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**EFFECT OF CHEMICAL COMPOSITION ON SALINE WATER  
EVAPORATION**

by

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**A Thesis**

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## **ABSTRACT**

The purpose of this work was to investigate the evaporation rates of various brines and to compare them to the evaporation rates of pure water under the same environmental conditions in the laboratory. NaCl, MgCl<sub>2</sub> and KCl were the salts used in the experiments, at three densities. Mixtures of the salts were also used. One set of experiments was conducted under free convection while the other was conducted under forced convection, both over pans. Temperature was relatively constant for the experiments but relative humidity was not controlled. Wind profiles were measured during the forced convection experiments and an aerodynamic equation used to calculate evaporation for comparison with the observed evaporation rates. Surface temperatures were also measured. Water activities of all the brine and brine mixtures were also measured and compared to predictions by Raoult's law. In general, it was found the evaporation rate of brines was lower than that of pure water and that the water activities and evaporation rates were density-dependent to a certain extent. More precisely, they were dependent on the actual constituents in the brine due to the different molecular weights, and the number of ions dissolving from a given weight of salt or salt mixture. Evaporation rates can better be estimated on this basis than on the basis of density alone, as one would expect from Raoult's Law.

## RÉSUMÉ

Le but de ce travail est d'étudier les taux d'évaporation de différentes saumures et de les comparer aux taux d'évaporation de l'eau pure lorsque ces derniers sont observés en laboratoire dans les mêmes conditions météorologiques. Le NaCl,  $\text{MgCl}_2$  et KCl sont les sels que nous avons utilisés lors des expériences, à trois densités différentes. Nous avons aussi utilisé des mélanges de sels. Une série d'expériences s'est déroulée en convection libre et une autre en convection forcée; les deux séries ont été menées au-dessus de bassins. La température est demeurée relativement constante durant l'expérience mais l'humidité relative n'a pas été contrôlée. Les profils des vents ont été mesurés lors des expériences avec convection forcée, et une équation aérodynamique a servi au calcul de l'évaporation pour la comparaison avec les taux d'évaporation observés. Les températures de surface ont aussi été mesurées. L'activité des eaux de toutes les saumures et de tous les mélanges de saumures a été mesurée et comparée aux prédictions de la loi de Raoult. En général, nous trouvons que les taux d'évaporation des saumures est inférieur à ceux de l'eau pure. Nous trouvons aussi que l'activité de l'eau et les taux d'évaporation dépendent jusqu'à un certain point de la densité, mais qu'ils dépendent encore plus précisément des constituants de la saumure, et cela à cause des différentes masses moléculaires et du nombre d'ions se dissolvant d'une quantité donnée de sel ou de mélange de sels. Les taux d'évaporation peuvent être estimés plus précisément sur cette base que sur la seule base de la densité, comme l'on s'y attendrait selon la loi de Raoult.

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## **CHAPTER 1**

### **1.0 Introduction**

As the world population increases, and more attention is being paid to increasing and diversifying food production, there is increasing pressure to conserve and protect fresh water resources. In particular, many regions around the world that are presently experiencing high population growth rates are also regions in which agricultural production is limited by low rainfall and insufficient fresh water resources. On the positive side, such regions do have ample land resources, which can be put into agricultural production if the existing problem of water salinity can be overcome. Fresh water resources are not only limited in these regions, but agricultural chemicals leaching into drainage waters tends to contaminate these resources and increase their salinity. Saline drainage water is one of the main agricultural sources of fresh water contamination. Saline drainage waters result from a combination of factors including: 1) climatic conditions (high temperature, low rainfall, low relative humidity) which lead to high evaporation and salt buildup in the soil, which is then released during short and intense periods of rainfall 2) leaching of applied fertilizers into drainage water, and 3) the use of saline irrigation water.

Many methods of circumventing the salinity problem in arid and semi-arid regions have been investigated, each looking at different aspects of the problem. A number of studies have focused on alternating fresh and brackish water for surface irrigation (Mao, 1994). The research to be presented here focuses on the problem of preventing

saline drainage waters from entering the fresh water resource network through the use of evaporation ponds, a technique adopted in the western United States, particularly in California, since 1985. There, about 90% of fresh water consumption is utilized for irrigation in agriculture (U.S. Geological Survey, 1983). Even though the water used to irrigate contains only dissolved salts, salinization due to huge quantities of irrigation water is a great threat to agriculture in the American west. A study carried out in California shows that evaporation basins in the San Joaquin Valley annually receive about 3.9 million m<sup>3</sup> of subsurface drainage water from about 22,700 ha of subsurface drained fields (Ford, 1988). This saline drainage water was disposed into evaporation basins having dissolved salt concentrations ranging from 2,500 to 65,000 mg/L (Ford, 1988), indicating that the ponds are loaded with approximately 800,000 tons of salts every year.

The use of evaporation ponds provides an effective means of protecting fresh water resources, that may be applicable to other arid and semi-arid regions. However there are high costs associated with this method, primarily due to the reduction of productive area required in making space for the ponds. Thus, investigations aimed at determining the factors involved in evaporation rate of saline solutions could lead to methods for reducing the land area required for evaporation ponds for a given drainage load. It is also necessary to develop techniques to recover and purify useful substances from these deposits. Most subsurface drainage waters are dominated by salts (NaSO<sub>4</sub> , NaCl, KCl and MgCl<sub>2</sub>) which upon dissolution in water dissociate into

their constituent cations ( $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ), and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ ). These cations (dissolved solids) may cause water molecules to coordinate around them because of electrostatic attraction, which in turn reduces the evaporation rate of water. These are common non-toxic elements that may become problematic only when they are highly concentrated in the soil.

There is evidence that evaporation rates under specific climatic conditions depend more on the density of the brine solution than on the types of salt present, whether considered individually or in a mixture (Turk 1970; Harbeck, 1955). The main objective of this thesis was, therefore, to substantiate or refute these findings since they have bearing on the design of drainage ponds. The design is not simply a function of the input of agro-chemicals, but also of the pedology and geology of the region, which determines the type of ionic species in drainage waters.

Saline drainage water occurs in areas with a wide variety of climatic conditions under which evaporation may occur. Knowledge of the effects of climatic variables and salt concentration would provide valuable information regarding the expected rates of evaporation. Information of this type would help in designing the size of ponds needed for disposal of the enormous quantity of saline drainage water, and also to determine how fast it will be evaporated when salts are mixed in solution or when a single salt dominates. As often occurs, the drain water may contain mixtures of two or more salts depending upon ionic composition of inflows. Moreover, the relative composition of

any drainage water may vary with time due to changes in inflow composition or, for highly concentrated water bodies, with differential precipitation. Therefore the principal objectives of this study will be as follows:

### **1.1 Objectives:**

Turk (1970) and Harbeck (1955) asserted that variations in total salinity, and hence in density, are much more important in controlling evaporation rate than is the actual chemical composition. However, according to Raoult's Law, the chemical composition can have a significant influence based on the mole fraction of the constituent. The aim of this study is therefore:

- 1) To investigate the relationships between chemical composition of brines at different densities and their water activities.
- 2) To measure the evaporation rates of brines under free and forced convection.
- 3) To evaluate the measured evaporation rates in terms of an aerodynamic equation, incorporating the water activities associated with the various combinations of density and composition.



## **1.2 Scope**

The experimental work on the determination of evaporation rates was limited to NaCl, and  $\text{MgCl}_2$  with KCl in a 1:1 ratio and a range of densities of 1.1 to 1.3 g/ml. The work was carried out under laboratory conditions at a single wind speed and at constant temperature.

## **CHAPTER 2**

### **2.0 LITERATURE REVIEW**

#### **2.1 Background**

In order to investigate the evaporation of salt water, it is necessary to know how the addition of an electrolyte to pure water alters its rate of evaporation. Any addition of solutes to the solvent may change the properties of the solution. These properties include osmotic pressure, melting temperature, boiling temperature and vapor pressure of the solvent.

Studies on saline water evaporation found in the literature focus on the relationship between vapor pressure reduction and the species of salt in the solution. The water activity of a salt in solution (ratio of vapor pressure of the salt water to vapor pressure of fresh water under the same climatic conditions) is the parameter used to describe the magnitude of this reduction.

Vapor pressure of saline water is lower than that of a similar body of fresh water under the same physical conditions. Harbeck (1955) states that this can be explained in terms of the energy balance, since there is less consumption of heat by evaporation from saline waters this permits less energy to escape as latent heat of vaporization. This may cause a build-up of sensible heat and consequently a rise of temperature of the liquid. In warming the saline water will suffer adversely in the exchange of sensible heat and long wave radiation between its surface and the

atmosphere. The resultant shift in energy balance towards greater (or lesser gain) and less efficient conversion of energy into latent heat means that the final evaporation rate of saline water must be lower than that of fresh water receiving the same initial input of energy. Other explanations have been given reaching to similar conclusions have been given: the presence of salt not only reduces the molecular activity of the water, but also causes a negative hydrostatic pressure which lowers the saturation vapor pressure, resulting in a lower relative humidity (Bonython, 1956; Turk, 1970; Salhotra et al., 1985).

The pioneering work in the development of saline water evaporation equations was undertaken by Harris and Robinson (1916), Lee (1927), Rohwer (1933) and Young (1947).

Lee (1927) compared the evaporation from distilled water with evaporation from Owens' Lake brine of varying densities, and presented results showing that up to a certain limit the ratio of evaporation of brine to that of distilled water decreased about 1 percent for a change in density of 0.01 g/ml. He also showed that the rate of evaporation decreased with an increase in salt content until the salt concentration reached about 30%, at which point a thin crust tended to form on the brine surface, preventing the escape of active water molecules into the air.

Work by Rohwer (1933) and Young (1947) indicated that for brine of varying concentrations of NaCl, the rate of evaporation decreases about 1% for each 1% increase in salt content. Their findings did not differ greatly from those of Lee (1927) or Harris and Robinson (1916).

Harbeck (1955) presented a detailed theory of the effect of salinity on evaporation. His experiments consisted of determining the effect of salts of different concentration on saturation vapor pressure at an arbitrary temperature of 15 °C. Assuming two identical insulated shallow pans similarly exposed, one containing pure water, the other one containing brine, the increase of temperature of brine will be greater than that of pure water. The temperature of the brine rises until the energy made available by the decrease in evaporation can be returned to the atmosphere. The amount of energy utilized for evaporation was lower because of the higher heat capacity of the brine solution than that of pure water. He assumed that if the amount of incoming energy was the same for both pans, the amount of outgoing energy must also be the same. It is therefore possible to determine the effect of salinity and other factors on the temperature rise of the brine. He determined this by employing the mass transfer theory, considering equivalent wind over both pans and assuming that the possible effect of a change in atmospheric stability resulting from a small increase in water temperature in the pan of brine would be negligible.

