Experimental Study on Specific Heat of Hot Brine for Salt Gradient Solar Pond Application

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Abstract: Sodium chloride (NaCl) solution of has been found to be widely used in the heat storage zone (HSZ) of salt gradient solar ponds (SGSP) in concentrations ranging from 20% to 25% (weight percentage) for the collection and storage of solar energy and retrieval of the same in the form of thermal energy. NaCl solution of concentrations ranging from 25% to 0% has been used to form the salinity gradient which is called as the non-convecting zone (NCZ) which are stacked over the HSZ of a SGSP. Less dense layer is floated above a heavy layer by keeping one over the other ultimately. The main purpose of the salinity gradient establishment is to prevent the convective heat loss from the Heat Storage Zone (HSZ) by suppressing the convection due to solar heating. Values of specific heat capacity at elevated temperature and concentration are helpful to have an accurate estimation of the thermal energy extractable by decanting the hot brine from the HSZ of the SGSP. A number of compilations of the thermo-physical properties of NaCl solutions have been published, but literatures giving details about the specific heat capacity of NaCl solution at different concentration and temperature necessary for SGSP efficiency estimation are found missing. In the present study, an attempt has been made to experimentally measure and to theoretically predict the specific heat capacity of the NaCl brine solution at elevated temperatures and at varying solution concentrations. An adiabatic calorimeter has been fabricated to determine the specific heat capacity of the brine solution at elevated temperatures above the ambient temperature.

Key words: solar pond; adiabatic calorimeter; salt concentration; specific heat.

Nomenclature

A  ammeter
\( a_1, a_2, a_3, a_4 \)  function coefficient
Bat  battery
\( C_v \)  specific heat of the calorimeter vessel in (J/kg°C)
\( C_p \)  is the specific heat capacity at constant pressure (J/kg°C)
\( \Delta C \)  rise in concentration in (%)
HSZ  heat storage zone
I  the current flowing through the heating coil in amperes
K  key
\( m_b \)  mass of brine solution in (kg)
\( m_c \)  mass of the calorimeter vessel in (kg)
NCZ = non convective zone
Rh = rheostat
SGSP = salt gradient solar pond
S = salinity in weight percentage
ΔT = temperature rise of the contents of the calorimeter in (°C)
T = temperature (°C)
t = total time duration of current passage in seconds.
UCZ = upper convective zone
V = the potential difference found across the heating coil in volts
ρ = density in (kg/m³)

1. Introduction

A great number of salt works are being operated along the sea coasts to harvest NaCl salt. All over the world salt gradient solar ponds are constructed to collect and store solar energy [1]. NaCl dissolved in water at near saturation concentration are widely used to store the sun’s light energy and to deliver it in thermal form. Conventionally, thermal energy recovery from the SGSP is done by withdrawing hot NaCl brine solution from the HSZ at a temperature ranging from 70°C to 75°C. On an experimental basis an NaCl based salt gradient solar pond (SGSP) of 500sq.m area has been constructed and operated to generate electric power at Pondicherry at a hot brine inlet temperature ranging from 70°C to 75°C.

The specific heat capacities of the NaCl brine solution at elevated temperature and at higher concentrations are essentially needed so as to have an assessment of thermal energy extractable from a SGSP. Podoski et al, have made the specific heat measurements 3,4 dimethylpyridine liquid in the temperature ranges of 265-380K using the adiabatic calorimeter[2]. A regression analysis is carried out on saturation concentration data at various temperatures [3, 4]. In the present study, an attempt has been made to experimentally determine the specific heat capacity of the NaCl brine at different concentrations and at different temperatures using adiabatic calorimetric method. Modeling studies have been made by developing a computer program to estimate the specific heat capacity of NaCl brine at elevated temperatures and at different concentrations. The results of both the experimental and theoretical values of specific heat capacity of NaCl brine solution have been presented.

