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# Theoretical Analysis of Saline Diffusion during Sodium Chloride Aqueous Solutions Freezing for Desalination Purposes

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**Abstract:** Considering the important demand of fresh water and its scarce availability, water desalination is an interesting technology, producing about 44 Mm$^3$/year worldwide, but, in general the most common desalination techniques are highly energy demanding. Freezing-Melting (F/M) desalination uses just up to 70% less thermal energy, but is the least used process mainly, due to the difficulty of the salt separation. This study proposes a model able to analyses the thermodynamic potential that allows the salt diffusion during the F/M process, using an aqueous solution of sodium chloride. This should allow to obtain a sensitive analysis of the process to promote the separation between the high concentration brine and the ice with liquid separation by physical process. The unidimensional model is based on the evolution of both processes: thermal and mass diffusions, depending on temperature and saline gradients, predicting whether the salt will remain inside the ice or not. Thus, the thermal potential is adjusted to frozen only when the salt has been "pushed" towards the brine. Mostly models have base their results on the assumption of a "certain value of saline concentration of the liquid fraction", value in which there is great disagreement. In this paper the calculations are based on the concentration in the solid-liquid interface, which has been extensively studied and there is a coincidence in those results, being the main advantage of the proposed model.

**Keywords:** freezing/melting desalination process; aqueous solutions of sodium chloride; theoretical diffusive models

## 1. Introduction

The desalination process aims to obtain water suitable for human consumption (Castillo and Pilatowsky, 2013), which is important but cost-and energy intensive process (Erlbeck *et al.*, 2017). Numerous methods have been used, nevertheless, until June 2016, the 51% of seawater on the world, was desalted by a Multi-Stage Flash (MSF), a thermal process accompanied with high environmental impact due to the high consumption of hydrocarbons (Guevara and Stabridis, 2008). About 10,000 tons of oil were used in the world to produce 1000 m3/day of desalinated water (Ghalavand, Hatamipour and Rahimi, 2014).

Freezing/Melting (F/M) has the advantage to be the most theoretically energy-efficient desalination processes. This low consumption is due to the fact that the latent heat of melting of the ice is only 334 kJ/kg against 2,257 kJ/kg for its vaporization, so the process of the F/M could save up to 70% of the energy required by the thermal conventional desalination processes (Williams *et al.*, 2015), (Mtombeni, T., Maree, J.P., Zvinowanda, C, 2013). The most commercial process is Reverse Osmosis, which is the more used technology for brackish water desalting, near to 84% on the world, (IDA Desalination, 2017). However, the problem of membrane replacement persists, no being the case of the F/M process.

The F/M process can remove dissolved salts in solutions during the formation of ice crystals (Johnson, 1976; Jungwirth, 2005; Blank, Tusel and Nisanc, 2007). Freezing has been used to separate a wide variety of contaminants from water, such as minerals, organic chemicals and dissolved particles. In addition to low energy consumption, it operates at low temperature, minimizing corrosion problems and allowing low cost materials such as plastic. A pre-treatment is not required, thus avoiding the use of chemicals and implies minimum environmental impact (Rahman et al. 2007, (Johnson, 1979; Mandri *et al.*, 2011).

During the decades of the 1960s and 1970s, there were several attempts to commercialize this technology, which has continued its development for 45 years, through many technological innovations (Thompson and Nelson, 1954; Marshall, Goff and Hartel, 1967; Curran, 1970; Rice and Chau, 1997) and countless pilot plants.

However, this operation stays having many drawbacks compared to reverse osmosis and thermal processes, such as high capital costs. However, the most difficult problem to solve has been the entrapment of salts in the ice during the crystallization, hindering their separation, and requiring for it, crushing and recrystallization of the ice, which increases operating costs (Wiegandt and Berg, 1980; Subramani and Jacangelo, 2015).

Ice quality depends on several factors linked mainly to freezing process kinetics. The objective is to eject salt in a small volume of unfrozen brine. However, it often occurs that some salts are trapped in the ice crystal, even independently of the solubility of the salts in ice (Jungwirth, Vrbka and Jungwirth, 2005). Research works have been oriented towards reaching a lower water salinity. Thus, Yoshihito Shirai proposed to use agitators and fan to circulate the solution and cold air to improve heat and mass transfer, additionally an seed ice was integrated (Shirai *et al.*, 1998). (Yu, Ma and Zhang, 2007) find that at low initial solution temperature (about 6oC), the temperature of coolant, the solution concentration and the re-crystallization process as important factors to obtain a mayor purity of the ice produced. Experiments have also been conducted at different salt concentrations, stirring velocity in the separation vessel, as well as increase the number of washing steps to determine if the mentioned parameters can reduce the effects on salt retention.

In an experimental study, the desalination rate positively correlated with freezing temperature while negatively correlated with freezing rate, the solid fraction, solution concentration and the surface area of the freezing container (Luo et al. 2010). Reddy et al proposed that an agitator can reduce the salts encapsulated in crystals (Reddy *et al.*, 2009).

(Erlbeck *et al.*, 2017), carried out important research on the effect on efficient desalination with different methods as cooled plate with several operation conditions and their dependence on ice production, the heat transfer via droplets of non-miscible organic fluids and classical crystallization with stirred, then, they add a post treatment to produce usable water.

### *1.1. Theoretical studies*

Some authors introduced the conditions prevailing in the interface, the latent heat and the rejection of the salts were accomplished (Körber, Scheiwe and Wollhöver, 1983). The position and advancement of the interface is not known a priori but should be determined through the mechanisms of mass transport and brine properties depending on concentration.