Moore and Runkles (1968) carried out the most complete work on evaporation from "sodium chloride" solutions under controlled laboratory conditions. They evaluated the effects of different atmospheric conditions on brine evaporation by systematically changing temperature, wind, and humidity for different salt concentrations. They found that brines of high salinity did not evaporate under laboratory conditions of low winds and high humidity, even with relatively high air temperature (90° F).

Numerous investigators (Dickson et al. 1965; Salhotra et al., 1985; 1987) have studied the influence of salinity and density on the activity of saline water. Dickson et al. (1965) measured the reduction of saturation vapor pressure for solutes ranging in density from 1.188 to 1.244 g/ml.

In measurements carried out at the southern edge of the Dead Sea, Oroud (1994) extended the work of Dickson et al.(1965) and Salhotra et al. (1985; 1987) regarding the effect of density on the water activity by using pans containing water with densities of 1.00 g/ml, 1.26 g/ml, 1.31g/ml, and 1.34 g/ml, respectively. The evaporation ratios of saline water to fresh water ( $\alpha = E_{\text{sal}} / E_{\text{fresh}}$ ) at that particular location were also compared to those presented by Turk (1970). This comparison was particularly useful because the densities of investigated brines were similar to some of those presented by Turk (1970). The differences in results were attributed to the difference in climatic conditions.

Even though research by various workers has led to this reasonable approach to estimating evaporation rates from fresh or saline water, the difficulty is to determine the activity of water for different situations such as one may face in designing evaporation ponds to treat agricultural drainage waters. In such a situation, the mix and concentration of dissolved salts can vary from one region to another due to different pedology and crop production, and can vary temporally due to rainfall patterns and timing of field operations. Thus, it is necessary to be able to predict water activity from the composition and concentration of the solution. The following sections will review the work that has been done in this regard.

## 2.2 Vapor Pressure Lowering Effect of Solutes

Dissolved salts influence many of the physical and chemical properties of pure water, including the boiling point, the freezing point, the osmotic potential, the electrical conductivity and the vapor pressure. When a solute is dissolved in a solvent, the solute lowers the vapor pressure of the solvent. Raoult's law states that the partial pressure of a solute in solution is equal to the vapor pressure of solvent times the mole fraction of the solute in solution. Therefore Raoult's law indicates that vapor pressure lowering is proportional to the mole fraction (or concentration) of water in the solution and inversely proportional to the water activity and is given (Atkins, 1982) as:

$$P_i = P_i^0 X_i \quad (2.1)$$

and the mole fraction can be written as:

$$X_i = \left( \frac{\left( \frac{W.Solv}{M.W} \right)}{\left( \frac{W.Solv}{M.W} \right) + \left( \frac{W.Solu}{M.W} \right)} \right) \quad (2.2)$$

Where,

$P_i$  is the vapor pressure lowering of solvent above the solution ( mbar )

$X_i$  is the mole fraction of solute, dimensionless,

$P_i^{\circ}$  is the vapor pressure of pure solvent (mbar),

W. Solu. is weight of the solute (kg),

W. Solv is weight of the solvent (kg),

M.W represents the molecular weight of the solute or solvent ( mole  $\text{kg}^{-1}$  ).

The vapor pressure lowering effect of a solute can also be described in terms of water activity,  $A_w$ , which is defined as the ratio of the vapor pressure of the solution to that of pure water.

$$A_w = \frac{P_i}{P_i^{\circ}} \quad (2.3)$$

Knowing water activity, evaporation rate of brines can then be easily calculated by employing the evaporation rate of fresh water:

$$\text{Evp}(b) = \text{Evp}(f) \cdot A_w \quad (2.4)$$

where,

$\text{Evp}(b)$  is the evaporation rate of brine (g/hr),

$\text{Evp}(f)$  is the evaporation rate of fresh water (g/hr).



Differential vapor pressure lowering (VPL) between a brine solution and a solvent is given by:

$$VPL = \frac{(P^o - P_i)}{P^o} \quad (2.5)$$

Harbeck (1955) showed that the water activity of mixed brines of known chemical composition can be approximated using a composite reduction factor obtained by summing the weighted reduction in saturation vapor pressure due to each of the constituent salts (which is a direct extension of Raoult's Law). Thus, for a solution of total concentration  $\chi$  containing N salts of partial concentration  $\chi_i$ ,

$$Aw(\chi) = (1/\chi) \sum [\chi_i * Aw_i(\chi_i)] \quad \text{with a summation from } i = 1 \text{ to } N \quad (2.6)$$

where,

$Aw(\chi)$  is the water activity in a solution of total concentration  $\chi$ ,

$\chi_i$  is the concentration in a solution of single salt i at total concentration ( $\chi$ ),

$Aw_i(\chi_i)$  is the water activity in a solution of single salt i.

## 2.3 Predicting Evaporation from a Water Body

The rate of evaporation of pure water is often described by the Penman equation (Penman, 1948):

$$E = \frac{\left[ \delta \frac{R_n}{\lambda} + \gamma E_a \right]}{(\delta + \gamma)} \quad (2.7)$$

where,

$E$  is the evaporation rate ( $\text{kg.m}^{-2}.\text{s}^{-1}$ ),

$\delta = (e_s - e_a)/(T_s - T_a)$ , is the slope of the saturated vapor pressure curve ( $\text{mbar.K}^{-1}$ ),

$e_s$ ,  $e_a$  are the saturated vapor pressures at the surface and of the air, at temperatures  $T_s$  and  $T_a$ , respectively,

$R_n$  is the energy flux of net incoming radiation ( $\text{W.m}^{-2}$ ),

$\lambda$  is the latent heat of vaporization of water per unit mass ( $\text{J.kg}^{-1}$ ),

$\gamma$  is the psychrometric constant  $0.66$  ( $\text{mbar.K}^{-1}$ ),

$E_a$  is the vapor flux into the air ( $\text{kg.m}^{-2}.\text{s}^{-1}$ ).

The first term in the right-hand numerator is the evaporation equivalent of the net radiant flux at the surface, whereas  $E_a$  is the aerodynamic term i.e. the driving power of the atmosphere.  $\gamma$  can be defined as:

$$\gamma = c_1/c_2 = [H/(T_s - T_a)] / [\lambda E/(e_s - e_d)] \quad (2.8)$$

(obtained from Feddes et al., 1978):

where,

$H$  is the sensible heat flux:  $H = c_1(T_s - T_a)/r_a$  ( $J\ m^{-2}\cdot s^{-1}$ ),

$\lambda E$  is the latent heat flux:  $\lambda = c_2(e_s - e_d)/r_a$  ( $J\ m^{-2}\cdot s^{-1}$ ),

$c_1/c_2$  are constant ( $mbar\cdot K^{-1}$ ),

$e_d$  is the actual vapor pressure of the air above the water body,

$r_a$  is the resistance to diffusion of heat or water vapor (assumed equal) from the water surface to the atmosphere ( $s\cdot m^{-1}$ ).

The influence of wind speed on evaporation is implicit in equation 2.7, since the fluxes  $H$  and  $\lambda E$  are functions of air movement. Thus, with appropriate meteorological measurements it is possible to estimate the evaporation from a body of pure water.

Equation 2.7 cannot be used directly to predict the rate of evaporation of water from a saline body given the necessary meteorological terms because the vapor pressure of pure water is not the same as that of saline water. The presence of solutes in water lowers its vapor pressure and increases the latent heat of vaporization of the solution.

Calder and Neal (1984) proposed a modification to the Penman equation that gives the evaporation rate from saline water bodies explicitly in terms of the salinity and the necessary meteorological variables. The modification is based on the activity of water in solution at a given temperature and is:

$$\lambda E = \{ (\partial e_s / \partial T) H + \rho c_p [ \{ (e_s(T) - e / A_w) / r_a \} / ((\partial e_s / \partial T) + \gamma / A_w) \} \quad (2.9)$$

where,

$\rho$  is density of the air ( $\text{kg.m}^{-3}$ )

$c_p$  specific heat of the air ( $\text{J.kg}^{-1} \cdot \text{K}^{-1}$ ).

Here,  $A_w$  is the activity of water in solution. Strictly speaking,  $\beta$  is a curvilinear function of temperature, increasing and then decreasing from 5 to 40°C. However, Calder and Neal note that for salinities up to 292‰, the variation is less than 7% and they treated it as a constant rather than as a function of temperature,  $A_w(T_o)$ . Although this equation permits the estimation of evaporation rates from saline and fresh water bodies, the authors state that the errors involved in the meteorological inputs and estimation of the aerodynamic resistance are high enough to limit the usefulness of the approach. However, they suggest that errors in estimated evaporation rates due to changes in  $A_w$  should not exceed 10-15% under constant meteorological conditions.

A year later, Salhotra et al. (1985 and, 1987) attempted various analytical procedures to compute an equation to determine the effect of both densities and the water activity based on particular ionic composition and salinity concentration on the reduction of saturation vapor pressure. Results were obtained using evaporation rates from eight saline pans, with density ranging from 1.03 to 1.24 g/ml. The evaporation rate was calculated by two different approaches. The commonly used approach to account for the salinity effects based on the ratios of salt water to fresh water is  $\alpha$  approach:

$$\alpha = E_{\text{salt}} / E_{\text{fresh}} \quad (2.10)$$

where the evaporation rate per unit area of salt water  $E_{\text{salt}}$  is given by:

$$E_{\text{salt}} = \alpha f(W) [e(T_s) - \psi e(T_a)] \quad (2.11)$$

and the evaporation rate per unit area of fresh water  $E_{\text{fresh}}$  is

$$E_{\text{fresh}} = f(W) [e(T_s) - \psi e(T_a)] \quad (2.12)$$

At a given water surface temperature the saturation vapor pressure over a planar surface  $e_o$  of a saline solution can be expressed as:

$$e_o = A_w(T_o) * e(T_o) \quad (2.13)$$

and saturation vapor pressure of fresh water is given by:

$$e_s(T_o) = 6.01078 e^{((17.269 T_o) / (237.3 + T_o))} \quad (2.14)$$

where,

$A_w(T_o)$  water activity at temperature  $T_o$  °C,

$e(T_o)$  the saturation vapor pressure of fresh water at temperature  $T_o$  °C  
(mbar),

$E_{salt}$  evaporation rate from a saline solution (mbar),

$E_{fresh}$  evaporation rate from fresh water (mbar),

$f(W)$  empirical function of wind speed  $W$ ,

$\psi$  relative humidity (expressed as a fraction),

$T_s$  temperature of water surface °C,

$T_a$  temperature of air °C,

The accuracy of the  $\alpha$  approach (Eq. 2.10) is limited by salinity and ionic composition functions.