2. Theoretical analysis

Thermo physical properties such as density, heat capacity, thermal conductivity, kinematic viscosity, thermal diffusivity, solute diffusivity, thermal expansion coefficient and solutal expansion coefficient for sodium chloride has been provided in the literatures [5-11]. The density of the NaCl brine solution is found to have a variation in the density values due to the concentration and the temperature of the solution. According to Xu [12] the density of brine solution could be determined using the following polynomial representation-

\[ \rho(S,T) = a_1 + a_2 T + a_3 T^2 + a_4 T^3 \] ........................(1)

Where ,

\[ a_1(S) = 999.9 + 7.6374S + 7.3624 \times 10^4 S^2 + 4.7088 \times 10^3 S^3 \]
\[ a_2(S) = 0.02592 - 0.039546 S + 7.7952 \times 10^4 S^2 - 9.3073 \times 10^6 S^3 \]
\[ a_3(S) = -5.9922 \times 10^3 + 3.7422 \times 10^4 S - 1.0436 \times 10^5 S^2 + 1.4816 \times 10^7 S^3 \]
\[ a_4(S) = 1.5332 \times 10^5 - 9.386 \times 10^7 S + 3.2836 \times 10^9 S^2 + 4.0083 \times 10^{10} S^3 \]

and S is the Salinity in percent by weight and T is the temperature in °C and ρ is the density in kilogram per cubic meter. The specific heat capacity of NaCl salt dissolved in water could be estimated using the following empirical relation obtained from the regression analysis carried out on saturation concentration data for NaCl solution. The relations given below are used in the simulation of saturated solar pond performance [13].

\[ C_p = 4180 - 4.396 \times (S/100) \times (\rho + 0.0048 (S/100)^2) \]

Where S is the salinity in weight percent and ρ is the density in kilogram per cubic meter. Using equation (1) the density values are obtained and the values are substituted in equation (2) to determine the specific heat capacity of NaCl brine solution. In order to do the above estimation a computer program has been developed and the specific heat capacity values at several elevated temperatures and for various concentration of the NaCl salt solution could be estimated.
3. Materials and methods

A calorimeter is a device used to measure the quantity of thermal energy gained or lost during the chemical reactions. In order to determine the specific heat capacity of the hot brine NaCl solution at different temperatures and at different concentrations a well insulated adiabatic calorimeter apparatus has been fabricated indigenously which will neither permit the outside heat to enter nor allow the heat of the calorimeter to go out from it. Using the adiabatic calorimetric technique the specific heat capacity of sodium chloride solution in the temperature range between 31°C to 75°C for the selected concentrations ranging from 1% to 26% has been estimated. The apparatus setup and electrical wiring diagram for estimating specific heat capacity by adiabatic calorimetric method has been described in Figure.1.

A Joule’s calorimeter apparatus was used as the basis for forming an adiabatic calorimeter. It mainly consisted of a polished aluminium cylindrical vessel enclosed inside a wooden box with sufficient thickness of insulating lining provided on the inner side of the box. A known quantity of NaCl brine was taken in the calorimeter vessel and its concentration and temperature were measured.

\[ C_p = \frac{V\Delta T - m_c \Delta C}{m_b \Delta T} \]  

(3)

Similar such experimentations on NaCl solution were performed for a concentration of 25%, 23% and 20% at a corresponding temperature of 70°C, 62°C and 57°C respectively. The specific heat capacity of NaCl brine obtained at the above mentioned concentrations and temperatures of the brine solution sampled out from the UCZ, NCZ and HSZ of SGSP under one atmospheric pressure have been recorded in Table.1 and plotted in Figure.2.

In order to check the validity of the results obtained from the experimentation, using the same procedure, a sample of top water of 1% concentration at a temperature of 31.0°C was collected from the top most part of the UCZ layer. Using the adiabatic calorimeter apparatus arrangement the specific heat capacity of the UCZ layer solution of 1% concentration at a temperature of 31°C was found to have a value of 4153 J/kg°C, which is very much close to the specific heat capacity values reported for distilled water and is of 4185 J/kg °C. The obtained values of specific heat capacity were found to be very close to the reported values and thus validated the method of measurement of the specific heat capacity of the NaCl brine solution. As the concentration of the brine increases along with the increase in the temperature the specific heat capacity was found to have a decrease in its value.

Table 1, gives the experimentally measured specific heat capacity values of NaCl brine solution. It is observed from the Table.1 that for a rise in the concentration (ΔC) = 6% and temperature increment ΔT of 18°C, the decrease in specific heat capacity (ΔC_p) is found to have a value of 200.2 J/kg°C. The reduction in specific heat capacity of NaCl brine for a unit rise in concentration (%) and for a unit rise in temperature in (°C) have been estimated as 1.85 J/kg°C.

![Fig.1. Schematic diagram of adiabatic Calorimeter experimental arrangement](image-url)
4. Results of the modeling studies

The experimental results of the specific heat capacity of NaCl brine obtained by adiabatic calorimetric method have been compared with the theoretically predicted result for the various temperatures and for different concentration of the NaCl brine solution and have been presented in the Fig.3.

