

# Computer Model for the Area and Performance of Solar Ponds

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## ABSTRACT

The increased price of fuel that has taken place since 1974 has enhanced the feasibility of other sources of energy. For the processing of saline minerals in zones of higher solar radiation the utilization of solar energy to concentrate brines has proven to be a valuable economical alternative to plant processing, especially in desert or remote areas far from adequate port facilities and fuel supply.

Consequently, a study has been made on the calculation of the surface area of solar evaporation ponds employing the variables rate of evaporation, porosity of crystallized salts and the leakage rate through the pond bottom. It has been shown that with leakage rates in the order of  $10^{-6}$  cm/sec., or more, permeability is the main variable. Evaporation rate is the most important variable when the leakage rates are better than  $5 \times 10^{-7}$  cm/sec.

## INTRODUCTION

For the processing of saline minerals in zones of high solar radiation the utilization of solar energy to concentrate brines has proven to be a valuable economical alternative to plant processing. Consequently, a study has been made on the calculation of the surface area of solar evaporation ponds employing the variable rate of evaporation, porosity of crystallized salts and the leakage rate through the pond bottom.

### 1. DEFINITION

It is assumed that during evaporation, brines are transferred successively through a series of ponds (each of which is called a stage or step), each with a higher concentration level. Thus, to calculate the pond area, the initial and final concentrations in each pond (stage) may be arbitrarily fixed, generally based upon the composition of the crystallized salts that would be deposited during that period of evaporation. The area of the solar pond, will then be based upon the rate of evaporation (which is a function of the composition of the brine), the phase chemistry of the brine along the evaporation path, the densities of the brine and crystallized salts, the salt porosity and the pond leakage rates.

In the sea water or similar quinary brine system the following relationships apply for the potassium ion present:

- 1.1  $K_i$   
( $i = 0, 1, 2, 3, \dots$ ): Mass flow output of K in pond  $i$ , present in the liquid phase (input to pond  $i + 1$ )

- 1.2  $Kocl_i$  Mass of K in the occluded (entrained) brine in the salts of pond  $i$   
1.3  $Kcris_i$  K crystallized in pond  $i$   
1.4  $Kl_i$  Mass flow of K present in the brines leaking from pond  $i$   
1.5  $A_i$  Evaporation area of pond  $i$   
1.6  $CK_i$  K concentration in the input brine to pond  $i$   
1.7  $YK_i$  K concentration in the crystallized salts (%) in pond  $i$

By definition we have:

$$\begin{aligned} 1.8 \quad \frac{K_{i-1} - K_{fi}}{K_{i-1}} &= \eta_{fi} \\ 1.9 \quad \frac{K_{i-1} - Kocl_i}{K_{i-1}} &= \eta_{och} \\ 1.10 \quad \frac{K_{i-1} - Kcris_i}{K_{i-1}} &= \eta_{cris} \end{aligned}$$

In a system of  $i$  ponds (steps),  $(8 \times i) + 1$  variables are involved. When using the above terms the following mass balances gives  $(3 \times i) - i$  equations.

### 2. MASS BALANCES

$$2.1 \quad K_{i-1} = K_i + Kocl_i + Kcris_i$$

with 1.8, 1.9 and 1.10 this becomes:

$$K_{i-1} = K_i + (1 - \eta_{och}) \cdot K_{i-1} + (1 - \eta_{fi}) K_{i-1} \\ + (1 - \eta_{cris}) K_{i-1}$$

Rearranging the previous equation:

$$K_i = K_{i-1} + K_{i-1}(\eta_{och} - 1) + K_{i-1}(\eta_{fi} - 1) \\ + K_{i-1}(\eta_{cris} - 1)$$

it follows that:

$$2.2 \quad K_i = K_{i-1}(\eta_{och} + \eta_{fi} + \eta_{cris} + 1 - 3)$$

We can define:

$$2.3 \quad \eta_{tot} = \eta_{och} + \eta_{cris} - 2 \\ = 1 - (1 - \eta_{och}) - (1 - \eta_{fi}) - (1 - \eta_{cris})$$

The following expression is obtained:

$$2.4 \quad K_i = K_{i-1} \cdot \eta_{tot}$$

Which becomes for stage i:

$$2.5 \quad K_i = K_0 \prod_{j=1}^i \eta_{totj}$$

The system requires  $(8 \times i) - 1 - i$  equations to be solved. The remaining relations are obtained with independent equations relating the occlusion (entrainment), crystallization, leakage rates, pond area and a fixed/or given variable.

### 3. GIVEN VARIABLE

For a more general solution, the given variable in this study will be  $K_0$ , or in other words, the input of K into the system (in tons/day).

### 4. LEAKAGE LOSSES IN POND i

The leakage losses of element K in pond i can be calculated with D'Arcy's permeability equation:

$$4.1 \quad FK_i = K_{fi} = \frac{k_i \cdot A_i \cdot h_0 \cdot \bar{CK}_i}{L_i};$$

where

- $K$  = permeability coefficient (mm/s)
- $h$  = height of brine column
- $L$  = depth of "impervious" bottom clay

We have defined

$$\eta_{fi} = \frac{K_{i-1} - K_{fi}}{K_{i-1}}$$

So

$$4.2 \quad 1 - \eta_{fi} = \frac{K_{fi}}{K_{i-1}}$$

### 5. OCCLUSION LOSSES OF K IN POND i

We have

$V_t$  = total volume of crystallized salts in pond i.

$V_h$  = voids.

$V_{sal}$  = volume of crystallized mass.

$$5.1 \quad V_t = V_h + V_{sal}$$

$$5.2 \quad p = \text{porosity (\%)}$$

So

$$5.3 \quad V_h = p \times V_t, \text{ and}$$

$$5.4 \quad V_{sal} = (1 - p) \cdot V_t$$

We will define M as:

$$5.5 \quad MK = \frac{\text{quantity of element K in entrained brines}}{\text{total mass of crystallized salts}}$$

So

$$5.6 \quad MK_i = \frac{K_{ochi}}{Sal_{crisi}}$$

$$5.7 \quad K_{ochi} = V_h \times db_i \cdot XK$$

Where

$db_i$  = density of entrained brines in pond i.