It has been found that the  $\beta$  approach, which is directly based on the effect of

salinity and ionic composition on saturation vapor pressure, is simpler and more accurate as illustrated in the following equation (Salhotra et al., 1987):

$$E_{\text{salt}} = f(W) [Aw(S_s)e(T_s) - \psi e(T_a)] \quad (2.15)$$

where  $Aw(S_s)$  is the water activity in the solution of salinity  $S$ .

## 2.4 Estimating Heat and Mass Transfer into the Atmosphere

The heat that passes through the laminar boundary layer over a surface can be expressed as (Oke, 1978 ):

$$F_H = \rho c_p h_H \Delta T \quad (2.16)$$

The moisture transfer to ambient air is then similarly given as:

$$F_M = h \Delta C \quad (2.17)$$

where,

$F_H$  is heat flux density ( $\text{J. m}^{-2} \cdot \text{s}^{-1} \cdot \text{deg}^{-1} = \text{W. m}^{-2} \cdot \text{K}^{-1}$ ),

$F_M$  is mass flux density ( $\text{kg m}^{-2} \text{ s}^{-1}$ ),

$c_p$  is specific heat of air at constant pressure ( $\text{J. kg}^{-1} \text{ K}^{-1}$ ),

$\rho$  is air density ( $\text{kg. m}^{-3}$ ),

$h$  is boundary layer conductance ( $\text{m. s}^{-1}$ ),

$\Delta T$ , is the temperature difference between the surface and ambient air,

$\Delta C$  is concentration difference between the surface and ambient air ( $\text{kg m}^{-3}$ ).



### 2.4.1 Boundary Layer Conductance

The quantitative description of the exchange between surface and ambient air depends on the nature of flow. The latter can be expressed in terms of the Reynolds number (Re) as follows (Jones 1992):

$$Re = \frac{uL}{\nu} \quad (2.18)$$

where the wind speed in the boundary layer "u" is largely controlled by the frictional drag imposed on the flow by the underlying rigid surface. The drag retards motion close to the ground and gives rise to a sharp decrease of mean horizontal wind speed ( $\bar{u}$ ) as the surface is approached. Therefore, the gradient of mean wind speed ( $\Delta\bar{u}/\Delta z$ ) is greater over a smooth object, and least over rough surface. Wind variation with height can be accurately described by the logarithmic profile equation (Plate 1971 ):

$$\bar{u}_z = \frac{u_*}{k} \ln \frac{z - d}{z_0} \quad (2.19)$$

In estimating boundary layer conductance for heat and mass transfer over objects of finite length, two dimensionless numbers that are functions of the Reynold's number are used. These are the Nusselt (Nu) and Sherwood (Sh) numbers which

are often called Pohlhausen equations that can be written as:

$$Sh = 0.66 Sc^{1/3} Re^{1/2} \quad (2.20)$$

and,

$$Nu = 0.66 Pr^{1/3} Re^{1/2} \quad (2.21)$$

where,  $Sc$  and  $Pr$  are the Schmidt and Prandtl numbers, respectively, and are defined further down.

Therefore boundary layer conductance ( $h$ ) can be calculated as follows:

$$h = \frac{Sh * D}{L} \quad (2.22)$$

Over extended areas, the boundary layer conductance ( $h$ ) may also be written in the form (Jones 1992):

$$h = \frac{u_*^2}{u} \quad (2.23)$$

where the friction velocity is given by:

$$u_* = (b * \bar{u}_z) \quad (2.24)$$

where,

$L$  is the length of laminar boundary layer building up over an object (m),

$\nu$  is kinematic viscosity ( $\text{m}^2 \text{s}^{-1}$ ),

$\bar{u}_z$  is mean wind speed at height  $z$  ( $\text{m s}^{-1}$ ),

$u_*$  is friction velocity ( $\text{m s}^{-1}$ ),

$k$  is von Kármán constant (0.40),

$z$  height (m),

$z_0$  roughness length (m),

$D$  is molecular diffusivity,

$d$  is displacement height,

$b$  is a surface-dependent parameter.

The nature of molecular properties of the fluid can be described by the Prandtl (Pr) and Schmidt (Sc) numbers. The Prandtl number is the ratio of the momentum diffusivity to the thermal diffusivity and indicates the relative ease of transport of momentum and heat; it is given by:

$$\text{Pr} = \frac{\nu}{\alpha} \quad (2.25)$$

The Schmidt number is given by:

$$Sc = \frac{\nu}{D} \quad (2.26)$$

where,  $\nu$ ,  $\alpha$  and  $D$  are the molecular diffusivities, with values of  $1.5 \times 10^{-5}$ ,  $2.06 \times 10^{-5}$ ,  $2.39 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ , respectively.

The Reynolds number (Re) can not be used in the case of free convection. The Grashof number can be applied in such cases:

$$Gr = \frac{g \kappa L^3 \Delta T}{\nu^2} \quad (2.27)$$

where,

Gr is the Grashof number,

$g$  is gravitational acceleration ( $9.81 \text{ m s}^{-2}$ ),

$\kappa$  is coefficient of thermal expansion ( $\kappa = 1/T \text{ dV/dT} = 1/T$ ,  $T$  expressed in  $^{\circ}\text{K}$ ),

$\Delta T$  is temperature difference between object and ambient air.

## **2.5 Summary**

It appears that the main problem in estimating evaporation rate from a salt-water body, besides being able to predict climatic conditions over the relevant time scale, is to determine the ionic composition of the brine. Given the ionic composition, the water activity can then be predicted fairly accurately over a wide range of densities using Raoult's Law in its extended form as presented by Harbeck (1955).

Once the brine water activities are determined, this can be used to predict saline water evaporation from the Eq 2.4.

Since evaporation rates of saline water may also be estimated from aerodynamic equations, it is necessary to estimate boundary layer conductance by one of the two approaches. The first approach use Reynold number to assess the nature of the flow, and then to compute the Sherwood number (Eq. 2.20). The second approach is to measure wind velocity profile to determine friction velocity; the value of wind friction was then used in the Eq. 2.23.

## **CHAPTER 3**

### **3.0 MATERIALS AND METHODS**

#### **3.1 Room condition:**

The experiments were carried out in a laboratory at the Department of Agricultural and Biosystems Engineering, Macdonald Campus of McGill University. The relative humidity in this room was in the range of 19 to 40 %, reflecting conditions in arid regions. There was no noticeable air current in the testing room. The temperature of the room varied from 24° C to 28° C.

#### **3.2 Apparatus and Set-up**

The laboratory equipment consisted of:

**3.2.1 Evaporation Pans.** The pans used were made of stainless steel, and had a 220 mm inner diameter, and a rim height of 50 mm.

**3.2.2 Hygrometer.** A Vaisala HMI 32<sup>(1)</sup>, digital temperature-humidity gauge with an accuracy of  $\pm 1^{\circ}\text{C}$  for temperature and  $\pm 1\%$  for relative humidity was used to monitor general room conditions.

**3.2.3 Electric Fan.** The fan was a household variable speed type set to run at one speed without oscillating.

(1) : use of manufacture's name is for the readers information only, it does not suggest endorsement.

**3.2.4 Infrared Thermometer.** A portable infrared Minolta (land Cyclops compact) thermometer designed for measuring temperatures in the range of -50 to 500 °C with an accuracy of  $\pm 0.1$  °C was used to monitor water surface and air temperature at 50 mm above the evaporation pans. It has a response time of 0.5 seconds and three operation modes; continuous measure, peak measure and monitor. This thermometer is very sensitive to the emissivity of different materials, and must be adjusted according to settings provided in the manual.

**3.2.5 Balance.** A Mettler PM4000 electronic balance, with accuracy of 0.1 grams for loadings of up to 4 kg was used to determine changes in the mass of water.

**3.2.6 Thermo-anemometer.** The anemometer was an Alnor Compuflow hand-held unit, which has an accuracy of  $\pm 3$  % of the indicated reading over a range from 0.10 m/s to 15 m/s. This anemometer provides automatic averaging from memory and provides a hardcopy printout.

**3.2.7 Aqualab.** A Model CX2 Aqualab was used for water activity measurement. This equipment uses the chilled-mirror dewpoint technique to measure the water activity ( $A_w$ ) of a solution in the range 0.003 to 1.000. When a sample is measured with Aqualab CX2, a stainless steel mirror within the chamber is repeatedly cooled and heated while dew forms and is driven off. Each time dew forms on the mirror, Aqualab measures the temperature and  $A_w$  of the sample,

saving these values to compare to previous values as it repeats its reading.  
When the  $A_w$  values are less than 0.001 apart, the measurement process is complete.



### 3.3 Test Solutions

Salts solution of chemical elements (NaCl, KCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) were chosen to simulate agriculture saline drainage waters since these waters are composed largely of these types of salts solutions.

The brines were either sodium chloride or a 1:1 ratio of potassium chloride and magnesium chloride. The magnesium chloride was available as a hydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), and the actual molecular weight of the magnesium chloride fraction was considered in preparing the brines. These two types of brine were made up to densities of 1.1 g/ml, 1.2 g/ml or 1.3 g/ml using, 400 g of tap water plus salt (Table 3.1). Test solutions of different concentrations were also prepared, to determine their water activities.

Table 3.1. Amount of salts and tap water used for brine solutions.

Brine of	Density		
	1.1 g/ml	1.2 g/ml	1.3 g/ml
NaCl	40 <sup>(TW)</sup>	80 <sup>(TW)</sup>	120 <sup>(TW)</sup>
$\text{MgCl}_2$ / KCl	20 / 20* <sup>(TW)</sup>	40 / 40* <sup>(TW)</sup>	60 / 60* <sup>(TW)</sup>

\*<sup>(TW)</sup> : 20 g of  $\text{MgCl}$  plus 20 g of KCl plus 400 ml of tap water.

<sup>(TW)</sup> : tap water.

The experiments were conducted under two conditions:

- with a wind of speed  $2.56 \text{ m s}^{-1}$ , and,
- without wind

Room relative humidity, the general room temperature, the water surface temperature and the air temperature at 50 mm above the water surface were monitored.

### **3.4 Experiment Under Forced Convection**

#### **3.4.1 Preliminary Work of the Forced Convection Experiment**

Since one of the objectives of this research was to compare evaporation rates of different brines at different densities under the same conditions, it was important to determine a proper fan placement relative to the pans. In order to have the same wind effects, an effort was made to determine optimum placement of the pans relative to the fan.

If placed in a straight line perpendicular to the airstream, the central pan tended to experience about 1% less evaporation. Moving the central pan closer to the fan by 15 to 20 cm resulted in raising the evaporation rate of this pan by about 1%. But, at the same time, due to general room air turbulence and non linearity of the fan wind-stream, it was noted that all three pans experienced variance in evaporation of about 1%. It was therefore decided to simply place the three pans in a straight line as shown in Fig 3.1. To determine at which level the wind velocity becomes stable, the wind velocity was measured from at height of 0.5 to 10 cm above the pans. A stable wind velocity of  $2.56\text{-m s}^{-1}$  was measured at 10 cm above the surface of each pan. This wind velocity was kept constant throughout all wind trials.

