Deposition of Sodium Chloride from Supercritical Water

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Supercritical water oxidation (SCWO) is a new technology that promises successful destruction of organic material from hazardous aqueous wastes without harmful emissions. SCWO is made possible due to the special properties of supercritical water (SCW). The very same properties of SCW are also responsible for the low solubility of inorganic salts (coming from processed waste streams or formed during reaction) and consequent salt precipitation and fouling of the system. There are several proposed or implemented systems that attempt to solve the fouling problem by either removing the salt from the stream prior to the reactor or preventing deposition in the reactor itself. Designing a solution to the fouling problem in a SCWO system is closely related to the understanding of the deposition mechanism. Deposition from sodium chloride-water system was the subject to this study because of the system's phase behavior and because no previous deposition studies had been performed on it.

Sodium chloride deposition was investigated in a fully developed turbulent flow of SCW through a horizontal, electrically heated test section of the 1 l/min UBC/NORAM SCWO plant. The solubility measurements performed at 24.1, 24.45 and 25.67 MPa and temperature 461-560 °C agreed with the semi-empirical Martynova-Galobardes-Armellini solubility model that assumed equilibrium between solid and vapor as a solvation type reaction. Various flow conditions and concentrations that were higher than the vapor concentration at the three-phase equilibrium were used in deposition experiments. Sodium chloride-water solution in the bulk passed through the two-phase vapor-liquid region before the vapor-solid region was entered. There were two distinct regions of deposition observed, one in the vapor-liquid region and one in the vapor-solid region. The heat transfer coefficient increased by 1-6 kW/m²·K (20-75 %) when a salt solution was introduced to the system. The salt thickness profiles were inferred from outer surface temperatures. The average porosity of the deposit in the vapor-liquid region was calculated as 0.1 and of the deposit in the vapor-solid region as 0.6. These porosities could be uncertain to ±50%.
Heat and mass transfer were modeled in both regions. The buoyancy effects for pure water and salt solution were neglected. Three deposition models were developed for vapor-liquid region. The first model assumed molecular mass transfer from the bulk to the wall from both vapor and liquid phases with the same mass transfer coefficient. The second model assumed mass transfer from the vapor phase only (liquid phase frozen). The third model assumed mass transfer from the vapor phase with the vapor and liquid phases in equilibrium (infinitely fast mass transfer between phases). A model assuming combination of molecular mass transfer and particle deposition as a deposition mechanism was developed for the vapor-solid region. All models assumed no surface resistance to molecules or particle attachment. A comparison between experimental results and model predictions showed that the deposition in vapor-liquid region was governed by the mass transfer from the vapor phase with some mass transfer from the liquid phase involved. Deposition in the vapor-solid region was greatly affected by the amount of liquid phase remaining just before the three-phase temperature was exceeded.
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LIST OF SYMBOLS

$A_c =$ reduction factor $[-]$  
$A_{hyd} =$ the activity of hydrate NaCl $n\text{H}_2\text{O}_{(v)}$ $[-]$  
$A_s =$ the activity of the solid NaCl $[-]$  
$A_w =$ the activity of water $[-]$  
$C =$ critical point of the solution at the constant temperature $[-]$  
$c =$ the critical curve $[-]$  
$C_0 =$ initial concentration of salt [ wt % ]  
$C_{0HT} =$ initial concentration of the salt solution for the HT region [kg s / kg]  
$C_b =$ total salt concentration in the bulk [kg s / kg]  
$C_{b1} =$ the bulk concentration at the beginning of the length step [kg s / kg]  
$C_{b2} =$ the bulk concentration at the end of the length step [kg s / kg]  
$C_{bat} =$ solubility limit at the bulk temperature (vapor-solid equilibrium) [kg s / kg]  
$C_{Lb} =$ concentration of salt in liquid phase [kg s / kg]  
$C_{Lb1}$ and $C_{Lb2} =$ concentrations of the salt in the liquid phase at the beginning and at the end of the step [kg s / kg]  
$C_{\text{liq}} =$ the concentration of the salt in the dense liquid phase at vapor-liquid equilibrium [kg s / kg]  
$C_{NaCl} =$ concentration of NaCl in vapor phase [ ppm ]  
$C_{\text{oute}} =$ measured concentration of the solution at the outlet of the test section [ppm]  
$C_p =$ concentration of salt particles [kg s / kg]  
$c_p =$ average specific heat capacity [kJ/kg-K]  
$c_p =$ specific heat capacity [kJ/kg-K]  
$C_{pB} =$ concentration of salt in particles in the bulk [kg s / kg]  
$CPS =$ the critical point of salt $[-]$  
$CPW =$ the critical point of water $[-]$  
$C_{vb} =$ concentration of dissolved salt in vapor phase [kg s / kg]  
$C_{vb1}$ and $C_{vb2} =$ the concentrations of the dissolved salt in the vapor phase at the beginning and at the end of the step respectively [kg s / kg]
C_{v,sat}= saturation concentration for vapor phase at vapor-liquid equilibrium [kg_s/kg]

C_{w,sat}= solubility limit at the wall temperature (vapor-solid equilibrium) [kg_s/kg]

D = diffusion coefficient [m^2/s]

d = the tube diameter [m]

\(d_m\) = the effective hydrodynamic diameter of molecule [m]

\(d_p\) = the diameter of the salt particle [m]

\(d_t\) = time step [s]

\(d_t\) = time of deposition [s]

\(d_z\) = length step [m]

f = friction factor [-]

H = specific enthalpy [kJ/kg]

\(h_1\) = modified heat transfer coefficient to account for the effect of salt [kW/m^2-K]

\(h_0\) = heat transfer coefficient obtained for pure water flow in a clean tube [kW/m^2-K]

\(h_m\) = mass transfer coefficient [m/s]

HTE = High Temperature Experiments (bulk fluid in vapor-liquid and vapor-solid region) [-]

\(K_b\) = Boltzmann's constant [J/K]

\(K_c\) = equilibrium constant [-]

\(k_{\text{fluid}}\) = thermal conductivity of the fluid in pores [kW/m-K]

\(k_f\) = thermal conductivity [kW/m-K]

\(k_{\text{layer}}\) = thermal conductivity of the porous salt layer [kW/m-K]

\(k_{\text{salt}}\) = thermal conductivity of NaCl [kW/m-K]

\(k_w\) = thermal conductivity of the tube wall [kW/m-K]

L = length of the tube [m]

LTE = Low Temperature Experiments (the bulk fluid in vapor-liquid region) [-]

\(\dot{m}\) = mass flow rate [kg/s]

\(m_{\text{fluid}}\) = mass of distilled water [kg]

\(m_{\text{NaCl}}\) = mass of the salt [kg]

\(m_s\) = the experimentally obtained mass of deposited salt [kg]
\( m_{\text{salt}} = \text{calculated mass of deposited salt} \) [kg]
\( \text{Nu} = \text{Nusselt number} \) [-]
\( N = \text{number of hydrated water molecules attached to the dissolved NaCl} \) [-]
\( p = \text{absolute pressure} \) [MPa]
\( P = \text{the critical end point (the intersection between critical curve and the three phase equilibrium area)} \) [-]
\( q = \text{heat flux supplied to fluid} \) [kW/m²]
\( q_L = \text{the heat flux} \) [kW/m]
\( Q_{\text{loss}} = \text{heat loss} \) [kW]
\( Q_s = \text{salt mass flux} \) [kg/s/m²]
\( Q_{\text{sm}} = \text{salt mass flux due to the molecular mass transfer} \) [kg/s/m²]
\( Q_{\text{sp}} = \text{salt mass flux due to the deposition of particles} \) [kg/s/m²]
\( Q_t = \text{power supplied to the test section} \) [kW]
\( R = \text{the critical end point (the intersection between critical curve and the three phase equilibrium area)} \) [-]
\( \text{Re} = \text{Reynolds number} \) [-]
\( r_i = \text{inner tube radius} \) [m]
\( r_o = \text{outer tube radius} \) [m]
\( r_s = \text{distance from the center of the tube to the salt layer} \) [m]
\( \text{Sc} = \text{Schmidt number} \) [-]
\( \text{Sh} = \text{Sherwood number} \) [-]
\( S_t = \text{salt thickness} \) [m]
\( T = \text{temperature} \) [K]
\( T_{b0j}, T_{b1j} = \text{bulk temperature at the location} j \text{ and times} t_0, \text{ and} t_1 \text{ respectively} \) [K]
\( T_0 = \text{measured outer surface temperature} \) [K]
\( T_{oc} = \text{calculated temperature at the outer tube surface} \) [K]
\( T_{pc} = \text{pseudo critical temperature} \) [K]
\( T_s = \text{temperature at the interface between the salt layer and the fluid} \) [K]
\( T_{sw} = \text{temperature at the inner tube wall} \) [K]
\( T_{tp} = \text{three phase equilibrium temperature} \) [K]
$T_{V,L}$ = the temperature at the vapor-liquid equilibrium curve corresponding to the initial concentration of the solution $C_0$ [K]

$T_w$ = inner wall temperature [K]

$T_{w0j}, T_{wij}$ = inner surface temperatures calculated from the measured outer surface temperatures at the location $j$ and times $t_0, t_1$ respectively [K]

$u$ = bulk stream fluid velocity [m/s]

$u^*$ = the wall friction velocity of the fluid [m/s]

$V_d^+$ = dimensionless particle deposition velocity [-]

$V_p$ = particle deposition velocity [m/s]

$V_{rms}$ = root mean square voltage across the test section [V]

$V_{scr}$ = root mean square voltage supplied to secondary transformers [V]

$w, b$ = subscripts referring to properties taken at inner wall temperature $T_w$ and bulk temperature $T_b$.

$Y_{thick}$ = thickness of the salt layer [m]

**Greek Symbols**

$\Delta C$ = concentration gradient [kg$_s$/kg]

$\Delta h_j$ = change of the heat transfer coefficient [kW/m$^2$-K]

$\varepsilon$ = surface roughness [mm]

$\phi_{HT}$ = porosity of the salt layer in high temperature region [-]

$\phi_{LT}$ = porosity of the salt layer in low temperature region [-]

$\phi$ = porosity of the salt layer [-]

$\mu_j$ = viscosity [kg / m-s]

$\rho_s$ = salt density [kg/m$^3$]

$\rho$ = bulk density of the solution taken to be same at the wall [kg/m$^3$]

$\rho_w$ = pure water density [g/cm$^3$]

$\sigma$ = electrical conductivity of the salt solution [$\mu$S/cm]

$\tau_p$ = the particle relaxation time [s]

$\tau_{p1}$ = dimensionless particle relaxation time [-]

$\tau_w$ = the wall shear stress [N/m$^2$]
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1. INTRODUCTION

1.0. Supercritical water oxidation process

The supercritical water oxidation (SCWO) is a process for the destruction of aqueous organic wastes that is made possible due to the special properties of supercritical water (SCW). Water at temperatures and pressures above the critical temperature and pressure exists as a one phase supercritical fluid with properties that are different from its properties at atmospheric conditions. With a low density, a small dielectric constant and a low dissociation constant, supercritical water exhibits great solvation potential for non-polar covalent solutes and organic compounds. This enhanced solvation ability is used to bring into contact molecules of organic compounds and oxygen resulting in rapid oxidation of organic materials. The SCWO process involves pressurizing of the aqueous waste and oxidant to the working pressure which is typically between 24 and 30 MPa, mixing the pressurized streams followed by preheating to the temperature at which reaction starts, oxidation reaction with the subsequent cooling, depressurizing and separating of the gaseous, liquid and solid products which are mostly H\textsubscript{2}O, CO\textsubscript{2} and ash. A schematic of the process is given in Figure 1.1.

\begin{center}
\begin{tikzpicture}
    \node [rectangle] (oxygen) at (0,0) {Oxygen};
    \node [rectangle] (water) at (0,-1) {Water \& Organics};
    \node [rectangle] (heating) at (1,-1) {Heating};
    \node [rectangle] (reaction) at (2,-1) {Single Phase Reaction};
    \node [rectangle] (cooling) at (3,-1) {Cooling};
    \node [rectangle] (separation) at (4,-1) {Separation};
    \node [rectangle] (co2) at (5,-1) {CO\textsubscript{2}};
    \node [rectangle] (water) at (5,-2) {Water};
    \node [rectangle] (ash) at (5,-3) {Ash};

    \draw [->] (oxygen) -- (water);
    \draw [->] (water) -- (heating);
    \draw [->] (heating) -- (reaction);
    \draw [->] (reaction) -- (cooling);
    \draw [->] (cooling) -- (separation);
    \draw [->] (separation) -- (co2);
    \draw [->] (separation) -- (water);
    \draw [->] (separation) -- (ash);
\end{tikzpicture}
\end{center}

\textit{Figure 1.1. Schematic of the SCWO process.}
The SCWO process promises the following features:

- destruction of organic aqueous wastes that have 1-20% solids concentration with little or no pre-dewatering of the waste
- destruction efficiencies comparable to incineration
- separation of solid, liquid, and gaseous effluents
- given the relatively low operating temperatures (400-600°C), exhaust gases do not contain NO\textsubscript{x}
- calculations show that the process can sustain itself through heat recovery with auxiliary fuel needed only for startup of the system
- portable SCWO plants can be moved to sites, which means that the cost of waste transport is eliminated

Depending on the type of the aqueous waste that is processed, the following problems may arise in a SCWO system:

- corrosion
- pumping
- fouling

The fouling is caused by low solubility of ionic compounds in SCW. Due to their low solubility, certain salts precipitate in the heaters and the reactor causing deposits on the reactor walls and finally plugging. Solutions to the fouling problems in the SCWO systems may arise from a fundamental understanding of salt formation and deposition. A starting point in gaining that understanding would be examining the behavior of a binary salt-water system. The present study is concerned with the behavior of the two component NaCl-H\textsubscript{2}O solution under SCWO operating conditions. This study is a continuation of the work done earlier (Teshima, 1997) on sodium sulfate and its ultimate goal is to model fouling in SCWO systems equipped with a tubular reactor. Sodium chloride was chosen because it
can be found in potential wastes for SCWO treatment, it has simple phase diagram and represents one of two typical types of salts.

SCW as a solvent is introduced in the section 1.1. Since various salts in the processed waste can cause fouling in a SCWO system, the salt’s origins are given in a review of waste treatments and corrosion studies in the section 1.2. Different approaches to the fouling problem solution are summarized in the section 1.3. and possible solutions for SCWO systems with a tubular reactor are given in 1.4.

1.1. Properties of supercritical water

Pure water has been subjected to numerous studies and its thermodynamic and transport properties are well known. For pure water, the critical point corresponds to 22.09 MPa and 374.14°C (Van Wylen, et al. 1994) meaning that above this temperature or pressure there is no liquid-vapor phase change. However, as it can be seen from the Figure 1.2 for a constant pressure of 25 MPa (typical operating pressure of the SCWO facility), the density of water drops rapidly around the critical temperature\(^1\). The density of supercritical water at the temperatures and pressures that are used in SCWO process is around 100 kg/m\(^3\), so SCW can be viewed as a very dense gas.

The change of dielectric constant with the temperature at 25 MPa is given also in the Figure 1.2. The dielectric constant of pressurized water decreases from its value of around 80 for room temperature to value of 2 for typical operating temperatures in the SCWO process. This value is similar to those of non-polar species. Such a low dielectric constant actually shows how disorientated and unstructured water becomes at supercritical conditions (Franck, 1976).

\(^1\) At pressures above 22.09 MPa, the compressibility and other property derivatives go through a maximum at the "pseudocritical" temperature, which increases with pressure.
Figure 1.2. Density and dielectric constant of pure water as a function of temperature at 250 bar. (Haar et al. (1984), Adapted from DiPippo, (1998))

Gas-like density and low dielectric constant are the reasons why SCW is such a good solvent for gases and organics and such a poor solvent for ionic species. At supercritical conditions water becomes a non-polar solvent. The hydrogen and oxygen
atoms in a molecule of water are bonded by polar covalent bonds. Those covalent bonds exist at an angle of 105° and they are not symmetric, resulting in a dipole (Figure 1.3.).

![Diagram of a water molecule with covalent bonds at an angle of 105°.]

**Figure 1.3** Water molecule is a dipole with covalent bonds at an angle of 105°.

Molecules of water are bonded together via hydrogen bonds. In the solid phase, molecules of water are highly ordered in hexagonal packing with hydrogen bonds spacing the molecules out and leaving a "hole" amongst them which is responsible for the lower density of the ice (Figure 1.4.A, Cherim and Kallan, 1976). The maximum number of hydrogen bonds per one water molecule is four.
At ambient conditions the hexagonal structure of ice is distorted by the dynamics of bond bending and rotation (Cochran et al., 1992) so that orientational order persists only for two or three molecular diameters (Figure 1.4.B). Cochran et al. (1992) in a molecular dynamics study looked at solvation structure in SCW. By using "the minimum geometric criterion" of Beveridge et al. (1983), Cochran et al. found that the number of hydrogen bonds per water molecule at ambient conditions approached 2.3, whereas a less rigid criterion which would count bent hydrogen bonds would give number closer to four. As liquid water is heated, the kinetic energy of its molecules increases, hydrogen bonds get weaker, the number of hydrogen bonds per oxygen atom goes down and the density decreases again.

![Figure 1.4. Molecular structure of water in solid phase and at ambient conditions.](image)

At supercritical conditions hydrogen bonding is highly reduced and hydrogen bonds that are formed are very, very weak leaving a picture of a very disordered fluid (Figure 1.5.). Cochran et al. (1992) in their molecular dynamics study found that the number of hydrogen bonds per water molecule in SCW was about one-third the number in
ambient water which comes approximately to one hydrogen bond per one water molecule (Cochran et al., 1992).

![Supercritical water](image)

**Figure 1.5. Hydrogen bonding in supercritical water.**

Because of its non-polar character, SCW is poor solvent for ionic species. That is quite the opposite of the behavior of the water at atmospheric conditions. At atmospheric conditions the attractive forces between ions and water dipoles are stronger than ion-ion attraction which is shown in Figure 1.6. for sodium chloride. Most salts have high solubility at atmospheric conditions.

At supercritical conditions due to the low density of water and decreased number of hydrogen bonds, only small fraction of ions is shielded by water molecules (Figure 1.7) and solubility of the ionic compound decreases. Low solubility at supercritical conditions causes salt precipitation and consequent deposition to the walls in a SCWO facility. Precipitation and deposition mechanisms depend on the type of salt and the phase behavior of the salt solution. Various salts can be found in processed wastes as discussed in the following section.
Figure 1.6. Sodium chloride and water as a solvent at atmospheric conditions.

Figure 1.7. Sodium chloride and water as a solvent at supercritical conditions (water molecules are smaller relative to NaCl molecule).
1.2. Origins of salts in a SCWO system

Fouling is directly related to the chemical content of the aqueous waste that is being treated in the SCWO plant. There are two possible origins of salts in the SCWO system. One origin is directly related to their presence in the waste. So, to avoid plugging of the SCWO system one might restrict SCWO system application only to wastes that do not contain salts. Even in that case, destruction of some organic compounds (e.g. halides) can result in salt formation following oxidation and neutralization.

