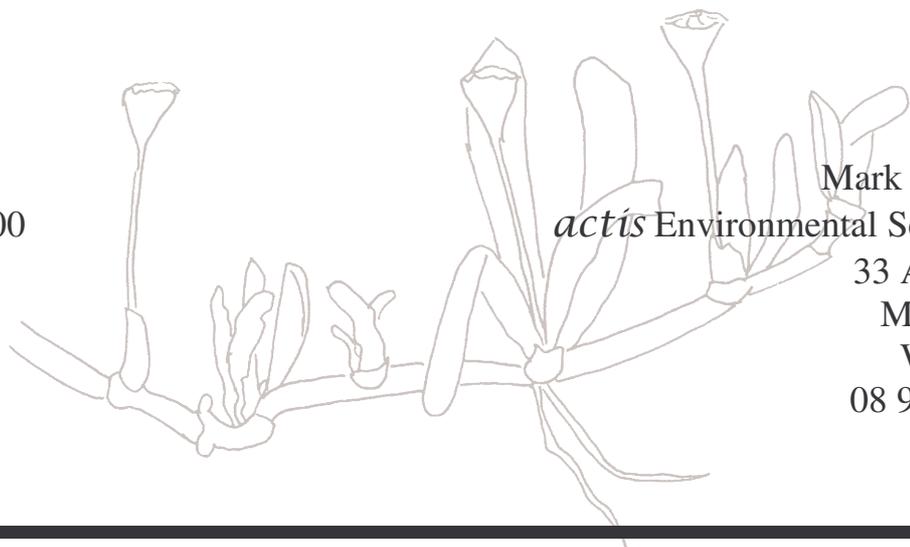# Review and Discussion on the Evaporation Rate of Brines

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Contents

1 Executive Summary

Evaporation of water from saline groundwater stored in disused pits at Placer (Granny Smith) is seen as an important mechanism for reducing the volume of groundwater stored. This report reviews some of the fundamental processes involved in the phenomena of evaporation, highlights the strengths and weaknesses of methods used to model evaporation, speculates on the expected evaporation in the practical application of filling a pit, and discusses methods of increasing evaporation from the pit.

A term introduced in this report, although it is common in other fields, is the term effective evaporation. This term simply refers to the expected evaporation of water, expressed as height loss, from the body of water under discussion. Effective evaporation is often derived from the evaporation reported by the Bureau of Meteorology as pan evaporation that refers to evaporation of freshwater from a small pan of water.

The lack of air circulation, a greater rainfall catchment area than evaporation area, and reduction of incident solar energy on the water surface will reduce the effective evaporation from a pit. Effective evaporation will also be reduced by the following factors irrespective of whether the evaporation takes place in a pit; reduced vapour pressure due to salinity and increased local humidity.

Spraying the discharge water into the air is considered a method of significantly increasing evaporation, as is wetting the rock face of the pit which is being heated by the solar rays.

It was estimated that the effective evaporation from a saline water body at the surface would be on average 1400 mm per year. If the brine were sprayed over a full pit the effective evaporation would be approximately 1800 mm per year (128%). If the brine were sprayed over an empty pit the effective evaporation would be approximately 900 mm per year (61%). This figure is conservative, as the spray would collect additional energy from the heated rocks on the pit wall. The effective evaporation from a nearly empty pit would be approximately 600 mm per year (43%).

Various commercial 'vaporisation' units are available, which would greatly enhance the effectiveness of spraying the brine over a pit. These units are energy intensive, but would probably return a higher rate of evaporation of approximately 130%.

It is suggested that the loss of solar energy for evaporation in a less than full pit be estimated and potential methods of validating effective evaporation estimates be investigated. If the brine is to be sprayed over the pit, the risk of increased corrosion in existing plant should be assessed amongst other costs.

2 Introduction

The scope of this report is to review the literature relevant to the evaporation of brines, and collate the basic principles of evaporation in a single document.

3 Evaporation Principles

3.1 Definition of Evaporation

Interestingly evaporation is often not defined in pure chemical and physics texts (for instance (Weast, Astle et al. 1986)). This is because evaporation is a non-technical interpretation of more fundamental physical processes. Evaporation or condensation occur when a liquid is not in equilibrium with its vapour or gas phase. Therefore, evaporation can be defined as the physical process in which a liquid is changed into a gas by molecular transfer. Condensation is the reverse process.

Evaporation is often misleadingly defined as '*the transfer of water from the liquid state*" ((Linsley, Franzini et al. 1992) p.28), though this definition is adequate for most purposes. It is, however, misleading because water is not the only substance evaporated in ambient temperatures. All liquids evaporate, including glass, mercury and ethanol. It is also misleading because it does not impart any understanding of the process of evaporation.