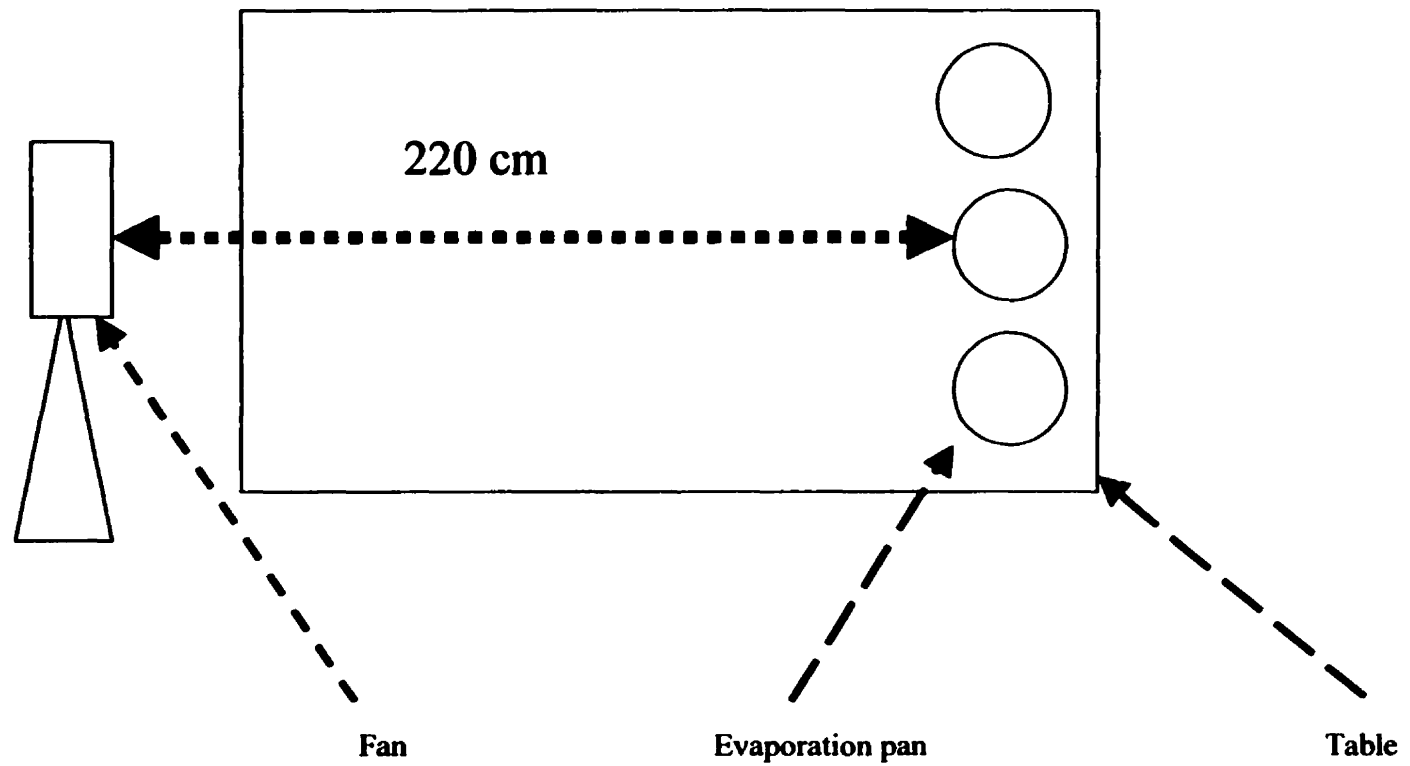
### **3.4.2 Experimental Design.**

For statistical purposes each brine density and fresh water was replicated three times over the course of the experiment. The location of the pans containing NaCl, MgCl<sub>2</sub>/KCl and fresh water was changed between runs.

The design permitted comparison of evaporation of the six test solutions under the same conditions. In each wind run, only three pans could be used at a time given the fact that there was only one fan available. One pan contained fresh water, one the NaCl brine at a given density, and the other pan contained the MgCl<sub>2</sub>/KCl mixture at the same density. See Figure 3.1, for the general set-up.

### **3.4.3 Test Procedure**

Each run lasted 12-hours. Water loss, air temperature at 5 cm above the pan and water surface temperatures were measured after each 12-hour period. After the 12-hour reading, fresh tap water of similar temperature as the test solutions was added to each pan and stirred vigorously in an effort to redissolve precipitated salts. This was done to compensate for the evaporative water loss and to restore the original density. Wind speed was recorded at heights of 0.5 cm, 5 cm and 10 cm above the surface of each pan. For the first few experiments, wind speed was monitored more frequently but no changes were noted.



**Figure 3.1 Plan view schematic of wind condition**  
**(not to scale)**

### **3.5 Experiment Under Free Convection**

Once the trials with wind were completed, trials were repeated in the absence of wind. Unlike the wind-driven evaporation experiment, the free convection experiment involved six brine solutions (NaCl and MgCl<sub>2</sub>/KCl at three densities each) plus the control tap water, for a total of seven pans. Water loss by evaporation in these runs was only measured at the end of the 24 hour period. A run was performed and repeated four times for each density level (1.1, 1.2, 1.3 g/ml). The locations of the pans were randomized.

## **CHAPTER 4**

### **4.0 RESULTS AND DISCUSSION**

The raw data are presented in appendix "A". Summary data and graphs are given in the text.

#### **4.1 Water Activities of Various Brines**

The first part of this study was to measure the water activity of various brines including those used in the free and forced convection experiments. This was to verify: 1) that the vapor pressure reduction by the salts used followed Raoult's Law, and 2) that in a mixed-salt environment, the vapor pressure could be explained by equation 2.6. The water activities for the various brines at different densities are given in Table 4.1 (single salts) and Table 4.2 (mixed salts). The values predicted by Raoult's Law are also given in these tables.

It is clear that the water activity corresponds very closely to that predicted by Raoult's Law in all cases (Table 4.1 and 4.2). It is also clear that it is not the density as such that determines the vapor pressure lowering. It is rather the molarity that must be taken into account since it is this that determines the mole fraction of water as per Raoult's Law. As the molarity increases, the water activity decreases, and the vapor pressure lowering due to different salts is directly comparable when expressed in molar terms. Whenever the brine solutions reaches saturation, the water activities become almost equal. See Table 4.1.

The observed water activity of the mixed brine  $\text{MgCl}_2/\text{KCl}$  is 1 to 11.5% higher, than that of  $\text{NaCl}$  brine. This was probably was due to the additional ion provided during dissolution of  $\text{MgCl}_2$ . Similar information can be found in a chart presented in the International Critical Tables (National Research Council, 1928) that show that  $A_w$  for  $\text{MgCl}_2$  at equal density is lower than that for  $\text{KCl}$  and  $\text{NaCl}$  solutions.



**Table 4.1 Water activity for single brine of NaCl, KCl, MgCl<sub>2</sub>**

<u>Brine NaCl</u>					<u>Brine KCl</u>				<u>Brine MgCl<sub>2</sub></u>			
Density g/ml	m	Obs	Calc. Raoult's Eq (2.2)	Percent Diff (%)	m	Obs	Calc* Raoult's Eq (2.2)	Percent Diff (%)	m	Obs	Calc* Raoul's Eq (2.2)	Percent. Diff. (%)
1		1			1				1			
1.05	0.67	0.98	0.97	1	0.67	0.97	0.98	1	0.28	0.98	0.98	-
1.1	1.71	0.95	0.94	1	1.34	0.96	0.95	1	0.58	0.97	0.97	-
1.15	2.38	0.92	0.92	-	2.01	0.93	0.93	-	0.86	0.96	0.96	-
1.2	3.42	0.91	0.89	2.2	2.68	0.91	0.91	-	1.15	0.95	0.94	1
1.3	5.13	0.85	0.83	2.2	4.024	0.85	0.87	2	-	0.92	0.92	-

m. stands concentration expressed in term of molarity

For the mixed brine solutions, the water activity agreed closely with that predicted by equation (2.6) which is essentially a weighted average of the water activities of the individual brines. See Table 4.2.

Table 4.2 Water activity for mixture brine of NaCl/KCl, KCl/MgCl<sub>2</sub> and MgCl<sub>2</sub>/KCl

Density g/ml	<u>Brine NaCl+KCl</u>			<u>Brine KCl+MgCl<sub>2</sub></u>			<u>Brine MgCl<sub>2</sub>+NaCl</u>		
	Obs	Calc. Raoult's Law Eq (2.2)	Calc. Eq.(2.6)	Obs	Calc. Raoult's Law Eq (2.2)	Calc. Eq.(2.6)	Obs	Calc. Raoult's Law Eq (2.2)	Calc. Eq.(2.6)
1	1			1			1		
1.05	0.97	0.97	0.97	0.98	0.98	0.97	0.97	0.97	0.98
1.1	0.95	0.95	0.95	0.96	0.97	0.96	0.96	0.96	0.95
1.15	0.92	0.93	0.92	0.95	0.95	0.94	0.94	0.95	0.93
1.2	0.90	0.90	0.91	0.93	0.93	0.92	0.91	0.92	0.92
1.3	0.84	0.86	0.85	0.90	0.90	0.87	0.86	0.89	0.87

Salhotra et al (1987) state that there is limited information regarding evaporation from mixture brine solutions. However, it appears that one could simply use the mixed brines ionic composition to compute the water activity and then account for this in the evaporation equations as done by several authors (see Literature Review). For large-scale estimations, however, the problem is more complex. Over a large body of water with different depths, there can be significant variations of water temperature, particularly close to shore where salts may deposit more rapidly. Furthermore, the evaporative conditions relative to the

turbulence field can vary widely, depending on the surrounding topography. Finally, it is not a simple matter to account for the temporal variations of drying potential over large areas. These are among the reasons why evaporation estimates on a large scale cannot be better than about 15-30% on a relevant time-scale.

## **4.2 Evaporation Experiments**

The second part of this experiment consisted in: 1) measuring evaporation rates of brines and fresh water under forced convection to be compared to estimates of evaporation rates based on boundary layer theory, aerodynamic equations, or evaporation rates calculated by the water activity method; 2) the measured evaporation rates of brines and fresh water under free convection to investigate the decrease in evaporation with increase in the density.

