $y = 1$, and $z = 1$ corresponds to pure salts: 1 lb $\text{H}_3\text{BO}_3/\text{lb S}$, 1 lb $\text{NaCl}/\text{lb S}$ and 1 lb $\text{Na}_2\text{SO}_4/\text{lb S}$ respectively. Lines xy , zy and zx correspond to binary mixtures of salts $\text{H}_3\text{BO}_3\text{-NaCl}$, $\text{Na}_2\text{SO}_4\text{-NaCl}$ and $\text{Na}_2\text{SO}_4\text{-BO}_3$ respectively. The vertical axis gives the amount of water associated with any mixture composition.

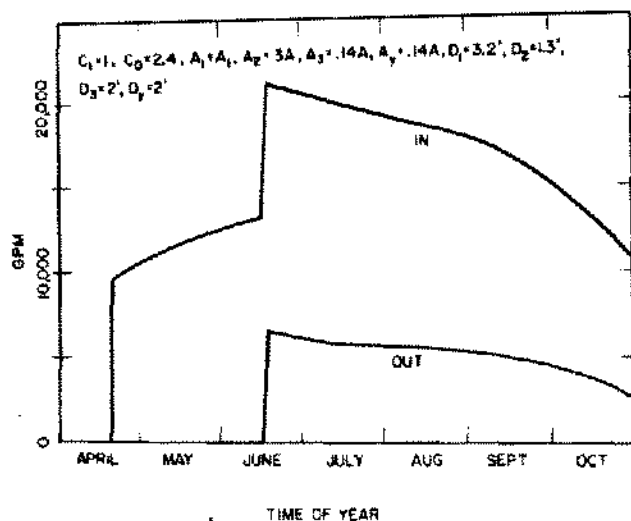


Figure 8. Typical Solution to Equation 28 for Four Ponds in Series.

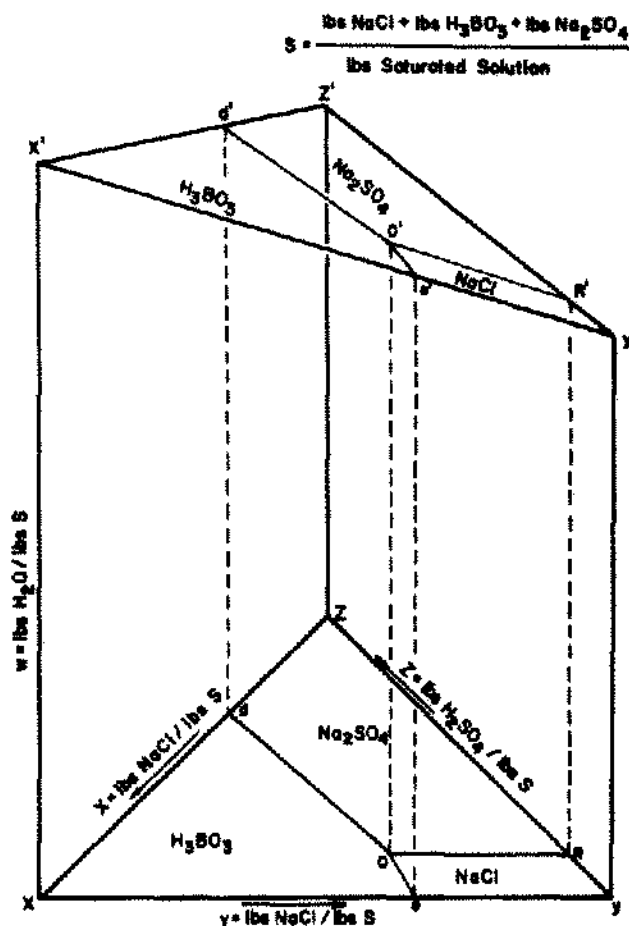


Figure 9. Three dimensional Projection for System: $\text{NaCl-H}_3\text{BO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 35°C .

To simplify the procedure, the equations, the three dimensional projection can be projected in two two-dimensional diagrams as shown in Figure 10. Using the equilibrium data the tie lines: de , op , $d'e'$, $o'p'$ can be represented by equations of the form:

$$y_1 = n_1 + m_1 x^* \quad (29)$$

$$y_2 = n_2 + m_2 x^* \quad (30)$$

$$y_1' = n_1' + m_1' x^* \quad (31)$$

$$y_2' = n_2' + m_2' x^* \text{ etc.} \quad (32)$$

For instance, for line de :

$$n = \text{lb Na}_2\text{SO}_4 / \text{lb S at } y = 0$$

$$m = (1-d)/(1-e)$$

$$x^* = \text{lb NaCl} / \text{lb S}$$

The values of n and m are calculated from the equilibria data, corresponding to the pond temperature. Since the equilibrium lines are probably not straight lines, they