$XK_i$  = % of K in entrained brines (wt. %)

$$5.8 \quad Sal_{crisi} = V_{sal} \cdot d_{sal}$$

Where

$d_{sal}$  = density of crystallized salts in pond i

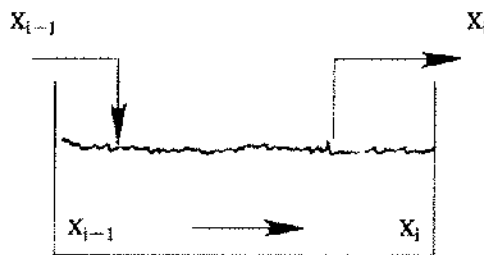
Dividing 7 by 8, we have

$$5.9 \quad MK_i = \frac{K_{ochi}}{Sal_{crisi}} = \frac{V_h \cdot db_i \cdot XK_i}{V_{sal} \cdot d_{sal}}$$

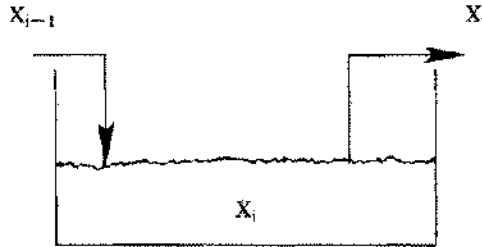
$$5.10 \quad MK_i = \frac{K_{ochi}}{Sal_{crisi}} = \frac{p \cdot db_i \cdot XK_i}{(1 - p) \cdot d_{sal}}$$

In a pond system we can work with a continuous or semi-batch operation, the latter by feeding and removing brines at intervals. In the first case, a concentration gradient along every pond is obtained, from  $X_{i-1}$  to  $X_i$ , where  $X_{i-1}$  is equal to the concentration of the feed brine to pond i.

A continuous feed system:



In a semibatch system, we have approximately the following:



The above reasoning is based on the assumption that the brine volume in the ponds is considerably larger than the input or output.

So:

$$\begin{aligned} K_{ocl_i} &= MK_i \times \text{Sal cris}_i \\ 5.11 \quad K_{ocl_i} &= \frac{p \cdot db_i \cdot XK_i \cdot \text{Sal cris}_i}{(1-p) \cdot d_{sal}} \end{aligned}$$

$$5.12 \quad \text{Sal cris}_i = \frac{K_{cris_i}}{YK_i} = \frac{Na_{cris_i}}{YNa_i}$$

Where

$$\begin{aligned} K_{cris} &= K \text{ crystallized in pond } i \text{ (ton)} \\ Na_{cris_i} &= Na \text{ crystallized in pond } i \\ YK_i &= \% \text{ of } K \text{ crystallizing in pond } i. \\ YNa_i &= \% \text{ of } Na \text{ crystallizing in pond } i. \end{aligned}$$

Replacing these terms in the previous equations we have:

$$5.13 \quad K_{ocl_i} = \frac{p \cdot db_i \cdot XK_i \cdot K_{cris_i}}{(1-p) \cdot d_{sal} \cdot YK_i}$$

$$5.14 \quad K_{ocl_i} = \frac{p \cdot db_i \cdot XNa_i \cdot Na_{cris_i}}{(1-p) \cdot d_{sal} \cdot YNa_i}$$

Either 5.13 or 5.14 can be used to calculate  $K_{ocl_i}$ . 5.13 is recommended when  $YK_i > 0.1$ ; 5.14 should be employed when  $YK_i = 0$ .

In 1.9 we had defined

$$K_{ocl_i} = (1 - \eta_{ocl_i}) \cdot K_{i-1}$$

And in 1.10

$$K_{cris_i} = (1 - \eta_{crisK_i}) \cdot K_{i-1}$$

By analogy

$$Na_{cris_i} = (1 - \eta_{crisNa_i}) \cdot Na_{i-1}$$

Replacing in 5.13 and 5.14 respectively we obtain:

$$5.15 \quad (1 - \eta_{ocl_i}) K_{i-1} = \frac{(p) \cdot db_i \cdot (1 - \eta_{crisK_i}) \cdot K_{i-1} \cdot XK_i}{(1-p) \cdot d_{sal} \cdot YK_i}$$

$$5.16 \quad (1 - \eta_{ocl_i}) K_{i-1} = \frac{(p) \cdot db_i \cdot (1 - \eta_{crisNa_i}) \cdot Na_{i-1} \cdot XK_i}{(1-p) \cdot d_{sal} \cdot YNa_i}$$

But

$$\frac{Na_{i-1}}{K_{i-1}} = \frac{CNa_{i-1}}{CK_{i-1}}$$

Where

$$\begin{aligned} CNa_{i-1} &= \text{input concentration of Na in pond } i. \\ CK_{i-1} &= \text{input concentration of K in pond } i. \\ Na_{i-1} &= \text{ton of Na input in pond } i. \\ K_{i-1} &= \text{ton of K input in pond } i. \end{aligned}$$

Replacing in 5.15 and 5.16 we obtain:

$$5.17 \quad (1 - \eta_{ocl_i}) K_{i-1} = \frac{p \cdot db_i \cdot (1 - \eta_{crisK_i}) \cdot K_{i-1} \cdot XK_i}{(1-p) \cdot d_{sal} \cdot YK_i}$$

$$\begin{aligned} 5.18 \quad (1 - \eta_{ocl_i}) K_{i-1} &= \frac{p \cdot db_i \cdot (1 - \eta_{crisNa_i}) \cdot CNa_{i-1} K_{i-1} \cdot XK_i}{(1-p) \cdot d_{sal} \cdot YNa_i \cdot CK_{i-1}} \end{aligned}$$

Rearranging:

$$5.19 \quad 1 - \eta_{oclK_i} = \frac{MK_i}{YK_i} \times (1 - \eta_{crisK_i})$$

$$5.20 \quad 1 - \eta_{oclK_i} = \frac{MK_i}{YNa_i} \times (1 - \eta_{crisNa_i}) \times \frac{CNa_{i-1}}{CK_{i-1}}$$

In a continuous system we have to use  $\overline{XK_i}$ , and  $XK_i$  in a semibatch, to calculate  $MK_i$ . In agitated tank reactors,  $XK_i$  must be employed as the concentration of entrained brines.

## 6. CRYSTALLIZATION

During evaporation we have:

- Changing brine concentration due to evaporation.
- Losses of element K due to leakage.
- Losses of element K due to occlusion and crystallization.

We will arbitrarily divide each pond into two. One of these subdivisions will have an impervious bottom. In the second subdivision all leakage losses will take place, but this pond will not have a brine output. On the other hand, entrained losses will be calculated independently.