The values of specific heat capacity has been compared for the LCZ solution concentrations ranging from 20% to 26% and also for 1% concentration solution normally found in the UCZ. In general it is found that there is a decrease in specific heat capacity values of brine solution when there is an increase in the concentration and temperature. Referring to Fig.3, the practically estimated values are found to have a slightly higher value than the theoretically predicted values. The difference in specific heat capacity value found for all concentrations are reported to have a slightly difference in \( C_p \) value.

![Graph showing experimental evaluation of specific heat capacity at different temperature with time](image)

**Table 1. Experimental determination of the specific heat capacity of NaCl solution for different concentrations and at different temperatures**

<table>
<thead>
<tr>
<th>NaCl Brine Sampling Region</th>
<th>Temperature (°C)</th>
<th>Concentration (Weight %)</th>
<th>Specific heat Capacity ( C_p ) (J/kg°C)</th>
<th>( \Delta C ) (%)</th>
<th>( \Delta T ) (°C)</th>
<th>( \Delta C_p ) (J/kg°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCZ</td>
<td>31</td>
<td>1</td>
<td>4153.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCZ</td>
<td>35</td>
<td>20</td>
<td>3480.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCZ</td>
<td>57</td>
<td>20</td>
<td>3460.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCZ</td>
<td>62</td>
<td>23</td>
<td>3377.3</td>
<td>26-20</td>
<td>75-57</td>
<td>3260.6~3460.8</td>
</tr>
<tr>
<td>LCZ</td>
<td>70</td>
<td>25</td>
<td>3341.4</td>
<td>=6</td>
<td>=18</td>
<td>=200.2</td>
</tr>
<tr>
<td>LCZ</td>
<td>75</td>
<td>26</td>
<td>3260.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. A representative values of the predicted specific heat capacity for NaCl solution for discrete set of concentration and temperature pair

<table>
<thead>
<tr>
<th>S.No</th>
<th>Temperature °C</th>
<th>Concentration %</th>
<th>Specific heat capacity of NaCl solution (J/kg°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>5</td>
<td>3965.07</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>10</td>
<td>3764.34</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>15</td>
<td>3583.60</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>20</td>
<td>3428.22</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>25</td>
<td>3303.84</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>28</td>
<td>3247.45</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>29</td>
<td>3232.99</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>30</td>
<td>3219.94</td>
</tr>
</tbody>
</table>
Heat extraction is obtained from the stored heat of the highly concentrated NaCl brine solution stacked in the LCZ of the SGSP by withdrawing NaCl brine solution using motor pumps. In order to withdraw a specific quantity of thermal energy from the SGSP the necessary brine flow rate is to be estimated with the estimated value of specific heat capacity of the brine solution. Temperature of the brine withdrawn from the HSZ of SGSP may range from 50°C to 75°C depends upon the demand of the load and the necessary NaCl brine concentration would range from 20% to 26%. The experimentally estimated and theoretically predicted \( C_p \) values of NaCl brine have been compared and presented in Fig.4. It is found that the \( C_p \) values are almost having the same value for a concentration of 20% at a temperature of 35°C. It is found that the experimental \( C_p \) values are higher than the theoretically predicted values. The difference in \( C_p \) values are found to have a gradual increase with the increase of temperature in the range from 57°C to 70°C and at a corresponding concentration ranging from 20% to 25%.

5. Conclusions

The variation in the specific heat capacity of NaCl salt solution at different temperature and at different concentration have been studied both experimentally and theoretically. The specific heat capacity of NaCl brine experimentally determined at different constant elevated temperatures are found to have a general decrease in specific heat capacity values. A best fit relation for the estimation of specific heat capacity suited for SGSP applications has been obtained for the NaCl brine of higher concentration (20% to 26%) and for higher temperatures (57°C to 75°C). These ranges of concentration and temperature are associated with the brine environment of the Heat Storage Zone of any SGSP. The \( C_p \) value obtained from the simulation study has been compared with the experimental values. The experimental values of \( C_p \) are slightly higher than that of the theoretical results and the deviation is found to be close to 1% only, which validates the simulation program developed for the study.

6. References

6. Kaufmann DW, Sodium Chloride; the Properties and Production of Salt and Brine, Reinhold, New York 1960.

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