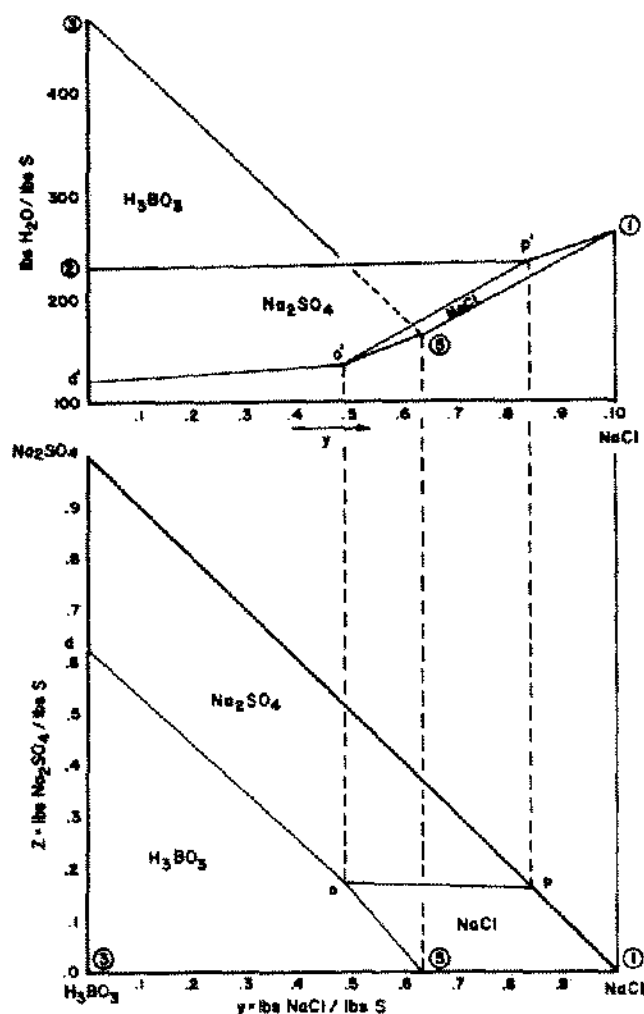


Figure 10. Janeka Projection for System: NaCl-H₃BO₃-Na₂SO₄-H₂O.

might be represented by a correlation, which would give corresponding x and y values for each point of the line.

The third salt is expressed as function of the other two

$$z = 1 - (x + y) \quad (33)$$

Material balance equations for each component for the liquid phase can be written using the general equation:

For H₃BO₃:

$$A\rho_B \frac{dD}{dt} X_B = Q_I \rho_{B,I} X_{I,B} - Q_O \rho_{B,O} X_{O,B} - \Delta V \rho_B X_B \quad (34)$$

where X is the weight fraction of H₃BO₃ in the streams indicated by the subscripts. Similar equations can be written for the other components. As expressed before, ΔV includes losses due to evaporation (ΔV_E), losses due to entrainment (ΔV_{ES}), losses due to precipitation (ΔV_S) and losses due to seepage (ΔV_L).

The salt precipitation (ΔV_S) and the liquid phase composition are functions of the rate of evaporation (ΔV_E). By using the material balance and equilibria equations, as sets of simultaneous equations the mother liquor composition and salt precipitated can be evaluated as function of rate of evaporation for selected time increments. The thus determined mother liquor composition can then be used to evaluate the losses of each component in seepage and entrainment. This procedure is repeated along the crystallization path, till the operation is completed.

In connection with this, there are a number of optimization techniques (such as linear programming) which can effectively be used in the solution of this problem. The objective would be to minimize water in the brine. The constraints will be set by the equilibria equations as we want to use solar evaporation for concentration purposes only or as a fractional crystallization operation. Whatever procedure is used, the approach should consider small increments of time to have a more reliable evaporation rate through the year, since the entire operation is based on this data.

SUMMARY

An energy balance may be used as a tool to determine evaporation rates. Its primary value lies in extrapolation of data for pure water to obtain evaporation rates for concentrated brines. If evaporation rates and leakage rates are known, complex pond operations may be described in terms of mathematical models. A model of a single stage pond was found to describe the concentration and surface elevation profile of an operating pond. A model of a series of ponds was developed and used to predict pumping rates for specific operating conditions.

A procedure to predict mother liquor composition, and salt deposition as a function of evaporation rate and equilibria data through the pond operation cycle is presented. Such data is essential to control pond operation especially when multicomponent systems are involved.

NOTATION

A	Pond area, cm ²
C	Tracer concentration, weight fraction
D	Pond depth, cm
E	Evaporation rate, cm/hr
h	Heat transfer coefficient, cal/cm ² -hr°C
H	Elevation, cm
k	Mass transfer coefficient, g/cm ² -hr-mm Hg
q	Net incoming radiant energy, cal/cm ² -hr
Q	Volumetric flow rate, cm ³ /hr
m,n	Parameters of the line equations
n	Number of ponds in a series
P	Partial pressure of water vapor, mm of Hg

r	Heat transfer coefficient for black body radiation, $\text{cal}/\text{cm}^2\text{-hr-}^\circ\text{C}$
S	Weight of soluble key salts per pound of saturated solution: $(\text{NaCl} + \text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4)$ per pound saturated solution
t	Time, hr
x	Mass fraction
x,y,z	Weight fraction of key salts in saturated solution $x = \text{lb H}_3\text{BO}_3/\text{lb S}$ $y = \text{lb NaCl}/\text{lb S}$ $z = \text{lb Na}_2\text{SO}_4/\text{lb S}$

Greek symbols

β	Leakage rate, cm/hr
ΔP	Vapor pressure lowering due to dissolved salts, mm of Hg
ΔV	Rate of loss of brine volume, cm^3/hr
ϵ	Porosity of salts deposited, fraction
λ	Latent heat of vaporization, cal/g
ρ	Density, g/cm^3
τ	Thickness of salts deposited, cm

Subscripts

a	Atmosphere
B	Brine
E	Evaporation
ES	Entrained in the salts
i	Pond number
I	Inlet
j	Time increment number
L	Leakage
O	Outlet
S	Salt
W	Water

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