We have the following for any given pond i:

T will be defined as a tracer (no crystallization) in pond i and whose final concentration in the entrained brine is approximately equal to the concentration in the pond brine  $CT_i$ . So

$$\begin{aligned} \text{Sad}_{i-1} &= \text{Input brine in subdivision pond (b) of pond i} \\ \text{XT}_{i-1} &= \% \text{ by weight of T in } \text{Sad}_{i-1} \\ \text{Tf}_i &= \text{leakage losses of T in subdivision pond (b)} \end{aligned}$$

According to D'Arcy we have (see formula 4.1)

$$6.1 \quad \text{Tf}_i = \overline{CT}_i \cdot (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i = \text{T}_{i-1}^{**}$$

We know that:

$$6.2 \quad \text{Sad} = \frac{\text{Tf}_i}{\text{XT}_{i-1}}$$

The quantity of input K into subdivision pond (b) is:

$$\begin{aligned} K_{i-1}^{**} &= \text{Sad} \cdot \text{XK}_{i-1} = \text{Tf}_i \cdot \frac{\text{XK}_{i-1}}{\text{XT}_{i-1}} \\ 6.3 \quad K_{i-1} &= \overline{CT}_i \cdot (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i \cdot \frac{\text{XK}_{i-1}}{\text{XT}_{i-1}} \cdot t_i \end{aligned}$$

Leakage losses of K in subdivision pond (b) (equal to leakage losses in pond i) are:

$$\text{Kf}_i = \overline{CK}_i \cdot (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i \cdot t_i$$

The difference between  $K_{i-1}$  and  $\text{Kf}_i$  is equal to the quantity of K crystallized in subdivision pond (b).

$$\begin{aligned} \text{Kcris}_i &= K_{i-1}^{**} - \text{Kf}_i \\ &= \overline{CT}_i \cdot (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i \cdot \frac{\text{XK}_{i-1}}{\text{XT}_{i-1}} \cdot t_i \\ &\quad - \overline{CK}_i (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i \cdot t_i \end{aligned}$$

We will define  $r_K$  as the % of element K crystallized in subdivision pond b.

$$\begin{aligned} 6.4 \quad r_K &= \frac{\text{Kcris}_i}{K_{i-1}^{**}} = \frac{K_{i-1}^{**} - \text{Kf}_i}{K_{i-1}^{**}} \\ r_K &= 1 - \frac{\text{Kf}_i}{K_{i-1}^{**}} \end{aligned}$$

Replacing  $\text{Kf}_i$  and  $K_{i-1}$  in the previous equation, we have:

$$r_K = 1 - \frac{\overline{CK}_i (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i}{\overline{CT}_i (\bar{h}\bar{o}/L) \cdot k_i \cdot A_i \cdot (\text{XK}_{i-1}/\text{XT}_{i-1})}$$

As:

$$\frac{\text{XK}_{i-1}}{\text{XT}_{i-1}} = \frac{\text{CK}_{i-1}}{\text{CT}_{i-1}}$$

So

$$6.5 \quad 1 - r_K = \frac{\overline{CK}_i}{\overline{CT}_i} \cdot \frac{\text{CT}_{i-1}}{\text{CK}_{i-1}}$$

We know that (formula 1.10):

$$\begin{aligned} 1 - \eta_{\text{cris}_i} &= \frac{\text{Kcris}_i}{K_{i-1}^{**}} \\ 6.6 \quad \text{Kcris}_i &= \text{Kcris}_i^* + \text{Kcris}_i^{**} \end{aligned}$$

By definition, in pond (a)

$$6.7 \quad \text{Kcris}_i^* = K_{i-1}^* \cdot \text{NTK}$$

Where  $\text{NTK}$  = theoretical crystallization yield of element K in pond i. We know that (see 6.4):

$$6.8 \quad \text{Kcris}_i^{**} = r_{K_i} \cdot K_{i-1}^{**}$$

Replacing 6.8 and 6.7 in 6.6 we obtain:

$$6.9 \quad \text{Kcris}_i = K_{i-1}^* \cdot \text{NTK} + r_{K_i} \cdot K_{i-1}^{**}$$

So

$$6.10 \quad 1 - \eta_{\text{cris}_i} = \frac{K_{i-1}^*}{K_{i-1}^{**}} \cdot \text{NTK} + \frac{K_{i-1}^{**}}{K_{i-1}^{**}} \cdot r_{K_i}$$

From 6.4 we know that:

$$6.11 \quad K_{i-1}^{**} = \frac{\text{Kf}_i}{1 - r_K}$$

From 1.8

$$\text{Kf}_i = (1 - \eta_h) \cdot K_{i-1}$$

Replacing in 6.11

$$K_{i-1}^{**} = K_{i-1} \cdot \left( \frac{1 - \eta_h}{1 - r_K} \right)$$

Replacing in 6.10

$$\begin{aligned} 1 - \eta_{\text{cris}_i} &= \frac{K_{i-1}^*}{K_{i-1}^{**}} \cdot \text{NTK} + \frac{K_{i-1}^{**}}{K_{i-1}^{**}} \cdot r_{K_i} \\ &= \frac{K_{i-1}^* - K_{i-1}^{**}}{K_{i-1}^{**}} \cdot \text{NTK} + \frac{K_{i-1}^{**}}{K_{i-1}^{**}} \cdot r_{K_i} \\ &= \text{NTK} - (\text{NTK} - r_K) \cdot \left( \frac{K_{i-1}^*}{K_{i-1}^{**}} \right) \\ &= \text{NTK} - (\text{NTK} - r_K) \cdot \left( \frac{K_{i-1}^*}{K_{i-1}^{**}} \right) \cdot \left( \frac{1 - \eta_{f_K}}{1 - r_K} \right) \\ 6.12 \quad 1 - \eta_{\text{cris}_i} &= \text{NTK} - (\text{NTK} - r_K) \cdot \left( \frac{1 - \eta_{f_K}}{1 - r_K} \right) \end{aligned}$$

Let  $\text{Na}$  be another arbitrary element. By analogy with element K, we have (see 6.12):

$$6.13 \quad 1 - \eta_{\text{cris}_{\text{Na}_i}} = \text{NTNa} - (\text{NTNa} - r_{\text{Na}_i}) \cdot \left( \frac{1 - \eta_{f_{\text{Na}}}}{1 - r_{\text{Na}_i}} \right)$$