### **4.2.1 Evaporation Under Forced Convection**

Information derived from the literature review shows that evaporation of brine solutions generally decreases as their density increases. This was not experienced in the wind experiment, because of different experimental conditions (temperature and humidity) that occurred between repeated observation. Figures 4.1, 4.2, and 4.3 show the evaporation rates for the three different densities as well as the changes in relative humidity. Although one would expect the evaporation rates to follow the changes in RH, this was not always the case. Part of the problem was that the evaporation rates were calculated on a 12-hour basis, which was perhaps too long without replenishing the water. During this period, evaporation would cause the density of the solution to increase, and thus sometimes overcompensate for a drop in RH. Furthermore, the comparison of evaporation rates with respect to density and composition are difficult since the density changes over the 12-hour periods are dependent on

the initial values. Thus, one cannot expect a clear relationship. The lower density brines should evaporate more quickly during the same time periods, so that an analysis based on density cannot be referred to the initial values. Nevertheless, the data are presented.

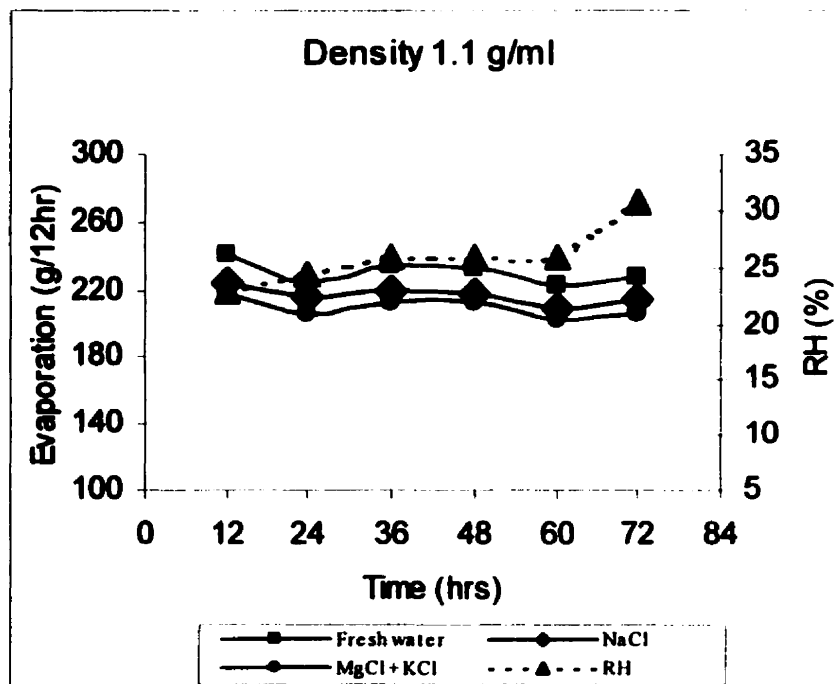


Figure 4.1 Evaporation of fresh water versus brine solutions of density 1.1 g/ml.

**Note:** After each measure, the quantity of water evaporated was replaced.

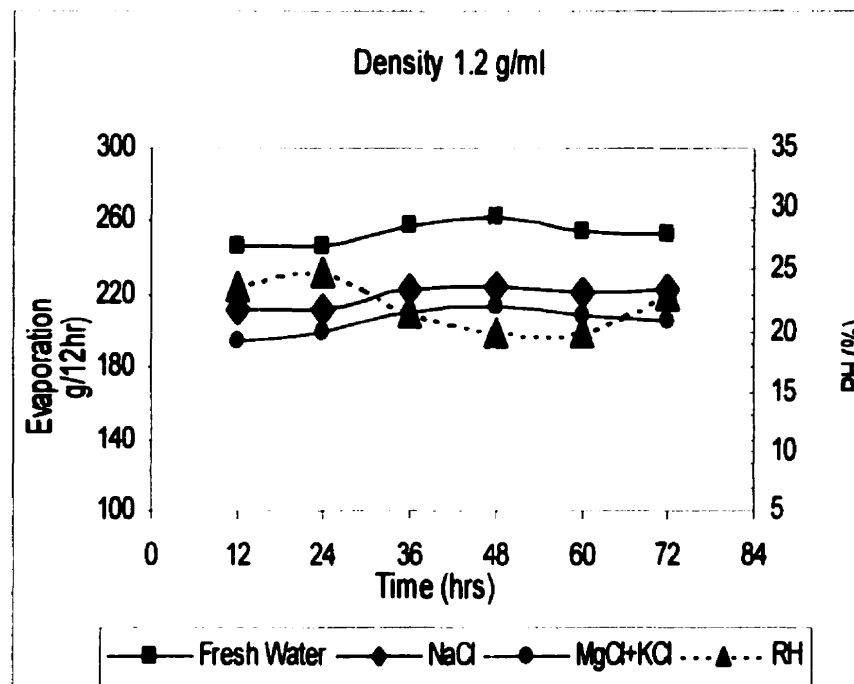
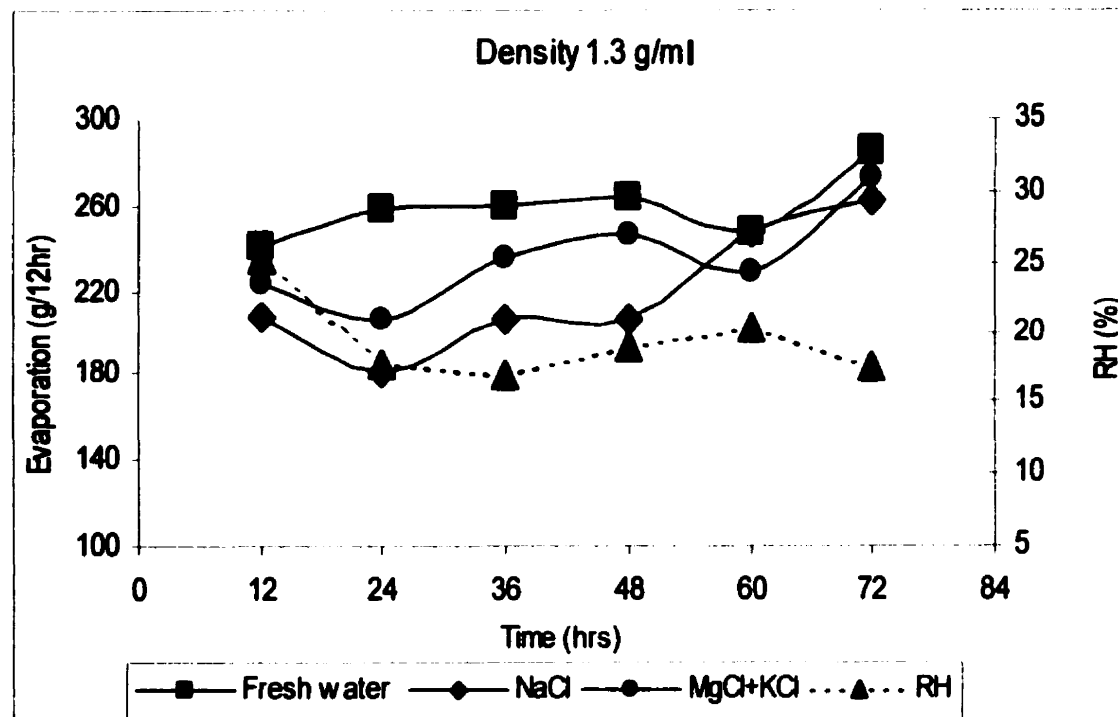


Figure 4.2 Evaporation of fresh water versus brine solutions of density 1.2 g/ml.

**Note:** After each measure, the quantity of water evaporated was replaced.



**Figure 4.3** Evaporation of fresh water versus brine solutions of density 1.3 g/ml.

**Note:** After each measure, the quantity of water evaporated was replaced.

#### **4.2.1.1 Data Analysis**

Table 4.3. presents the mean surface water temperature and mean evaporation rate for solutions of different densities, i.e. for two brine solutions and fresh water. The evaporation rate of each brine solution and fresh water is inversely related to the surface water temperature. In all replications, the surface temperatures of the NaCl and MgCl<sub>2</sub>/KCl brines were higher than that of fresh water, corresponding to lower evaporation rates. Since the brine solutions result in a lower vapor pressure and higher temperature than that over fresh water, less energy escapes as latent heat. This is due to the higher specific heat ( $C_p$ ) of the brine solutions, which corresponds to a higher surface water temperature of the brine solutions in the pan, as discussed by Harbeck (1955). In the present experiment, there was no correlation between evaporation rate and surface temperature of the brine solutions, and this disagrees with the theory of Harbeck (1955). Although the surface temperature of the NaCl brine was 1°C higher than that of the MgCl<sub>2</sub>/KCl brine at densities of 1.2 and 1.3 g/ml, the evaporation rate of NaCl was also higher. This was not as expected from Harbeck's theory, which would suggest a lower evaporation rate for NaCl.



**Table 4.3. Average evaporation of six-replications of fresh water and brine solutions of density of 1.1, 1.2 and 1.3 g/ml versus average surface water temperature.**

Density	Fresh water		Brine of NaCl		Brine of MgCl <sub>2</sub> /KCl	
	Avg. Evp. ( g/12hr )	Avg.Temp. ( °C )	Avg. Evp. ( g/12hr )	Avg.Temp. ( °C )	Avg. Evp. ( g/12hr )	Avg. Temp. ( °C )
1.1	230.34	14.7	216.78	15.8	209.27	15.6
1.2	253.41	14.7	219.08	17.0	203.73	16.1
1.3	258.38	14.4	213.59	18.2	205.56	17.1

Avg. Evp: average evaporation rate.

Avg. Temp: average surface temperature.

Table 4.4 shows the observed average percentage evaporation rate difference between fresh water and brines NaCl, MgCl<sub>2</sub> /KCl in a 12-hour period.

**Table 4.4. Percent average evaporation rate differences**

Density	Brine NaCl	Brine MgCl <sub>2</sub> /KCl
1.1	5.9	9.2
1.2	13.6	19.6
1.3	17.4	20.5

The observed evaporation rate of the brine NaCl was higher than that of the MgCl<sub>2</sub>/KCl mixture in all cases, see Table 4.5.

**Table 4.5. Percent differences between brine NaCl and MgCl<sub>2</sub>/KCl**

Density	Percent. Diff.
1.1	3.5
1.2	7.0
1.3	3.5 *

\*: Subject to error

Evaporation rates at the highest density may be subject to error, since salts were deposited on the walls of the pans after some time as the solution approached saturation. Although an effort was made to prevent surface water crystallization by stirring periodically or continuously, the same phenomenon occurred during the several attempts. This was also experienced by Bonython, (1956), and Dickson, (1965), who showed that the evaporation rates agree well at the lowest density, but at higher densities it was difficult to obtain good data due to salt crystallization on the walls of the pans and at the surface of the water. This indicates that there may be local high concentrations of salts where the surface of the water meets the pan.