Other theoretical works studied the combination of thermal behavior, heat transfer and liquid-solid phase-change. (Voller and Cross, 1981), describe an extension to the explicit finite difference solution to the enthalpy formulation, which describe an accurate solution to Stefan problems. The temperature distribution, the phase of change position and its velocity, using a finite difference method for a melting problem for different materials were evaluated (Savović and Caldwell, 2003). A complete list of studies of phase-change phenomena from solid to liquid or solid to gas was presented (Yao and Prusia, 1989).

In other research, mathematical models used finite differences to approximate the crystal growth and the temperature distribution, as well as the position and velocity of the interface in motion (Orcutt, 1969), in relation to solute distribution during freezing, (Terwilliger and Dizio, 1970; Körber, Scheiwe and Wollhöver, 1983). The solute distribution coefficients were also determined. Measurements of temperature and concentration profiles were performed (Weeks and Lofgren, 1967; Grange, Viskanta and Stevenson, 1976; Wollhöver *et al.*, 1985; Kapembwa, Rodríguez-Pascual and Lewis, 2014). The phenomenon of solute or impurity rejection at the solid-liquid interface stayed far from understanding (Grange, Viskanta and Stevenson, 1976). However, most of the works do not consider the physical properties changes of the saline solution which have no constant concentration, leading to inaccuracies in their calculations. The present work aims to analyze profiles of both temperature and salinity applying the mains heat and mass transfer equations, providing information to promote the diffusion of the salt, by the temperature gradient. Other factors as the initial saline concentration, recipient dimensions or geometry for instance should be considered to obtain a better of salt separation from ice being the temperature gradient the most important to produce an acceptable fresh water quality. This process has not been widely commercially used for desalination purposes but however this technology had been applied in the food Industries.

## 2. Physical model

Based on the literature reviewed a lack information about saline solution freezing and salt rejection was found. Especially the effect of concentration gradient on the physical properties of the solution, such as: density, freezing point, thermal conductivity, thermal coefficients, kinematic viscosity, etc. consequently, a physical model is proposed, which allows their calculation.

### *2.1. Description*

This physical model consists in a horizontal transparent cylinder which was thermal insulated except in one flat side to drive the heat flow in a unidimensional x-direction. The non-insulated surface was exposed to the cold air at temperatures Ta below the freezing point of saline solution. Depending on both, brine and air temperatures; Tb and Tair, respectively, ice formation evolution take place at the solid-liquid interface. When Tair is below saline solution freezing point and Tb higher than the temperature of interface surface of ice, the heat transfer should be performed from brine towards the cold air. The heat transfer is carried out by natural convection between the brine and the ice formed and between the cylinder surface and cold air. By conduction through the ice and the cylinder material thickness. Figure 1 shows the container of saline water.

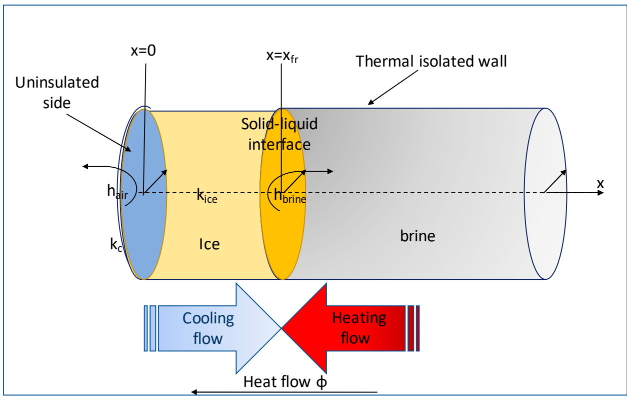

**Figure 1.** Scheme of the physical model

Temperature values and their gradients should be defined to: 1. produce ice at the solid-liquid interface, and 2. Operate the cooling flow to remove both solidification latent heat of water and heat sensible for ice sub-cooling. The correlation between the ice formation kinetics and the diffusion time. Ice formation should be performed progressively so that it allows to transfer the ions to the brine.

### *2.2. Heat transfer Model description*

#### 2.2.1. Main equations

Freezing cannot be simulated as a simple general equation of heat conduction, which only governs the solid phase. For the sensible heat transfer, the model is normally formulated for one-dimension thermal conduction.

At x=0, convection heat transfer is performed between cooling air and cylinder surface no insulated, with a cooling rate:

$$\varphi_{air} = h_{air}(T_{x=0} - T_{air})$$

**Eq.1**

At time t, freezing interface is located at x=$x_{Fr}$ and Eq.1 is only adequate for 0≤x<$x_{Fr}$. At x=$x_{Fr}$, the convection heat transfer is performed between brine and ice surface:

$$\varphi_b = h_b(T_b - T_o)$$ **Eq.2**

Combining the equations 1, and 2 (Eq.3), the solution of the evolution of temperature and global heat flow as function of x and t is obtained. The progression of the position of ice-brine interface $x_o$=$x_i$ and the heat flow allows identifying the development of ice production as function of time, at $x_o$=$x_i$:

$$\varphi_{brine} - \varphi_{ice} = -\rho L_f \frac{dx_o}{dt_o}$$ **Eq.3**

Where $\frac{dx_o}{dt}$ is the rate of volume of ice formed per unit area on the growing surface (m$^3$/(s m$^2$)) and $\rho L_f$ is the latent fusion heat per volume (J/m$^3$). When the distribution of temperatures allows that the total generated heat flow to be negative, ice rate increases and consequently $\frac{dx_o}{dt_o}$ is positive.