By definition, we have:

$$(1 - \eta_{f_{\text{Na}}}) = \frac{\text{Naf}_i}{\text{Na}_{i-1}}$$

By mass balance:

$$6.14 \quad \frac{Na_{i-1}}{K_{i-1}} = \frac{CNa_{i-1}}{CK_{i-1}}$$

According to D'Arcy (see 4.1) we have:

$$Naf_i = k_i \cdot A_i \cdot \bar{h}_o \cdot L_i^{-1} \cdot \overline{CNa}_i \cdot t_i$$

$$Kf_i = k_i \cdot A_i \cdot \bar{h}_o \cdot L_i^{-1} \cdot \overline{CK}_i \cdot t_i$$

Dividing:

$$6.15 \quad Naf_i = Kf_i \times \left( \frac{\overline{CNa}_i}{\overline{CK}_i} \right)$$

Replacing 6.15 and 6.14 in 1 -  $Nf_{Na}$  we have

$$1 - \eta_{fNa} = Kf_i \cdot \left( \frac{\overline{CNa}_i}{\overline{CK}_i} \cdot \frac{CK_{i-1}}{CNa_{i-1}} \cdot \frac{1}{K_{i-1}} \right)$$

$$6.16 \quad 1 - \eta_{fNa} = (1 - \eta_{fK}) \cdot \left( \frac{K_{i-1}}{K_{i-1}} \cdot \frac{\overline{CNa}_i}{\overline{CK}_i} \cdot \frac{CK_{i-1}}{CNa_{i-1}} \right)$$

In ponds where K does not crystallize, it may be employed as a tracer. By definition (formula 6.5):

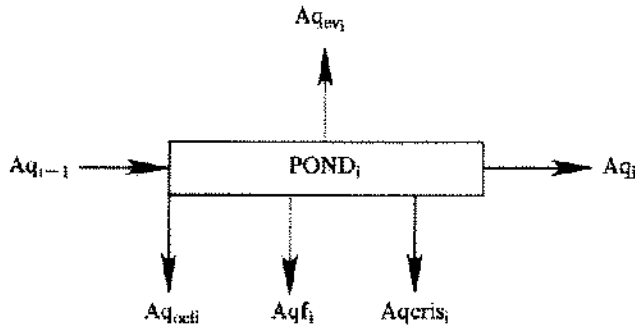
$$6.17 \quad 1 - \eta_{fNa} = (1 - \eta_{fK}) \cdot (1 - r_{Na})$$

Replacing 6.17 in 6.13 we obtain:

$$6.18 \quad 1 - \eta_{crisNa} = NTNa - (NTNa - r_{Na}) \cdot (1 - \eta_{fK})$$

## 7. COMPUTATION OF THE EVAPORATION AREA IN POND i

In pond i we have the following water mass balance



- $Aq_{i-1}$  = Water input in pond i.
- $Aq_i$  = Water output in pond i.
- $Aq_{ev_i}$  = Evaporation in pond i.
- $Aq_{ocli}$  = Entrained water in pond i.
- $Aq_{cris_i}$  = Water of crystallization.
- $Aq_{fi}$  = Water loss in leaking brines.

$$7.1 \quad Aq_{i-1} = Aq_i + Aq_{ev_i} + Aq_{ocli} + Aq_{fi} + Aq_{cris_i}$$

For any given period T of operation, where the evaporation rate for a pond i is equal to  $ev_i$ , we have:

$$7.2 \quad Aq_{ev_i} = A_i \cdot T \cdot ev_i$$

Expressing the above equations as a function of the previously defined variables we have the following relationships:  
According to D'Arcy

$$F_{H_2O_i} = Aq_{fi} = k_i \cdot A_i \cdot T \cdot \left( \frac{\bar{h}_{o_i}}{L_i} \right) \cdot \overline{CH_2O_i}$$

Using 4.1

$$7.3 \quad Aq_{fi} = \frac{\overline{CH_2O_i}}{\overline{CK}_i} \cdot K_{fi}$$

Using 1.8

$$7.4 \quad Aq_{fi} = \frac{\overline{CH_2O_i}}{\overline{CK}_i} (1 - \eta_{fi}) \cdot K_{i-1}$$

The following equations apply

$$7.5 \quad Aq_{i-1} = K_{i-1} \cdot \left( \frac{XH_2O_{i-1}}{XK_{i-1}} \right)$$

$$= K_{i-1} \cdot \left( \frac{CH_2O_{i-1}}{CK_{i-1}} \right)$$

$$7.6 \quad Aq_i = K_i \cdot \left( \frac{XH_2O_i}{XK_i} \right) = K_i \cdot \left( \frac{CH_2O_i}{CK_i} \right)$$

$$7.7 \quad Aq_{ocli} = K_{ocli} \cdot \left( \frac{XH_2O_i}{XK_i} \right) = K_{ocli} \cdot \left( \frac{CH_2O_i}{CK_i} \right)$$

$$7.8 \quad Aq_{cris_i} = Sal_{cris_i} \cdot YH_2O_i = K_{cris_i} \cdot \left( \frac{YH_2O_i}{YN_{2i}} \right)$$

$$= Nacris_i \cdot \left( \frac{YH_2O_i}{YN_{2i}} \right)$$

$Z_i$  = Water of crystallization (in wt. %) divided by % of K in crystallized salts.

Rearranging 7.7 and 7.8 we obtain:

$$7.9 \quad Aq_{ocli} = (1 - \eta_{ocli}) \cdot \left[ \frac{XH_2O_i}{XK_i} \right] \cdot K_{i-1}$$