Testing of different types of wastes has been performed by various research groups and some of them identified fouling with some salts as a significant problem. While processing military dyes and pyrotechnic compounds, Rice et al. (1994) encountered formation of sulfate and chloride salt deposits in the reactor. Oldenburg et al. (1993) treated propellants, explosives and pyrotechnics by combined hydrolysis-SCWO treatment and reported possible sodium carbonate fouling. Kimberly–Clark corporation studied deinking sludge from paper recycling in the SCWO pilot plant at the University of Texas – Austin (Blaney et al. 1996). No plugging was mentioned by the authors for this type of waste. Pharmaceutical waste (1-3 wt% of salts), deinking sludge (0.1 wt % of salts) and municipal sludge (< 0.1 wt % of salts) were treated in Institut fur Technische Chemie, Karlsruhe. The destruction of deinking sludge was successfully completed without plugging. Plugging was observed after two hours of treatment of the pharmaceutical waste (Goldacker et al. 1996). A mixture of primary and secondary sludge from a pulp & paper mill was treated in SCWO by MODEL Development Corporation. It remained unclear if they solved any reactor plugging problems (Modell, 1988). Pulp and paper industry waste was also treated by NORAM Engineering and Constructors Ltd. with the MODEC pilot plant in Karlsruhe (Cooper et al. 1998). Plugging occurred during treatment of secondary sludge that was generated from mill wastewater containing effluent from an old chlorine bleaching process. This secondary sludge had high concentration of chlorinated organics. Bramlette et al. (1990) reported sulfate and phosphate fouling while testing three classes of simulated wastes: inorganic streams containing mixed hazardous and radioactive waste.
Another origin of salts is related to corrosive reactions in the reactor. Most severe corrosion occurs near the pseudocritical temperature. The solution for corrosion is either to use special materials or to neutralize acids formed during the oxidation reactions in which case different salts are formed. When chloride, fluoride, sulphur or phosphorus are present in the waste that is oxidized in the SCWO plant, acids like HCl, HF, H$_2$SO$_4$ or H$_3$PO$_4$ are produced. Their neutralization results in the formation of chlorides, fluorides, sulfates and phosphates. It was observed that chloride was one of the most corrosive species in wastes treated under SCWO conditions (Fodi et al. 1998). Sulfate was reported to be less aggressive than chloride. Possible reactions of HCl and H$_2$SO$_4$ formation are given for oxidation of dioxin and mustard gas:

Dioxin: \[ \text{Cl}_2\text{-C}_6\text{H}_2\text{-O}_2\text{-C}_6\text{H}_2\text{-Cl}_2 + 11 \text{O}_2 = 12 \text{CO}_2 + 4 \text{HCl} \]

Mustard gas: \[ \text{Cl-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-Cl} + 7 \text{O}_2 = 4 \text{CO}_2 + 2 \text{H}_2\text{O} + 2 \text{HCl} + \text{H}_2\text{SO}_4 \]

Extensive research has been going on in the area of materials that can resist corrosion. Of the tested materials, nickel based alloys showed high susceptibility to corrosion particularly in hydrochloric and sulfuric acid environments for temperatures below the pseudocritical temperature of water (Mitton et al. 1998). Corrosion rates for titanium based alloys were two orders of magnitude lower than for nickel based alloys in acidic chloride containing solutions and an order of magnitude lower in acidic sulfate and phosphate containing solutions (Boukis et al. 1998).

It is obvious that the inorganic content of any SCWO processed waste is important to fouling issues. At this time, I am not aware of any detailed study done on the chemical content of processed wastes in terms of the effect of the chemical content on fouling,
types and concentrations of salts present in the waste, and types and concentrations of salts formed during reaction. However, the above summary shows that chlorides, sulfates, phosphates and carbonates can cause fouling during SCWO treatment of various wastes.

1.3. Possible solutions to fouling problems

Depending on their solubility in SCW, some salts precipitate at temperatures around the pseudocritical temperature which is usually reached in the preheating system of a SCWO facility and others precipitate at higher temperatures that are reached in the reactor. Depending on the types of salts present in the system and the operating conditions, salt deposits can be formed in the preheaters, in the reactor or in both. There are several approaches to the solution of the fouling problem.

One suggested approach is to use a salt separation system before the reactor. Such a system would have two functions: preheating of the waste feed to the reaction temperature and removal of salt from the feed stream. Kirts (1994) described a salt separator as a long, vertical, pipe-like pressure vessel with the waste stream introduced at the top and heated by direct mixing with part of the effluent coming from the reactor (heat recovery). Precipitated salts collect at the bottom and on the sides of the vessel and are removed at service intervals by redissolving them in subcritical water and blowing them out with low pressure air. This type of the solution would be beneficial only to the removal of salts that precipitate at lower temperatures since the maximum temperature in the separator would be the one at which reaction starts, which is usually below 400 °C for the pressure of 25 MPa. Also, downtime for the separator cleanup would be needed.

Rice et al. in 1994 proposed a number of input tubes that feed one reactor. When one tube becomes restricted, the feed is switched to the next tube, while the first one is being cleaned. I think, with this design that, if the walls of the preheating tubes were hotter than the bulk fluid, it would be possible to reduce the concentrations of salts that precipitate at lower and higher temperatures and to provide adequate bulk temperature
needed for the reaction to start at the end of the preheating system. The same idea applied to reactor cycling is already jointly patented by Abitibi-Price, Inc. at Mississouga, Canada and General Atomics, San Diego, California (Bond et al. 1996). Two reactors are used in a way that feeding and flushing streams are continuously alternated. The flushing stream is usually clean water at temperatures at which scale buildup can be redissolved.

A more universal solution to the fouling problem would be to prevent or lessen salt deposition in the reactor itself. Different reactor designs could be implemented to lessen fouling. Even though existing designs are more or less successful in lessening scale buildup, the complete elimination of the salt deposition has not been achieved yet and eventually some way of cleaning of the fouled surfaces is needed.

One of the reactor designs targeting fouling is a MODAR type reactor (Barner et al. 1992, Figure 1.8.). This reactor is a vertical pressure vessel in which the waste feed, supercritical water and oxidant are introduced at the top through a coaxial nozzle. The aqueous waste is preheated to approximately 300 °C and then introduced to the reactor. In the reaction zone, the feed is rapidly mixed with supercritical water and oxidant. Salts that precipitate in the reaction zone fall down to the bottom of the reactor which is kept at lower temperatures (200 °C) by injecting continuous stream of cold water. There, precipitated salts get redissolved and are drained from the bottom of the reactor. However, there is still a scale buildup in the reaction zone due to the fraction of precipitated salts being carried to the walls and sticking there. Some salts also precipitate in the preheating zone.
Figure 1.8. MODAR vessel type reactor (Adapted from Barner et al. 1992).

Sandia National Laboratories, Foster Wheeler Development Corporation and Gencorp, Aerojet jointly developed a SCWO reactor with a transpiring wall (Haroldsen et al., 1996) by using a platelet device. Platelets are liners that provide uniform distribution of the fluid through small transpiration pores along their surfaces. The reactor itself is a vertical, three feet long, pressure containment tube with the platelet centered inside by welded rings. The space between the tube and the platelet is divided into three zones. The aqueous waste and oxidant are preheated to 320°C and introduced into the first part of the reactor which is 5 inches long where SCW is injected through bigger holes distributed amongst the pores of the platelet. Waste, SCW and oxidant are mixed in this zone and the
reaction starts. The second zone is 26 inches long and supplied with 450 °C SCW for transpiration. This is the reaction zone. In the third five inch long zone room temperature water is injected to redissolve precipitated salts. Haroldsen et al. (1996) report that the rate of scale buildup and corrosion are significantly reduced. However, after experiments with sodium sulfite it was noted that deposition was significant around the injection holes in the first zone of the reactor.

1.4. Solutions to fouling in SCWO systems with a tubular reactor

The tubular type reactor (Figure 1.9.) is a long horizontal tube in which a preheated mixture of waste and oxidant is introduced at the temperatures at which the reaction starts. The first commercial SCWO system operates with a tubular reactor and was used by Huntsman Petrochemical Corporation (Salt Lake City, Utah) for mixed organic waste streams coming from Huntsman’s Austin Laboratories. Materials that were used for the plant to resist corrosion were not identified for proprietary reasons. The authors claim that plant can operate 320 day/year, 24 hour/day and it needs maintenance once every two weeks for carbonate scale removal from its heat exchangers (McBrayer and Griffith, 1996).

The possible solutions to fouling in a tubular reactor might include reactor cycling (Bond et al. 1996), preheaters cycling (Rice et al. 1994), salt separation system (Kirts, 1994), increase of the operating pressure which for certain salts increases their solubility limit (Rice et al. 1994), and usage of the salt blends that have higher solubility limit (McBrayer et al. 1996). Probably the combination of several approaches will work successfully in a SCWO system with a tubular reactor. For any approach, formation of a salt deposit over time is inevitable and some cleaning method of fouled surfaces will have to be employed. The design of the appropriate solution to the fouling problem depends highly on the location of the deposit (preheaters, reactor) and the plugging time which are defined by the phase behavior of the salts and their deposition mechanism. Given the complexity of the problem, the starting point in the development of the solution would be
to examine the behavior of a binary salt-water system under SCWO operating conditions. Chapter 2 summarizes previous work on phase behavior and deposition studies for two typical salts that can be found in potential wastes: sodium chloride and sodium sulfate. This summary leads to the objectives of the thesis.

![MODEC reactor for SCWO treatment](image-url)

**Figure 1.9.** MODEC reactor for SCWO treatment. Adapted from Modell (1990).
2. BEHAVIOR OF COMMON SALTS IN SCWO SYSTEMS

2.0. Introduction

More understanding of the salt deposition process is needed in order to design an SCWO system that can process salty wastes. Binary salt-water systems were examined by several research groups as the first and the simplest step in gaining a better understanding of the deposition process. Sodium chloride and sodium sulfate are common salts in the waste streams and representatives of the two types of salt-water systems. They have been subjected to intensive research that included phase behavior, precipitation phenomena and deposition studies. There were no deposition studies performed on sodium chloride-water solutions in SCWO systems with a tubular reactor.

The following sections describe the phase behavior (section 2.1.), and precipitation phenomena (section 2.2.) of sodium sulfate-water and sodium chloride-water systems and deposition studies on sodium sulfate (section 2.3.). This review of the work done on salt behavior in SCWO systems leads to the objectives of the thesis that are given in the section 2.4.

2.1. Phase behavior

The phase behavior of salt water systems (binary and ternary) at elevated pressures and temperatures has been examined extensively for the last 40 years because of its importance in different disciplines from geochemistry to power plant engineering. Binary salt water systems at high temperatures and pressures, according to their phase behavior, can be divided in two basic groups (Valyashko, 1977). In general, their phase diagrams \((p,T,x)\) are three-dimensional. A characteristic of a binary salt-water system phase diagram is its critical curve. The critical curve extends from the critical point of the first component to the critical point of the second component of the system and gives \(p, T, x\) for which the composition of the vapor and the liquid phases are identical (Franck 1967).
Salt-water systems that belong to the first group of binary systems (Type I systems) have components with similar molecules, low melting temperature of the salt (around 900 °C), and critical curves that are uninterrupted (Valyashko, 1977, Franck, 1967). A typical representative of these Type I salts is sodium chloride and more details on the phase behavior of NaCl-H₂O solution are given in the section 2.1.1. Salts that form Type II binary systems exhibit a decrease in the solubility when temperature approaches the critical temperature of the water and have a critical curve that is interrupted and interferes with the three phase solid-liquid-gas surface (Valyashko, 1977, Franck, 1967). The typical representative of this group is sodium sulfate. (More details are provided in the section 2.1.2.)

### 2.1.1. Phase behavior of the NaCl-H₂O system

The pressure-temperature-concentration (p-T-x) diagram of the sodium chloride-water solution is given in Figure 2.1. and shows the boundaries between the different phases of the solution. The pure water component is on the left side and the pure salt component is on the right side of the concentration axis. Triple points of pure water and pure salt are denoted with TP and critical points of pure components with CP. A constant temperature cross-section and a constant pressure cross-section of the phase diagram are given in the Figures 2.2.A and 2.2.B. The whole p-T-x diagram has four regions: a one phase fluid region, a liquid-vapor region, a vapor-solid region and finally a liquid-solid region. The liquid-vapor region is defined by three areas that are bounded by three curves. (Figure 2.1.) The first curve is the curve that connects the critical point of water to the critical point of the salt and is called the critical curve (c) of the solution. At conditions determined by this curve, the liquid phase and the vapor phase have the same composition. The second curve, denoted with v, is the curve on the left side of the critical curve and it represents the composition of the vapor phase at three phase equilibrium. The surface between that curve and the critical curve is the surface that represents vapor composition at vapor-liquid phase equilibrium. The curve on the right side of the critical curve, denoted
Figure 2.2.A

TP – the triple point
CPW – the critical point of water
CPS- the critical point of salt
\(c\) – the critical curve
\(v\) – the composition of vapor phase at three-phase equilibrium
\(l\) – the composition of liquid phase at three-phase equilibrium

- VLS the three-phase (vapor-liquid-solid) equilibrium surface

C – critical point of the solution at the constant temperature

Figure 2.1. Phase diagram for the binary NaCl-water system (adapted from Gehrig et al. 1986).
$l$, determines the composition of the liquid phase at the three phase equilibrium. The area between this curve and the critical curve gives the composition of the liquid phase at the vapor-liquid equilibrium. The area between curves $v$ and $l$ is a three-phase equilibrium area (VLS). The critical curve does not interfere with the three phase equilibrium area and is uninterrupted. That means that the equal composition of phases in the solution (critical phenomena) exists only for liquid-vapor equilibrium and not for three phase equilibrium.

When a constant temperature cross section is taken between the critical point of water and the maximum of the critical curve, p-x diagram for NaCl-water solution shown in the Figure 2.2.A. is obtained. The point C is the critical point of the solution for the given temperature.

*Figure 2.2.A. Constant temperature cross section of the $p$-$T$-$x$ phase diagram: $p$-$x$ phase diagram for NaCl-water solution.*
The line V- L is a three-phase line, part of the three-phase surface from the p-T-x diagram. The point V corresponds to the curve v on the p-T-x diagram and gives the composition of the vapor phase at the three phase equilibrium. The point L corresponds to the curve l and gives composition of the liquid phase at the three phase equilibrium. The curve V-C is the composition of the vapor phase at the vapor-liquid equilibrium and the curve L-C gives the composition of the liquid phase at the vapor-liquid equilibrium. The vapor-solid equilibrium is given by the curve v-s.

Of particular interest for this study is T-x phase diagram for pressure taken between the critical point of water and the maximum of the critical curve (Figure 2.2.B). The critical point C is obtained as an intersection between the critical curve c and the p = const. plane. The three phase line is given as V-L and represents the intersection between the p=const. and the three phase equilibrium surface. The curve C-V gives the composition of the vapor phase at the two phase equilibrium and the curve C-L gives the composition of the liquid phase at the two-phase equilibrium. The line v-s is vapor-solid equilibrium line.

Since the sodium chloride-water system plays a significant role in power plant engineering and geochemistry, its phase behavior was investigated in detail in the past. In particular, vapor-liquid, vapor-liquid-solid and vapor-solid curves were obtained for constant temperatures and constant pressures. Armellini (1992) summarized previous experimental work on phase equilibrium in NaCl-H\textsubscript{2}O systems as well as thermodynamic models describing the system phase behavior. Armellini incorporated results obtained for isothermal (constant temperature) phase equilibria at temperatures of 450, 500 and 550 °C. The isobaric phase equilibrium diagrams were obtained by Armellini as an interpolation of the isothermal data of the various researchers. Armellini performed isobaric phase equilibrium experiments to obtain the vapor-liquid equilibrium curve as well as to investigate solid salt formation. He used an optically accessible cell (Figure 2.3.) that could withstand temperatures up to 700 °C and pressures up to 340 bar.
$C$ — critical point of the solution, $v-s$ — vapor-solid equilibrium curve,
$V, L$ — the composition of the vapor and liquid phase respectively at the three phase equilibrium

**Figure 2.2.B.** Constant pressure cross section of the $p$-$T$-$x$ phase diagram: $T$-$x$ phase diagram for NaCl-water solution.
Figure 2.3. Cross-sectional view of high-temperature and high pressure optically accessible cell (Armellini, 1992).
The cell was first filled at room temperature with the salt solution of known concentration that was varied from 0.1–20.0 wt % for different experimental runs. After that, the heating of the cell was done at the rate of 1.5°C per minute while the pressure was kept constant at 250 bar. A one-phase solution would pass into the vapor-liquid region during heating. Formation of liquid phase was visually observed and recorded by video taping. The bulk temperature as well as the cell wall temperature were recorded during the experiment. Those two temperatures corresponding to the to the first appearance of the second phase provided a lower and an upper bound for the real phase nucleation temperature since bubbles appeared to emerge from the cell wall. The experimental results obtained from the research above for the vapor-liquid equilibrium curve in the isobaric phase diagram at the constant pressure of 25 MPa (typical operating pressure of a SCWO facility) are plotted in the Figure 2.4. At this pressure, the critical point of the solution is around 387°C and the three phase equilibrium temperature around 450°C. The vapor and the liquid phases are two-component and the solid phase is assumed to be 100% sodium chloride.

Bischoff (1991) provided a complete tabulated summary of the pvTx liquid-vapor surface of NaCl-H\textsubscript{2}O between 300 and 500°C from a compilation of experimental data. The change of the vapor concentration at two phase equilibrium with pressure and temperature is obtained from Bischoff's summary and plotted in Figure 2.5. The change of the concentration of liquid phase at the vapor-liquid equilibrium with temperature and pressure is plotted in Figure 2.6. From the same summary, the change of three-phase equilibrium temperature with pressure is obtained and plotted in Figure 2.7. These interpolations are used to model the experiments described in the present thesis. Pitzer (1998) developed an equation of state for the NaCl-H\textsubscript{2}O system that very well represents experimental data in the temperature range 300 – 700 °C. The equation of state is based on theoretical modeling for mixtures of hard spheres. So the vapor-liquid equilibrium curve is well defined by experimental data and Pitzer's equation of state.
Figure 2.4. Temperature - Composition NaCl-H₂O phase Diagram
Figure 2.5. The change of vapor concentration at two phase equilibrium with pressure and temperature (based on the data published in Bischoff, 1991).
Figure 2.6. The change of the concentration of liquid phase at the vapor-liquid equilibrium with temperature and pressure plotted from data published in Bischoff (1991).
Figure 2.7. The change of three-phase equilibrium temperature with pressure obtained from data published in Bischoff (1991).

\[ T_p = 0.1136p^2 + 0.9077p + 356.16 \]
For deposition studies in a SCWO system for a process at constant pressure, the vapor-solid equilibrium curve is of equal if not greater importance. NaCl vapor-phase solubility studies from seven different research groups were examined and their results summarized by Armellini and Tester (1993). In Armellini and Tester's review it is said that flow methods were used by Styrikovich et al. (1955), Martynova and Samoilov (1962) and Galobardes et al. (1981). Solubility experiments done by Olander and Liander (1950), Sourirajan and Kennedy (1962) and Bischoff et al. (1986) involved sampling with a direct measurement of Na\(^+\) and/or Cl\(^-\) concentration. The change of solubility with pressure for the temperature of 500 °C obtained from the research groups above is given in Figure 2.8. It can be seen that there were certain discrepancies in their results. The inconsistencies among solubility data could have been caused by errors associated with an experimental procedure or errors caused by the high temperature hydrolysis of solid NaCl. The hydrolysis reaction can be written as:

\[
\text{NaCl}_{(s)} + \text{H}_2\text{O}_{(v)} = \text{NaOH}_{(s)} + \text{HCl}_{(v)} \quad (2.1.)
\]

Besides dissolved NaCl, HCl may be another source of chlorine in the vapor phase. Hydrolysis would affect solubility measurements if the measurements were chlorine-based. Hydrolysis of solid NaCl was studied by several researchers (Martynova and Samoilov, 1957; Armellini and Tester 1993). It was observed that the extent of hydrolysis depended on pressure and temperature. For their solubility measurements Armellini and Tester used 20-25 cm long salt bed in an Inconel 625, 1.43cm OD and 0.91cm ID tube that was 42 cm long. During their experiments pure deionized water flowed continuously through the salt bed. Armellini and Tester measured the concentrations of hydrogen, sodium and chloride ions in their samples. Sodium chloride solubility experiments were performed for temperatures of 450°, 500° and 550°C and pressures from 100-250 bar. Flow rates varied from 0.0002-0.003 kg/min. The effect of the hydrolysis on solubility measurements is given as a molar ratio [Cl\(^-\)]/[Na\(^+\)] in Table 2.1. as well as the solubility results. The hydrolysis reaction was the most significant for temperatures greater than 500 °C and pressures of 100 bar. The hydrolysis was not very significant at a pressure of 25 MPa.
<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Pressure (bar)</th>
<th>Density (kg/ m³)</th>
<th>NaCl solubility (ppm)</th>
<th>[Cl]/[Na] (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>100</td>
<td>33.61</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>450</td>
<td>150</td>
<td>54.22</td>
<td>12.5</td>
<td>1.1</td>
</tr>
<tr>
<td>450</td>
<td>200</td>
<td>78.73</td>
<td>63.6</td>
<td>1.0</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>30.5</td>
<td>0.9</td>
<td>5.5</td>
</tr>
<tr>
<td>500</td>
<td>150</td>
<td>48.08</td>
<td>13.7</td>
<td>1.2</td>
</tr>
<tr>
<td>500</td>
<td>200</td>
<td>67.7</td>
<td>31.4</td>
<td>1.1</td>
</tr>
<tr>
<td>500</td>
<td>250</td>
<td>89.9</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>28.07</td>
<td>0.9</td>
<td>8.3</td>
</tr>
<tr>
<td>550</td>
<td>200</td>
<td>60.43</td>
<td>33.8</td>
<td>1.2</td>
</tr>
<tr>
<td>550</td>
<td>250</td>
<td>78.64</td>
<td>98</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Table 2.1 NaCl solubility and hydrolysis results at pressures 100-250 bar and temperatures 450-550 C (Armellini and Tester 1993).*
Figure 2.8. Comparison of experimentally obtained isothermal solubility of NaCl to solubility model predictions at 500 °C (Adapted from Armellini 1993).
For the vapor-solid equilibrium curve Styrikovich 1969, Martynova 1964, Galobardes et al. 1981 used a simple semi-empirical solubility model to correlate the experimental data. In this model, it was assumed that equilibrium between solid NaCl and its vapor exists as a solvation type reaction:

\[
NaCl(s) + nH_2O(v) = NaCl \cdot nH_2O(v) \tag{2.2}
\]

\(n\)-number of hydrated water molecules attached to the dissolved NaCl

Since NaCl that is dissolved in SCW stays as a bound ion pair (Mesmer et al. 1989, Cui and Harris, 1994) the equilibrium relationship for 2.2 was written as:

\[Kc = A_{hyd} / (A_w^n A_s) \tag{2.3}\]

Where:

- \(A_{hyd}\)- the activity of hydrate NaCl \(nH_2O(v)\)
- \(A_w\)- the activity of water
- \(A_s\)-the activity of solid NaCl

It was assumed that activity of of the solid NaCl \(A_s\) was equal to 1, and that the vapor phase was ideal. The water activity was taken as proportional to the density of pure water \(\rho_w\) and the following expression for equilibrium constant was obtained:

\[Kc \cong C_{NaCl} / \rho_w^n \tag{2.4}\]

Where,

- \(C_{NaCl}\)- concentration of NaCl in vapor phase
Figure 2.9. Comparison of experimentally obtained isobaric solubility of NaCl to solubility model predictions at 250 bar.