An adequate analytic solution of these coupled partial differential equations is very difficult and may be obtained only for specific cases. Moreover, the particular solution is known at the actual physical conditions on the border. The repartition of temperature should modify the physical and thermal properties within the ice. In order to simplify the solution and adopt practical values, it is assumed that the homogeneity of physical properties of the subcooled solid phase (ice), such as density $\varrho_{ice}$, heat capacity $c_{ice}$, conductivity $k_{ice}$, and thermal diffusivity $\alpha_i$). Further simplifications were implemented by assuming that the cooling air temperature $T_{air}$ keeps constant, while liquid (brine) temperature $T_b$ kept slightly higher than solidification temperature of water ($T_o$=$T_{Fr}$≈0 °C) and lower than brine freezing.

The temperature gradients $(T_i - \mathrm{T}_{air}) = (T_b - \mathrm{T}_i)$ generated, the heat flow rate; acting as thermal resistances in series from the ice, the plate, and the air:

$$\varphi_{ice} = \frac{T_i - T_{air}}{\frac{1}{h_{air}} + \frac{1}{\frac{k_c}{l_c}} + \frac{1}{\frac{k_{ice}}{x_o}}}$$ **Eq.4**

The heat flow rate from the brine section is given by Eq. 2, it is exclusive from convection heat transfer. Combining the equations 2 and 4 (in Eq. 5) to vanish the heat flow rates:

$$\frac{T_i - T_{air}}{\frac{1}{h_{air}} + \frac{1}{\frac{k_c}{l_c}} + \frac{1}{\frac{k_{ice}}{x_o}}} - h_b(T_b - T_i) = \rho L_f \frac{dx_o}{dt_o} \qquad \textbf{Eq.5}$$

It manages to relate the ice depth xo to the freezing time $t_o$. If the process starts at t=0 and continue until $t_{fr}$ time, $dt_{fr}$ needs to increase dx of ice generation becomes:

$$dt_{fr} = \frac{\rho L_f}{\frac{T_i - T_{air}}{\frac{1}{h_{air}} + \frac{1}{\frac{k_c}{e_c}} + \frac{1}{\frac{k_{ice}}{x}}} - h_b(T_b - T_i)} dx_o \qquad \text{Eq.6}$$

This Eq. 6 is used to identify the time tfr necessary to freeze a thickness xo of brine. Obviously, the increase of ice thickness as function of time implies that the coefficient of dxo should be positive.

### 2.2.2. Complementary equations

In order to obtain the thermal properties, (Yunus Cengel, 2011), it was used the following relations:

$$Nu = \left\{0.825 + \frac{0.387 * Ra^{1/6}}{\left[1 + [0.492/Pr]^{9/16}\right]^{8/27}}\right\} \qquad \text{Eq.7}$$

It is a function of:

$$Ra_{air} = \frac{g\beta_{air}(T_c - T_{air})d_c^3}{{v_{air}}^2} Pr \qquad \text{Eq.8}$$

$$Ra_b = \frac{g\beta_w(T_b - T_i)d_c^3}{{v_w}^2} Pr \qquad \text{Eq.9}$$

And then, finally:

$$h_{air} = \frac{k_{air}}{d_c} Nu_{air} \qquad \text{Eq.10}$$

$$h_b = \frac{k_b}{d} Nu_b \qquad \text{Eq.11}$$

For both air and brine sides, respectively.

While saline solution freezing process occurs the salt contained homogeneously at the beginning of the process is displaced towards the non-frozen section, consequently, the concentration increases as ice (now free of salt) grows, and the factors affecting the heat transfer phenomena (described in Eqs. 7-11), depend on the characteristics of the actual solution.

To simplify the model and give an accurate approach, we used sodium chloride (NaCl) to estimate the brine behavior as the evolution of seawater, sodium chloride is the main salt in seawater and values for density, dynamic viscosity and specific heat are in good agreement with literature values of sea water (Melinder and Ignatowicz, 2015). The freezing temperature $T_i(°C)$ of the brine salt solution was estimated using the equation proposed in (Fofonoff and R.C., 1983):

$$T_i(°C) = -5.75\ 10^{-2}S + 1.710523\ 10^{-3}S^{\left(\frac{3}{2}\right)} - 2.154996\ 10^{-4}S^2 - 7.53\ 10^{-4} \quad \text{Eq.12}$$