$$7.10 \quad Aq_{cris_i} = Z_i \cdot (1 - \eta_{cris_i}) \cdot K_{i-1}$$

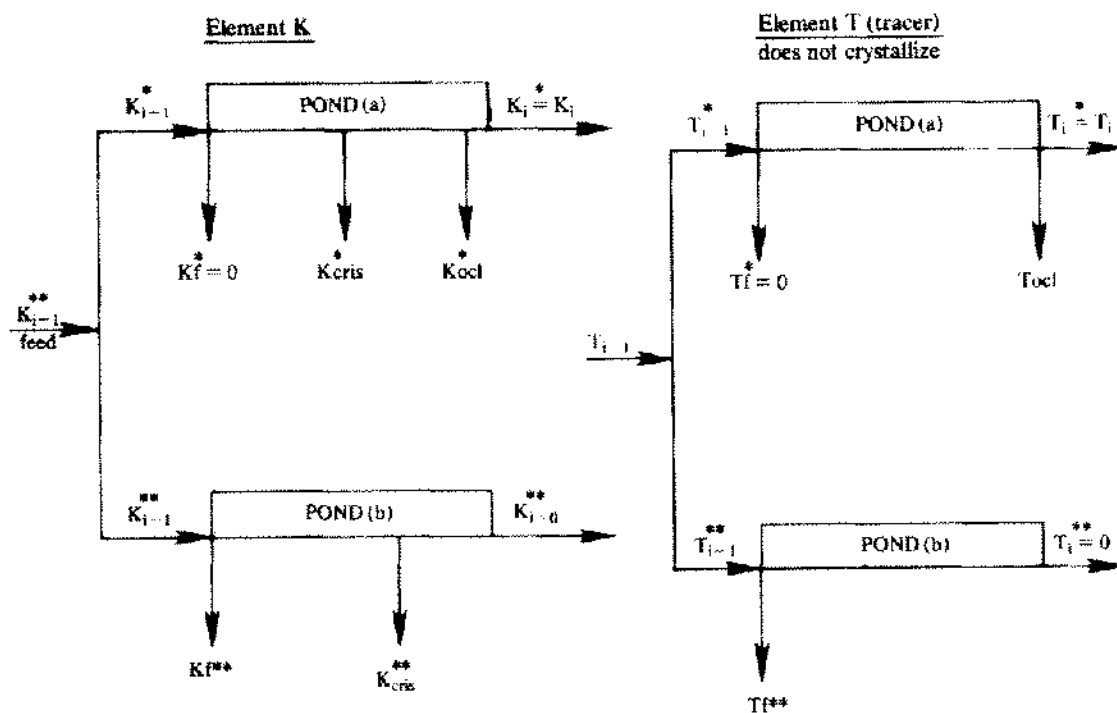
According to 7.2

$$A_i = \frac{Aq_{ev_i}}{T \cdot ev_i}$$

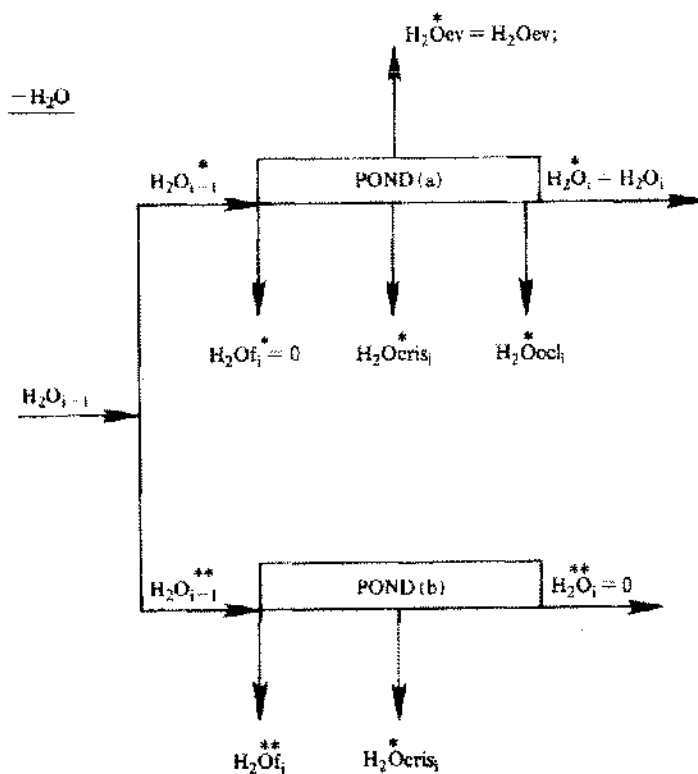
Replacing in 7.2

7.11

$$A_i = \frac{1}{T \cdot ev_i} \cdot \left( K_i - \left\{ \frac{XH_2O_{i-1}}{XK_{i-1}} \right\} - \left\{ \frac{XH_2O_i}{XK_i} \right\} \cdot K_i \right. \\ \left. - K_{i-1} \cdot (1 - \eta_{ocli}) \cdot \frac{XH_2O_i}{XK_i} - \frac{\overline{CH_2O_i}}{\overline{CK}_i} (1 - \eta_{fi}) \right. \\ \left. \cdot K_{i-1} - Z_i (1 - \eta_{cris_i}) \cdot K_{i-1} \right)$$



$$\begin{aligned}
 K_{i-1}^* &= K_{cris}^* + K_{ocl}^* + K_i^* \\
 &= NTK \cdot K_{i-1}^* + K_{ocl}^* + K_i^* \\
 K_{i-1}^{**} &= K_f^{**} + K_{cris}^{**} \\
 &= K_f + K_{cris}^{**} \\
 K_{cris, i-1} &= K_{cris}^* + K_{cris}^{**}
 \end{aligned}$$



Utilizing the following relations, and since  $K_{i-1}$  is a common factor, we obtain:

$$2.4 \quad K_i = K_{i-1} \cdot \bar{\eta}_{\text{tot}_i}$$

$$2.5 \quad K_i = K_0 \cdot \prod_{i=1} \bar{\eta}_{\text{tot}_i}$$

$$\frac{XH_2O_i}{XK_i} = \frac{CH_2O_i}{CK_i}$$

$$\frac{XH_2O_i}{\bar{X}K_i} = \frac{CH_2O_i}{\bar{C}K_i}$$

7.12

$$A_i = \left( \frac{K_{i-1}}{T \cdot \text{ev}_i} \right) \left\{ \left( \frac{CH_2O_{i-1}}{CK_{i-1}} \right) - \eta_{\text{tot}} \left( \frac{CH_2O_i}{CK_i} \right) - (1 - \eta_{\text{ocli}}) \frac{\bar{CH}_2O_i}{\bar{C}K_i} - (1 - \eta_f) \frac{\bar{CH}_2O_i}{\bar{C}K_i} - Z_i (1 - \eta_{\text{crisi}}) \right\}$$

In ponds where no K crystallizes the last term is undetermined because

$$Z_i = \frac{YH_2O}{YK} \rightarrow 0$$

If we employ any crystallizing element, such as Na, we know that:

$$\text{Sal crist}_i = \frac{Aq_{\text{crisi}}}{YH_2O_i} = \frac{Nacris_i}{YNa_i} = \frac{Keris_i}{YK_i}$$

$$Aq_{\text{crisi}} = Nacris_i \cdot \left[ \frac{YH_2O_i}{YNa_i} \right] = Nacris_i \cdot Z^*$$