3.2 Vapour Pressure

Evaporation can be better understood by understanding the notion of vapour pressure of a liquid. Molecules in a liquid are in constant movement. The average rate of movement depends on the kinetic energy of the system, which is indirectly measured as temperature. Molecules with high kinetic energy will often move away from the attraction of the other molecules into the ambient gas or air, as it mostly is. These molecules may remain as a gas or vapour or return to the liquid phase. All liquids emit these molecules as a vapour, causing the liquid to have a vapour pressure over the surface of the liquid. The liquid will continue to have a net movement of molecules to the ambient gas until equilibrium is reached. The vapour pressure at equilibrium (Vapour Pressure) is dependant on the kinetic energy (i.e. temperature) and the property of the liquid. Glass, for instance, has a very low Vapour Pressure at ambient temperatures. As the temperature of the liquid increases then so the equilibrium vapour pressure of the liquid increases. As the temperature of the ambient gas (air) increases then the partial pressure of liquid in the gas (relative humidity) decreases for a constant mass of vapour.

The principles of the evaporation process are rather simple. Evaporation is the process of equilibrating the vapour pressure of the liquid to the equilibrium partial vapour pressure of the liquid in the ambient gas or air. Increasing evaporation means doing one of the following,
- increasing the equilibrium vapour pressure of the liquid,
- decreasing the equilibrium partial pressure of the liquid in the ambient gas or air, or
- increasing the rate of transfer from the liquid to the gas state.

For the purposes of this report, the following discussion will focus on the evaporation of water from an aquatic solution or brine in ambient air. This will allow for a more specific discussion.

3.3 Equilibrium Vapour Pressure of Brines

The equilibrium vapour pressure of pure water is well known and defined in many texts (for instance (Weast et al. 1986)).

The difference in vapour pressure between water at 30 degrees (31.824 mm Hg) and 40 degrees (55.324 mm Hg) Celsius is an increase of 73%. Temperature increases the amount of vapour suspended over of body of liquid (water) at equilibrium.

The temperature of a brine or water in a field situation is dependant on the incident solar radiation as the (only) source of energy input. To maximise the temperature of an evaporating solution, it is important to expose the water/brine to the greatest solar radiation and retain as much of the incident radiation as possible; minimising heat loss in reflection and absorption through the ground, with the only energy loss through evaporation.

The area of the evaporating brine exposed to incident radiation is therefore critical; this is normally interpreted as surface area of the evaporation pond but may not always. As the area covered by brine increases, the greater the potential incident radiation.

Loss of incident radiation through reflection is an important consideration when the water being evaporated is brine. This is because the salt precipitated from brine increases the reflection and therefore heat loss. This is countered commercially by the use of dyes to increase solar absorption or by increasing the depth of the brine being evaporated. Increasing the depth of brine reduces the chance of the solar energy being reflected before the energy has been absorbed. The optical density of brines increase with salinity (Buch, Chaudhari et al. 1993) meaning more efficient light absorption and the conversion of light to heat is higher for a smaller depth of brine than pure water. In practice, if the depth of brine is greater than 50cm then changing the absorption and reflective characteristics of the brine is not considered commercially viable for salt production. The criteria, of course would be different for the current application.

In theory, it is possible to lose energy through diffusion of heat to the atmosphere. In practice this is not a major heat loss compared to the loss of heat through water vapour or evaporation.

Dissolved salts decrease the vapour pressure of an aqueous solution. Brines have a lower equilibrium vapour pressure at the same temperature as pure water. This effect is well recognised by solar salt and vacuum salt manufactures (Forrest and Worthley 1964; Bonython 1966; Garrett 1966; Deflers P 1970; Salhotra, Adams et al. 1985; Steinhorn 1991). Buch et al. (1993) is a particularly good reference for the physical properties of seawater concentrates, including vapour pressure and surface tension. Laborde (1983) provides a mechanism for calculating evaporation rates from the concentration of magnesium in brines. To minimise the effect of the equilibrium vapour pressure decreasing with salinity in commercial solar evaporation plants, brines are separated into an evaporating sequence over a number of ponds, from lowest salinity to highest salinity, with the highest salinity ponds windward of the lower salinity ponds. The mean vapour pressure of the brines in ponds in a salinity sequence is higher than the vapour pressure of sole pond with homogenous brine (this can be demonstrated using calculus).

The author is not aware of any method of increasing the equilibrium vapour pressure of the brine without diluting, which is contrary to the objective of reducing the volume of brine. Reducing the surface tension may have the effect of increasing the evaporation rate but the surfactants can also cause a film to form over the surface increasing the energy needed for water vapour to escape the water body.

3.4   Partial Pressure of Water in Air

As for the vapour pressure of water, the equilibrium partial pressure of water in air is mostly dependant on the temperature of the air and is not easily manipulated.