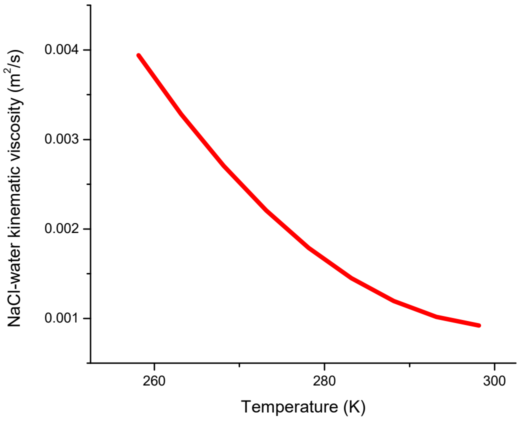

Figure 2 Kinematic viscosity for NaCl-water solutions

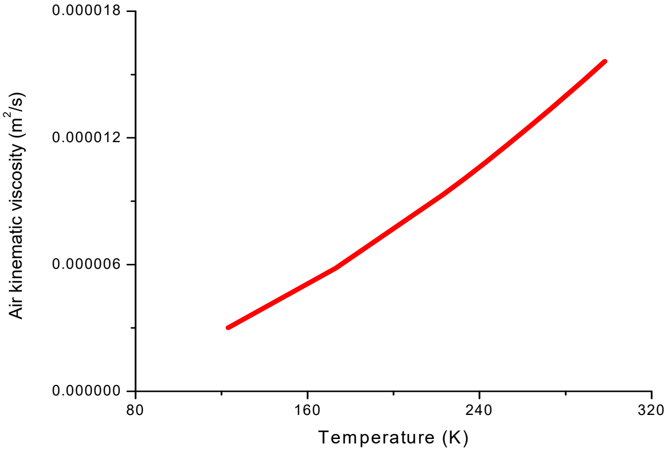

Figure 3 Air kinematic viscosity at low temperatures

The characteristics of dilute solutions, depend on salt concentration. Thus, the freezing point decreases, the density increase, such as the coefficient of volumetric expansion and osmotic pressure. Given the lack information and because the literature gives no values for the variables to be used below 0ºC, the functions have been extrapolated mainly based on the freezing point and the properties of sodium chloride-water solutions.

The values for the modified properties during the freezing process, were obtained from the literature, (Å. Melinder, 2007; Cengel and Boles, 2011; Frank Dreith, Raj M. Manglik, 2011), adapting for low temperatures for air and NaCl-water solution, shown in Figure 2 and 3.

The correlations for kinematic viscosities are:

$$v_{air} = 0.0001{T_{air}}^2 + 0.227T_{air} - 1.6 \qquad \text{Eq.13}$$

and

$$v_b = 2 * 10^{-6}{T_b}^2 - .001T_b + .1471 \qquad \text{Eq.14}$$

for air and NaCl-water solution, respectively.

The values of kinematic viscosity, thermal conductivity which depend on brine concentration during the process are defined by many authors. (Å. Melinder, 2007; Sharqawy, Mostafa H., Lienhard V, John H., 2013; Melinder and Ignatowicz, 2015). Their results agree with measurements of thermal conductivity reported by Ryedel, (Granryd and Melinder, 2005; A. Melinder, 2007).

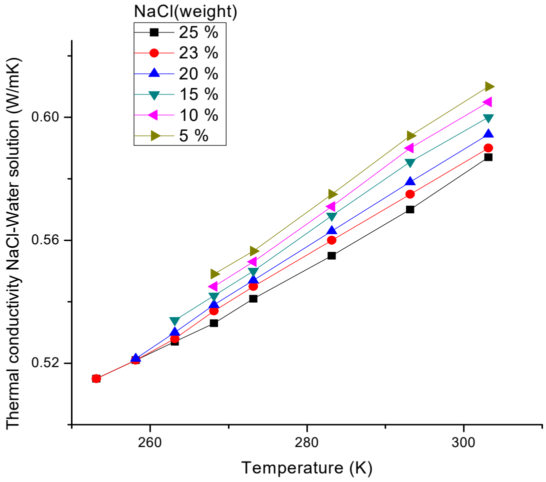

Figure 4 Thermal conductivity for NaCl-Water solutions at different salinity

$$k_b = -6.29 - 0.73logW_{\%} + 5688.8/T_b - 0.13{logW_{\%}}^2 - \frac{1.59 * 10^6}{{T_b}^2} + \frac{231logW_{\%}}{T_b} - 2.45 * 10^{-3}{logW_{\%}}^3 + \frac{1.49 * 10^8}{{T_b}^3} - \frac{1.24 * 10^4 logW_{\%}}{{T_b}^2} + \frac{30.8{logW_{\%}}^2}{T_b} \qquad \textbf{Eq.15}$$

Prandtl number (Pr) for air low temperature, kinematic viscosity and thermal conductivity can be obtained by many ways. In this work the tables presented by Holman (1998) are used.

The equation for Pr number obtained is:

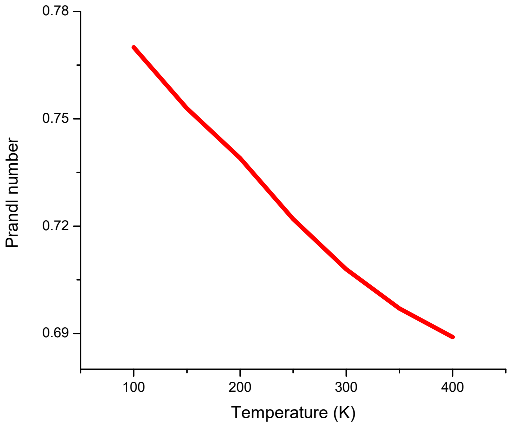

Figure 6 Prandtl Number for low temperatures

$$Pr_{air} = 3\ 10^{-7}{T_b}^2 - 4\ 10^{-4}T_b + 8.109 \qquad \textbf{Eq.16}$$

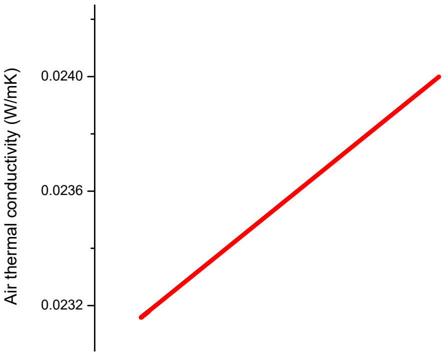

**Figure 5 Air thermal conductivity for at low temperatures**

And the equations obtained for thermal conductivity:

$$k_{air} = -3x10^{-8}{T_{air}}^2 + 8x10^{-5}T_{air} + 0.0236 \qquad \textbf{Eq.17}$$

The minimum coefficient of multiple correlations for all the equations were $R^2$=0.9983.