But

$$\frac{Na_{i-1}}{K_{i-1}} = \frac{CNa_{i-1}}{CK_{i-1}}$$

and

$$Nacris_i = (1 - \eta_{\text{crisNa}}) Na_{i-1}$$

So, rearranging

$$\begin{aligned} Aq_{\text{crisi}} &= YH_2O_i \cdot \text{Sal crist}_i \\ &= YH_2O_i \cdot \left[ \frac{Nacris_i}{YNa_i} \right] \\ &= \left[ \frac{YH_2O_i}{YNa_i} \right] \cdot (1 - \eta_{\text{crisNa}}) \cdot K_{i-1} \cdot \left[ \frac{CNa_{i-1}}{CK_{i-1}} \right] \end{aligned}$$

$$7.13 \quad Aq_{\text{crisi}} = Z^* (1 - \eta_{\text{crisNa}}) \cdot K_{i-1} \cdot \frac{CNa_{i-1}}{CK_{i-1}}$$

This expression replaces  $Z_i(1 - \eta_{\text{cris}})$  in 7.12 when K does not crystallize.

$$\begin{aligned} 7.14 \quad A_i &= \frac{K_{i-1}}{T \cdot \text{ev}_i} \cdot \left[ \frac{CH_2O_{i-1}}{CK_{i-1}} - \eta_{\text{tot}} \left( \frac{CH_2O_i}{CK_i} \right) - (1 - \eta_{\text{ocli}}) \frac{CH_2O_i}{CK_i} - (1 - \eta_f) \frac{CH_2O_i}{CK_i} - Z_i (1 - \eta_{\text{crisi}}) \right] = \frac{K_{i-1}}{T \cdot \text{ev}_i} \cdot [\alpha] \end{aligned}$$

In a reactor no leakages take place, except the final output brine. Rearranging we have:

$$7.15 \quad A_i = \frac{K_{i-1}}{T \cdot \text{ev}_i} \left[ \frac{CH_2O_{i-1}}{CK_{i-1}} - \left\{ \eta_{\text{tot}} \frac{CH_2O_i}{CK_i} - (1 - \eta_{\text{ocli}}) \left\{ \frac{CH_2O_i}{CK_i} \right\} - Z_i (1 - \eta_{\text{crisi}}) \right\} \right]$$

We have then:

$$A_i = \left[ \frac{K_{i-1}}{T \cdot \text{ev}_i} \right] \cdot \left\{ \frac{CH_2O_{i-1}}{CK_i} - \left[ \frac{CH_2O_i}{CK_i} \right] \eta_{\text{crisi}} - Z_i (1 - \eta_{\text{crisi}}) \right\}$$

## 8. CALCULATIONS

Summarizing the previous relations we have the following independent variables:

$$K_i, \quad \eta_{\text{fi}}, \quad \eta_{\text{ocli}}, \quad \eta_{\text{cris}}, \quad A_i$$

For each of them a relation must be obtained according to the experimental studies.

The experimental variables are:

- Concentration of element K, tracer T, element Na (crystallizes), and water in brines and salts.
- Crystallization yields of K and Na.
- Densities of brines and salts.
- Salts porosity.
- Leakage rates and pond characteristics (depth of impermeable layer and height of brine column) in order to calculate  $NTK_i$  and  $NTNa_i$ .

That is to say, we require the following data:  $K_0$ ,  $XK_i$ ,  $CK_i$ ,  $XK_2O_i$ ,  $XT_i$ ,  $YK_i$ ,  $Z_i$ ,  $Z_i^*$ ,  $XNa_i$ ,  $YNa_i$ , densities, porosities and leakage rates. With these the following are obtained:

$$r_i \quad \text{and} \quad M_i$$

## EQUATIONS FOR SOLAR EVAPORATION PONDS

$$2.4 \quad K_i = K_{i-1} (\eta_{\text{fi}} + \eta_{\text{ocli}} + \eta_{\text{cris}} - 2)$$

$$4.2 \quad 1 - \eta_f = \left[ \frac{Kf_i}{K_{i-1}} \right]$$

$$6.2 \quad 1 - \eta_{\text{crisK}_i} = NTK_i + \left[ \frac{NTK_i - rK_i}{1 - rK_i} \right] (1 - \eta_i)$$

$$5.20 \quad (1 - \eta_{\text{ocl}}) = \left[ \frac{MK_i}{YNa_i} \right] (1 - \eta_{\text{crisNa}_i}) \cdot \left[ \frac{CNa_{i-1}}{CK_{i-1}} \right]$$

$$7.13 \quad A_i = \frac{K_{i-1}}{T \cdot ev_i} [\alpha]$$

### CONCLUSION

This work shows that it is possible to calculate the area of solar ponds once the basic data is on hand, utilizing empirical variables and leakage rates as parameters.

The above formulas assume that ponds of any given size can be constructed, a situation which is not usually true.

If the phase chemistry data can be expressed in terms of a variable, for instance density, then for a given set (sequence) of ponds the brine composition along the evaporation path can be obtained.

This can be done with small hand calculators. In this case, for each pond the initial composition of the brine is given and iteratively, for different compositions of the end brine, areas may be calculated until the given and calculated areas are insignificantly different.

### EXAMPLES

#### Example 1

**Introduction.** A brine must be concentrated in solar ponds between the following compositions:

TABLE 1  
Concentration (grams/liter)

	Density	K	Na	Mg	SO <sub>4</sub>	H <sub>2</sub> O
Feed	1.225	21.9	100	11.6	17	864
Final	1.237	31.8	84	16.8	24.5	865

TABLE 2

Memory Number	Terminology	Description	Data in This Example
0	$K_{i-1}$	Potassium feed (tons/day)	500
1	$(h_o/L) \times 0.864$	Brine height clay thickness $\times$ factor	$h_o = L = 50$ (cm)
2	NTNa	% of input sodium crystallized	Calculated through the program
3	$Z^*/CH_2O^*$	See below	0
4	$CH_2O \times 10^3$	Water concentration (grams/liter)	865
5	—		
6	F	Scale factor	$F = 0.7$
7	$C_0$ or $ev$	Evaporation rate equation of metallic pans	$C_0 = -79.58$
8	$C_1$		$C_1 = 175.27$
9	$C_2$		$C_2 = -81.62$
S0	$CK_i$	Final concentration of K (g/l)	$CK_i = 31.8$
S1	$CK_{i-1}$	Initial concentration of K (g/l)	$CK_{i-1} = 21.9$
S2	$CT_i$	Final concentration of tracer (g/l)	$CK_i = 31.8$
S3	$CT_{i-1}$	Initial concentration of tracer (g/l)	$CK_{i-1} = 21.9$
S4	$CNa_{i-1}$	Initial concentration of sodium (g/l)	$CNa_i = 100$
S5	$CNa_i$	Final concentration of sodium (g/l)	$CNa_{i-1} = 84$
S6	YNa	Wt. % of Na in crystallized salts	$YNa = 0.393†$
S7	$1 - \eta_{\text{crisNa}}$		
S8	$q^{-1}$	Coefficient	$q = 21.61$
S9	$d_o$	Coefficient	$d_o = 1.223$
A	$d_{i-1}$	Initial brine density	$d_{i-1} = 1.223$
B	$d_i$	Final brine density	$d_i = 1.237$
C	$p^*$	$p^* = (p/1 - p) \times (1/d_{\text{sal}}) \times (1/02000);$ $p = \text{porosity}$ $d_{\text{sal}} = \text{salt density}$	$p = 0.34$ $d_{\text{sal}} = 2.10$
D	$1 - \eta_i$	Wt. % of K lost through leakage	Calculated
E	$1 - \eta_{\text{ocl}}$	Wt. % of K lost through entrainment	Calculated
J	$1 - \eta_{\text{crisK}}$	Wt. % of K lost by crystallization	0