#### **4.2.1.2 Comparisons of Evaporation Rate Determined in Aerodynamic and Water Activity Method to the Observed.**

Observed brine evaporation rates and those computed using fresh water evaporation multiplied by water activity are compared; this comparison was also extended to the aerodynamic method (see Tables 4.8, 4.9, 4.10, and 4.11).

In order to evaluate evaporation rates of the brines and fresh water via the aerodynamic method, the laminar boundary layer conductance ( $h$ ) was estimated. Three approaches were used:

- 1) The first approach used to calculate  $h$  (Eq. 2.22) was to compute the Sherwood number (Eq. 2.20); this itself is based on a calculation of the Reynold number by (Eq. 2.18). Further by assuming a realistic boundary layer length ( $L$ ) of 0.22 m, was found to be of  $0.01\text{-m s}^{-1}$ .
- 2) Using the same approach but assuming a shorter boundary layer length ( $L$ ) of 0.10 m to correct for the presumably unrealistic expectation that a boundary layer extends over whole evaporation pan, gave  $h = 0.03\text{ m s}^{-1}$ .
- 3) The measured velocity of the wind profile was used to calculate friction velocity in (Eq.2.24), where roughness length  $Z_0$  and displacement height ( $d$ )

were estimated from the best-fit to the log profile (See Table 4.6).

The value of  $u^*$  was also taken from the best-fit profile. This value of  $u^*$  was then used in Eq. 2.23 to estimate the boundary layer conductance, yielding a value of  $0.021 \text{ m s}^{-1}$ .

Table 4.6. Wind profile data

$u^*/k$ $\text{m s}^{-1}$	$u^*$ $\text{m s}^{-1}$	$z_0$ m	$z$ m	$d$ m	$z-d$ m	$uz$ $\text{m s}^{-1}$	$\ln(z-d/z_0)$
0.51	0.22	0.007	0.0173	0.005	0.0123	2	0.564
			0.0189		0.0139	2.07	0.686
			0.0302		0.0252	2.37	1.281
			0.0415		0.0365	2.56	1.651
			0.0667		0.0617	2.86	2.176

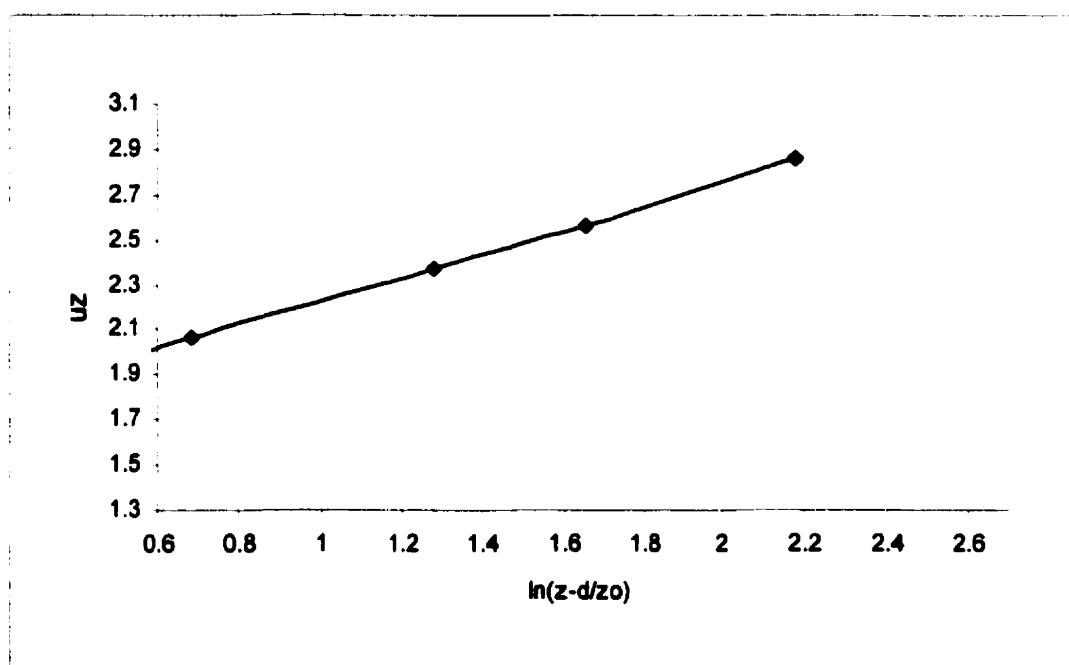


Figure 4.4 Logarithmic decay of wind profile measured above evaporation pans.

Table 4.7 and Figure 4.5. shows observed evaporation rates of six replication of fresh water and evaluated evaporation rates via the aerodynamic method under three laminar boundary layer conductances: In the case of  $h = 0.01 \text{ m s}^{-1}$ , the estimated evaporation rates were only half of the observed values, whereas those based on  $h = 0.03 \text{ m s}^{-1}$  tended to be considerably larger. The best agreement was obtained using  $h=0.021 \text{ m s}^{-1}$ .

**Table 4.7** Computed evaporation rates under three different boundary layer, and the observed evaporation rate.

			L = 0.22 m h = 0.01 m s <sup>-1</sup>		L = 0.10 m h = 0.03 m s <sup>-1</sup>		L = 0.22 m h = 0.021 m s <sup>-1</sup>		
Rep.	Vapor Pressure Density g/m <sup>3</sup>		Evaporation		Evaporation		Evaporation		Observed Evaporation g/12hrs
			h*ΔC g/m <sup>2</sup> s	g/12 hrs	h*ΔC g/m <sup>2</sup> s <sup>-1</sup>	g/12 hrs	h*ΔC g/m <sup>2</sup> s	g/12 hrs	
1	12.11	4.79	0.0732	120.18	0.220	360.54	0.154	252.38	240.47
2	11.13	4.65	0.0648	106.36	0.194	319.08	0.136	223.35	223.84
3	11.88	5.15	0.0673	110.47	0.202	331.40	0.141	231.98	234.98
4	12.27	5.29	0.0698	114.55	0.209	343.64	0.147	240.55	232.84
5	12.35	5.49	0.0686	113	0.206	337.93	0.144	236.55	222.16
6	12.59	5.98	0.0661	108.49	0.198	325.47	0.139	227.83	227.74
	S.D.			4.90		14.71		10.298	7.02
	Average			112.11		336.34		235.44	230.34

L : length of laminar boundary layer

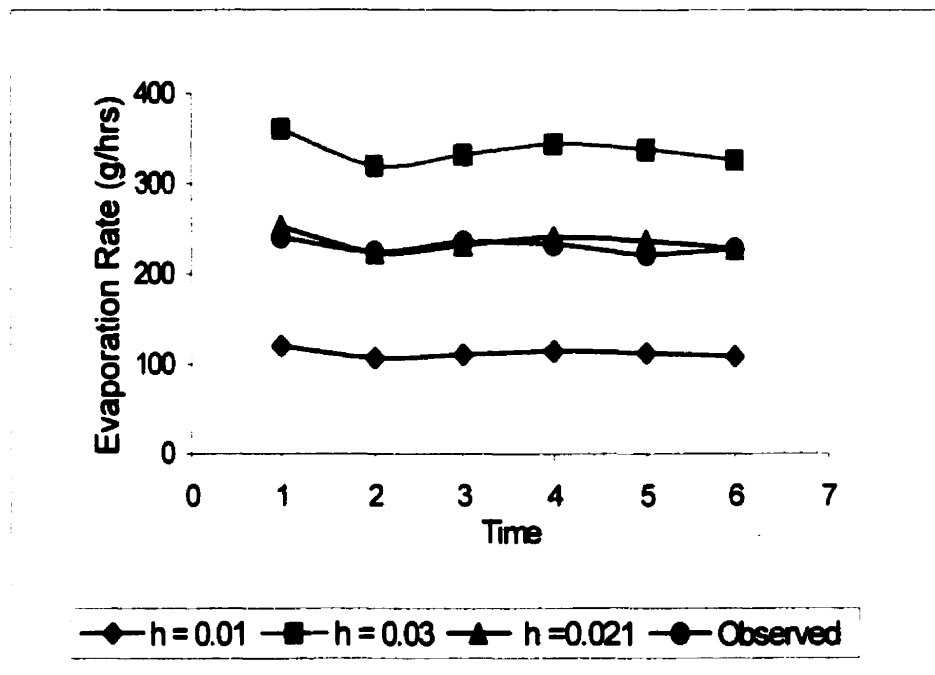


Figure 4.5 Evaporation rates under three different boundaries layer, and the observed evaporation rate.



Table 4.8 contains data from fresh water and Tables 4.9, 4.10 and 4.11 contain data from NaCl brine, and  $\text{MgCl}_2/\text{KCl}$  brine, including: vapor pressure density, observed evaporation rates and evaporation rates calculated by the aerodynamic method (Eq. 2.17) for 12-hours periods, and percent difference between observed and calculated evaporation. Tables 4.9, 4.10 and 4.11 also include calculated evaporation rates determined by the water activity Eq 2.4. The brine evaporation rates computed by the method of water activity were shown to be closer to the observed brine evaporation rates than those calculated by the aerodynamic equation.