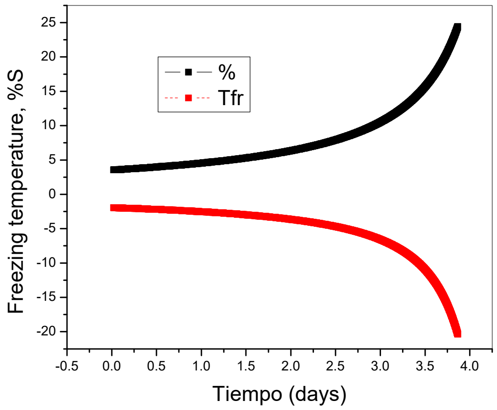

**Figure 7 Salinity and freezing temperature evolution**

Figure 7 shows freezing temperatures derived from the modeling and it can be observed the evolution of saline concentration and freezing temperature, which should continue until reaches cryostatic point, corresponding at -21ºC and 23.4% of concentration, (A. Melinder, 2007), which agrees with colligative properties of diluted solutions.

*2.3. Salt diffusion analysis*

For salt diffusion during freezing, the model proposed by Allaf is used (Allaf *et al.*, 2011), issued from Fick law, (Allaf, 1982):

$$\frac{\rho_s}{\rho_w}(\overrightarrow{v_s}-\overrightarrow{v_w}) = -D\vec{\nabla}\left(\frac{\rho_s}{\rho_w}\right) \qquad \textbf{Eq.18}$$

The salinity of solution is $\frac{\rho_s}{\rho_w}$, subsequently, if it is assumed that the water velocity in the brine was globally: $\overrightarrow{v_w} \approx 0$, and the movement of salt should be uniaxial towards one dimension; Eq.18 became:

$$Sv_s = -D\frac{\partial S}{\partial x} \qquad \textbf{Eq.19}$$

Since the grow ice aims reaching a new equilibrium phase change (Fukui and Maeda, 2002), solidification process is responsible of a partial or total expulsion of salt towards the residual more concentrated brine. The requirement of a complete expulsion of salt ions from dx layer of ice implies that $S_{(x+dx,t)}$ should be twice that $S_{(x,t)}$, then:

$$Sv_s = -\frac{D(S_{(x+dx,t)} - S_{(x,t)})}{dx} \qquad \textbf{Eq.20}$$

And

$$Sv_s = -\frac{D(2S_{(x,t)} - S_{(x,t)})}{dx} \qquad \textbf{Eq.21}$$

Then, since the diffusion time $t_{dif}$ is correlated with dx ice layer, we have:

$$S\frac{dx}{dt_{dif}} = -\frac{D\left(S_{(x,t)}\right)}{dx} \qquad \textbf{Eq.22}$$

and:

$$\frac{dx}{dt_{dif}} = -\frac{D}{dx} \qquad \textbf{Eq.23}$$

Thus, the time $dt_{fr}$ needed for diffusing salt out of dx layer should be:

$$dt_{dif} = \left|\frac{dx^2}{D}\right| \qquad \textbf{Eq.24}$$

Accordingly, the study of mass transfer requires estimation of diffusivity D of salt in the brine. There are several accurate experimental methods for the measurement of D, for example, optical (Krahn, Schwelger and Lucas, 1983), spectroscopic (Stejskal and Tanner, 1965) the Taylor method (Ouano, 1972; Atwood and Goldstein, 1984). However, the value of D has frequently been estimated because of the problems due the expensive instrumentation.

There are several literature correlations for this purpose (Wilke and Chang, 1955; Hayduk and Laudie, 1974; Robert C. Reid, John M. Prausnitz, 1987; Miyabe, 2011). We use the Nernst-Haskell for electrolyte solutions, (Robert C. Reid, John M. Prausnitz, 1987):

$$D = \frac{RT[1/n_+] + [1/n_-]}{F^2[1/\lambda_+^o] + [1/\lambda_-^o]} \qquad \textbf{Eq.25}$$

The limiting ionic conductance in water at 298 K for $Cl^-$ is 76.3 and for $Na^+$ 50.1 ($(A/cm^2)V/cm)(g\text{-}equiv/cm^3)$ (Harned and Benton B., 1943).

**Table 1 Values obtained of diffusivity of salt in water, Temperature and Salinity**

| Salt diffusivity in water | Temperature °C | Salinity S g/l |
|---|---|---|
| $8.42X10^{-6}$ | 0.717 | 35.5 |
| $8.3517X10^{-6}$ | -1.497 | 52.04 |
| $8.2841X10^{-6}$ | -3.686 | 124.03 |
| $8.1921X10^{-6}$ | -9.347 | 198.34 |

## 3. Conditions for F/M desalination

The F/M process requires at least three essential conditions:

1. A positive evolution of grow ice through thickness x:

$$dx_o = \boldsymbol{a}\, dt_{fr} \qquad \textbf{Eq.26}$$

From Eq. 6, since coefficient $\boldsymbol{a}$should be positive, it is proposed:

$$a = \frac{\dfrac{T_i - T_{air}}{\dfrac{1}{h_{air}} + \dfrac{1}{\frac{k_c}{e_p}} + \dfrac{1}{\frac{k_i}{x}}} - h_b(T_b - T_i)}{\rho L_f} > 0 \qquad \textbf{Eq.27}$$

Consequently:

$$\frac{T_i - T_{air}}{\dfrac{1}{h_{air}} + \dfrac{1}{\frac{k_c}{e_p}} + \dfrac{1}{\frac{k_i}{x}}} - h_b(T_b - T_i) > 0 \qquad \textbf{Eq.28}$$

This is to say that Eq. 26 and 27 are conditions which strictly depends on air temperature ($T_{air}$) as well as brine temperature ($T_b$).