\*Z\* =  $YH_2O/YNa$  (Wt. % of water of crystallization in salts)  
Wt. % of sodium in salts.

†YNa: in this pond only NaCl crystallizes, so theoretically

$$YNa = \frac{\text{Mol. weight of Na}}{\text{Mol. weight of NaCl}} = 0.393$$



It can be acknowledged from Phase Diagram Charts that sodium chloride is the only saturated salt. In solar ponds the porosity of the crystallized salts has proven to be in the order of 34%. In this example, and in the followings, the brine height in the ponds will be 0.50 meters as well as the thickness of the impervious bottom seal.

The following parameters are also required

(a) Evaporation rate.

In this example we will use the following equation:

$$ev = \{C_0 + C_1 \cdot \bar{d} + C_2 \cdot \bar{d}^2\} \cdot F$$

$$ev = \{-79.58 + 175.27 \cdot (\bar{d}) - 81.62 \times (\bar{d}^2)\} \cdot F$$

where

$\bar{d}$  = average density of the brine in each pond.

$F$  = scale factor (between metallic pans and industrial ponds).

(b) Estimation of crystallized salts.

It has been stated that sodium chloride is the only salt that crystallizes in this example. The following equation will be employed (derivation unpublished):

$$NTNa = \frac{d_i - d_{i-1}}{q^{-1} - (d_{i-1} - d_o)}$$

where

$q$  = coefficient, specific to this example.

$d_{i-1}$  = input density

$d_i$  = output density

$d_o$  = 1.223 (coefficient)

$$NTNa = \frac{\text{Crystallized sodium in pond}}{\text{input sodium to pond}}$$

Data employed in program (HP-67).

**Results.** It was stated that no potassium crystallizes in this pond, so  $\eta_{crisk} = 1$ .

The first column of this table shows the potassium that leaves the pond through leakage (1). The pond area requirement has been estimated for each of the above stated potassium losses, as well as the permeability coefficient of the bottom seal, the potassium output (in output brine), and the coefficient which calculates the potassium lost because of entrainment ( $1 - \eta_{ocl}$ ).

$$(1) \quad 1 - \eta_l = \frac{Kf}{K_{i-1}} \frac{\text{potassium in leaking brine}}{\text{input potassium}}$$

Once the real value of  $k$  is known, estimated in independent experiences to this calculation, the real behavior of the pond can be guessed. Assuming that a coefficient of permeability equal to  $5 \times 10^{-8}$  cm/second applies, the pond area requirement is 1,595,000 m<sup>2</sup> and the pond potassium output is 485 tons/day, approximately.

## Example 2

**Introduction.** Now the input brine of example 1 will be concentrated as follows:

TABLE 4

	Density (gr/cc)	Concentration (grams per liter)				
		K	Na	Mg	SO <sub>4</sub>	H <sub>2</sub> O
Feed brine	1.237	31.8	84	16.8	24.6	864
Output brine	1.253	46.4	65.5	27.1	39.7	864

From Phase Diagram Charts it is known that only NaCl crystallizes in this pond. It will be assumed that porosity  $p = 34\%$  and that the same formulas shown in Example 1, apply in this example. (NTNa and  $ev$  estimation).

We know that  $K_{i-1} = 485$  (t/day).

Data employed in program (HP - 67).

TABLE 3

$1 - \eta_l$ (1)	Pond Area (thousand of m <sup>2</sup> )	$k$ (cm/sec)	$K_i$ (tons/day)	$\eta_{cdx}$	$\eta_{ocl}$	$\eta_l$	$\eta_{tot}$
0.005	1593.8	$6.76 \times 10^{-8}$	485.1	1.0	0.975	0.995	0.9703
0.010	1590.5	$1.36 \times 10^{-7}$	482.7	1.0	0.975	0.990	0.9653
0.020	1584.0	$2.72 \times 10^{-7}$	477.7	1.0	0.975	0.980	0.9554
0.040	1570.9	$5.49 \times 10^{-7}$	467.8	1.0	0.976	0.960	0.9358
0.080	1544.8	$1.12 \times 10^{-7}$	447.9	1.0	0.976	0.920	0.8953

TABLE 5

Memory Number	Terminology	Description	Data In This Example
0	$K_{i-1}$	Potassium feed (tons/day)	485
1	$(h_0/L) \times 0.864$	Same as example 1	$h_0 = L = 50$ cm.
2	NTNa	Same as example 1	NTNa = $f(d)$
3	$Z^*/CH_2O$	Same as example 1	0
4	$CH_2O \times 10^3$	Same as example 1	$CH_2O = 865$
5	—	—	—
6	F	Scale factor	$F = 0.70$
7	$C_0$	Same as example 1	$C_0 = -79.58$
8	$C_1$	Same as example 1	$C_1 = +175.27$
9	$C_2$	Same as example 1	$C_2 = -81.62$
S0	$CK_i$	Same as example 1	$CK_i \times 46.4$
S1	$CK_{i-1}$	Same as example 1	$CK_{i-1} = 31.8$
S2	$CT_i$	Same as example 1	$CM_{gi} = 27.1$
S3	$CT_{i-1}$	Same as example 1	$CM_{gi-1} = 16.8$
S4	$CNa_{i-1}$	Same as example 1	$CNa_{i-1} = 84.0$
S5	$CNa_i$	Same as example 1	$CNa_i = 65.5$
S6	$YNa_i$	Same as example 1	$YNa = 0.376^*$
S7	$1 - \eta_{crisNa}$	Same as example 1	Calculated through the program.
S8	$q^{-1}$	Same as example 1	$q = 21.61$
S9	$d_0$	Same as example 1	$d_0 = 1.223$
A	$d_{i-1}$	Same as example 1	$d_{i-1} = 1.237$
B	$d_i$	Same as example 1	$d_i = 1.253$
C	$p^*$	Same as example 1	$p = 0.34$
D	$1 - \eta_f$	Same as example 1	—
E	$1 - \eta_{ocl}$	Same as example 1	—
F	$1 - \eta_{crisk}$	Same as example 1	$1 - \eta_{crisk} = 0.02^\dagger$

\*We have assumed 98% NaCl and 2% other salts as the salts composition.