Another factor that affects the equilibrium partial pressure of water in the air is the air pressure itself. A drop in air pressure will often result in precipitation of water (rain). There are local changes in the partial pressure of water in air. A cold area out of the sun is likely to have a higher relative water partial pressure but these situations are indicative of disequilibrium states.

3.5 Rate of Transfer

The rate of water transfer from a water body to the air is directly dependent on the surface area, and the relative difference between the equilibrium vapour pressure of the water to the existing partial pressure of water in the air.

Water bodies can effectively form an insulating cover of water vapour over the surface. The air immediately adjacent to the water body can be at equilibrium pressure and gradually becoming less at a distance from the surface. This phenomenon is well known and has been experienced by most people in the form of a cool sea breeze or lake breeze. Bonython (1966) describes the factor in his paper. The initial laminar layer (only millimetres thick) adjacent to the water body is controlled by molecular diffusion. At a greater height above the water, the water vapour is mixed via a process of eddy diffusion. In a small water body such as the Class A evaporating pan the eddy diffusion would not be a limiting factor at all. The larger the water body, the larger the influence or resistance to evaporation due to water vapour in the upper layers. This layer has been found to be only several metres thick in open lakes but in an enclosed pit situation it may be 50 metres thick or more. Figure 1 in Bonython (1966) allows us to postulate that evaporation in a large lake would be 73% of a Class A evaporation pan, while evaporation in a deep pit, given constant values for all other variables would be 65% of a Class A pan. The wind velocity in a pit would not reach the levels of that at the surface so the loss of evaporation in a pit would be much greater than 8-9%.

The surface area issue is important from the point of extending the potential total solar radiation. It is also important in increasing the rate of water vapour transfer to the atmosphere. Surface area can be increased by spraying water droplets, aeration, waterfalls, wave action, and as mentioned before increasing the flat area of the evaporating water body. Small droplets have a much larger surface area to a flat surface. Evidence from AgWA experiments suggest that spraying in an irrigation situation increases the evaporation by 25%. This figure should be used with some caution as a) the water was freshwater and b) the data was collected in an experiment where the question was how much water is reaching the plants, not how much additional water is lost using sprays. It is a reasonable hypothesis to make that the spraying of brine negates the resistance to evaporation by eddy diffusion, and that the evaporation rate from sprays approaches that of a Class A pan.

4 Measurement of Evaporation

Evaporation is not a simple phenomenon to measure, as it is a cumulation of a number of chemical, physical and meteorological variables. It should not be surprising that the measurement of evaporation has been approached from a number of different levels and using different technologies.

The Bureau of Meteorology itself has used a number of methods over time. These include evaporating pan designs starting with a tiled pit in the ground that was replenished with water every day. This was followed by a 'sunken pan', which is a hybrid of the tiled pit, and finally the present day 'Class A' pan. The sunken pan was phased out approximately 50 years ago. The tiled pit suffered from leaks that were not identifiable until they were major. The sunken pan was a useful compromise as the temperature of the evaporating pan did not fluctuate wildly with the ambient temperature and was more representative of what was happening in larger ponds or lakes. The 'Class A' is quite different from the other pans in that it does not have an insulating layer and is elevated in the air by 20cm or so. Measurements are affected by wind velocity and ambient temperature in a more erratic fashion than the other direct evaporation methods. More recently, in the 1980's all official evaporation pans were fitted with a birdcage to stop birds and small mammals drinking and bathing in the water. The birdcage has the effect of reducing the apparent evaporation by 8% by reducing the wind velocity and maintaining the water vapour envelope over the water. BOM stations were not required to note the addition of birdcages to the pans, as it can only be assumed that it was thought the loss to animals was of an equal but undefined magnitude. Evaporation from a pan is expressed as millimetres per day. The direct reading of changes in height of water in the pan (nett evaporation) is converted to gross evaporation by adding the rainfall to the daily height differences in the pan. This latter figure is what is recorded.

Pan evaporation provides the basis for the mass balance calculation of evaporation. By itself it is a pointless expression of lake evaporation either freshwater or saline, but as a variable in calculating local potential evaporation it is very useful.

A common equation for estimating evaporation from a large saline water body is as follows:
Evaporation = Lake Factor * Salinity Factor * (Pan Evaporation – Rainfall)

Evaporation, Pan Evaporation and Rainfall have the same units and are normally expressed in millimetres per day. As mentioned before the Lake Factor is normally assumed to be 70% or 0.7 but this may be less as in the example of a pit where it would drop to at least to 0.65. The Salinity Factor is normally assumed to be 0.7 for saturated brines. An algorithm determined from empirical data is:
Salinity Factor = 1-salinity ($^0/_{00}$)*0.00086
Another useful reference is Joshi and Bhatt (1983).