2. Requirements of high value of diffusivity D: Since diffusion time $t_{dif}$ normally depends on the diffusivity, which is a function of salinity (Eq. 26 and Table 1), it is means that the higher the salinity, the lower value of D.

3. Requirements of diffusion time lower than freezing time to get salt-free ice:

$$\frac{dt_{dif}}{dt_{fr}} < 1 \qquad \text{Eq.29}$$

Freezing conditions should be carried out to perform ice formation as slow as possible, that it allows salt ions to “escape” into brine solution before reaching the solidification of a considered layer (dx).

## 4. Results

Salt separation should be considered as the most important condition of an appropriate F/M desalination. From the three conditions established, it is possible to regulate the process in terms of the most convenient initial temperatures and salt concentration to allow freezing without salt trap into frozen water.

The Table 2 presents some result of these interesting parameters. Excessive gradient of temperatures will result on entrapment of salts on ice and contrary, the diffusion occurs at low freezing velocity.

**Table 2. Properties obtained from the model proposed**

| d/length | $T_{air}$ | $T_i$ | $l_i$ | Solution viscosity | **S** (g/l) | Freezing temperature (°C) | $\beta_{air}$ |
|---|---|---|---|---|---|---|---|
| 0.12/0.6 | -15 | 25 | 0.1 | 0.00272 | 42.6 | -2.37 | 0.0038 |
| 0.12/0.6 | -15 | 25 | 0.2 | 0.02259 | 53.3 | -3.01 | 0.0039 |
| 0.12/0.6 | -30 | 25 | 0.4 | 0.02280 | 106.5 | -6.69 | 0.0081 |

**Table 3. Continuation. Properties obtained from the model proposed**

| $h_{air}$ | $k_w$ | $h_w$ | $\varrho_b$ | $\frac{dt_{dif}}{dt_{fr}}$ | a (m/s) | Ice salt free? |
|---|---|---|---|---|---|---|
| 7.950 | 0.459 | 4.43 | 1036 | 0.04369 | 3.65E-07 | YES |
| 7.953 | 0.453 | 4.46 | 1045 | 0.03322 | 3.03E-07 | YES |
| 12.15 | 0.432 | 4.69 | 1093 | 1.00045 | 1.69E-07 | NO |

**S**: Salt concentration on liquid.

## 5. Conclusions

New fundamental model was defined to obtain the conditions able to achieve a suitable saline solution desalination. This model is based on the comparison of both freezing process and salt diffusion in saline water. It involves the effect of thermal parameters, which normally depend on salt concentration (conductivity, freezing temperature, etc.), physical characteristics (density, expansion coefficient, kinematic viscosity, salt diffusivity, etc.), and equipment geometry. The model is at the same time simple and effective and provides an approach tool to conduct F/M desalination process. Important information has been collected to achieve data closer to observed in experimentation in a complex problem. The ice grow rate value must be around 3E-07 to ice salt separation and the freezing temperature must be lower than -15°C to achieve 233 g/l on liquid. The results of this model will help the design and build high-performant adequate F/M prototypes and industrial plants.

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## 6. References

Allaf, K. (1982) *Transfer phenomena and industrial applications*. First. Lebano: Lebanese University, Faculty of Science.

Allaf, K. *et al.* (2011) 'Drying diffusing model', in *6th International CIGR Technical Symposium - Towards a Sustainable Food Chain: Food Process, Bioprocessing and Food Quality Management 2011,*. Nantes, France: Elsevier B.V., p. 89672.

Atwood, J. G. and Goldstein, J. (1984) 'Measurements of Diffusion Coefficients in Liquids at Atmospheric and Elevated Pressure by the Chromatographic Broadening Technique', *J. Phys. Chem.*, 88(2), pp. 1875–1885. doi: 10.1021/j150653a041.

Blank, J. E., Tusel, G. F. and Nisanc, S. (2007) 'The real cost of desalted water and how to reduce it further', *Desalination*, 205(1–3), pp. 298–311. doi: 10.1016/j.desal.2006.05.015.

Castillo, B. and Pilatowsky, I. (2013) *Análisis técnico y económico del potencial de la aplicación de la tecnología de congelación para la desalación de agua de mar.* Universidad Nacional Autónoma de México.

Cengel, Y. a. and Boles, M. E. (2011) 'Termodinamica - Cengel 7th', *Termodinamica*, p. 1456. Available at: http://www.mediafire.com/download/7a3idxrs2gxjbpu/Termodinamica+-+Cengel+7th.pdf.

Curran, H. M. (1970) 'Water desalination by indirect freezing', *Desalination*, 7(3), pp. 273–284. doi: 10.1016/S0011-9164(00)80201-5.

Erlbeck, L. *et al.* (2017) 'Investigation of the depletion of ions through freeze desalination', *Desalination*. Elsevier B.V., 407, pp. 93–102. doi: 10.1016/j.desal.2016.12.009.

Fofonoff, N. P. and R.C., M. J. (1983) 'Algorithms for computation of fundamental properties of seawater', *Unesco technical papers in marine science*.