**Table 4.8 Comparison between observed evaporation rates and rates calculated from the aerodynamic equation for fresh water (eighteen replications).**

<u>Vapor Pressure</u> <u>Density</u> ( g/m <sup>3</sup> )						<u>Evaporation Rates</u> ( g/12hrs )		
Rep.	e <sub>s</sub>	e <sub>a</sub>	RH %	h m s <sup>-1</sup>	Pan area m <sup>2</sup>	Calc.	Obs	Percent. Diff.
	Eq (2.14)							
1	12.11	4.79	21	0.021	0.038	252.38	240.47	4.7
2	11.13	4.65	23			223.35	223.84	-0.2
3	11.88	5.15	25			231.98	234.98	-1.3
4	12.27	5.29	26			240.55	232.84	3.2
5	12.35	5.49	26			236.55	222.16	6.1
6	12.59	5.98	28			227.83	227.74	0.0
S.D						10.298	7.02	3.00
Average						235.44	230.34	2.2
7	12.03	5.54	25			223.68	246.08	-10.01
8	12.43	5.36	24			243.73	247.14	-1.40
9	14.67	5.07	23			253.77	258.14	-1.72
10	14.67	4.57	20			244.19	262.78	-7.61
11	11.65	4.22	20			256.13	253.66	0.96
12	12.03	4.33	21			265.61	252.68	4.87
S.D						14.38	6.38	5.49
Average						247.85	253.41	-2.49
13	12.19	5.51	25			230.18	240.48	-4.47
14	11.88	4.66	21			248.87	258.14	-3.72
15	11.65	3.94	17			265.87	260.38	2.07
16	11.57	3.94	18			263.12	263.31	-0.07
17	12.03	4.24	19			268.53	242.84	9.57
18	11.28	4.13	20			246.24	285.14	-15.80
S.D						14.76	16.16	8.41
Average						253.80	258.38	-2.07

**Table 4.9 Comparisons between observed evaporation rates and rates calculated from the aerodynamic equation and the water activity method of brines NaCl and MgCl<sub>2</sub>/KCl at density 1.1 g/ml for six replications**

<b><u>Brine of NaCl</u></b>									
<b><u>Vapor Pressure Density</u></b>					<b><u>Evaporation Rates</u></b>				
( g/m <sup>3</sup> )					( g/12hrs )				
(e <sub>s</sub> ) (Eq.2.13)	(e <sub>a</sub> ) (Eq.2.14)	RH %	h m s <sup>-1</sup>	Pan area m <sup>2</sup>	Calc.	Obs.	Percent. Diff.	Aw analy.lab.	Evp*Aw (Eq. 2.4)
11.37	4.79	21	0.021	0.038	226.83	224.75	-0.93	0.94	226.04
10.42	4.65	23			198.84	215.2	7.60	0.94	210.41
11.16	5.15	25			207.21	219.98	5.81	0.94	220.88
11.52	5.29	26			214.74	218.42	1.68	0.94	218.87
11.52	5.49	26			208.01	208.8	0.38	0.94	208.83
11.81	5.98	28			200.99	213.52	5.87	0.94	214.08
S.D					10.210	5.54	3.47		6.60
Average					209.44	216.78	3.40		216.52

<b><u>Mixed Brine MgCl<sub>2</sub>/KCl</u></b>									
11.74	4.79	21			239.58	218.47	-9.66	0.97	233.26
10.76	4.65	23			210.56	205.42	-2.50	0.97	217.12
11.51	5.15	25			219.27	212.38	-3.24	0.97	227.93
11.88	5.29	26			227.15	212.08	-7.11	0.97	225.85
11.88	5.49	26			220.42	202	-9.12	0.97	215.50
12.18	5.98	28			213.75	205.26	-4.14	0.97	220.91
S.D					10.43	6.10	3.09		6.81
Average					221.79	209.27	-5.96		223.43

Table 4.10. Comparisons between observed evaporation rates and rates calculated from the aerodynamic equation and the water activity method of brines NaCl and MgCl<sub>2</sub>/KCl at density 1.2 g/ml for six replications

<b><u>Brine NaCl</u></b>									
<u>Vapor Pressure</u>		<u>Evaporation Rates</u>							
<u>Density</u>									
( g/m <sup>3</sup> )		( g/12-hrs )							
e <sub>s</sub> (Eq.2.13)	e <sub>a</sub> (Eq. 2.14)	RH %	h m s <sup>-1</sup>	Pan area m <sup>2</sup>	Calc.	Obs	Percent. Diff.	Aw Analy. lab	Evp*Aw (Eq. 2.4)
10.58	5.44	25	0.021	0.038	177.33	211.82	16.28	0.89	219.01
10.92	5.31	24			193.28	212.04	8.85	0.89	219.95
10.92	5.00	23			204.04	223.22	8.59	0.89	229.74
10.24	4.35	20			203.09	224.12	9.38	0.89	233.87
10.24	4.22	20			207.53	220.99	6.09	0.89	225.76
10.58	4.25	21			218.30	222.28	1.79	0.89	224.89
S.D					13.961	5.63	4.74		5.68
Average					200.59	219.08	8.50		225.54
<b><u>Brine MgCl<sub>2</sub>/KCl</u></b>									
11.18	5.44	25			198.01	193.32	-2.43	0.93	228.85
11.54	5.31	24			214.65	197.06	-8.93	0.93	229.84
11.54	5.00	23			225.41	208.74	-7.99	0.93	240.07
10.82	4.35	20			223.08	212.12	-5.17	0.93	244.39
10.82	4.22	20			227.52	206.90	-9.97	0.93	235.90
11.18	4.25	21			238.98	204.22	-17.02	0.93	234.99
S.D					13.843	7.19	4.96		5.94
Average					221.28	203.73	-8.58		235.67

Aw. Analy. lab.: water activity analyzed in the laboratory.

Table 4.11. Comparisons between observed evaporation rate and rates calculated from the aerodynamic equation and the water activity method of brines NaCl and MgCl<sub>2</sub>/KCl at density 1.3 g/ml for six replications

<b><u>Brine NaCl</u></b>									
<u>Vapor Pressure</u>									
<u>Density</u>		<u>Evaporation Rates</u>							
( g/m <sup>3</sup> )		(g/12hrs)							
e <sub>s</sub>	e <sub>a</sub>	RH	h	Pan	Calc.	Obs	Percent.	Aw	Evp*Aw
(Eq.2.13)	(Eq. 2.14)	%	m s <sup>-1</sup>	area			Diff.	Anly. lab	(Eq. 2.4)
				m <sup>2</sup>					
10.12	5.51	25	0.021	0.038	158.75	207	23.31	0.83	199.60
9.86	4.66	21			179.25	180.44	0.66	0.83	214.26
9.67	3.94	17			197.60	205.42	3.81	0.83	216.12
9.60	3.94	18			195.31	205.46	4.94	0.83	218.55
9.99	4.24	19			198.01	220.46	10.18	0.83	201.56
9.36	4.13	20			180.15	262.78	31.44	0.83	236.67
S.D					15.36	27.36	12.28		13.42
Average					184.84	213.59	12.39		214.46
<b><u>Brine MgCl<sub>2</sub>/KCl</u></b>									
11.34	5.51	25			200.77	194.06	-3.46	0.9	216.43
11.05	4.66	21			220.20	176.44	-24.80	0.9	232.33
10.83	3.94	17			237.76	205.24	-15.84	0.9	234.34
10.76	3.94	18			235.20	215.9	-8.94	0.9	236.98
11.19	4.24	19			239.49	198.34	-20.75	0.9	218.55
10.49	4.13	20			219.02	243.37	18.45	0.9	256.63
S.D					14.98	22.67	15.61		14.55
Average					225.41	205.56	-9.22		232.54

#### **4.2.1.3 Comparisons of Data From the Literature With the Present Experiment of Brine Evaporation Reduction.**

There are two ways to compare the reduction in evaporation rate due to salts;

1) the water activity approach that uses the ratio of vapor pressure of brine over that of fresh water; 2) the  $\alpha$  approach, where the ratio ( $\alpha$ ) is computed as the evaporation from saline solutions (E) divided by evaporation from fresh water ( $E_o$ ), assuming constant meteorological conditions.

Oround (1994), Turk (1970), Bonython (1956), and Salhotra et al. (1985, 1987) used " $\alpha$  approach, evaporation ratios" to express the amount of reduction in evaporation due to salts in a solution. Here, the experimental data are compared with those of Oround (1994) and Turk (1970). Computed values of  $\alpha$  for the three pans of different density, as computed from (Eq. 2.10) are presented in Tables 4.12 and 4.13. These tables show the value of  $\alpha$  for each replication of each brine. Also included is the mean value of the 6 replications.

Table 4.12. Computed values of  $\alpha$  (ratio of evaporation from brines and fresh water ) of density 1.1 g/ml.

Rep	$\alpha$ NaCl	$\alpha$ MgCl/KCl
1	0.93	0.91
2	0.96	0.92
3	0.94	0.90
4	0.94	0.91
5	0.94	0.91
6	0.94	0.90
S.D	-	-
Mean	0.94	0.91

Table 4.13. Computed values of  $\alpha$  (Ratio of evaporation from brines and fresh Water ) of density 1.2 g/ml.

Rep.	$\alpha$ NaCl	$\alpha$ MgCl/KCl
1	0.82	0.71
2	0.84	0.72
3	0.80	0.69
4	0.70	0.60
5	0.73	0.62
6	0.80	0.69
S.D	0.1	0.05
mean	0.78	0.67

Notes: Rep. Means replications

$$\alpha_{\text{NaCl}} / \alpha_{\text{MgCl/KCl}} = (\text{Evap. NaCl} / \text{Fresh water}) \text{ and } (\text{MgCl}_2 + \text{KCl} / \text{Fresh water})$$

Comparisons with previous work are rather difficult, because many of the evaporation ratios reported were average values resulting from a variety of climatic conditions. In order to get good agreement between the previous studies and the findings of this study on the relations between salinity and evaporation reduction, one would have to have brines of similar density. Table 4.14. presents

the ( $\alpha$ ) ratio reported by Oround (1994), Turk (1970) and present study.

**Table 4.14. The mean ( $\alpha$ ) of the present study and those presented by other investigators.**

	<u>1.1 g/ml</u>	<u>1.2 g/ml</u>	<u>1.3 g/ml</u>
Oround	0.92	-	0.37
Turk	0.92	0.72	0.35
Present Study	* 0.90 / 0.94	* 0.78 / 0.67	-

\* values for  $\alpha_{\text{NaCl}}$  /  $\alpha_{\text{MgCl/KCl}}$

Dickson et al. (1956) found that synthetic brine solutions at 1.2 g/ml exhibited a lower  $\alpha$  than did samples of the Dead Sea, also at 1.2 g/ml. This suggests that ionic composition can effect  $\alpha$  independently of solution density. The data in Table 4.12 to 4.13 do not exhibit this behavior. This may be due to the simplified nature of the solution chemistry.



#### 4.2.2 Evaporation Under Free Convection

In the trials of evaporation under free convection, the temperature and humidity remained almost constant during data collection and the evaporation rates were much lower. It is therefore possible to show the relationship between evaporation rates and density more clearly. Figure 4.6 shows evaporation rate decrease as the density increases.

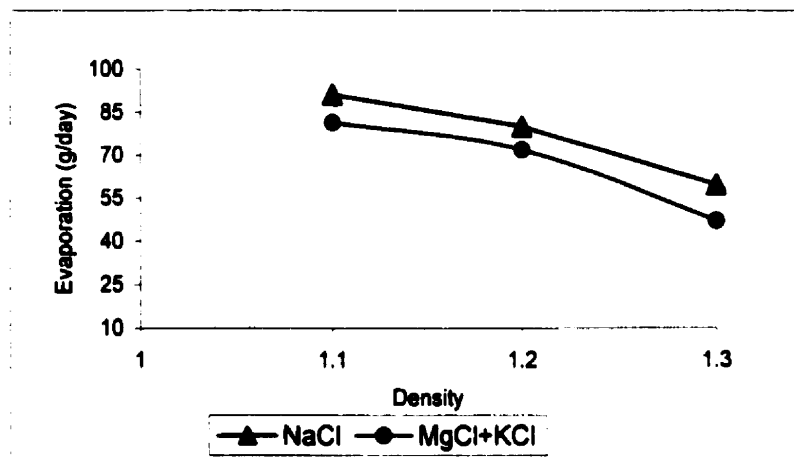


Figure 4.6. Brine evaporation rate versus density.