Surprisingly its use is not commonly reported in the literature, although it is used in practical applications such as solar salt operations and agricultural irrigation. The reason for this, it is felt, is that it makes assumptions that, while are useful for long term average estimates, are suspect outside of basic well tested environments. Also, until the common use of computers, it was the only easy and relatively accurate means of estimating long-term evaporation.

A common mass balance equation in use is known as the Dalton Equation. It does not include a pan evaporation variable and relies on water vapour and wind velocity readings to determine evaporation.

The Dalton equation is:

$Eo = k*u*(e_s - e)$ kg/(m2.s)

where k is a factor related to surface roughness (in units of 0.01 s2/m2), u is the wind speed (m/s), e_s is the saturation water vapour pressure at screen temperature (hPa), e is the vapour pressure of the air (hPa).

Mass balance models are not considered by some (Hargraves 2000 pers. comm.) as being robust because of the unique scaling factor needed for lake size, and also hot air thermals can disrupt laminar flow calculations. Although this view is not unanimous (see Jacobsen and Ore (1974)).

A more common method used in the literature for determining evaporation is based on the solar energy input to the system. This method is apparently more reliable and does not require such an extensive history of meteorological data. Apparently, the Penman's Equation and its various modifications, is the most common (see 6.1).

It has been the experience of the author that the Dalton and Penman methods of determining evaporation are sensitive to the data used to estimate the estimated evaporation. They both rely on constant monitoring of meteorological parameters, and are influenced to a large degree by local conditions that may not reflect the body of water that is being modelled. Typically, field data records are not complete and the estimation suffers because of this. The advantage of these equations is that with a complete data set collected from an appropriate location, the equations will model water bodies in atypical situations, like that in a pit. The evaporation pan method has not the finesse of the Dalton and Penman methods but the method is very robust in approximating evaporation over long periods. It is suggested that pan evaporation is always used where possible as fall back for other estimations.

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6 Appendix

6.1 Formula

Penman's equation for lake evaporation taken from
http://web.bham.ac.uk/ceu716/msc/node49.html.

Penman published an important paper in 1948, which allows calculation of the rate of evaporation
Eo from a water surface like that of a lake, too large to be much affected by the additional
evaporation that occurs at the edge. It is founded on six basic equations -

1. The Dalton equation (Note 4.E)

$$Eo = k.u \ (es - e) \qquad kg/(m2.s)$$

where k is a factor related to surface roughness (in units of 0.01 s2/m2), u is the wind speed (m/s),
es is the saturation water vapour pressure at screen temperature (hPa), e is the vapour pressure of
the air (hPa).

2. The definition of the 'diffusion resistance' ra between water and air -

$$ra = r.c/ \ (Ks.L.k.u) \qquad s/m$$

where r is the density of the air (kg/m3), c is its specific heat (J/kg.K), Ks is the pyschrometric
constant in Regnault's equation (hPa/K - see Section 6.3), L is the latent heat of evaporation
(J/kg).

3. The definition of the 'saturation deficit' S -

$$S = es - e \qquad hPa$$

4. The 'psychrometric slope' D, the tangent to the saturation vapour pressure/temperature curve,
defined as follows -

$$D = (es - ew) / (T - Ts) \qquad hPa /K$$

where ew is the saturation water vapour pressure at the water surface temperature Ts, and T is the
air temperature (°C).

5. The convective heat flux H from water surface to air -

$$H = r.c \ (Ts - T) / ra \qquad W/m2$$

6. The energy balance at an insulated ground surface (see Section 5.1) -

$$Rn = L. \ Eo + H \qquad W/m2$$

where Rn is the net radiation inflow.

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Then those equations can be combined:

7. First 1 & 2 can be combined to produce

$$E_o = r.c \ (e_w - e) \ / \ K_s \ . \ r_a$$
$$\text{kg/(m2.s)}$$

(*)8. Then split the term (e_w - e), using equations 3 & 4, as follows -

$$e_w - e = (e_w - e_s) + (e_s - e) = D \ (T_s - T) + S$$
$$\text{hPa}$$

9. Combine equations 7 & 8 -

$$E_o = r.c \ [D(T_s - T) + S] \ / \ K_s.L.r_a$$
$$\text{kg/(m2.s)}$$

10. Rearrange 9 thus -

$$r.c.D(T_s - T) = K_s.L.E_o. \ r_a - r.c.S$$
$$\text{J.kg/(m4.s2.K)}$$

11. Combine 5 & 10 -

$$H = [K_s.L. \ E_o - r.c.S/ \ r_a] \ / \ D$$
$$\text{W/m2}$$

12. Then join 6 & 11 -

$$L. \ E_o = (D.R_n + r.c.S/ \ r_a) \ / \ (D + K_s)$$
$$\text{W/m2}$$

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Penman, H.L. 1948: Natural evaporation from open water, bare soil and grass. Proc. Roy. Soc. A, 193, 120-45.