Frank Dreith, Raj M. Manglik, M. S. (2011) *Principles of Heat Transfer*. seventh, *Handbook of Phase Change: Boiling and Condensation*. seventh. United States: Cengagle Learning, Inc.

Fukui, K. and Maeda, K. (2002) 'Effects of crystal growth rate and heat and mass transfer on solute distribution', *Chemical Engineering Science*, 57(15), pp. 3133–3140. doi: 10.1016/S0009-2509(02)00174-4.

Ghalavand, Y., Hatamipour, M. S. and Rahimi, A. (2014) 'A review on energy consumption of desalination processes', *Desalination and Water Treatment*, (February 2015), pp. 1–16. doi: 10.1080/19443994.2014.892837.

Grange, B. W., Viskanta, R. and Stevenson, W. H. (1976) 'Diffusion of heat and solutescraped surface freezer during freezing of salt solutions', *International Journal of Heat and Mass Transfer*, 19, pp. 373–384. doi: 10.1016/0017-9310(76)90093-4.

Granryd, E. and Melinder, A. (2005) ‘Using property values of aqueous solutions and ice to estimate ice concentrations and enthalpies of ice slurries’, *International Journal of Refrigeration*, 28(1), pp. 13–19. doi: 10.1016/j.ijrefrig.2004.07.013.

Guevara, A. and Stabridis, O. (2008) ‘Desalación mediante el uso de energías renovables: Una reflexión desde la perspectiva económica’, in Márquez, R. (ed.) *Biblioteca Jurídica Virtual del Instituto de Investigaciones Jurídicas de la UNAM*. Primera. México, D.F., pp. 1–18.

Harned, H. S. and Benton B., O. (1943) *The Physical Chemistry of Electrolytic Solutions*. First. Edited by A. C. S. Monograph. New Haven, Connecticut: Reingold Publishing Corporation.

Hayduk, W. and Laudie, H. (1974) ‘Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions’, *AIChE Journal*, 20(3), pp. 611–615. doi: 10.1002/aic.690200329.

Holman, J. P. (1999) *Transferencia de calor*. Octava (pr. Edited by C. Fernández. Madrid, España: McGRAW-HILL/INTERAMERICANA.

IDA Desalination (2017) *IDA Desalination Yearbook 2016-2017*. 1st edn. Oxford, UK: Media Analytics Ltd. Available at: https://www.paperturn.com/flipbook/id/global-water-intelligence/ida-desalination-yearbook-2016-2017?pid=NzU7549#/7 (Accessed: 23 March 2017).

Johnson, W. E. (1976) ‘State of the art of freezing processes, their potential and future.’, *Desalination*, 19, pp. 349–358.

Johnson, W. E. (1979) ‘Indirect freezing’, *Desalination*, 31(1–3), pp. 417–425. doi: 10.1016/S0011-9164(00)88545-8.

Jungwirth, P. (2005) ‘Brine Rejection from Freezing Salt Solutions : A Molecular Dynamics Study’, (111).

Jungwirth, P., Vrbka, L. and Jungwirth, P. (2005) ‘Brine rejection from freezing salt solutions: A molecular dynamics study’, *Physical Review Letters*, 95(September), pp. 1–4. doi: 10.1103/PhysRevLett.95.148501.

Kapembwa, M., Rodríguez-Pascual, M. and Lewis, A. E. (2014) ‘Heat and Mass Transfer Effects on Ice Growth Mechanisms in Pure Water and Aqueous Solutions’, *Crystal Growth & Design*, 14, pp. 389–395. doi: 10.1021/cg401428v.

Körber, C., Scheiwe, M. W. and Wollhöver, K. (1983) ‘Solute polarization during planar freezing of aqueous salt solutions’, *International Journal of Heat and Mass Transfer*, 26(8), pp. 1241–1253. doi: 10.1016/S0017-9310(83)80179-3.

Krahn, W., Schwelger, G. and Lucas, K. (1983) ‘Light scattering measurements of mutual diffusion coefficients in binary liquid mixtures’, *J. Phys Chem*, (2), pp. 4515–4519.

Luo, C., Chen, W. and Han, W. (2010) 'Experimental study on factors affecting the quality of ice crystal during the freezing concentration for the brackish water', *Desalination*, 260(1–3), pp. 231–238. doi: 10.1016/j.desal.2010.04.018.

Mandri, Y. *et al.* (2011) 'Parametric study of the sweating step in the seawater desalination process by indirect freezing', *Desalination*, 269(1–3), pp. 142–147. doi: 10.1016/j.desal.2010.10.053.

Marshall, R. T., Goff, H. D. and Hartel, R. W. (1967) *The Freezing Process for desalting Saline Waters, Office of Saline Water*. Washington, DC. 20402: U.S. Government Printing Office.

Melinder, A. (2007) *Thermophysical Properties of Aqueous Solutions Used as Secondary Working Fluids*. Royal Institute of Technology, KTH, Stockholm, Sweden.

Melinder, Å. (2007) *Thermophysical Properties of Aqueous Solutions Used as Secondary Working Fluids*.

Melinder, A. and Ignatowicz, M. (2015) 'Properties of seawater with ice slurry use in focus', *International Journal of Refrigeration*. Elsevier Ltd, 52, pp. 51–58. doi: 10.1016/j.ijrefrig.2014.12.022.

Miyabe, K. (2011) 'Estimation of molecular diffusivity in aqueous solution of acetonitrile by the Wilke-Chang equation', *Journal of Separation Science*, 34(19), pp. 2674–2679. doi: 10.1002/jssc.201100385.