Observed evaporation rates of brine  $\text{MgCl}_2/\text{KCl}$  were lower compared to that of the  $\text{NaCl}$  brine since, at the same density, more ions are present due to the contribution of the tri-atomic constituent  $\text{MgCl}_2$ . The ionic ratio at the same weight (w) is :

$$\frac{\frac{w}{58.45}}{\left( \frac{0.5 * w}{74.45} + \frac{0.75 * w}{95.23} \right)} = 1.17$$

This shows that the vapor pressure lowering effect of a given weight of NaCl in solution should be 3 -10 % greater than that of the same weight of an  $\text{MgCl}_2/\text{KCl}$  mixture in equal proportions, as would be predicted by Raoult's Law, up to the saturation limits.

## 5.0 CONCLUSIONS

The following conclusion can be drawn from the current study:

It is important to consider the ionic species present in a brine of a given density in order to permit estimation of the evaporation rate by accepted equations (Eq. 2.4) involving meteorological conditions. This conclusion issues from the confirmation that Raoult's Law of equation (Eq. 2.2) and Harbeck's (1955) equation (Eq. 2.6) apply. Neither of these equations is directly density-dependent. Furthermore, observed differences in evaporation rates between the NaCl brine and the  $\text{MgCl}_2/\text{KCl}$  mixture at the same density indicate a difference explainable by the ionic ratio between the two brines.

This conclusion disagrees with previous statements that indicate that the density is the overriding consideration in determining evaporation rates from brines. The work done here proves that although density is important, significant errors in predicting evaporation rate can occur if the ionic composition is ignored. For example, the vapor pressure reduction due to NaCl should be 3 -10% greater than that expected due to an  $\text{MgCl}_2/\text{KCl}$  mixture (1:1 ratio) of the same density. It is therefore necessary to know what the dominant salt constituent is in a given brine if the evaporation rate is to be predicted more accurately than presently possible basing the analysis on density alone.

The evaporation rates calculated by the aerodynamic equations at a boundary layer conductance of  $0.021 \text{ m s}^{-1}$ , and by the water activity method, were shown to be close to the observed evaporation rates.

The free convection experiment demonstrated that brine evaporation rates decreases as solution density increase.

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## **APPENDIX "A"**

**DATA - WITH WIND EXPERIMENT  
AND  
DATA OF - NO-WIND EXPERIMENT**

Date	Time hour	Room Temp & RH		Fresh Water		solution 2 NaCl (1.1) g/ml		solution 3 MgCl + KCl (1.1) g/ml		Air Temp.
		RH (%)	T °C	evap (g)	T, °C	evap (g)	T, °C	evap (g)	T, °C	
26/2	9 <sup>30</sup>	24.7		-	-	-	-	-	-	
	10 <sup>30</sup>	24.7	27.1	25.48		23.34		23.46		
	11 <sup>30</sup>	24.7	26.6	21.16	-	20.24	-	20.36	-	-
	12 <sup>30</sup>	24.7	26.3	19.76		18.76		18.96		
	13 <sup>30</sup>	24.8	26.2	19.92		18.82		18.20	-	-
	14 <sup>30</sup>	-	26.0	19.74		18.68		18.80		
	15 <sup>30</sup>	-	-	19.30		18.24		18.64	-	-
	16 <sup>30</sup>	-	-							
	17 <sup>30</sup>	24.3	26.1	39.48		36.70		37.50		
	18 <sup>30</sup>			18.16		17.42		17.26		
	19 <sup>30</sup>	22.2	25.9	19.08		17.62		18.14		
	20 <sup>30</sup>	21.9	26.0	18.60		16.72		17.46		
	21 <sup>30</sup>	21.4	26.0	19.79	14.8	18.21	16.3	18.69	15.9	25
27/2	12 <sup>hour</sup>			240.47		224.75		218.47		
	21 <sup>30</sup>	--	--	--	--	--	--	--		
28/2	12 <sup>hour</sup>		24.6	223.84	13.5	215.20	14.5	205.42	14.2	23

Date	Time	Room Temp & RH		Fresh Water		solution 2 NaCl (1.1) g/ml		Solution 3 MgCl <sub>2</sub> + KCl (1.1) g/ml		Air Temp
	Hour	RH (%)	T °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	Evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C
28/2	10 <sup>25</sup>	24.3	25.5	-	-	-	-	-	-	
	22 <sup>25</sup>	25.8	26.7	234.49	14.5	219.98	15.9	212.38	15.6	23.3
	22 <sup>45</sup>	-	-	-	-	-	-	-	-	-
28/2	10 <sup>45</sup>	25.8	27.8	232.84	15	218.42	16.1	212.08	15.7	23.1
	11 <sup>00</sup>	-	-	-	-	-	-	-	-	-
	23 <sup>00</sup>	25.8	28.9	222.16		208.80		202	16.1	23.7
	23 <sup>10</sup>	-	-	-	-	-	-	-	-	-
1/3	11 <sup>10</sup>	30.8	25.4	227.74	15.4	213.52	16.1	205.26	16.2	23.9

Date	Time	Room Temp & RH		Fresh Water		solution 2 NaCl (1.2) g/cm <sup>3</sup>		solution 3 MgCl <sub>2</sub> + KCl (1.2) g/cm <sup>3</sup>		Air Temp
	hour	RH (%)	T °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C
4/3	20 <sup>10</sup>	25.8	26.4	-	-	-	-	-	-	
5/3	8 <sup>10</sup>	23.6	26.8	246.08	14.7	211.82	16.7	193.32	16.5	24.2
	8 <sup>20</sup>	-	-	-	-	-	-		-	-
5/3	20 <sup>20</sup>	24.9	26.8	247.14	15.2	212.04	17.3	197.06	16.5	24.5
	20 <sup>30</sup>	-	-	-	-	-	-		-	-
6/3	8 <sup>30</sup>	21.6	26.8	258.14	15.2	223.22	17.8	208.74	16.8	24.2
	8 <sup>40</sup>	-	-	-	-	-	-		-	-
	20 <sup>40</sup>	20.0	26.9	262.78	14.2	224.12	16.7	212.12	15.6	24.2
	20 <sup>55</sup>	-	-		-	-	-		-	-
7/3	8 <sup>55</sup>	19.8	26.7	253.66	14.2	220.99	16.8	206.9	15.6	23.7
	9. <sup>00</sup>	-	-	-	-	-	-		-	-
7/3	21. <sup>00</sup>	23	26.5	252.68	14.7	222.28	16.8	204.22	15.8	23.0

Date	Time	Room Temp (°C) & RH (%)		Fresh Water		Brine 1 NaCl (1.3) g/ml		Brine 2 MgCl <sub>2</sub> + KCl (1.3) g/ml		Air Temp
	Hour	RH. (%)	T °C	evap (g)	T <sub>s</sub> °C	Evap. (g)	T <sub>s</sub> °C	Evap. (g)	T <sub>s</sub> °C	T <sub>a</sub> °C
10/3	10 <sup>05</sup>	25.0	27.2	-	-	-	-		-	
	220 <sup>5</sup>	25.3	26.6	240.48	14.9	207.00	18.4	191.83	17.8	24.3
11/3	9 <sup>15</sup>	25.0	27.2							
	21 <sup>15</sup>	17.6	26.6	258.14	14.5	180.44	17.9	174.27	17.5	-
	21 <sup>30</sup>	17.6	26.6	-	-	-	-		-	-
12/3	9 <sup>30</sup>	16.9	26.6	260.38	14.2	205.42	17.7	203.07	16.8	
14/3	12 <sup>30</sup>	23.4	25.4	-	-	-	-		-	-
15/3	0 <sup>30</sup>	18.4	27.5	263.31	14.1	205.46	18.2	213.73	16.8	-
	0 <sup>40</sup>						-		-	-
15/3	12 <sup>40</sup>	20.3	28.4	242.84	14.7	220.46	18.4	196.17	17.6	-
15/3	040	17.4	27.5	285.14	13.7	262.78	18.8	241.20	16.4	

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.1 g/ml	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C		T °C
Pan # 1	95.2	22.3	84.3	21.8				40	25
Pan # 2	98.8	22.2	86.7	21.8					
Pan # 3	97.2	22.1	79.32	21.6					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.1 g/ml	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH %	T °C
Pan # 1	93.10	22.3	73.31	21.7				40	25
Pan # 2	82.24	21.8	72.95	21.8					
Pan # 3	87.45	21.9	85.45	21.6					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.1 g/ml	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH %	T °C
Pan # 1	86.51	21.8	83.43	21.9				40	25
Pan # 2	87.8	21.9	76.61	21.8					
Pan # 3	90.69	21.9	91.20	22.2					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.2g/ml	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH %	T °C
Pan # 1	75.14	21.8	61.59	22	106	20.5	25.5	40	25
Pan # 2	70.34	21.2	100.39	20.1					
Pan # 3	84.17	21.8	81.38	21.1					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp	Room Condition	
Density 1.2g/ml	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH %	T °C
Pan # 1	72.28	21.7	69.63	22	102	20.5	25.5	40	25
Pan # 2	77.75	21	101.46	21.8					
Pan # 3	83.13	21.9	76.48	21.3					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.2g/ml	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH %	T °C
Pan # 1	66.36	20.7	44.99	22	100.5	20.5	25.5	40	25
Pan # 2	85.4	22.2	62.38	21.1					
Pan # 3	71.93	21.9	48.98	23					

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.3 g/ml	evap (g)	T <sub>s</sub> °C	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH (%)	T °C
Pan # 1	51.28		43.91		104.72			40	27
Pan # 2	63.02		50.39						
Pan # 3	56.72		49.41						

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.3 g/ml	evap (g)	T <sub>s</sub> °C	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH (%)	T °C
Pan # 1	65.25		53.94					40	27
Pan # 2	53.12		78.28						
Pan # 3	59.55		84.42						

	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.3 g/ml	evap (g)	T <sub>s</sub> °C	Evap (g)	T <sub>s</sub> °C	evap (g)	T <sub>s</sub> °C	T <sub>a</sub> °C	RH (%)	T °C
Pan # 1	62.61		43.1					40	27
Pan # 2	53.12		75.35						
Pan # 3	69.21		84.14						



	NaCl		MgCl <sub>2</sub> /KCl		Fresh Water		Air Temp.	Room Condition	
Density 1.3 g/ml	evap (g)	T, °C	Evap (g)	T, °C	evap (g)	T, °C	T <sub>a</sub> °C	RH (%)	T °C
Pan # 1	64.94		43.67					40	27
Pan # 2	59.38		41.37						
Pan # 3	56.56		45.25						