Martynova-Galobardes-Armellini solubility model (Eq. 2.6.)
By taking the logarithm of both sides of the equation 2.4. and expressing the dependence of equilibrium constant on temperature as a Gibbs-Helmholtz type relationship the following expression was obtained:

$$\log C_{\text{NaCl}} = n \log \rho_w - E \div T + F \quad (2.5.)$$

E,F- constants

Armellini et al. applied the above form of the solvation model (2.5) to regress their data. They included data of Galobardes' (1981) and Bischoff et al. (1986) in their fit. The resulting model equation (Martynova-Galobardes-Armellini solubility model) has the form:

$$\log C_{\text{NaCl}} = 3.866 \log \rho_w - 1233.4 \div T + 7.772 \quad (2.6.)$$

Where:

$C_{\text{NaCl}}$ - concentration of NaCl in ppm

$\rho_w$ - pure water density in g/cm$^3$

T - temperature in K

This solvation model very well represented Armellini's solubility data at 450, 500 and 550 °C. However, at the constant pressure of 25 MPa Armellini obtained only two data points for the temperatures of 500 and 550 °C (Figure 2.9.). These data points are not in agreement with results obtained by Sourirajan and Kennedy (1962) for the same pressure. Armellini comments that Kennedy's results were affected by errors associated with the dilution of the samples before analysis. Since our UBC study is in particular concentrated on the sodium chloride deposition at a constant pressure of approximately 25 MPa, more experimental data are needed for sodium chloride solubility to verify the adequacy of the simple solubility model.
2.1.2. Phase behavior of Na$_2$SO$_4$-H$_2$O solution

The system sodium sulfate–water exhibits phase behavior of the second type meaning that the critical curve in the p-T-x diagram is interrupted and that the solubility of sodium sulfate in water decreases when the temperature approaches the critical temperature of water (Valyashko, 1977, Armellini, 1992). The critical curve (c) intersects with vapor composition at the three-phase equilibrium curve (v) and liquid composition at the three-phase equilibrium curve (l) at two points: P and R (Figure 2.10). The point P is very close to the critical point of pure water and it occurs at a temperature of 374°C and a pressure of 221 bars. The intersection at the point R happens at approximately 440°C and 1160 bars (Armellini, 1992). The region of the phase diagram below the point P is called the lower two- and three-phase equilibrium region. The region above the point R is defined as the upper two and three-phase equilibrium region. The region between points P and R is the metastable portion of the critical curve and three phase immiscibility regions. To show the phase boundaries, the constant temperature cross sections were taken at three different temperatures and resulting p-x diagrams are shown in the Figure 2.11. The p-x diagrams are obtained at the temperature below point P [Figure 2.11.a.], at the temperature between P and R [Figure 2.11.b.] and at the temperature above R point [Figure 2.11.c.]. Given that a typical operating pressure in a SCWO facility is around 25 MPa, the phase diagram of the interest for the deposition studies (T-x diagram) is located in the region between the critical end points P and R. As it can be observed from Figure 2.11.b only two phases, vapor and solid phase, exist in equilibrium in this region.

One set of data for the vapor-solid equilibrium curve at the pressure of 25 MPa was obtained in a study done at UBC in 1997 (Teshima, 1997, Rogak and Teshima, 1999). For his solubility measurements Teshima used an electrically heated test section (the same one used in the present study). The test section was equipped with bulk and surface temperature measurements and was kept isothermal within 1°C during the solubility
Figure 2.10. Phase diagram for the binary Na$_2$SO$_4$-water system (Adapted from Valyashko 1977).
a) Constant T cross section through the lower region at a temperature lower than the temperature corresponding to point P

b) Constant T cross section through the metastable region at a temperature between points P and R

c) Constant T cross section through the upper region at a temperature higher than the temperature corresponding to point R

Figure 2.11. Pressure–composition Na$_2$SO$_4$–water diagram (Armellini, 1992).
Figure 2.12. Summary of data for solubility of sodium sulphate in water at 25 MPa (Rogak and Teshima, 1999).
experiments. The basic assumption was that the whole test section was at the same temperature and that all salt above the solubility limit would deposit in the test section. The concentration of the salt in the effluent was measured with a conductivity meter. Twenty two data points were obtained in the temperature range 374 – 505 °C using two different flow rates. Results from this and other studies are given in the Figure 2.12. More details can be found in Teshima, (1997).

2.1.3. Ternary NaCl-Na$_2$SO$_4$-H$_2$O system

The phase behavior of the NaCl-Na$_2$SO$_4$-H$_2$O ternary system was examined by Hong et al. (1995), Armellini (1992), and DiPippo (1998 at MIT). DiPippo determined what phases existed in equilibrium at pressures of 200 and 250 bar and temperatures ranging from 320 to 400°C. The total salt in the ternary mixture was varied from 5-20 wt %. The phase equilibria for 10 wt % total salt at 250 bar is shown in Figure 2.13. For the high concentrations of sodium sulfate in the mixture, solid-liquid equilibrium was observed. In the mixtures with higher concentrations of sodium chloride, vapor-liquid equilibrium exists. It seems that solid phase formation can be avoided in the temperature range 340–400°C if sodium chloride is added in a sufficient amount to wastes containing sodium sulfate.

2.2. Precipitation phenomena for sodium chloride and sodium sulfate

Experiments simulating rapid precipitation of sodium chloride and sodium sulfate in Modar type reactors (section 1.3.) were performed by Armellini et al. (1994). Aqueous salt solutions with salt concentrations of 0.1-10wt% were injected into a coaxially flowing SCW stream at constant pressure of 25 MPa. Experiments involved particle collection and laser transmission measurements. The experimental apparatus included an optical cell and laser transmission equipment (Figure 2.14.).
Figure 2.13. Temperature-composition diagram for NaCl-Na$_2$SO$_4$-H$_2$O system at 250 bar and 10 wt% total salt (DiPippo, 1998).
Results from scanning electron microscopy (SEM) of collected solids, in situ laser transmission measurements, and low magnification microscopic or visual observation of the jets showed that, at this pressure, the sodium chloride solution first passed through the two-phase/liquid-vapor region before particles are formed, whereas with sodium sulfate the solid phase was formed directly from a homogeneous supercritical solution (Armellini et al. 1994). Sodium sulfate particles were smaller in size, 1-3μm. Two models were
proposed for particle formation by Armellini. The first model assumed homogeneous nucleation of sodium sulfate particles followed by mass transfer limited growth of solids. The second model assumed that particles were growing by agglomeration. Sodium chloride particles that were collected from a 0.5 wt % solution ranged from 5 to 25µm in size and particles formed from a 10 wt% solution had size in the range of 20-100µm(Figure 2.15.). The sodium chloride particles were hollow inside.

Figure 2.15. SEM photomicrographs of particles collected during shock crystallization experiments (Armellini and Tester, 1991).

The authors assumed that highly concentrated liquid droplets were precursors for nucleation of the solid sodium chloride phase. This mechanism of shock crystallization was also responsible for the porous structure and the size of particles.
2.3. Deposition rate experiments and modeling

2.3.1. UBC sodium sulfate deposition study

The aims and methods of the present work are closely related to Teshima's study (1997), which will now be reviewed in some detail. Sodium sulfate solubility measurements (see section 2.1.2.), deposition experiments and deposition modeling were performed by Teshima at the UBC/NORAM pilot plant. The detailed description of the pilot plant can be found in the Chapter 3., section 3.1. or in Teshima (1997).

![Figure 2.16. The UBC/ NORAM test section (not to scale).](image)

The objective of the deposition experiments was to measure salt thickness profiles along the test section (Figure 2.16) for different experimental conditions for turbulent flow in a heated horizontal pipe and compare them to model predictions. Salt thickness profiles were inferred from outer surface temperature measurements (at the locations of salt deposits outer surface temperature increases due to the decreased thermal conductivity of the wall plus salt). Teshima (1997) performed 14 deposition experiments with sodium sulfate concentrations varying from 0.652 to 1.066 wt % and flow rates in the range 0.62 - 2.22 kg/min (Reynolds numbers 33,000 to 180,000). The inlet bulk temperature in the test section was varied from 363 to 375°C and the outlet bulk temperature ranged from 384 to 388 °C. The variation in the heat flux was from 0.8 to 5.73 kW/m. Teshima concluded that
buoyancy was not important under the conditions of his study. When the temperature profiles were obtained, the next step was to calculate salt thickness profiles. The basis for this calculation was a heat transfer model based on properties and correlations for pure water. To calculate salt thickness profiles along the tube, an additional heat transfer model for the salt layer was added. Knowing the conductivity of the salt layer, its thickness could be inferred from changes in tube surface temperature. The salt layer was assumed to be porous with parallel columns of salt and stagnant water at a constant porosity $\phi$ of 0.71 (taken from Hodes 1994). The conductivity of the salt layer was calculated from:

$$k_{\text{layer}} = (1 - \phi) k_{\text{salt}} + \phi k_{\text{water}}$$  \hspace{1cm} (2.7)$$

The thermal conductivity of sodium sulfate was not available at the conditions of interest for this study. To assess thermal conductivity Teshima used mass balances from six experiments. For each of six runs, Teshima assumed an initial thermal conductivity of the sodium sulfate ($k_{\text{salt}}$) to calculate the conductivity of the porous salt layer ($k_{\text{layer}}$). When the salt thickness profile was obtained as described in the procedure above, he calculated the mass of the salt deposited in the whole tube and compared it to the mass measured in the experiments. Then he adjusted thermal conductivity of salt until the two masses agreed within 0.5 grams in values. The thermal conductivity obtained in this way ranged from 2.5 to 9.8 W/m-K. An average was taken of all obtained values of thermal conductivity with a result of 5.8 W/m-K that was used to calculate salt thickness profiles for all experimental runs that were analyzed (at times when 0.024 kg of salt was delivered to the test section). It is not known how strong a function of temperature the thermal conductivity of sodium sulfate is. However, Teshima underlined that the salt thickness profiles were as accurate as the estimation of the thermal conductivity of salt.

Another issue related to this calculation was pointed out by Hodes (1998) in his literature review. This issue was Teshima's assumption that the porosity of the salt layer in all experiments was uniform and equal to 0.71. With this assumption Teshima obtained values of thermal conductivity ranging from 2.5 to 9.8 W/m-K for a very small
temperature variation. For example, the thermal conductivity of sodium chloride at room temperature (20°C) and 175°C is 6 and 4 W/m-K respectively. If we extrapolate thermal conductivity data to the temperature of 375°C (average temperature for Teshima's deposition experiments) the value of thermal conductivity comes to 3 W/m-K. So, the change of thermal conductivity for sodium chloride from 20 to 375°C is from 6 to 3 W/m-K, whereas Teshima obtained change of thermal conductivity of sodium sulfate from 9.8 to 2.5 W/m-K in the temperature range 363-388°C. If, in the same procedure that was used to obtain the thermal conductivity that is described above, the thermal conductivity of salt was kept constant, the porosity of the salt layer would not be constant and would change from run to run to satisfy the mass balance. Hodes (1998) in his review of Teshima's work performed a calculation showing how sensitive salt thickness profile was to porosity. At a temperature of 375°C and pressure of 25 MPa, the thermal conductivity of water is 0.41 W/m-K. If we approximate the thermal conductivity of sodium sulfate with the thermal conductivity of sodium chloride at this temperature which is 3 W/m-K for the values of porosity of 0.6 and 0.8 we would obtain the conductivity of salt layer (from the expression above) as 1.44 and 0.92 W/m-K respectively. It is obvious that the value of porosity definitely affects calculated salt thickness profiles. I would conclude that salt thickness profiles were as accurate as the assumptions that thermal conductivity of sodium sulfate was equal to 5.8 W/m-K and that porosity was constant in all runs and equal to 0.71. Hodes suggested performing the mass balances for the same experimental run at different times and calculating porosity (if the conductivity of salt was known) to see how porosity changed with time. For this to be done reliably, an accurate mass balance and salt thermal conductivity data are needed. Once the salt thickness profiles were available they were compared to the mass transfer model predictions. The four different mass transfer models were developed to predict the thickness of the salt layer as a function of distance from the test section inlet. All models assumed no surface resistance to the salt molecules and/or particles attachment to the wall. Also, they took into account the effect of hot walls on deposition (except "Model 3"). "Model 1" (Suspended Particles) assumed that salt particles were formed in the bulk fluid when the bulk concentration exceeded the solubility limit and were carried along the tube without being deposited to the wall. "Model 2" (No
Nucleation) assumed that the bulk solution was supersaturated without homogeneous nucleation of the particles. For “Model 3” (Chan et al., 1994) the amount of salt deposited on the wall was calculated from Chan et al. model. The assumption used in this model was that all salt above the solubility limit in the bulk was immediately transported to the wall. For “Model 4” (Complete) both particle deposition and molecular mass transfer were taken into account. It was assumed that all particles nucleating homogeneously in the bulk had diameters of 2 µm (based on Armellini’s precipitation studies, see section 2.2.). Figure 2.17. gives a comparison of the predictions from the four models to the experimentally obtained salt thickness profile along the tube for the deposition experiment number 11 (Init. Conc. = 1.066 wt %, Mass flow = 2.16 kg /min, Temp. range =365-386 ° C, Heat flux = 5.58 kW/m, Time = 80 sec.).

Figure 2.17. Comparison of experimental and predicted salt deposition profiles for sodium sulphate in a heated tube at 25 MPa and near critical temperatures.
As you can see models 1, 2, and 4 produced the same salt thickness profiles. The magnitude of the peak in the profiles is about 30% below the experimental result. The location of the peak is at 0.5 m whereas the experimentally obtained profile gives the location of the peak at 1.25 m. “Model 3” is not consistent with other models. This is not surprising since this model does not take into account the effect of the hot walls on deposition. The models gave similar predictions as above for all experimental runs which indicated that molecular mass transfer was a more important mass transfer mechanism than deposition of particles. Moreover, the models suggested that bulk solution was always below saturation and no particles in the bulk were nucleated at the investigated experimental conditions.

Teshima pointed out that model predictions were as accurate as the solubility equation and mass transfer coefficient calculation.

2.3.2. MIT/ NIST deposition rate study

Hodes (1998) at MIT in cooperation with NIST performed solubility and deposition rate studies with sodium sulfate and potassium sulfate. The MIT test cell was a six port chamber with a centrally placed hot finger that was optically accessible. The test cell was modified from a ¾ inch (1.91 cm) diameter, stainless steel 316, Swagelok cross. The inner surfaces of the chamber were gold plated to prevent corrosion. The four chamber ports were used for instrumentation access (bulk thermocouple), visual access (sapphire windows), and mounting of an internally heated cylinder in the center of the test cell (plug, Figure 2.18.). The fluid entered the test cell through the hole drilled at the bottom of the cross and exited through the hole drilled at the top of the cell (in and out of paper in Figure 2.18.). The hot finger had two parts: an Inconel 625 base (used for mounting ) and the actual heated cylinder that was 2.76 cm long with the diameter of 0.559 cm. The heated cylinder was made of copper with a Hastelloy C276 sleeve and an Inconel 625 cap. Heating of the finger was provided with Watlow C1E14 Firerod cartridge heater that was placed into 0.125 inch diameter hole in the hot finger. Power
supplied by the heater was 10.61 watts. Five K type thermocouples were located on the surface of the hot finger to measure axial and azimuthal temperature profiles (Hodes, 1998). In this experimental setup, a pump provided flow rate of up to 25 ml/min at STP.

![Diagram of the optically accessible test cell with the hot finger](image)

**Figure 2.18. The optically accessible test cell with the hot finger. The flow is in and out of the page.** (Hodes, 1998)

Solutions (2 to 8 wt % of salt) were pressurized to 250 bar and preheated to a temperature close to the solubility limit for the given pressure and initial concentration. The final heating was provided in the hot finger. In that way, deposition was restricted to the hot finger only. The duration of the deposition experiments varied from 6 to 12 minutes. Twenty one experimental runs were performed with the bulk temperature ranging from 340.8 to 374.7 °C. During the experiments temperatures were recorded at 1 – 2
minute intervals and the pressure drop across the cell was recorded as well. It was noticed that the bulk temperature in each run increased by 3 °C.

After the purging of the cell with nitrogen that was done to prevent salt re-dissolving during the cool-down, the hot finger was removed, the salt deposit examined and the mass of salt measured. The obtained deposition rate from the experiments was on the order of one gram per minute. The porosity of the salt layer was measured as well and it was approximately 70 %. The heat and mass transfer mechanism for all experiments was natural convection.

In the deposition modeling, Hodes assumed that there was no homogeneous salt nucleation in the boundary layer around the finger and that salt molecules were transported from the solution to the hot finger surface by natural convection only. Salt would then nucleate heterogeneously at the finger-solution interface. This assumption was partially validated by visual observation during the experiments. Another validation was provided with a model that was developed to show if nucleation in the boundary layer would occur or not at the experimental conditions.

Two deposition rate models were developed. The first model assumed an analogy between heat and mass transfer, and a linear relationship between salt solubility and temperature. This model neglected buoyancy forces (Hodes, 1998). The second (rigorous) model took into account buoyancy forces and the heat of precipitation when salt was nucleating. Salt deposition within a porous salt layer was not accounted for. The predictions of the second model agreed well with the experimental results for concentrations up to 4 wt %. For higher concentrations the model under predicted the experimental data by a factor of two. Hodes pointed out that disagreement of the model predictions with the experimental data for higher concentrations was caused by the significant deposition within the porous salt layer. It was concluded that no homogeneous nucleation was happening and that the dominant mass transfer mechanism was diffusion of
salt molecules across the boundary layer from the solution to the finger-fluid interface and consequent heterogeneous nucleation at the interface.

2.5. Objective and outline of the thesis

In general, the salt deposition studies described above had a purpose of gaining better understanding of the fouling process in the SCWO systems, so that the fouling problem could be overcome. The sodium sulfate studies done by Hodes (1998) and Teshima (1997) showed that homogeneous nucleation was not happening at the conditions of their experimental work. Given the differences in the phase behavior, morphology of solid particles, and temperature range at which precipitation occurs at a pressure of 25 MPa for sodium chloride and sodium sulfate, one might argue that their deposition rates and deposition mechanisms are different. We could find no research on deposition rates from sodium chloride-water solution under supercritical conditions done to this time. So in this work, the deposition of sodium chloride at supercritical conditions in turbulent flow through a horizontal, electrically heated (constant heat flux), insulated pipe is examined. This work is undertaken with the goal of obtaining an appropriate model for sodium chloride deposition in a SCWO plant with a tubular reactor which would approach sodium chloride’s behavior in reality and be able to predict salt thickness profiles with particular interest in the location and height of their peaks in the electrically heated tube. In this study I investigated which mass transfer mechanism was the most dominant mechanism in deposition from a sodium chloride-water solution. The problem is complicated by the existence of the two phase vapor-liquid region. This region can affect heat and mass transfer in an electrically heated tube. Since the liquid phase is much denser than the vapor phase, phase separation might occur along the tube. According to Armellini, dense liquid droplets are precursors for solid particle formation. That indicates that the concentration and size of droplets could affect deposition mechanism as well.