Mtombeni, T., Maree, J.P., Zvinowanda, C, M. (2013) 'Evaluation of the performance of a new freeze desalination technology', *Int. J. Environ. Sci. Technol. (2013)*, (10), pp. 545–550. doi: 10.1007/s13762-013-0182-7.

Orcutt, J. C. (1969) 'Nucleation and growth of ice crystals in secondary refrigerant freezing', *Desalination*, 7(1), pp. 75–96. doi: 10.1016/S0011-9164(00)80275-1.

Ouano, a C. (1972) 'Diffusion in Liquid Systems. I. A Simple and Fast Method of Measuring Diffusion Constants', *Industrial & Engineering Chemistry Fundamentals*, 11(2), pp. 268–271. doi: 10.1021/i160042a019.

Rahman, M. S., Ahmed, M. and Chen, X. D. (2006) 'Freezing-Melting Process and Desalination: I. Review of the State-of-the-Art', *Separation & Purification Reviews*, 35(September 2005), pp. 59–96. doi: 10.1080/15422110600671734.

Rahman, M. S., Ahmed, M. and Chen, X. D. (2007) 'Freezing melting process and desalination: review of present status and future prospects', *International Journal of Nuclear Desalination*, 2(3), p. 253. doi: 10.1504/IJND.2007.013549.

Reddy, S. T. *et al.* (2009) 'Investigating Factors That Affect Separation in a Eutectic Freeze Crystallisation Process', *Africa*, pp. 649–655.

Rice, W. and Chau, D. S. C. (1997) ‘Freeze desalination using hydraulic refrigerant compressors’, *Desalination*, 109(2), pp. 157–164. doi: 10.1016/S0011-9164(97)00061-1.

Robert C. Reid, John M. Prausnitz, B. E. P. (1987) *The properties of gases and liquids*. Fourth. Edited by McGraw-Hill. New York, NY: McGraw-Hill.

Savović, S. and Caldwell, J. (2003) ‘Finite difference solution of one-dimensional Stefan problem with periodic boundary conditions’, *International Journal of Heat and Mass Transfer*, 46, pp. 2911–2916. doi: 10.1016/S0017-9310(03)00050-4.

Sharqawy, Mostafa H., Lienhard V, John H., Z. S. M. (2013) ‘The thermophysical properties of seawater : A review of existing correlations and data’.

Shirai, Y. *et al.* (1998) ‘Effect of seed ice on formation of tube ice with high purity for a freeze wastewater treatment system with a bubble-flow circulator’, *Water Research*, 33, pp. 1325–1329. doi: 10.1016/S0043-1354(98)00335-2.

Stejskal, E. O. and Tanner, J. E. (1965) ‘Spin diffusion measurements: spin echoes in the presence of a time-dependant field gradient’, *The Journal of chemical physics*, 42(1), pp. 288–292. doi: 10.1063/1.1695690.

Subramani, A. and Jacangelo, J. G. (2015) ‘Emerging desalination technologies for water treatment: A critical review’, *Water Research*. Elsevier Ltd, 75, pp. 164–187. doi: 10.1016/j.watres.2015.02.032.

Terwilliger, J. P. and Dizio, S. F. (1970) ‘Salt rejection phenomena in the freezing of saline solutions’, *Chemical Engineering Science*, 25, pp. 1331–1349. doi: 10.1016/0009-2509(70)80010-0.

Thompson, T. G. and Nelson, K. H. (1954) *Desalting sea water by freezing*. Washington, DC.

Voller, V. and Cross, M. (1981) ‘Accurate solutions of moving boundary problems using the enthalpy method’, *International Journal of Heat and Mass Transfer*, 24, pp. 545–556. doi: 10.1016/0017-9310(81)90062-4.

Weeks, W. F. and Lofgren, G. (1967) ‘The Effective Solute Distribution Coefficient During the Freezing of NaCl Solutions’, *U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, N. H., U.S.A.*, p. 20.

Wiegandt, H. and Berg, R. Von (1980) ‘Myths about freeze desalting’, *Desalination*, 33(July 1979), pp. 287–297. Available at: http://www.sciencedirect.com/science/article/pii/S0011916400885719 (Accessed: 13 October 2014).

Wilke, C. R. and Chang, P. (1955) ‘Correlation of diffusion coefficients in dilute solutions’, *AIChE Journal*, 1(2), pp. 264–270. doi: 10.1002/aic.690010222.

Williams, P. M. *et al.* (2015) 'Technology for freeze concentration in the desalination industry', *DES*. Elsevier B.V., 356, pp. 314–327. doi: 10.1016/j.desal.2014.10.023.

Wollhöver, K. *et al.* (1985) 'Unidirectional freezing of binary aqueous solutions: an analysis of transient diffusion of heat and mass', *International Journal of Heat and Mass Transfer*, 28(4), pp. 761–769. doi: 10.1016/0017-9310(85)90226-1.

Yao, L. S. and Prusia, J. (1989) *Advances in heat transfer: Melting and freezing*. United States: Academic Press, Inc.

Yu, T., Ma, J. and Zhang, L.-Q. (2007) 'Factors affecting ice crystal purity during freeze concentration process for urine treatment', *Journal of Harbin Institute of Technology (New Series)*, 14(5).

Yunus Cengel, A. G. (2011) *Transferencia de Calor y Masa*. 4ta edn, *Mc Graw Hill*. 4ta edn. Mc Graw Hill.