†It has been assumed that 2% of potassium crystallizes in the last stages of evaporation in the pond.

**Results.** During the evaporation (and concentration) process daily and seasonal temperature differences take place. It has been assumed that 2% of the potassium feed crystallizes during the last stages of concentration in the pond, due to brine changes.

TABLE 6

$1 - \eta$	Pond Area (thousands of $m^2$ )	$k$ (cm/sec)	K (tons/day)	$\eta_{crisk}$	$\eta_{ocl}$	$\eta_f$	$\eta_{tot}$
0.024	1201.5	$7.11 \times 10^{-8}$	448.7	0.98	0.969	0.976	0.925
0.071	1179.1	$1.17 \times 10^{-7}$	426.0	0.98	0.970	0.929	0.878
0.143	1145.4	$4.48 \times 10^{-7}$	391.9	0.98	1.971	0.857	0.808
0.238	1100.6	$7.77 \times 10^{-7}$	346.4	0.98	0.972	0.762	0.714

If  $k = 5 \times 10^{-8}$  is accepted as the pertinent permeability coefficient, then the pond area is 1,220,000  $m^2$  and 450 tons/day the potassium output, which will be the input to the next stage of concentration (sylvinite field).

### Example 3

The output brine of Example 2, is saturated in NaCl and KCl; so if evaporation continues, sylvinite should crystallize. The aforementioned brine will be concentrated between the following compositions:

TABLE 7

	Density (gr/cc)	Concentration (gr./liter)			
		K	Na	H3BO3	H2O
Feed	1.253	46.4	65.5	10.2	859
Final	1.285	37.9	30.0	18.8	859

As in Examples 1 and 2, porosity equals 34% as well as the density of the crystallized salts will be the same = 2.1. The potassium input (feed) is 450 tons/day.

The crystallization yield of potassium can be calculated with the following expression (unpublished):

$$NTK = \frac{\gamma(d_i - d_{i-1})}{(\delta \times d_{i-1} - 1) \cdot (\delta \times d_i - 1)}$$

where

- $d_{i-1}$  = brine input density  
 $d_i$  = brine output density  
 $\gamma$  and  $\delta$  = coefficients (specific to this example)

The evaporation rate will be calculated employing the same expression as in Examples 1 and 2.

On the other hand, it is known that the crystallized salt (syvinitite) has 14.1% of potassium (26.9% KCl).

#### Data employed in program (HP-67).

TABLE 8

Memory Number	Terminology	Description	Data in This Example
0	$K_{i-1}$	Same as previous examples	450 ton/day
1	$(h_o/L) \times 0.864$	Same as previous examples	$h_o = L = 50$ cm.
2	NTK	Same as previous examples	—
3	$Z/CH_2O$	†	—
4	$CH_2O \times 10^3$	Same as previous examples	$CH_2O = 859$
5	—	—	—
6	F	Scale factor 0.6	$F = 0.6$
7	$C_0$ or ev	Same as previous examples	$C_0 = -79.58$
8	$C_1$	Same as previous examples	$C_1 = +175.27$
9	$C_2$	Same as previous examples	$C_2 = -81.62$
S0	$CK_i$	Same as previous examples	$CK_i = 37.9$
S1	$CK_{i-1}$	Same as previous examples	$CK_{i-1} = 46.4$
S2	$CT_i$	Same as previous examples	$CH_3BO_3 = 18.8$
S3	$CT_{i-1}$	Same as previous examples	$CH_3BO_{3i-1} = 10.2$
S4	$CNa_{i-1}$	Same as previous examples	$CNa_{i-1} = 65.5$
S5	$CNa_i$	Same as previous examples	$CNa_i = 30$
S6	YK	Same as previous examples	$YK = 14.1\%$
S7	$1 - \eta_{cris Na}$	Same as previous examples	—
S8	$\gamma$	Coefficients	$= 0.0339$
S9	$\delta$	Coefficients	$= 0.8201$
A	$d_{i-1}$	Same as previous examples	$d_{i-1} = 1.253$
B	$d_i$	Same as previous examples	$d_i = 1.285$
C	$p^*$	Same as previous examples	$p = 0.34; d_{sat} = 2.1$
D	$1 - \eta_f$	Same as previous examples	—
E	$1 - \eta_{ocl}$	Same as previous examples	—
I	$1 - \eta_{erisk}$	Same as previous examples	—

$$\dagger Z = \frac{YH_2O}{YK} \quad \begin{array}{l} \text{(Wt. \% of water of crystallization in salts)} \\ \text{(Wt. \% of potassium in salts)} \end{array}$$

TABLE 9

$1 - \eta_f$ (leakage losses)	Pond Area (thousands of m <sup>2</sup> )	k (cm/sec)	K (tons/day)	$\eta_{crisK}$	$\eta_{oclK}$	$\eta_f$	$\eta_{tot.}$
0.0087	1455.2	$1.70 \times 10^{-8}$	148.3	0.385	0.953	0.992	0.330
0.060	1402.4	$1.32 \times 10^{-7}$	135.2	0.406	0.954	0.940	0.300
0.12	1341.6	$2.76 \times 10^{-7}$	119.9	0.430	0.956	0.880	0.266
0.20	1260.4	$4.90 \times 10^{-7}$	99.4	0.462	0.959	0.800	0.229
0.30	1158.9	$8.00 \times 10^{-7}$	74.0	0.503	0.962	0.700	0.164

If  $k = 2 \times 10^{-8}$  (cm/sec) applies, then the pond area required is 1,455,200 m<sup>2</sup>. The quantity of K crystallized is

equal to:  $K_{i-1} (1 - \eta_{erisk}) = 450 \times 0.615 = 276.8$  (ton/day) and 148 tons/day the potassium pond output.