The objectives of this work include following:
I. Modeling of the deposition of sodium chloride from a sodium chloride-supercritical water solution in fully developed turbulent flow in a heated tube with constant heat flux

II. Verifying the modeled profiles with the experimental results:

1. when the bulk temperature in the test section is below the three phase temperature (vapor-liquid region, Low Temperature Region) which is a situation that might in reality correspond to the temperature profile in the preheaters of the SCWO plant, and

2. when the bulk temperature in the test section is above the three-phase temperature (vapor-solid region, High Temperature Region) which is the situation that would arise in the reactor.

In order to meet the objectives, the following was done:

a) Experiments to determine sodium chloride solubility in SCW.

In the modeling of salt deposition a vapor-solid equilibrium model is needed. To verify the applicability of the Martynova-Galobardes-Armellini solubility model (Armellini, 1992) described in the section 2.1., solubility measurements were performed. The hydrolysis effect on solubility measurements was tested with two methods of sample analysis.

b.) Experiments to determine salt thickness profiles for various initial concentrations, heat fluxes, and flow rates when:

1. the bulk temperature is below the three phase temperature (Low Temperature Region) and

2. the bulk temperature is above the three-phase temperature (High Temperature Region)

The experimental data were obtained to verify our sodium chloride deposition model. The deposition experiments followed Teshima’s experimental work (see 2.3.). The salt thickness profiles were inferred from the outer surface temperature measurements.
However, the method was improved with a better mass balance procedures (mass balance performed at different times during one experiment) and sampling at the inlet and the outlet of the test section. Another improvement came from the availability of thermal conductivity data for sodium chloride. The porosity effect on the salt thickness profile calculation was examined as suggested by Hodes (1998). The effect of vapor-liquid region on deposition was investigated as well.

c) Three models were developed for deposition of sodium chloride from the vapor-liquid region and one model for deposition from the vapor-solid region. Modeled deposition profiles were compared to the experimental results and the deposition mechanisms discussed.
3. UBC/NORAM EXPERIMENTAL FACILITY

3.0. Introduction

The UBC/NORAM experimental facility was used to provide data on the solubility of sodium chloride in SCW at constant pressure and to measure sodium chloride deposition rates in turbulent flow of SCW through an electrically heated horizontal pipe. During the experiments, steady conditions were first reached with distilled water and then bulk and surface temperatures, pressures, flow rate, and power recorded. The feed was then switched to the salt solution of a specified concentration. During the solubility and deposition experiments, in addition to real-time temperature and pressure measurements, the conductivity of the effluent was recorded. In the salt deposition studies, salt thickness profiles were inferred from the outer surface temperature measurements on the test section of the pilot plant. The pressure drop along the test section was recorded as well. The fluid at the inlet and the outlet of the test section and at the outlet of the system was sampled at different times to perform mass balance. A detailed description of the pilot plant, its components and instrumentation is given in the following sections.

3.1. UBC/NORAM pilot plant

Two different experimental set-ups were used in the course of this study since the UBC/NORAM pilot plant had been constructed in two phases. The facility constructed in the first phase (initial experimental set-up) provided a test section for heat transfer and deposition studies. The test section was used for temperature and pressure measurements. The second phase facility (revised experimental set-up) was extended with a 115.8 meter long reactor (mounted after the test section) that was used for oxidation studies. This increased the total length of the facility and consequently the residence time of the plant. The revised pilot plant was improved with sampling ports and new electrical connections. NaCl solubility studies and some of the NaCl deposition measurements were performed with the initial experimental set-up.
The initial configuration of the pilot plant (Figure 3.1., approximately 23.2 m of Inconel 625 tubing) includes a Regenerative Heat Exchanger (6.2 m long), Preheater 1 (4.7 m long), Preheater 2 (4.7 m long), Test Section (3.8 m long), Test Section-Heat Exchanger connection (3.8 m long), and Process Cooler (6.2 m long, made of 0.952 cm (3/8) stainless steel). The plant was constructed from Inconel 625 high pressure 0.622 cm ID (0.952 cm OD) tubing to operate at temperatures up to 600 °C (650 °C maximum) and pressures around 25 MPa (28 MPa maximum) with flow rates ranging from 0.6 to 2.2 l/min. The tubing is joined together with high pressure unions designed by NORAM. The bodies of the unions are made of Inconel 625 and the nuts are made of stainless steel. The revised facility consists of the same sections as the initial configuration with the addition of a Reactor (115 m long) located after the test section and before the regenerative heat exchanger. The total length of Inconel tubing in the revised facility is approximately 140 m. All heated parts of the system are thermally insulated in ceramic board (Kaowool) boxes (15.2 x 15.2 cm).

Feed can enter the plant (Figure 3.1) from either of two 500 l polyethylene tanks. One tank was used to store distilled water. The other one stored salt solution during deposition and solubility studies and provided solution stirring with a mixer installed on the top of the tank.

The feed was pumped into the system with a high pressure, triplex positive displacement metering pump (GIANT P57). The pump provides flow rates from 0.6 to 2.2 l/min. The variation of the flow rate is accomplished with a Variable Frequency Drive (VFD, Reliance Electric ISU21002) control of the rpm of the pump motor. The maximum outlet pressure is 45 MPa. The positive displacement pump produces small flow fluctuations which are filtered with a pulsation damper (Hydrodynamics Flowguard DS-10-NBR-A-1/2" NPT) installed immediately after the pump.
Figure 3.1. UBC/NORAM pilot plant.
The fluid is first preheated in a regenerative heat exchanger which is a counter flow, tube-in-shell-type heat exchanger. The shell side is constructed from 1.27 cm Schedule 80 pipe (SS 347). The regenerative heat exchanger uses hot fluid coming from the test section (reactor) and flowing through shell side to heat up incoming cold fluid going through the tube side of the regenerative heat exchanger.

The feed is further heated in two preheaters that are electrically heated by running AC current through the tube wall. The power for the tube heating is supplied from silicon controlled rectifiers (SCR). The power goes from the SCR Panel through two step-down transformers (Hammond Manufacturing 240/24 VAC specified by manufacturer but found as 11:1 in our measurements, Appendix B, section B.2.) to each preheater. Each transformer delivers maximum 24 volts at 450 amps. The wiring from the SCR Panel to two transformers is done in series and from the transformers to a preheater in parallel (see Figure 3.2.). Heavy 2.5 cm thick copper cables are used to connect the transformers to barrel connectors attached to stainless steel rods (SS 304). In the initial configuration of the system, the stainless steel rods were silver soldered onto the preheater tube. This type of the connection after awhile caused generation of hot spots. In the revised experimental set-up, the connectors design was improved providing greater contact area. "Hot" connections (24 VAC maximum) are placed in the middle of the each preheater and the ground connections at their ends which provide a balanced power supply to each half of the preheater. The preheaters are controlled separately from the SCR panel. The power to Preheater 1 is adjusted manually on the SCR Panel. The power to Preheater 2 can be adjusted from Panel 2 with a feedback temperature controller that has manual and automatic mode. The deposition experiments performed on the revised facility used automatic power control for preheater two.
The preheated fluid enters the test section that is also electrically heated. The heating is achieved in the same way as described above for the preheaters (Figure 3.2.). Power control is provided manually from the SCR Panel. The test section is comprised of four tube sections. Two shorter sections (0.3 m long), placed at the inlet and the outlet of the test section, are not heated. The longer sections are each 1.52 m long and are electrically heated (Figure 3.3.). There are five union fittings connecting the test section tubing. They are used for disassembly and cleaning of the test section.

The hot fluid from the test section goes into the shell side of the regenerative heat exchanger for the initial configuration of the plant. In the revised experimental setup hot fluid enters a reactor that is not electrically heated. After the regenerative heat exchanger, the fluid is finally cooled down to below 50 °C in the process cooler and depressurized in a back pressure regulator (Tescom # 54-2162T24S) to atmospheric pressure. In the revised setup, the cold depressurized fluid goes into a gas/liquid separator before going
into the collection tank. During these NaCl studies, the collected fluid could be safely discharged into the drain.

![Diagram of the test section of the UBC/NORAM SCWO pilot plant](image)

**Figure 3.3.** The test section of the UBC/NORAM SCWO pilot plant

### 3.1.1. Safety issues

The major concerns were over-pressurization and over-heating of the system. The over-pressurization is prevented with three relief valves placed at different locations in the system. Each of them is capable of releasing the full pump flow rate at pressure of 29 MPa. To prevent over-heating, high-temperature alarms are placed at the outlet of the preheaters, the outlet of the test section, inlet and outlet of the reactor and outlet of the process cooler. If a temperature exceeds the manually set value, the alarms turn off the power to the heaters. Six surface temperatures along the system are also monitored with thermocouples clamped to the surface and temperatures digitally displayed on the Control Panel 2. The flow switch is also used to shut off the heaters if there is no flow. The system is enclosed with 18 gauge steel sheet to prevent high temperature, high velocity sprays. The plant is always operated with at least two qualified operators. More details on the safety features can be found in the UBC/NORAM Plant User’s Guide.
3.2. Instrumentation

3.2.1 Temperature measurements

All bulk and surface temperatures on the UBC/NORAM pilot plant were measured with K type (Chromel - Alumel) thermocouples.

Surface temperature measurements

The test section was equipped with twenty-nine surface thermocouples (high-temperature thermocouple wire with ceramic fiber insulation) that were extended to the data acquisition system with twisted, shielded extension wire. In the initial experimental setup there were 20 surface thermocouples on the top and 9 on the bottom of the test section (Figure 3.4).

![Diagram of thermocouple positions](image)

**Figure 3.4.** Position of thermocouples on the test section in the initial experimental setup.

The revised system had 19 top surface thermocouples and 10 bottom ones (the first section of the test section in the Figure 3.4. was rotated by 180°). The axial locations of the surface thermocouples for the heated part of the test section are given in Appendix
A. The unheated part of the test section between the electrical clamps located at the middle fitting was considered isothermal. The surface thermocouples were attached to the test section by spot welding of the chromel and alumel wires to the tube surface that was used as a junction between wires (Figure 3.5). The bare wires were then insulated by ceramic rods to prevent junction formation at some location other than the tube surface. For the rest of the thermocouple, wires were encased in a high temperature, ceramic fiber overbraid (Figure 3.5).

The thermocouples that were used for temperature alarms were Inconel-sheathed and clamped onto the tube surface with steel straps.

![Figure 3.5. Surface thermocouple attachment.](image)

**Figure 3.5. Surface thermocouple attachment.**

**Bulk temperature measurements**

Bulk temperature measurements were performed with Inconel-sheathed and ungrounded K type thermocouples. Five bulk temperature thermocouples were inserted into thermocouple ports placed on the top of five unions on the test section in the initial setup. In the revised experimental setup bulk thermocouples were also placed in the thermocouple ports at the inlet and the outlet of the preheater two. Bulk temperatures were measured in the sampling ports as well. The sampling ports used in this study were
located at the outlet of Preheater 2 (inlet of the test section) and at the outlet of the test section (after first section of the reactor).

The measurements of heat capacity of pure water in our facility showed that the test section thermocouples had an offset in temperature measurements of 2.2 °C (reading too high, Rogak 1999).

### 3.2.2. Pressure measurement: absolute and differential

Absolute and differential pressure transducers were located on the test section as shown in Figure 3.6 for the initial experimental setup and Figure 3.7 for the revised experimental setup. In the initial experimental setup two variable reluctance differential pressure transducers (DP427, DP429 Validyne DP303, with 55 kPa diaphragm each) were connected to pressure ports located on the unions of the test section. The signal output for each DP cell ranges from 0 to 10 volts. Each DP cell had a bypass line with a needle valve which was open only at the beginning of the experimental run to purge the DP cell line and prevent damage of the diaphragm. The total maximum pressure drop that could be measured along the test section of the initial experimental setup, without the DP cells going out of range, was 110 kPa. This pressure drop was too low to be used as an indication of tube plugging. In the revised experimental setup, only one differential pressure transducer (DPT 429-5-56) measured pressure drop along the test section (Validyne DP 303, with 2.5 MPa diaphragm). The absolute pressure transducer (Validyne Model P2) was placed at the outlet of the test section in the initial experimental setup. In the revised experimental setup its placement was changed to the beginning of the test section. This change was made to exclude pressure drop effect on the absolute pressure measurements (absolute pressure measurements are of the order of MPa and pressure drop is measured in kPa).
Figure 3.6: Differential (DP) and absolute pressure (P) transducers in the test section of the initial experimental setup.

Figure 3.7: Differential (DP) and absolute pressure (P) transducers in the test section of the revised experimental setup.

The calibration of the DP cells was performed with a hand pump (Omega, PCL-2HP) and portable manometer (Omega, PCL-200) by adjusting the zero and the span on the carrier demodulator. The calibration of the DP cell was performed with air as a fluid. The pressure drop that diaphragm of the DP cell DPT 429-5-56 was designed for was 2.5
MPa. The DP cell was pressurized up to 500 kPa (differential pressure) with a hand pump (Omega, PCL-2HP) attached to the positive (+) pressure port. This was the maximum pressure that hand pump could deliver. The negative port (-) was open to the atmosphere. The differential pressure was read on the portable manometer (Omega, PCL-200) and the voltage output from the carrier demodulator was read from the computer display. The calibration was performed by adjusting the zero and the span on the carrier demodulator for the minimum and maximum pressure. Zero voltage corresponded to the zero differential pressure. The maximum pressure of 2.5 MPa would give 10 V output. Since the maximum pressure used in calibration was 500 kPa, the span was adjusted to give the maximum voltage output possible at that pressure. The calibration of DP427 and DP429 was performed for the full pressure range. The absolute pressure transducer was calibrated with a dead weight tester up to the pressure of 24.09 MPa and this calibration was validated with the digital calibrator up to 26.7 MPa. The calibration data and charts are given in the Appendix B. The following expressions were derived from the data fit.

\[
\text{DP427} \quad \Delta p_{[\text{kPa}]} = 0.70092 + 5.99304 (V) \quad (3.1.)
\]

\[
\text{DP429} \quad \Delta p_{[\text{kPa}]} = 1.68013 + 5.9042 (V) \quad (3.2.)
\]

\[
\text{DPT 429-5-56} \quad \Delta p_{[\text{kPa}]} = 250 (V) \quad (3.3.)
\]

\[
\text{APT} \quad p_{[\text{MPa}]} = (405*V + 20*V^2 - 1.2*V^3 - 20)*6894.8*10^{-6} \quad (3.4.)
\]

### 3.2.3 Flow rate measurement

The flow rate was measured with a stop-watch and a graduated cylinder at the outlet of the system and at the sampling ports. During deposition experiments that were performed with the revised facility two sampling ports at the inlet (sampling port one) and the outlet (sampling port two) of the test section were used and kept open throughout the whole experiment. The flow rate in the test section was taken as a sum of the flow rate at the outlet of the system and the flow rate at the outlet of the test section from the sampling port two. A flow meter with a flow switch was placed at the outlet of the system and was used only for safety purposes (see section 3.1.1.)
3.2.4. Conductivity measurements

The conductivity of the effluent was measured in real time with a conductivity meter (Omega CDH-287-KIT) that was placed after the back pressure regulator. The conductivity probe was inserted in a T-fitting as shown in the Figure 3.8. The maximum output voltage signal of the conductivity meter was 100 mV with the accuracy of 0.3 % of the full scale.

![Diagram of conductivity meter probe installation](image)

*Figure 3.8: Conductivity meter probe installation*

The relationship between the conductivity measurements and the concentration of the sodium chloride in the effluent was determined by the calibration of the conductivity meter. The calibration was performed two times. The calibration was done with ACS certified sodium chloride (used throughout all experiments) that had been first oven dried before samples of seven different concentrations ranging from 0.001 to 1 wt % (ten concentrations used in the second calibration from 0.0001 to 5 wt %) were prepared. The calibration data from both calibrations agreed very well (Figure 3.9). The data fit was
done with two curves. The first one covers the range from 0.001 to 1 wt % (data fit 1) and the second one (data fit 2) covers the concentration range from 0.001 to 5 wt %.

Figure 3.9: Calibration of the conductivity meter with sodium chloride
The data fit 1 is given with the following expression:

\[ C_1 = 0.7235 + 10^{-2}(0.5399 - 0.746\sigma)^{0.5} \]  

(3.5)

The data fit 2 is given as follows:

\[ C_2 = 10^{-\log_{10}(\sigma/0.9559875 - 4.384858)} \]  

(3.6)

Where,

\( \sigma \)-is the electrical conductivity (\( \mu \text{S/cm} \))

\( C \)- is the concentration of the salt solution (wt %)

3.2.5. Atomic absorption and pH measurements

Atomic absorption measurements were used to obtain the concentration of Na\(^+\) in samples collected during our solubility measurements and exclude hydrolysis effect by comparing them to concentrations obtained from conductivity measurements. The pH of the samples was measured with the same goal. The atomic absorption measurements were performed at the Chemical Engineering Department at UBC and pH measurements at Pulp and Paper Center UBC.

3.2.6. Heat Flux Measurements

The SCR control panel displays RMS voltages (Vscr) supplied to the secondary transformers of the Preheater 1, Preheater 2 and Test section. This RMS voltage could not be used for the heat flux calculation because of the uncertainties associated with the secondary transformer ratio, resistance of the tube, and heat losses. The RMS voltage could not be measured directly on the tube during experiments because the AC voltage signal was not a perfect sinusoid. The calibration of the heat flux was performed as
described in the Appendix B but was not used in the heat flux calculation from the reasons stated above. The heat flux supplied to the fluid was calculated from the bulk enthalpies as described in the Appendix C, section C.2.

3.2.7. Data acquisition equipment

The data acquisition board Omega MultiScan/1200 with 24 differential thermocouple or voltage inputs was used to acquire temperature, pressure and conductivity data. The channels were isolated one from another. This was needed because of the direct electrical heating that was used in our system. The board provides one cold junction sensor for every 8 input channels. The calibration of the temperature sensors is software controlled and was performed at temperatures of ice bath and boiling water for each cold junction sensor. The same software provided gain calibration for voltage inputs at ±100.0 mV, ±1.0 V, ±5 V, and ±10 V. Out of 24 channels available on the board, 20 were used for temperature measurements, 3 for pressure measurements and 1 for conductivity. The board was connected to a personal computer that provided data display and storage. The software used for data acquisition was Tempview version 4.14.

The chosen measuring mode was a line cycle integration mode with sampling frequency of 1.92 kHz or once every 520.83 µs. The board can sample and average 32 measurements per line cycle which eliminates noise from AC line pickup. For further noise filtering, it is possible to average over 2, 4 or 8 line cycles. We chose 8 line cycles (average over 256 measurements). An expression given in Omega MultiScan/1200 manual was used to calculate the length of time needed to acquire one scan. With 256 measurements the time for one scan was calculated as 3.35 s and the scan interval of 5 s chosen as the closest time to the calculated one.
4. SOLUBILITY EXPERIMENTS FOR NaCl-H₂O SOLUTION

4.0. Introduction

The Martynova-Galobardes-Armellini solubility model that assumes that equilibrium between solid and vapor exists as a solvation type reaction (see Section 2.1.) needed verification with our solubility data in order to be employed in our sodium chloride deposition modeling. The solubility experiments at the UBC/NORAM facility were performed to determine the solubility of sodium chloride in supercritical water at constant pressures of 24.1, 24.45 and 25.67 MPa for temperatures ranging from 461 to 559.5 °C. The experiments were performed on the test section of the initial experimental setup (no bulk temperatures measured in preheaters, no sampling ports) with two experimental procedures. The general idea behind the solubility measurements was to deposit all salt above the solubility limit in the test section for the given bulk temperature and to measure the concentration of the effluent that would correspond to the solubility limit for that temperature. The concentrations of the samples were measured with a conductivity probe and by atomic absorption to exclude the effect of hydrolysis on the solubility data. Both methods gave consistent results. The pH of the samples was taken as well. The solubility results were compared to the simple model predictions and agreed very well. The following sections give more details on the experimental procedure, a summary of the measurements and a comparison between our experimental results and the solubility model output.

4.1. Experimental procedure

The salt used in the experiments was ACS certified sodium chloride that was oven dried before the NaCl solution was prepared. The concentration of the feed was chosen as 0.03 wt % which is the concentration of the vapor phase at the three phase equilibrium for the pressure of 25 MPa and the three phase equilibrium temperature $T_{tp}$ of 450 °C (Bischoff, 1991). This was to ensure that all of the salt above solubility limit would deposit
in the test section and that the effluent concentration would correspond to the solubility limit. The feed was prepared by dissolving the mass of salt (measured with digital scale) needed for the given concentration in a 4 liter beaker and stirring the high concentration solution thoroughly. After that, the high concentration solution was added into the solution tank and distilled water, in the amount needed to obtain 0.03 wt%, poured in. The final mixing was performed with an electric mixer. The mass of the salt \( m_{NaCl} \) was determined with the following expression:

\[
C_0 = 100 \cdot \frac{m_{NaCl}}{m_{NaCl} + m_{fluid}}
\]

where \( C_0 \) is wt % of salt and \( m_{fluid} \) is mass of distilled water.

When the salt solution was prepared, its conductivity as well as the conductivity of distilled water were recorded and the corresponding concentrations were calculated from the conductivity meter calibration curve. During the experiments steady state in the test section was first reached with distilled water. The flow rate was then measured at the outlet of the system and data logging begun. The average flow rate used in the solubility experiments was 1.2 l/min. The effect of flow rate on solubility measurements was not investigated. This effect was studied for sodium sulfate by Teshima (1997) and showed to be insignificant. When temperatures were steady, the feed was switched to the sodium chloride solution. The conductivity of the effluent was recorded in real time as well as visually observed on the conductivity meter display (the computer reading would go off scale for certain values of conductivity)\(^1\). During the transient, the conductivity of the effluent would peak and then decrease to reach a constant value (Figure 4.1.). When the conductivity of the effluent stopped changing with time (this was observed on the conductivity meter display), its value was recorded from the meter display and a sample of the effluent taken.

\(^1\) The magnitude of conductivity could not be determined from the computer reading alone since the data acquisition input signal remained in the range of 0-100 mV when the conductivity meter changed its range.
The flow rate was measured again and recorded. The bulk temperatures at the inlet and the outlet of the test section were recorded as well. After that, the feed was switched back to distilled water and heaters turned off for the system clean-out.

Figure 4.1. Single temperature experimental run.

Initially, each p-T-x point was supposed to be measured in a separate run as described above. This approach introduced the problem of reproducibility of the pressure in different runs. In runs #3 (p=24.1 MPa) and #6 (p=25.67 MPa, see Table 4.1) several p-T-x points were obtained during one experiment. In this second experimental procedure the test section reached the steady state with distilled water for the highest temperature of our interest at the given pressure. The salt solution was run through the system as described above for the single temperature run. Then, instead of a complete cool down, clean water was introduced into the system without shutting off the heaters. The heat flux was decreased to a value corresponding to the next temperature and system cleaned till the effluent concentration decreased to the level of the conductivity of distilled water (Figure 4.2.). When the steady state at the new temperature was reached, salt solution was
introduced in the system and procedure described above repeated. Temperatures and conductivity data were saved in a separate file for each bulk temperature.

![Figure 4.2. Multiple temperature experimental run.](image)

In our experimental procedure the test section was kept isothermal as closely as possible. In some runs a small temperature gradient existed in the test section (2 – 6 °C). The bulk temperature profile was chosen so that bulk temperature in the test section would dictate the solubility limit as the highest bulk temperature in the system. Figure 4.3. gives the typical modeled axial temperature profile along the preheaters and the test section in a solubility experiment. During the solubility experiments the three phase temperature ($T_{tp}$) was always exceeded first in the preheaters because the bulk temperatures that were looked at during our solubility experiments were ranging from 461 to 559 °C. For example, in an experiment at the pressure of 25 MPa and the test section bulk temperature of 460 °C, the three phase temperature (450 °C) would be reached in preheater two. That means that deposition would start in the preheaters first. As long as the deposition would end in the test section, our $T$-$p$-$x$ point (based on the average test section bulk temperature) would be as accurate as our measurements. This
assumption could have been affected by heterogeneous deposition happening at the hot walls but the effect of hot walls in the test section was probably not significant due to the small difference between the bulk and the wall temperatures.

**Figure 4.3:** The axial temperature profile for a typical solubility experiment and location of the salt deposit in the system.
The heat flux supplied to the preheaters was usually very high (see Figure 4.3.) and the modeled wall temperature at the outlet of preheater two exceeded the bulk temperature in the test section. That might have caused the deposition ending in preheater two and the solubility limit being determined by the wall temperature in preheater two instead of being determined by the average bulk temperature in the test section. However, the surface temperatures in the test section would increase during the experiment which indicated deposition in the test section.

4.2. Results of the solubility measurements

The results of our solubility measurements are summarized in the Table 4.1. The experimental runs #1 and #2 were single temperature runs performed at average pressures of 24.45 and 24.49 MPa respectively. There was some temperature variation (3 - 4 °C) with time during runs #1 and # 2 and the conductivity of the effluent was taken from the data file as an average value over period of time for the temperatures given in the Table 4.1. Runs #3 and #6 were performed following the second procedure described in the section 4.2. In run # 3, solubility limits at five temperatures (samples 1 to 5) ranging from 470.65 to 534 °C (taken as average bulk temperatures in the test section) and a pressure of 24.1 MPa were obtained. In run #6, p-T-x points were obtained for four temperatures (samples 1 to 4) ranging from 461 to 559.5 °C and an average pressure of 25.67 MPa. For all temperatures, in runs #3 and #6, samples were taken at the outlet of the system as described in the section 4.2. and the concentration of the sodium chloride in samples measured with the conductivity probe and with atomic absorption (Na+ based) to investigate hydrolysis. Armellini (1993, as discussed in the section 2.1.) observed that molar ratio [Cl]/[Na] obtained from Cl− and Na+ based solubility measurements was 1.1 at the temperature of 550 °C and pressure of 25 MPa which indicated some hydrolysis occurrence. The results from our analysis are given in the Table 4.1 and the Figure 4.4. Atomic absorption gave consistently lower values of sodium concentration for all temperatures and both pressures.
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<th>Effl. C wt %</th>
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<td>5 1/20/98</td>
<td>NaCl2004</td>
<td>485.8</td>
<td>1.21</td>
<td>24.1</td>
<td>0.031</td>
<td>241.5</td>
<td>0.0126</td>
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<td>N.A.</td>
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<td></td>
<td></td>
<td>485.5</td>
<td>1.21</td>
<td>24.1</td>
<td>0.031</td>
<td>242.9</td>
<td>0.0126</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
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<td></td>
<td></td>
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<td>24.1</td>
<td>0.031</td>
<td>245.7</td>
<td>0.0128</td>
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</tr>
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<td>24.1</td>
<td>0.031</td>
<td>297.2</td>
<td>0.0155</td>
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<td></td>
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<td>24.1</td>
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<td>304.8</td>
<td>0.0159</td>
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<td>1.21</td>
<td>24.1</td>
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<td>307.0</td>
<td>0.0160</td>
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<td>N.A.</td>
</tr>
<tr>
<td>6 2/3/98</td>
<td>Sample1</td>
<td>559.5</td>
<td>1.21</td>
<td>25.66</td>
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<td>198.0</td>
<td>0.0103</td>
<td>5.78</td>
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</tr>
<tr>
<td></td>
<td>Sample2</td>
<td>493.0</td>
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<td>25.63</td>
<td>0.033</td>
<td>314.0</td>
<td>0.0164</td>
<td>5.89</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>Sample3</td>
<td>472.5</td>
<td>1.21</td>
<td>25.64</td>
<td>0.033</td>
<td>408.0</td>
<td>0.0214</td>
<td>5.85</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>Sample4</td>
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<td>1.20</td>
<td>25.74</td>
<td>0.033</td>
<td>546.0</td>
<td>0.0287</td>
<td>5.72</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

Table 4.1. Summary of UBC solubility measurements.
Figure 4.4: UBC sodium chloride solubility results for two pressures obtained from conductivity and atomic absorption measurements.
The percentage difference between conductivity and atomic absorption concentration measurements varied from 8 to 10%. This difference was lower at higher temperatures which was quite the opposite of the expected measurements if hydrolysis was happening. If we assume that the difference between two methods at lower temperatures was associated with errors due to the calibration of the instruments then, if hydrolysis was taking place, this difference should become greater at higher temperatures. Since that was not the case, it was concluded that the hydrolysis did not affect our results.

The measured pH of the distilled water was 5.64. All samples had consistent readings with the distilled water except samples 3 and 4 in the run #3.

Runs #4 and #5 were not separate runs. They were part of run #3 in the sense that solubility data were extracted from the cool-down period between two temperatures within run #3 (experimental procedure explained in 4.2.). In this cool-down period, distilled water was run through the system in parallel with heat flux decrease and salt that had been deposited in the test section at the previous temperature acted as a salt bed. The data for the run #4 were obtained from the data file for sample 3 (run #3) in the period of cool-down from the temperature of 503.3 to 486.8 °C. The same approach was used to obtain data for run #5. Data were taken from the file for sample 4 (run #3) in the period of cool-down from temperature of 486.8 to 470.7 °C. In this way 14 solubility data points were obtained at the pressure of 24.1 MPa and temperatures ranging from 470.8 to 500.8 °C.

The solubility change with temperature for pressures of 24.1 and 25.67 MPa is plotted in Figure 4.5 and compared to results of Armellini (1993) and Sourirajan and Kennedy (1962) obtained for 25 MPa. Our results show that solubility decreases as temperature increases. Solubility increases with pressure.
Figure 4.5. UBC/NORAM solubility results compared to solubility data of other research groups.
4.3. Comparison with the Martynova-Garobaldes-Armellini solubility model prediction

The simple sodium chloride solubility model (see section 2.1. for details) used by Martynova (1964), Styricovich (1969), Galobardes et al. (1981) and Armellini (1993) gives the change of sodium chloride concentration with temperature and density. By fitting his data and data of Galobardes' (1981) and Bischoff et al. (1986) Armellini obtained the following form of the solubility model:

\[ \log C_{NaCl} = 3.866 \log \rho_w - \frac{1233.4}{T} + 7.772 \]  \hspace{1cm} (4.2)

Where,

- \( C_{NaCl} \) - concentration of NaCl in ppm
- \( \rho_w \) - pure water density in g/cm\(^3\)
- \( T \) - temperature in K

This model provides the connection between sodium chloride solubility and density of pure water and follows the premise that solvation ability of supercritical water greatly depends on its density.

Figure 4.6 compares the UBC results and the solubility model prediction at pressures of 24.1, 24.45 MPa and 25.67 MPa. The density of pure water used in the model was obtained for temperature-pressure points from EQTEST.f program (Pruss and Wagner, 1994) that provides the thermodynamic properties of pure water.

At all three pressures a good agreement between our sodium chloride solubility data and simple solubility model predictions was achieved. It was concluded that this solubility model was suitable for sodium chloride deposition modeling.
Figure 4.6. Comparison between UBC/NORAM solubility data and Martynova-Garobaldes-Armellini solubility model predictions at pressures of 24.1, 24.45 and 25.67 MPa.
5. DEPOSITION EXPERIMENTS: DESCRIPTION AND MEASUREMENTS

5.0. Introduction

The sodium chloride deposition experiments were designed to study salt deposition in a horizontal, electrically heated tube. The salt thickness profiles were measured indirectly by recording surface temperatures for the clean and the fouled tube. The salt layer on the inside of the tube caused a decrease in the thermal conductivity of the tube wall and a consequent surface temperature increase. The observed temperature increase depended not only on the thickness of the deposit but also on the heat flux, fluid velocity and the deposit roughness. To take into account these effects, a model of heat transfer from the outer surface of the tube to the bulk fluid was developed.

The experimental measurements were used to provide input for the heat transfer model. The most suitable heat transfer correlation for smooth tubes was selected using pure water measurements. The smooth-tube correlation was then modified using observed temperature changes that were occurring immediately after initiation of fouling. The measured outer surface temperature increase gave a preliminary picture of the shape and the location of the deposit. The amount of the deposited salt was found from the mass balance.

In Chapter 6, the salt thickness profiles are calculated using the information on heat transfer and mass balances contained in this chapter.

5.1. Experimental procedure

For each experimental run, steady state in the system was first reached with distilled water. In ten out of twelve experiments, the power settings to preheaters and test section were chosen so that there was no deposition in the preheaters (deposition
restricted to the test section only). In two experiments, deposition in the preheaters was purposely induced.

In the initial experimental setup, there was a problem with hot spots in the preheaters due to the bad electrical connections. The restriction of deposition to the test section was accomplished by trial and error. The power to Preheater 1 was set to the maximum with zero power to Preheater 2 and the test section. When steady-state was reached with clean water, the feed was switched to the salt solution and the conductivity of the effluent measured at the outlet of the system. Since the conductivity of the effluent agreed with the conductivity of the influent, Preheater 1 was eliminated as a cause of deposition. The next step was to set the power to Preheater 1 to the maximum, power to the test section to zero and power to Preheater 2 to the value that would give bulk and wall temperatures in Preheater 2 and test section below the three phase temperature. Since the conductivity reading of the effluent indicated that there was deposition happening, it was clear that hot spots were generated in Preheater 2. Hence, it was decided to use very low or zero power to Preheater 2 until the problem with electrical connections was fixed. In the revised experimental setup (no hot spots generation), the temperature controller was used to adjust the power to Preheater 2 by setting the wall temperature at the outlet of Preheater 2 to a certain value. In that way, the bulk temperature at the inlet of the test section was kept constant throughout an experiment. Whether deposition in the preheaters was occurring or not was also checked by analysis of the sample taken between Preheater 2 and the test section.

Salt solutions were prepared as discussed in section 4.2. When steady-state was established with the distilled water, the computer recording of temperatures, absolute pressure, pressure drop, and conductivity of the effluent was started. During experiments performed on the initial experimental setup, bulk temperatures were measured at the inlet, mid-point, and outlet of the test section. Bulk temperature measurements were done at the inlet and outlet of Preheater 2, and the inlet and the outlet of the test section, as well as at the sampling ports during experiments performed on the revised experimental facility. The flow rate at the outlet of the system was measured with a stopwatch and a beaker.
For the revised experimental facility, sampling ports at the inlet and the outlet of the test section were kept open throughout the whole experiment and their flow rates measured and recorded. The power setting was recorded as well.

After one to two minutes of data logging with distilled water running through the system, the feed was switched to the salt solution. The recording of the deposition time \( t=0 \) was started with the stopwatch when the conductivity of the effluent started increasing. The zero time of deposition was set to the moment when the salt solution reached the outlet of the test section. Given the physical distance between the outlet of the test section and the outlet of the system, there was a time lag between the conductivity reading at the outlet of the system and temperature measurements. During data analysis, the conductivity reading was corrected by the time that was needed for the fluid to travel from the outlet of the test section to the outlet of the system. This time was assessed from the data files by examining temperatures and conductivity after power was shut off. There was a sudden drop in all measured temperatures which was assumed to coincide with the sudden change in the conductivity reading. By matching the two changes, the conductivity reading was synchronized with the temperature reading in all experiments.

Collection of the effluent in 20 l jugs was started at \( t=0 \). The collection of the effluent was ended when 10 g \([±10\%]\) of salt was delivered to the test section in the experiments performed on the initial experimental setup. In the revised experimental setup, effluent was collected in separate jugs for 10, and 20 \([±10\%]\) g delivered to the test section. At the same instants when 10, or 20 g of salt were delivered to the test section, sampling of the solution was performed at the inlet and the outlet of the test section, and at the outlet of the system.

After effluent collection, the salt solution was switched back to the clean water, the heat flux to the test section was decreased and collection of the clean-out started. In experiments performed with higher salt concentrations, the clean-out water started when the surface temperature in the test section exceeded the design temperature of the system.
In some experiments, the decrease of the heat flux was sudden, which caused significant leakage at several fittings located after the test section. Given the fact that the salt solution was highly concentrated during the clean-out, a certain amount of the salt was lost through the leakage and hence, the mass balance could not be closed in some experiments. The other, less severe, effect on the mass balance was sinking of the heavy solution in the sampling ports that were located after the test section and were not used in the experiments. These sampling ports were purged after an experiment had been ended. The amount of the salt that was lost in this way amounted to less than one gram. The collection of the clean-out water was over when the conductivity of the effluent approached the conductivity of distilled water. The collected effluent was weighed and its conductivity measured. The conductivity of the samples was measured as well.

5.2. Summary of deposition experiments

A summary of the twelve deposition experiments with the listed experimental conditions (initial concentration, flow rate, pressure, bulk temperature range, heat flux, and three phase equilibrium temperature for the given pressure) is given in the tables 5.1.A and 5.1.B.

The first group of six experiments, Low Temperature Experiments (LTE) was performed with maximum bulk temperature lower than three phase equilibrium temperature (table 5.1.A). In these Low Temperature Experiments, the bulk temperature at the inlet of the test section was set around the vapor-liquid phase equilibrium temperature (based on Bischoff 1991, section 2.1.). For example, the vapor-liquid equilibrium temperature is equal to 400 °C at a pressure of 25 MPa and a concentration of 0.1 wt%. At pressures ranging from 23.5 to 25 MPa and a concentration of 0.1 wt %, the vapor- liquid equilibrium temperature is between 390 and 400 °C. At pressures ranging from 25 to 26 MPa, this temperature falls between 400 and 410 °C. At a concentration of 0.912 wt % used in experiment 7, the vapor-liquid region was entered at

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1 Due to the leakage, the mass of deposited salt collected during clean-out was by 40-50% lower than the mass of deposited salt obtained from the mass balance.
a temperature close to the critical temperature (at 25 MPa, the critical point of the solution is at 387 °C and 1 wt%). This means that the inlet of the test section (397 °C) was already in the vapor-liquid region in experiment 7.

The outlet temperature in all Low Temperature Experiments was set below the three-phase equilibrium temperature \( T_{\text{tp}} \). The change of the three-phase equilibrium temperature with pressure is given in the section 2.1.

In the Low Temperature Experiments the bulk fluid in the whole test section was in the vapor-liquid region and the three-phase temperature was exceeded at the wall only (Figure 5.1.).

<table>
<thead>
<tr>
<th>EXP.</th>
<th>DATE</th>
<th>DATA FILE</th>
<th>INIT. CONC.</th>
<th>FLOW</th>
<th>PRESS.</th>
<th>BULK TEMP. RANGE</th>
<th>HEAT FLUX</th>
<th>THREE PHASE TEMP.</th>
<th>EXP. SETUP</th>
</tr>
</thead>
<tbody>
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<td>.txt</td>
<td>wt%</td>
<td>l/min</td>
<td>MPa</td>
<td>°C</td>
<td>kW/m</td>
<td>°C</td>
<td>*</td>
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<td>1</td>
<td>10/22/98</td>
<td>Nac2o22</td>
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<td>1.16</td>
<td>24.63</td>
<td>397-443.3</td>
<td>2.36</td>
<td>447.4</td>
<td>2</td>
</tr>
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<td>0.62</td>
<td>25.63</td>
<td>400.4-450.1</td>
<td>1.37</td>
<td>454.1</td>
<td>2</td>
</tr>
<tr>
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<td>1.9</td>
<td>25.55</td>
<td>396.4-449.7</td>
<td>4.85</td>
<td>453.5</td>
<td>2</td>
</tr>
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<td>2.53</td>
<td>450.2</td>
<td>2</td>
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<td>1.94</td>
<td>24.35</td>
<td>387.6-440.6</td>
<td>5.55</td>
<td>445.6</td>
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</tbody>
</table>

* 1- initial experimental setup, 2-revised experimental setup

**Table 5.1.A. Summary of Low Temperature Experiments (the bulk fluid in vapor-liquid region).**
The amount of the heat supplied to the fluid per meter of the heated length of the tube varied from 1.37 kW/m to 5.55 kW/m. The heat fluxes were obtained from the energy balance (Appendix C, section C.2.).

The second group of experiments, High Temperature Experiments (HTE), is listed in the table 5.1.B. In these High Temperature Experiments, the effects of the vapor-liquid and the vapor-solid regions on deposition were investigated. For experiment 3, the concentration at the inlet of the test section was measured at sampling port one (located at the inlet of the test section) and was 0.065 wt %. In experiment 5, the measured concentration at the sampling port was three times higher than the feed concentration at the initial sampling times, probably due to the phase separation and sinking of the heavy, highly concentrated liquid droplets to the bottom of the sampling port. However, the concentration at the inlet of the test section that was measured at the sampling time when
20 g were delivered was lower than the feed concentration. This value of 0.077 wt % was assumed to be the inlet concentration in the experiment 5. The heat flux in this experimental group ranged from 0.73 kW/m to 3.89 kW/m.

Table 5.1.B. Summary of High Temperature Experiments (bulk fluid in vapor-liquid and vapor-solid region)

<table>
<thead>
<tr>
<th>EXP.</th>
<th>DATE</th>
<th>DATA FILE</th>
<th>INIT. CONC.</th>
<th>FLOW</th>
<th>PRESS.</th>
<th>BULK TEMP. RANGE</th>
<th>HEAT FLUX</th>
<th>THREE PHASE TEMP.</th>
<th>EXP. SETUP</th>
</tr>
</thead>
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<tr>
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<td>10/22/98</td>
<td>Nac4o22</td>
<td>0.106</td>
<td>1.15</td>
<td>25.04</td>
<td>399.6-493</td>
<td>3.68</td>
<td>450.1</td>
<td>2</td>
</tr>
<tr>
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<td>Nac5o22</td>
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<td>1.12</td>
<td>25.14</td>
<td>437.7-484</td>
<td>1.39</td>
<td>450.8</td>
<td>2</td>
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<td>Nac6o23</td>
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<td>0.65</td>
<td>25.71</td>
<td>441.1-481.8</td>
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<td>454.6</td>
<td>2</td>
</tr>
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<td>24.1</td>
<td>395.5-480.6</td>
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<td>444.0</td>
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</tr>
<tr>
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<td>1.23</td>
<td>24.04</td>
<td>402.9-507</td>
<td>3.9</td>
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<td>1</td>
</tr>
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<td>23.85</td>
<td>387.3-484</td>
<td>2.33</td>
<td>442.4</td>
<td>1</td>
</tr>
</tbody>
</table>

* Actual test section inlet concentration lower due to deposition in preheaters
** 1-initial, 2-revised

The temperature at the inlet of the test section was set around the vapor-liquid equilibrium temperature in experiments 2, 8, 11, and 12. The temperature at the outlet of the test section was higher than the three-phase temperature. The first part of the tube was in the vapor-liquid region and the second part of the tube was in the vapor-solid region in the experiments 2, 8, 11, and 12 (Figure 5.2.).
Figure 5.2. The test section view for High Temperature Experiments (HTE: 2, 8, 11, and 12) when the inlet bulk temperature is close to the two-phase equilibrium temperature and the outlet temperature is above three-phase equilibrium temperature.

A small portion of the bulk fluid at the inlet of the test section was in the one-phase region for some experiments. This depended on whether the inlet bulk temperature was slightly below or slightly above the vapor-liquid equilibrium temperature for the given pressure. In experiments 3 and 5 (Figure 5.3.) the inlet bulk temperature was 40 degrees higher than in other HTE and some deposition was occurring in Preheater 2. These two experiments were performed to examine the effect of buoyancy on deposition (Appendix C2). In these experiments, the concentration of the solution at the inlet of the test section was determined by sample analysis from sampling port one. This analysis showed that the concentration of two out of three samples was much higher than the
Figure 5.3: The test section view for High Temperature Experiments (HTE: 3 and 5) when the inlet bulk temperature is close to the three-phase equilibrium temperature and the outlet temperature is above three-phase equilibrium temperature.

The concentration of the feed in the experiment 5. This was probably caused by the sinking of heavy liquid droplets to the bottom of the sampling port. Such phase separation was more likely to happen if the concentration (density) of the liquid phase was high. The salt concentration in the liquid phase depended on the temperature. For example, the salt concentration in the liquid phase increases from 17 wt % at 400 °C to 52.5 wt % at 450 °C at a pressure of 25 MPa (section 2.1). The ratio of liquid density to vapor density is 4.7 at 400 °C and it is 10.2 at 450 °C which means that the density ratio increases approximately two times for a temperature increase of 50 degrees. However, only in one out of the two HTE performed with high inlet bulk temperature was the phase separation observed.
For the High Temperature Experiments, having the vapor-liquid region confined to the test section was important for three reasons. The first one was keeping the fouling restricted to the test section because the preheaters were not equipped for deposition investigation. The second one was preventing sinking of the liquid phase in sampling port one (located at the inlet of the test section) that could occur due to phase separation. The third reason for having the vapor-liquid region constrained to the test section was providing experimental data to compare with the results of the Low Temperature Experiments assuming that the same behavior observed in the Low Temperature Experiments would repeat itself in the vapor-liquid region (Low Temperature region) of High Temperature Experiments.

5.3. Heat Transfer to the Clean Tube

Six different correlations proposed by various authors for heat transfer in pure water were tested for the conditions of this study (Appendix C, section C.3.). The heat transfer coefficient to supercritical water is generally a strong function of heat flux as well as bulk temperature, flow rate and tube diameter, and none of the previously developed correlations are accurate for all conditions.

Figures 5.4 and 5.5 give comparisons between the calculated and measured surface temperatures for the clean tube with the pure water flow (T\textsubscript{\textit{w0}}) and they give the modeled heat transfer coefficient (h\textsubscript{0}) for a typical LTE and HTE respectively. These Figures show that the correlation proposed by Swenson et al. (1965) is quite good for the low temperature experiments (low temperature generally) while the Jackson-Fewster correlation (Ghajar and Asadi 1986) is better for conditions encountered in the high-temperature experiments. A detailed discussion of these correlations is given in Appendix C.
Exp. #1
P=24.63 MPa
Q=120.73 kW/m²
m=0.019 kg/s

Nu number correlations:
1. - Gnielinsky (1976)
2. - Shitsman-Miropolskii (1957)
3. - Jackson –Fewster (Ghajar and Asadi 1986)
4. - Swenson et al. (1965)
5. -Yamagata et al. (1971)
6. - Petukhov et al. (1961)

Figure 5.4. Comparison between modeled inner surface temperatures and experimentally obtained ones for the experiment 1 (LTE).
Exp. #2
P = 26.04 MPa
Q = 198 kW/m²
m = 0.019 kg/s

Nu number correlations:

1 - Gnielinsky (1976)  
2 - Shitsman-Miropolkii (1957)  
3 - Jackson –Fewster (Ghajar and Asadi 1986)  
4 - Swenson et al. (1965)  
5 - Yamagata et al. (1971)  
6 - Petukhov et al. (1961)

Figure 5.5. Comparison between modeled inner surface temperatures and experimentally obtained ones for the experiment 2 (HTE).
5.4. Modeling of the effect of salt on heat transfer coefficient

An illustration of the change of the surface and bulk temperatures and effluent concentration with time is given in Figure 5.6. for a typical low temperature experiment (other experiments are summarized in Appendix D). The salt solution was introduced to the test section at time $t_0$ and some surface temperatures decreased significantly in a short period (until $t=t_1$). The measured surface temperature decrease suggested that there was a change in the heat transfer coefficient when the salt solution was introduced to the system. Since the temperatures were measured at the outer surface of the tube, it was necessary to calculate the inner surface temperatures first, before further analysis was done. The inner surface temperatures $T_{w0j}$ and $T_{wij}$ ($j$ stands for the location of the surface thermocouple) were calculated from measured outer surface temperatures at times $t_0$ and $t_1$ respectively, assuming no deposition had taken place at time $t_1$. The calculation was performed assuming uniform heat generation and conductivity across the tube wall (Chapter 6, section 6.1., Eq. (6.6)). When the inner surface temperatures $T_{w0j}$ and $T_{wij}$ were calculated, their difference $[T_{wij} - T_{w0j}]$ was plotted against the relative inner surface temperatures $[T_{w0j} - T_p]$ for all experiments (Figure 5.7). Figure 5.7. clearly shows that the surface temperatures decreased between $t_0$ and $t_1$ when the inner wall temperature exceeded the three phase equilibrium temperature by 5 to 10 °C.¹

Table 5.2 lists measured $T_b$ at times $t_0$ and $t_1$ for the LTE. The variation of bulk temperatures was within 1.3 °C for all LTE except experiment 7. Table 5.3 lists measured $T_b$ at times $t_0$ and $t_1$ for the HTE. The variation of the bulk temperatures in the HTE was more pronounced (3°C) but still probably not significant. This suggested that the major effect of introducing the salt solution to the test section in this time interval was the enhancement of heat transfer, probably caused by a thin, rough salt deposit.

¹ Recent measurements of water heat capacity have indicated that the thermocouples on the facility may have an offset of about 2.2 °C so that in fact the temperature drop actually occurs closer to $T_p$ than indicated here.
Exp. #1, LTE, FLOW = 1.16 l/min, Tin=397 C, Tout= 443.3 C
INIT. CONC.=1060 ppm

Figure 5.6. The change of the measured parameters with time in the experiment 1.
Figure 5.7. The surface temperature change at the time $t_1$ for all LTE and HTE.
<table>
<thead>
<tr>
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*Table 5.3. Bulk temperature change for HTE in the time segment $\Delta t_1$*
The change of the heat transfer coefficient ($\Delta h_j$) was calculated as:

$$\Delta h_j = \frac{q}{(T_{w_{ij}} - T_{b_{ij}})} - \frac{q}{(T_{wo_{ij}} - T_{bo_{ij}})}$$  \hspace{1cm} (5.1.)

Where,

$T_{w_{ij}}, T_{w_{ij}}$ - inner surface temperatures calculated from the measured outer surface temperatures at the location $j$ and times $t_0$, and $t_1$ respectively (section 6.1., Eq. (6.6.))

$T_{b_{ij}}, T_{b_{ij}}$ - bulk temperature at the location $j$ and times $t_0$, and $t_1$ respectively (calculated as described in the Appendix C, section C.2.)

$q$ - heat flux supplied to fluid [kW/m$^2$]

The bulk temperature variation was neglected in the calculation of $\Delta h_j$ ($T_{b_{ij}} = T_{b_{ij}}$). The calculated values of $\Delta h_j$ are summarized in Table 5.4. for the LTE. The summary of the heat transfer coefficient change for the HTE with low inlet bulk temperature is given in Table 5.5, and in Table 5.6. for the HTE with high inlet bulk temperature. The heat transfer coefficient change was plotted against the relative inner surface temperatures [$T_{w_{ij}} - T_{tp}$] in Figure 5.8. for all LTE and HTE. Figure 5.8. shows that the enhancement of heat transfer increases as wall temperature rises above $T_{tp}$, but tends to plateau at around 3 kW/m$^2$-K. This plateau coincides with the bulk fluid temperature being greater than $T_{tp}$. One would expect the enhancement to depend on flow rate, heat flux and roughness more directly than on temperature, but for this work a simple correlation for heat transfer coefficient change was used. For the bulk temperatures lower than $T_{tp}$ the following linear fit to the calculated values of $\Delta h$ was used (Figure 5.8):

$$\Delta h_{LT} = 0.1 (T_{w_{ij}} - T_{tp}) - 1 \quad \text{if} \quad T_{w_{ij}} > T_{tp} + 10 \quad \text{and} \quad T_{bo_{ij}} < T_{tp}$$  \hspace{1cm} (5.2)

where subscript LT refers to the conditions for which the bulk temperature is below three phase equilibrium temperature.
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Table 5.4. Heat transfer coefficient change for LTE in the time segment \(\Delta t_1\)
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Table 5.5. Heat transfer coefficient change for HTE with low inlet bulk temperature in the time segment $\Delta t_i$
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Table 5.6. Heat transfer coefficient change for HTE with high inlet bulk temperature in the time segment $\Delta t_1$. 
Figure 5.8. Heat transfer coefficient change for all LTE and HTE in the time segment $\Delta t$. 
For the bulk temperature greater than $T_{tp}$, it seemed that the heat transfer coefficient change was not as strong function of inner surface temperatures as in the LT region and its value could be taken as a constant. Its value was obtained as a heat transfer coefficient change $\Delta h_{LT}$ at $T_{w0(j-1)}$ for which $T_{b0(j)}>T_{tp}$ and $T_{b0(j-1)} \leq T_{tp}$:

$$\Delta h_{HT} = \Delta h_{LT(j-1)} = \text{const. \ if \ } T_{b0(j)}>T_{tp} \ \text{and} \ T_{b0(j-1)} \leq T_{tp} \quad (5.3)$$

where subscript HT refers to the conditions for which the bulk temperature is above three phase equilibrium temperature.

For the inner surface temperature below the three phase equilibrium temperature, there was no significant heat transfer coefficient change.

The heat transfer coefficient obtained for pure water flow in a clean tube ($h_0$, section 5.4.) was modified to account for the effect of salt as follows:

$$h_j = h_0 + \Delta h \quad (5.4.)$$

5.5. Shape and Location of the Deposit

The outer surface temperature ($T_0$) changes at times $t_2$ and $t_3$ (times when 10 g and 20 g of salt were delivered to the test section, Figure 5.6.) were plotted against the relative inner surface temperature [$T_{w0}-T_{tp}$] for all LTE and against the relative bulk temperature [$T_{b0}-T_{tp}$] for all HTE to observe the shape and the location of the deposit. In the LTE plot, the temperature change [$T_{o2}-T_{o1}$] had one distinct peak for experiments for which the outlet bulk temperature stayed below the three phase equilibrium temperature (Figure 5.9). The temperature peaks were located after the three phase equilibrium temperature was exceeded at the wall. The peaks did not agree in their location which was represented by relative inner surface temperature for the clean tube. For experiments 4, 6 and 9, the outlet bulk temperature exceeded the three phase temperature and these experiments had a second temperature peak forming (Figure 5.9). In the HTE plot, the
temperature change \([T_{02}-T_{01}]\) had two distinct peaks for all low concentration HTE (Figure 5.10). The first temperature peak was located in the low temperature region (LT vapor-liquid region) where the bulk temperature was below the three phase equilibrium temperature.

**Figure 5.9.** Temperature change \([T_{02}-T_{01}]\) at time \(t_2\) for LTE.
The second peak was located where the three phase equilibrium temperature was reached in the bulk fluid (HT vapor-solid region). The peaks agreed in their location for the HTE that were performed with low inlet bulk temperatures (2, 11, 12) and for the experiments with high inlet bulk temperatures (3 and 5). When temperature profiles obtained at times $t_2$ and $t_3$ were compared for all the LTE and HTE it was noticed that the shape of the temperature profile did not change with time.

**Figure 5.10.** Temperature change [$T_{02} - T_{01}$] at time $t_2$ for HTE
5.6. Bulk temperature variation during deposition

The change of the bulk temperature at times $t_2$ and $t_3$ is summarized in Table 5.7. for the LTE and in Table 5.8. for the HTE.

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<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>TS MID</td>
<td>402.2</td>
<td>403.4</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>441.8</td>
<td>444.1</td>
<td>445</td>
<td></td>
<td></td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>10(LTE)</td>
<td>TS IN</td>
<td>388</td>
<td>387.5</td>
<td>387.8</td>
<td>T=395</td>
<td>445.6</td>
<td>-0.5</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>TS MID</td>
<td>402.3</td>
<td>401.7</td>
<td>401.9</td>
<td></td>
<td></td>
<td>-0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>440.3</td>
<td>439.4</td>
<td>437.6</td>
<td></td>
<td></td>
<td>-0.9</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

Table 5.7. The change of bulk temperature in LTE at times $t_2$ and $t_3$

The outlet temperatures in some LTE increased and reached $T_p$ (experiments 4, 6, and 9) and in some experiments decreased. The outlet temperatures decreased in all HTE except experiment 11. This temperature decrease could have been attributed to salt nucleation. The bulk temperature variation was within 6 °C and was not taken into account when calculating the salt thickness profiles (Chapter 6).
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Bulk temp. Locat.</th>
<th>Bulk Temp. at Time 0</th>
<th>Bulk Temp. at Time 2</th>
<th>Bulk Temp. at Time 3</th>
<th>Two phase temp.</th>
<th>$T_{np}$</th>
<th>$\Delta T_2$</th>
<th>$\Delta T_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(HTE)</td>
<td>PH2 IN</td>
<td>391.2</td>
<td>393.1</td>
<td>393.5</td>
<td>T$\approx$400</td>
<td>450.1</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>TS IN</td>
<td>398.4</td>
<td>399.4</td>
<td>399.2</td>
<td></td>
<td></td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>496.2</td>
<td>491.8</td>
<td>490.2</td>
<td></td>
<td></td>
<td>-4.4</td>
<td>-6</td>
</tr>
<tr>
<td>3(HTE)</td>
<td>PH2 IN</td>
<td>390.7</td>
<td>393.9</td>
<td>395</td>
<td>T$\approx$400</td>
<td>450.8</td>
<td>3.2</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>TS IN</td>
<td>437</td>
<td>436.6</td>
<td>437.9</td>
<td></td>
<td></td>
<td>-0.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>485</td>
<td>483.4</td>
<td>483.4</td>
<td></td>
<td></td>
<td>-1.6</td>
<td>-1.6</td>
</tr>
<tr>
<td>8(HTE)</td>
<td>PH2 IN</td>
<td>387.2</td>
<td>389.7</td>
<td>390.1</td>
<td>T$\approx$390</td>
<td>444</td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>TS IN</td>
<td>395.9</td>
<td>396.5</td>
<td>396.5</td>
<td></td>
<td></td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>480.6</td>
<td>474.1</td>
<td>471</td>
<td></td>
<td></td>
<td>-6.5</td>
<td>-9.6</td>
</tr>
<tr>
<td>11(HTE)</td>
<td>TS IN</td>
<td>403.1</td>
<td>406.4</td>
<td>405.6</td>
<td>T$\approx$390</td>
<td>443.6</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>TS MID</td>
<td>441.6</td>
<td>447.1</td>
<td>448.1</td>
<td></td>
<td></td>
<td>5.5</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>508.9</td>
<td>512.9</td>
<td>515.1</td>
<td></td>
<td></td>
<td>4</td>
<td>6.2</td>
</tr>
<tr>
<td>12(HTE)</td>
<td>TS IN</td>
<td>387.4</td>
<td>389.1</td>
<td></td>
<td>T$\approx$390</td>
<td>442.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS MID</td>
<td>415.8</td>
<td>422.8</td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TS OUT</td>
<td>484.6</td>
<td>498.4</td>
<td></td>
<td></td>
<td></td>
<td>-4.1</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.8.** The change of bulk temperature in HTE at times $t_2$ and $t_3$

5.7. Mass balance

The mass of deposited salt $m_s$ (g_s) in the test section was found as:

\[
m_s = m_{sin} - m_{sout}
\]  \hspace{1cm} (5.5)

Where the mass of the salt that was delivered to the test section $m_{sin}$ in a time $t$ was found as a product of the flow rate $\dot{m}$, salt concentration at the inlet of the test section and time:

\[
m_{sin} = \dot{m} \cdot C_{in} \cdot t
\]  \hspace{1cm} (5.6)
The mass of the salt that came out of the test section $m_{\text{sout}}$ in a time $t$ was found as a product of the mass of the collected fluid $m_{\text{coll}}$ (kg) for a time $t$ and the measured concentration of the collected fluid $C_{\text{coll}}$ (kg/kg).

$$m_{\text{sout}} = m_{\text{coll}} \cdot C_{\text{coll}}$$ (5.7)

The mass balance was performed at times $t_2$ and $t_3$ when 10 and 20 g were delivered to the test section. The mass balance could not be closed with the mass of salt that was collected during the clean out $m_{\text{clean}}$ due to the leakage in the system (section 5.1.). The measured masses are given in Table 5.9. for LTE and in Table 5.10. for HTE.

The analysis of the collected samples at times $t_2$ and $t_3$ (10 and 20 g delivered) was used to provide the concentration of the effluent, and concentrations of the solution at the inlet and the outlet of the test section. The measured concentrations are summarized in Table 5.9. for LTE and in Table 5.10 for HTE. Concentrations at the inlet of the test section agreed with the feed concentration for low concentration LTE. In the experiment 7 (high concentration LTE), this measured concentration at the inlet of the test section was much higher than the feed concentration which indicated sinking of the liquid phase into the sampling port. The concentrations at the inlet of the test section indicated deposition in Preheater 2 for HTE 3 and 5 (which was purposely induced). For experiment 5, this concentration measured at sample time $t_2$ also indicated liquid phase sinking into sampling port. The concentrations at the outlet of the test section and of the effluent were close in their value. These concentrations were higher than the concentrations of the vapor phase at the three phase equilibrium for LTE and they were close to the solubility limit at the outlet bulk temperature for HTE.

Since the sampling was performed at times $t_2$ and $t_3$ (the same time segments when the effluent collection was performed), the samples provided additional means to control our mass balance. Based on the amount of deposited salt and measured time of the collection, the deposition rates were calculated and are also summarized in Table 5.9. and Table 5.10.
### Table 5.9. Sampling and mass balance results for LTE at $t_2$ and $t_3$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Flow Rate</th>
<th>Feed Conc.</th>
<th>$m_{in}$</th>
<th>$m_{in}$</th>
<th>$m_r$</th>
<th>Deposition rate/Delivery rate</th>
<th>Collected Effluent</th>
<th>Sample I (Test Section In)</th>
<th>Sample II (Test Section Out)</th>
<th>Sample III (Effluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/min</td>
<td>wt%</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>1.16</td>
<td>0.106</td>
<td>10</td>
<td>3.7</td>
<td>6.3</td>
<td>N.M.</td>
<td>0.63</td>
<td>385</td>
<td>1045</td>
<td>431</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>7.8</td>
<td>12.2</td>
<td>0.4</td>
<td>0.61</td>
<td>466</td>
<td>1055</td>
<td>472</td>
</tr>
<tr>
<td>2</td>
<td>0.62</td>
<td>0.103</td>
<td>10</td>
<td>4.2</td>
<td>5.8</td>
<td>N.M.</td>
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<td>433</td>
<td>1066</td>
<td>440</td>
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<tr>
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<td></td>
<td></td>
<td>20</td>
<td>8.2</td>
<td>11.8</td>
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<td>0.59</td>
<td>418</td>
<td>1048</td>
<td>471</td>
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<td>0.1</td>
<td>10</td>
<td>3.7</td>
<td>6.3</td>
<td>N.M.</td>
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<td>392</td>
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<td>20</td>
<td>8.1</td>
<td>12</td>
<td>0.2</td>
<td>0.6</td>
<td>460</td>
<td>1039</td>
<td>416</td>
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<tr>
<td>4</td>
<td>1.18</td>
<td>0.912</td>
<td>10</td>
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<td>487</td>
<td>24265</td>
<td>505</td>
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<td>1</td>
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<td>N.M.</td>
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<td></td>
<td></td>
<td>555</td>
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### Table 5.10. Sampling and mass balance results for HTE at $t_2$ and $t_3$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Flow Rate</th>
<th>Feed Conc.</th>
<th>$m_{in}$</th>
<th>$m_{in}$</th>
<th>$m_r$</th>
<th>(m_r - m_i) / m_i</th>
<th>Coll. Effluent conc.</th>
<th>Solubility limit at T boil</th>
<th>Sample I</th>
<th>Sample II</th>
<th>Sample III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/min</td>
<td>wt%</td>
<td>g</td>
<td>g</td>
<td>g</td>
<td></td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
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<td>0.106</td>
<td>10</td>
<td>1.6</td>
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<td>157</td>
<td>145</td>
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<td>160</td>
</tr>
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<td>995</td>
<td>1042</td>
<td>157</td>
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<td>0.065</td>
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<td>3</td>
<td>7</td>
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<td>656</td>
<td>178</td>
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<tr>
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<td></td>
<td>20</td>
<td>5.6</td>
<td>14.4</td>
<td>0.37</td>
<td>0.72</td>
<td>178</td>
<td>158</td>
<td>656</td>
<td>178</td>
</tr>
<tr>
<td>5</td>
<td>0.65</td>
<td>0.077</td>
<td>10</td>
<td>3</td>
<td>7</td>
<td>N.M.</td>
<td>0.7</td>
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<td>180</td>
<td>2384</td>
<td>219</td>
</tr>
<tr>
<td></td>
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<td>5.8</td>
<td>14.2</td>
<td>0.3</td>
<td>0.71</td>
<td>206</td>
<td>180</td>
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<td>219</td>
</tr>
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<td>-0.13</td>
<td>0.91</td>
<td>104</td>
<td>101</td>
<td>N.M</td>
<td>N.M</td>
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<td></td>
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<td>N.M.</td>
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<td>N.M</td>
<td></td>
<td>101</td>
<td>N.M</td>
<td>N.M</td>
</tr>
<tr>
<td>12</td>
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<td>0.102</td>
<td>10</td>
<td>1.6</td>
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<td>-0.21</td>
<td>0.84</td>
<td>108</td>
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<td>N.M</td>
</tr>
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<td>N.M.</td>
<td>N.M.</td>
<td>N.M.</td>
<td>N.M</td>
<td></td>
<td>107</td>
<td>N.M</td>
<td>N.M</td>
</tr>
</tbody>
</table>
6. CALCULATION OF SALT THICKNESS PROFILES

6.0. Introduction

Salt thickness profiles were needed to compare our experimental results to sodium chloride deposition model predictions. The salt thickness profiles were obtained indirectly by first experimentally determining the outer surface temperature profiles for the clean and the fouled test section at different time intervals (Chapter 5.) and then using a heat transfer model to calculate the thickness of the salt layer along the segmented tube. The salt thickness was varied to obtain a best fit to the measured bulk and outer surface temperatures for each segment of the tube. The porosity of the salt layer was used as a free parameter in the heat transfer modeling. The agreement between the calculated and the measured mass of salt deposited in the tube was used to estimate porosity of the salt layer. The change of the porosity with experimental conditions and time was obtained as well. For the calculation of the salt layer thickness, the program written by Teshima (1997), Salt.f, was adopted and new routines added to it to model NaCl solutions (SaltThick.f, Appendix F).

The heat transfer model, porosity and salt thickness calculations and results are described below.

6.1. Heat Transfer Model

The cross section of a fouled tube segment is given in Figure 6.1. The size of the increment of the tube $dz_j$ for which the thickness of the salt layer was calculated, was determined by the distance between the thermocouples used for the outer surface temperature measurements. Figure 6.1. illustrates the components of the heat transfer model. The bulk temperatures $T_b$ were determined at each thermocouple position j from the known inlet bulk temperature (measured at the inlet of the test section), heat flux, mass flow and step size (more details in Appendix C, section C.2.).
$T_s$ - temperature at the interface between the salt layer and the fluid [K]  
$T_{sw}$ - temperature at the inner tube wall [K]  
$T_{oc}$ - calculated temperature at the outer tube surface [K]  
$r_s$ - distance from the center of the tube to the salt layer [m]  
$r_i$ - inner tube radius [m]  
$r_o$ - outer tube radius [m]  
$Y_{thick}$ - thickness of the salt layer [m]

Figure 6.1. The increment of the fouled tube used in salt thickness calculation.
The temperature at the interface between the salt layer and the fluid, $T_{s\theta}$, was calculated using an empirical heat transfer coefficient described in section 5.5 as follows:

$$T_{s\theta} = T_{b\theta} + \frac{q}{(h_0 + \Delta h)}$$  \hspace{1cm} (6.1)

The calculation of $T_s$ followed the procedure described in Appendix C for the clean tube. The calculation of $T_s$ considered the increased fluid velocity resulting from the smaller tube radius,

$$r_s = r_i - Y_{thick}$$  \hspace{1cm} (6.2)

where,

$Y_{thick}$ - salt layer thickness.

The temperature at the interface between the salt layer and the tube wall $T_{swj}$ was estimated with following assumptions:

- a one-dimensional radial, steady state heat conduction throughout the salt layer
- porous salt layer
- constant porosity $\phi$ throughout the deposit

The temperature at the interface between the salt layer and the tube wall was calculated as follows:

$$T_{sw} = T_s + \frac{q_L}{2 \cdot \pi \cdot k_{layer}} \cdot \frac{\ln \left( \frac{r_i}{r_s} \right)}{r_s}$$  \hspace{1cm} (6.3)

Where,

$q_L$ -the heat flux [kW/m]

$k_{layer}$ - thermal conductivity of the porous salt layer [kW / m-K]
The thermal conductivity of the porous salt layer was calculated assuming the salt layer structure as a network of columns of water and salt in parallel.

\[ k_{layer} = (1 - \phi) k_{salt} + \phi k_{fluid} \]  \hspace{1cm} (6.4)

Where,

- \( k_{fluid} \) - thermal conductivity of the fluid in pores evaluated at \( T_s \) [kW / m-K]
- \( k_{salt} \) - thermal conductivity of NaCl evaluated at \( T_{av} \) [kW / m-K]
- \( T_{av} = \frac{T_s + T_{sw}}{2} \)

\( \phi \) - porosity (void volume divided by the total deposit volume)

The thermal conductivity of NaCl was extrapolated from the temperature-conductivity graph (Touloukian et al., 1970) and its change with temperature was determined as:

\[ k_{salt} = 10^{(1.462 - 1.07 \log T_{av})} \]  \hspace{1cm} (6.5)

A one-dimensional radial, steady state heat conduction with the internal heat source through the tube wall was applied to obtain the outer wall temperature. A uniform volumetric heat generation, no change of the conductivity of the tube material radially with temperature and a perfectly insulated tube were assumed. The outer surface temperature was calculated as follows:

\[ T_{o,e} = T_w + q \cdot \frac{r_i \cdot (A^2 - \ln(A^2) - 1)}{2 \cdot k_w (1 - A^2)} \]  \hspace{1cm} (6.6)

Where,

\[ A = \frac{r_i}{r_o} \]
In order to perform the salt thickness calculation for a segment $dz_j$, the porosity $\phi$ of the salt layer had to be known. There were no previous experiments performed to determine the porosity of sodium chloride deposits. The average porosity of a sodium sulfate deposit was experimentally found to be 0.7 by Hodes (1998), but this information was not very useful in this work because the two salts had different phase behaviors and probably different deposit structures. Furthermore, there were two distinct regions of deposition observed in sodium chloride deposition experiments (a low temperature region where bulk temperature was below three-phase temperature and a high temperature region where bulk temperature was above three-phase temperature). It is assumed here that porosity of the deposit in two regions was different. There was also a question if the porosity of the deposit was changing with time.

The porosity was first found for the low temperature region by performing calculations for the LTE with a good mass balance (Option 1 of SaltThick.f program). The algorithm for this calculation is given in Figure 6.2. The general procedure for porosity calculation involved first calculating a salt thickness and a mass of deposited salt with initial porosity set to zero for the whole tube. The salt thickness calculation started for the $z_j$ for which the inner surface temperature $T_w$ exceeded the three phase equilibrium temperature $T_{tp}$. In the salt thickness calculation, the measured outer surface temperature $T_o$ at the location $z_j$ was compared to the calculated temperature $T_{oc}$ at the same location and if they differed by more than 0.1°C, the program added a thin layer of salt. When the thin layer of salt was added, the outer surface temperature for the fouled tube segment was calculated as described in 6.1.
Figure 6.2. Algorithm for salt thickness and porosity calculation in the option 1.
The calculated outside wall temperature $T_{ocj}$ was again compared to the measured temperature $T_{oj}$. The thickness of the salt layer was increased till the two temperatures agreed within 0.1°C. When the program finished marching through the whole length of the tube and calculating salt thickness for each tube increment, the total mass of deposited salt was calculated as:

$$
\sum_{j=1}^{n} m_{salt} = \sum_{j=1}^{n} \left( r_i^2 - (r_i - Y_{thickj})^2 \right) \pi d_{zj} (1 - \phi) \rho_{salt} 
$$

The program then compared the calculated mass $m_{salt}$ to the experimentally obtained one $m_s$. If they differed, the program increased porosity by 0.01 and repeated the procedure till the two masses agreed within 0.5 g.

It was possible to calculate the salt thickness profiles for a fixed value of porosity if the deposited mass of salt was not measured or if the sensitivity to the porosity was investigated (Option 2). The calculation followed the same procedure as described in the Option 1 except that there was no fitting the porosity to the measured salt mass.

For calculation of the thickness profiles in the HTE (Option 3), it was assumed that the porosity of the low temperature region was similar to that found in the LTE. In this calculation, the porosity in the high temperature region was treated as a free parameter. Option 3 was actually a combination of options 1 and 2. For the bulk temperature below the three phase temperature (low temperature region), the fixed low temperature porosity was used to calculate the thickness of salt layer and the mass of deposited salt as described in option 2. The mass of salt deposited in the high temperature region (bulk temperature above three phase temperature) was calculated by subtracting the mass deposited in the low temperature region from the measured mass. This high temperature region mass was then used to find the high temperature deposit porosity and thickness by following the procedure described in option 1.
6.3. Results of porosity and thickness calculations in LTE and HTE

6.3.1 Summary of the porosity calculation results

6.3.1.1. Porosity of the salt deposit in low temperature (LT) region (bulk temperature below three phase equilibrium temperature)

Option 1 of the SaltThick.f program (section 6.2.) was used to calculate the porosity of the low temperature region and the thickness of the salt layer from the experimentally obtained mass of deposited salt at times \(t_2\) and \(t_3\) for LTE 1, 4, 6 and 7. Table 6.1. gives values of porosity that were obtained in this calculation. The calculated value of porosity \(\phi_{LT}\) varied from 0.0 to 0.3.

<table>
<thead>
<tr>
<th>Low Temperature Experiment</th>
<th>Porosity at time (t_2)</th>
<th>Porosity at time (t_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 6.1. Calculated porosity of salt layer in low temperature region

The average porosity for the LT region was found to be 0.1 and it was used to recalculate salt thickness and mass of deposited salt for experiments 1, 4, 6, and 7. For this calculation, the option 2 of the SaltThick.f program was used. This average porosity was also used to obtain salt thickness and the mass of deposited salt in LTE 9 and 10 for which a mass balance was not performed. The calculated mass of deposited salt with the porosity of salt layer taken as 0.1 is given in the Table 6.2. for all LTE. This calculated mass \(m_{salt}\) was compared to the measured mass \(m_s\) of deposited salt at the time \(t_2\) when 10 g of salt were delivered to the test section.
### Table 6.2. Mass of deposited salt calculated with average porosity of 0.1 in all LTE at the time $t_2$ when 10 g were delivered to the test section

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Calculated mass of deposited salt [g] with average porosity 0.1</th>
<th>Measured mass of deposited salt [g]</th>
<th>Error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>6</td>
<td>-17</td>
</tr>
<tr>
<td>4</td>
<td>7.9</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>7.7</td>
<td>9.4</td>
<td>-18</td>
</tr>
<tr>
<td>9</td>
<td>7.8</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>10</td>
<td>8.2</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

This calculation showed that porosity adjustment introduced an error of up to 30% in the amount of the salt deposited in the tube. However, the thickness of the salt layer was of greater importance for this study than the actual mass of deposited salt. To see what effect porosity adjustment induced to the thickness of the salt layer, a comparison was made between the salt layer profile calculated from option one (using the measured mass of deposited salt as an input) and the salt layer profile obtained with the average porosity of 0.1 from option two of SaltThick.f program. This comparison is given in Figure 6.3 for experiments 1 and 4. To stress the importance of porosity, the salt layer thickness that was calculated with an average porosity of sodium sulfate deposit of 0.7 (taken from Hodes, 1998) for the experiment 1 was plotted on the same graph as well. This comparison showed that using average porosity of 0.1 in salt layer thickness calculations would introduce an error of about 10%. Had the average porosity of a sodium sulfate deposit been used for salt layer thickness calculation, the salt layer thickness would have been 72% lower than the salt layer thickness obtained from option one of SaltThick.f program. Once the average porosity of the low temperature region was determined as $\phi_{LT} = 0.1$, the next step was to use it in the calculation of the porosity of the salt deposit in the high temperature region.
Figure 6.3. Comparison between salt layer profiles calculated with different porosity for LTE 1 and 4 at the time $t_2$ when 10 g of salt were delivered to the test section (salt thickness at the location $j$ is represented by a symbol, a line connecting two symbols shows the possible shape of the deposit, not the actual thickness).
6.3.1.2. Porosity of the deposit in high temperature (HT) region

Option 1 was first used to find the porosity for the HTE with good mass balance assuming the same porosity in the LT and HT regions (Table 6.3.). The average porosity of the LT and HT deposits was found as 0.5. This value was much higher than the average porosity of LT region of 0.1 that was calculated in the previous section. As an alternative analysis, option 3 of the SaltThick.f program was used to calculate porosity of the deposit in the HT region. In this calculation, the porosity of LT region was assumed to be lower than 0.5. An average porosity of 0.1 was used to find LT region's salt thickness and mass of deposited salt in HTE 2 and 11. In the experiments 3, 5 and 12, higher porosity of LT region than 0.1 had to be used (0.2, 0.3, and 0.6 respectively) in order to match the calculated to the measured mass of deposited salt (with LT region porosity of 0.1, too much salt would be spent in the LT region and there would be no salt left for HT region deposit). The calculated values of the HT deposit porosity from option 3 are also listed in the Table 6.3. The average porosity of the HT region from Option 3 was found as 0.6.

<table>
<thead>
<tr>
<th>HTE</th>
<th>LT &amp; HT porosity at $t_2$ (Option 1)</th>
<th>LT &amp; HT porosity at $t_2$ (Option 3)</th>
<th>LT&amp;HT porosity at $t_3$ (Option 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LT</td>
<td>HT</td>
<td>LT</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>0.1</td>
<td>0.65</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>0.2</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>0.55</td>
<td>0.3</td>
<td>0.75</td>
</tr>
<tr>
<td>11</td>
<td>0.4</td>
<td>0.1</td>
<td>0.45</td>
</tr>
<tr>
<td>12</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 6.3. Porosity of salt layer for HTE obtained from Option 1 and Option 3

Options 1 and 3 did not give a large discrepancy in the HT deposit porosity (0.5 and 0.6 respectively). The LT deposit porosity obtained from Option 1 for LTE and HTE was 0.1 and 0.5 respectively which according to the discussion in the previous section
(Figure 6.3.) could affect thickness calculations in LT region significantly if Option 1 was used to calculate thickness profiles in HTE.

6.3.2. Summary of the salt thickness calculation results

6.3.2.1. Salt thickness profiles in low temperature region

The salt thickness profiles in the low temperature region were calculated at times $t_2$ and $t_3$. The profiles were obtained for the LTE (from option 2 of the SaltThick.f program) and HTE (from option 3) with the porosity of the salt layer equal to 0.1 except in the low temperature region of the HTE 3, 5 and 12 for which the porosity was taken as 0.2, 0.3 and 0.6 respectively (in order to satisfy the mass balance).

The results are listed in the Table 6.4. The table gives the calculated salt layer thicknesses $Y_{thick_i}$ in terms of the axial distance $z_i$ and the relative inner surface temperature for the clean tube $T_{w0j} - T_{tp}$ (relative inner wall temperature at time $t_0$ before the salt solution was introduced to the system). It was observed that deposit in the low temperature region of all experiments had been formed in the inner clean wall temperature range from $T_{tp}$ to $(T_{tp} + 30°C)$. In LTE 4,6 and 9 the formation of a second deposit peak was observed because the outlet bulk temperature reached the three-phase equilibrium temperature.

Further analysis is concentrated on the location and the height of the deposit peaks because they are crucial to the plugging of the tube. The location of the peaks (given in terms of the surface temperature) varied from 5.5 °C to 23.9 °C above the three-phase temperature (Table 6.4.). The height of the peaks at time $t_2$ varied from 0.18 mm in experiment 12 to 0.95mm in experiment 7. At time $t_3$, the peak height variation was from 0.3 mm in experiment 11 to 1.56 mm in experiment 7. It was observed that in some experiments the location of the peak shifted with time (1, 3, 4, 6, 7, 10). In some experiments the height of the peak did not change significantly with time (2, 5, 8, 10, 11).
<table>
<thead>
<tr>
<th>Exper.</th>
<th>$z_i$ [m]</th>
<th>$T_{w^0}$-Ttp [°C]</th>
<th>Ythick at time $t_2$ [mm]</th>
<th>Salt thickness at time $t_3$ [mm]</th>
<th>Exper.</th>
<th>$z_i$ [m]</th>
<th>$T_{w^0}$-Ttp [°C]</th>
<th>Ythick at time $t_2$ [mm]</th>
<th>Salt thickness at time $t_3$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(LTE)</td>
<td>2.10</td>
<td>-1.2</td>
<td>0.00</td>
<td>0.00</td>
<td>7(LTE)</td>
<td>2.30</td>
<td>4.2</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>2.22</td>
<td>1.5</td>
<td>0.05</td>
<td>0.00</td>
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<td>2.44</td>
<td>6.8</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>2.30</td>
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<td>0.01</td>
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<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2.44</td>
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<td>0.41</td>
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<td>20.7</td>
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</tr>
<tr>
<td></td>
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<td>3.13</td>
<td>10.9</td>
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</tr>
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<td>0.18</td>
<td>1.16</td>
<td></td>
<td>3.26</td>
<td>13.8</td>
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</tr>
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<td>0.98</td>
</tr>
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<td>0.04</td>
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<td>0.33</td>
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<td>0.00</td>
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</tr>
<tr>
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<td>2.06</td>
<td>5.7</td>
<td>0.14</td>
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</tr>
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<td>0.37</td>
<td>0.62</td>
<td></td>
<td>2.28</td>
<td>16.1</td>
<td>0.57</td>
<td>0.46</td>
</tr>
<tr>
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<td>12.6</td>
<td>0.08</td>
<td>0.41</td>
<td></td>
<td>2.55</td>
<td>26.1</td>
<td>0.16</td>
<td>0.66</td>
</tr>
<tr>
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<td>0.47</td>
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<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
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<td>0.00</td>
<td></td>
<td>0.72</td>
<td>4.9</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
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<td>0.23</td>
<td>0.00</td>
<td></td>
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<td>10.2</td>
<td>0.32</td>
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</tr>
<tr>
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<td>0.82</td>
<td></td>
<td>1.02</td>
<td>17.2</td>
<td>0.19</td>
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</tr>
<tr>
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<td>0.27</td>
<td>0.02</td>
<td></td>
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<td>19.4</td>
<td>0.17</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
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<td>0.00</td>
<td></td>
<td>1.41</td>
<td>5.5</td>
<td>0.18</td>
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</tr>
<tr>
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<td></td>
<td>1.72</td>
<td>19.4</td>
<td>0.17</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
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<td>9.4</td>
<td>0.28</td>
<td>0.46</td>
<td></td>
<td>1.22</td>
<td>-3.2</td>
<td>0.00</td>
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</tr>
<tr>
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<td>12.1</td>
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<td>0.62</td>
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<td>5.5</td>
<td>0.18</td>
<td>n.a.</td>
</tr>
<tr>
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<td>18.0</td>
<td>0.15</td>
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<td>19.4</td>
<td>0.17</td>
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</tr>
<tr>
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<td>21.7</td>
<td>0.22</td>
<td>0.98</td>
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<td>1.22</td>
<td>-3.2</td>
<td>0.00</td>
<td>n.a.</td>
</tr>
<tr>
<td>6(LTE)</td>
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<td>27.5</td>
<td>0.28</td>
<td>0.70</td>
<td></td>
<td>1.22</td>
<td>-3.2</td>
<td>0.00</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

**Table 6.4.** Calculated salt thickness profiles in low temperature region of LTE and HTE at times $t_2$ and $t_3$
Although the peak moved spatially, the experimentally determined deposition rates were rather constant in all experiments for which mass balances were performed (section 5.7). This leads to the conclusion that the low temperature region deposit was not very stable and that salt peak was shifted from one location to the other.

To further define the location of the peaks, the resulting thickness profiles for salt deposits in the low temperature region of all performed experiments when 10 g and 20 g of salt were delivered to the test section were plotted in Figures 6.4.A and 6.4.B. The salt thickness was plotted against the relative temperature at the salt-fluid interface $T_S - T_p$ (the relative temperature that the solution sees). Calculated salt thicknesses at the locations $j$ (represented with symbols in Figure 6.4) were connected with a straight line to show the shape of the deposit. This line did not represent the actual thickness of the salt layer. This plot revealed that all profiles matched in their location and that their peaks were formed when the three phase temperature at the salt-fluid interface was exceeded by 3-5 °C except in experiments 2 and 10 which had their peaks at $T_p$ and 10 °C after $T_p$ respectively.

The effect of the bulk temperature on the deposit location is shown in the Figure 6.5. The salt thickness profiles were plotted against the relative bulk temperature $T_b - T_p$. The deposits formed in the experiments with the similar bulk temperature range agreed in their location.

When analyzing the heights of the peaks for all experiments, it was difficult to find any connection between the flow rate (heat flux) and the height of the peaks. The effect of concentration was shown only for the experiment with the highest concentration (LTE 7) that had the highest peak height.
Figure 6.4. Salt thickness profiles in the low temperature region (A, B: at the times $t_2$ and $t_3$ when 10 and 20 g were delivered to the test section) plotted against the relative temperature at the salt-fluid interface $T_{sj}-T_{tp}$.
Figure 6.5. Salt thickness profiles in the low temperature region (A, B: at the times $t_2$ and $t_3$ when 10 and 20 g were delivered to the test section) plotted against the relative bulk temperature $T_b-T_{tp}$
6.3.2.2. Salt thickness profiles in high temperature region

The salt thickness profiles in the high temperature region of HTE were calculated from Option 3 at times $t_2$ and $t_3$. The results are listed in the Table 6.5. The table lists salt thicknesses of the deposits formed in low and high temperature regions of the HTE. The location of the calculated thickness is given in terms of the axial location $z_f$ and the relative bulk temperature $T_b - T_{tp}$. The results showed that the deposit in the high temperature region had been formed in the bulk temperature range $(T_{tp}-16 \, ^\circ C)$ to $(T_{tp} + 40 \, ^\circ C)$. The location of the HT peaks varied from $T_{tp} + 5 \, ^\circ C$ to $T_{tp} + 11.4 \, ^\circ C$ (bulk temperature). The height of the peaks ranged from 0.17mm in experiment 5 to 0.59 mm in experiment 12 at time $t_2$. The peak height variation was from 0.16 mm in the experiment 3 to 1.05 mm in the experiment 2 at the time $t_3$. The location of the peaks did not shift with time as it did in the low temperature region (section 6.3.2.1). The height of the peak was increasing with time (except in the exp.3). In the low temperature region, it was difficult to see a connection between flow rate (heat flux) and peak height growth. It did appear that deposits in high temperature region were more stable than deposits in the low temperature region because the peak locations were not changing with time.

The calculated salt thickness profiles in the low and high temperature regions of the HTE at times $t_2$ and $t_3$ are plotted in Figure 6.6. It was inferred that in experiments 11 and 12 high temperature peaks appeared cut off, but this may be an artifact of the large axial distance between thermocouples here. The peaks in the low temperature region when compared to the peaks of the deposit in the high temperature region appeared lower in experiments 2, 11, and 12 (medium concentration) and higher in experiments 3 and 5 (low concentration). The difference between these two groups of the experiments was that there was deposition induced in Preheater 2 in experiments 3 and 5 and some salt was possibly removed from the Preheater 2 deposit and reattached to the low temperature deposit in the test section.
<table>
<thead>
<tr>
<th>Exper.</th>
<th>$z_j$</th>
<th>Tb-Ttp [C]</th>
<th>Salt thickness at time $t_2$ [mm]</th>
<th>Salt thickness at time $t_3$ [mm]</th>
<th>Exper.</th>
<th>$z_j$</th>
<th>Tb-Ttp [C]</th>
<th>Salt thickness at time $t_2$ [mm]</th>
<th>Salt thickness at time $t_3$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(HTE)</td>
<td>1.13</td>
<td>-27.2</td>
<td>0.05</td>
<td>0.04</td>
<td>11(HTE)</td>
<td>0.63</td>
<td>-27.0</td>
<td>0.04</td>
<td>0.05</td>
</tr>
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<td>0.46</td>
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<td>0.32</td>
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*Table 6.5. Calculated salt thickness profiles in low and high temperature regions of HTE at times $t_2$ and $t_3$*
Figure 6.6. Calculated salt thickness profiles for HTE at times $t_2$ and $t_3$. 
7. MODELLING OF SODIUM CHLORIDE DEPOSITION

7.0. Introduction

A model was developed to predict the location and the thickness of the sodium chloride deposit for conditions that were encountered in the deposition experiments. The program SaltDep.f written by Rogak was modified and new routines added to it to model sodium chloride deposition (Appendix F). Section 7.1. gives details of the SaltDep4.f program including the heat transfer and the mass transfer models. The results and discussion of the deposition modeling are given in 7.2.

7.1. Sodium chloride deposition model

In the SaltDep4.f program, the SCWO system was divided into a number of segments that corresponded to the heated parts of the system (preheaters and test section) including a small unheated tube length at the outlet of the test section. It was possible to model heat and mass transfer in all segments. The main body of the SaltDep4.f program allowed for parametric studies with the possibility to vary mass flow, radius of the tube and length of the segments. At each time step \( dt_n \) (determined as deposition time/10) the program would march along the length performing heat and mass transfer calculations for each length step \( dz_j \) with the subroutine STEP.f. The set of subroutines dealing with the thermodynamic and transport properties of water, heat and mass transfer calculations and phase behavior of the NaCl-H\(_2\)O solution was given in the program Thermo.f. The salt thickness \( S_y \) was calculated in the main program with the known salt mass flux \( Q_{sj} \), time of deposition \( dt_j \) and porosity of the salt layer \( \phi \) (Figure 7.1.). The following sections give details of the heat and mass transfer calculations.
7.2. Heat transfer calculation

The heat transfer routines provided bulk $T_b$ and surface temperature $T_w$ (or $T_s$) calculations. The subroutine DISCRETE.F was used to obtain bulk temperatures $T_{bj}$ and subroutine HEAT.f provided the inner wall temperature calculation $T_{wj}$ as described in Appendix C. The input data from the input file for this part of the program included inner radius of the tube $r_i$ [m], pressure $p$ [MPa], flow rate $m$ [kg/s], number of heated segments $N$, step size $dz$ (taken as 0.01 m), segment starting coordinate $z$ [m], and either bulk temperatures at the inlet and the outlet $T_{bin}$, $T_{bou}$ [K] or the heat flux $q$ [kW/m²] for the tube segments. The thermodynamic and transport properties were taken as described in Appendix C. The inner wall temperatures $T_w$ were first calculated for the clean tube. For the fouled tube, the temperatures at the fluid salt interface $T_s$ were obtained by taking into account the tube radius change with time due to the salt deposit formation (Figure 7.1.). Once the inner surface temperatures were known, the next step was to approach the mass transfer calculations.

\[ S_{i} = Q_{i} \frac{dt}{\rho/(1-\phi)} \]

\[ S_{ii} \text{ at } dt_{3} \quad S_{i2} \text{ at } dt_{2} \quad S_{i3} \text{ at } dt_{3} \]

\[ T_{s(i)} = T_{b(i)} + q/h_{0} \]

\[ T_{w(i)} = T_{b(i)} + q/(h_{0} + \Delta h) \]

Figure 7.1. The increment of the fouled tube used in sodium chloride deposition model.
7.3. Mass transfer calculation

The general procedure for the salt layer thickness calculation at each time step $dt$ for each length segment $dz$ involved calculating the salt mass flux $Q_s$ from the bulk to the wall first (Figure 7.1.). This calculation would start when the wall temperature reached the three phase equilibrium temperature $T_{tp}$. Since there were two regions of deposition, the first step was to define mass transfer modes in the LT (bulk temperature below $T_{tp}$) and HT (bulk temperature above $T_{tp}$) regions. This definition was based on the examination of the phase behavior of the NaCl-H$_2$O solution (Chapter 2), the results of our experimental work (Chapter 6) and previous research done on salt deposition (Chapter 2). With the assumed mass transfer modes, three deposition models were developed and used to calculate a salt mass flux. The models are summarized in Table 7.1. for the LT region and in Table 7.2. for the HT region. The modeling details are given in the Sections 7.3.1. and 7.3.2.

7.3.1. Mass transfer modeling in LT region

The mass transfer mechanism in the LT region was first investigated. At a location $z_j$ where the three phase equilibrium temperature $T_{tp}$ was exceeded at the wall ($T_w > T_{tp}$), the bulk fluid would be in the two-phase vapor-liquid region ($T_{v,L} < T_b < T_{tp}$, where $T_{v,L}$ is the temperature at the vapor-liquid equilibrium curve corresponding to the initial concentration of the solution $C_0$). The vapor-liquid equilibrium curve suggests that the concentration of the salt in the vapor phase $C_{v,sat}$ would decrease with temperature and the concentration of the salt in the dense liquid phase $C_{liq}$ would increase with temperature. Since $T_{tp}$ was exceeded at the wall first, it was assumed that heterogeneous nucleation would occur at the wall and that the wall concentration would be at the solubility limit for the wall temperature $C_{sat}(T_w)$ (solubility limit at the fluid salt interface temperature for the fouled tube). This would create a concentration difference $AC$ to drive salt molecules from the bulk to the wall. So, the assumed mass transfer mode in the LT region was
<table>
<thead>
<tr>
<th>Model</th>
<th>Low Temperature Region (LT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_w(T_b) &gt; T_{tp}, T_b &lt; T_{tp}$</td>
</tr>
<tr>
<td></td>
<td><strong>Mass flux:</strong> $Q_{sLT} = Q_{sm} - \rho_m \Delta C$</td>
</tr>
<tr>
<td>1</td>
<td>Assumes that mass transfer happens from both, vapor and liquid phases with the same mass transfer coefficient</td>
</tr>
<tr>
<td></td>
<td>$\frac{\partial C_b}{\partial z} = - \frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_b - C_{sat}(T_w))$</td>
</tr>
<tr>
<td>2</td>
<td>Assumes that mass transfer from the bulk to the wall happens from vapor phase only, without participation of liquid phase in mass transfer (liquid phase frozen)</td>
</tr>
<tr>
<td></td>
<td>$C_b = C_{vb} + C_{Lb}$</td>
</tr>
<tr>
<td></td>
<td>$C_{vb} \leq C_{vsat}(T_b)$</td>
</tr>
<tr>
<td></td>
<td>$\frac{\partial C_{vb}}{\partial z} = - \frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w))$</td>
</tr>
<tr>
<td></td>
<td>$\frac{\partial C_{Lb}}{\partial z} = 0$</td>
</tr>
<tr>
<td>3</td>
<td>Assumes mass transfer from bulk to the wall from vapor phase, with fast mass transfer between vapor and liquid phases (vapor concentration at vapor-liquid equilibrium)</td>
</tr>
<tr>
<td></td>
<td>$C_b = C_{vb} + C_{Lb}$</td>
</tr>
<tr>
<td></td>
<td>$C_b \geq C_{vsat}(T_b)$</td>
</tr>
<tr>
<td></td>
<td>$\frac{\partial C_{vb}}{\partial z} = \frac{\partial C_{vsat}}{\partial T_b} \cdot \frac{\partial T_b}{\partial z}$</td>
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<tr>
<td></td>
<td>$\frac{\partial C_{Lb}}{\partial z} = \frac{\partial C_{vsat}}{\partial T_b} \cdot \frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w))$</td>
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<td>$C_{vb} &lt; C_{vsat}(T_b)$</td>
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<td>$\frac{\partial C_{vb}}{\partial z} = - \frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w))$</td>
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<tr>
<td></td>
<td>$\frac{\partial C_{Lb}}{\partial z} = 0$</td>
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Table 7.1. Summary of Models in LT region (nomenclature given on the next page)
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<thead>
<tr>
<th>Model</th>
<th>High Temperature Region</th>
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<td></td>
<td>$T_w(T_v) \geq T_{tp}$, $T_v &gt; T_{tp}$</td>
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</table>

**Mass flux:**

$$Q_{air} = Q_{em} + Q_{sp} = h_m \rho \Delta C + V_p \rho \Delta C_p$$

<table>
<thead>
<tr>
<th>Driving Forces $\Delta C$ and $\Delta C_p$</th>
</tr>
</thead>
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<tr>
<td>$\Delta C = C_{vb} - C_{wsat}$</td>
</tr>
<tr>
<td>$\Delta C_p = C_{pb} - 0$ ($C_{pw}=0$)</td>
</tr>
<tr>
<td>$C_b = C_{vb} + C_{pb}$</td>
</tr>
</tbody>
</table>

1. Assumes combination of mass transfer from vapor phase and particle deposition (no mass transfer from particles to vapor)

2. $C_{vb} \leq C_{bsat}(T_b)$

$$\frac{\partial C_{vb}}{\partial z} = \frac{-h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w))$$

$$\frac{\partial C_{pb}}{\partial z} = \frac{-V_p \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot C_{pb}$$

$C_b$ - total salt concentration in the bulk

$C_{vb}$ - concentration of dissolved salt in vapor phase

$C_{lb}$ - concentration of salt in liquid phase

$C_{pb}$ - concentration of salt in particles

$C_{wsat}$ - solubility limit at the wall temperature (vapor-solid equilibrium)

$C_{vsa}$ - saturation concentration for vapor phase at vapor-liquid equilibrium

$C_{bsat}$ - solubility limit at the bulk temperature (vapor-solid equilibrium)

**Table 7.2. Summary of HT region model**
turbulent mass transfer of molecules from the bulk to the wall. It was further assumed that there was no resistance to the molecule attachment to the surface. With these assumptions, the salt mass flux in the low temperature region $Q_{SLT}$ was then calculated as follows:

$$Q_{SLT} = Q_{sm} = h_m \rho \Delta C$$  \hspace{1cm} (7.1)

Where,

$Q_{sm}$ - salt mass flux due to the molecular mass transfer [kg/m$^2$-s]

$h_m$ - mass transfer coefficient [m/s]

$\rho$ - bulk density of the solution taken to be same at the wall [kg/m$^3$]

C-salt concentration [kg/kg]

The next step was to obtain the mass transfer coefficient $h_m$ and the mass transfer driving force $\Delta C$. It was assumed that the same processes affected heat and mass transfer and an analogy between heat and mass transfer was applied to obtain mass transfer coefficient. Since,

$$Nu = f(Re, Pr)$$ \hspace{1cm} (7.2)

$$Sh = f(Re, Sc)$$ \hspace{1cm} (7.3)

the form of Swenson et al. Nu number correlation (Appendix C, Eq. (C.7)) was utilized to obtain correlation for the Sherwood (Sh) number. The Swenson Nu correlation was rewritten by replacing Pr number with the Schmidt number (Sc) that was evaluated at the wall. The following expression was obtained for the Sh number:

$$Sh = \frac{h_m \cdot d}{D_w} = 0.00459 \cdot Re^{0.923} \cdot Sc_w^{0.613} \left( \frac{\rho_w}{\rho_s} \right)^{0.231}$$ \hspace{1cm} (7.4)

Where,

$D$ - diffusion coefficient [m$^2$/s]

W-stands for wall
and the Schmidt number is given as:

$$Sc_w = \frac{\mu_w}{\rho_w \cdot D_w}$$  \hspace{1cm} (7.5.)

To get relationship between heat transfer coefficient $h$ and mass transfer coefficient, the equation (7.4.) was divided by the equation (C.7.) (Appendix C) and the following expression obtained:

$$h_m = \frac{h}{\rho_w \cdot \bar{c}_p \cdot Le_w^{0.387}}$$  \hspace{1cm} (7.6.)

where,

$\bar{c}_p$ - average specific heat capacity given by (C.12.), Appendix C [kJ/kg-K]

The Lewis number was evaluated at the wall.

$$Le_w = \frac{k_w}{D_{mW} \cdot \rho_w \cdot c_{pw}}$$  \hspace{1cm} (7.7.)

To calculate $Le$ number, the diffusion coefficient of sodium chloride in supercritical water was needed. Experimental data for the diffusion coefficient of NaCl molecules in SCW were not available so the diffusion coefficient was estimated from the Einstein-Stokes relation (Shaw et al., 1991) as follows:

$$D_{mW} = \frac{K_b \cdot T_w}{3 \cdot \pi \cdot \mu_w \cdot d_m}$$  \hspace{1cm} (7.8)

where,
In order to calculate the diffusion coefficient, the effective hydrodynamic diameter $d_m$ was required. The radius of Cl$^-$ ($r_{Cl}$) at atmospheric conditions is $1.81 \text{ Å} \ [10^{-10} \text{ m}]$ and of Na$^+$ ($r_{Na}$) $0.97 \text{ Å}$ (Lide 1991). The bound sodium chloride has center to center ion pair separation ($r_{sep}$) of $2.293 \text{ Å}$. Whether ion pairing in SCW exists or not depends on the temperature and pressure. Cui and Harris (1994) investigated ion association and liquid structure in supercritical water solutions of sodium chloride at pressure of 25 MPa and temperatures ranging from 427-727 °C. They used molecular dynamics simulations of pure water and water with one or more ions. Their calculation of the potential of the mean force between sodium-chloride, sodium-sodium, and chloride-chloride ion pairs showed that sodium chloride stayed as the bound ion pair in supercritical water. Based on that conclusion, the hydrodynamic diameter $d_m$ used in this study was estimated as $5.1 \text{ Å}$.

$$d_m = r_{Cl} + r_{Na} + r_{sep} \quad (7.8.1)$$

Protopopov et al. (1994) investigated diffusion of iron-corrosion products in SCW and took into account a dramatic decrease of the diffusion coefficient around the pseudocritical temperature by incorporating a reduction factor $A_c$ in the diffusion coefficient calculation.

The reduction factor $A_c$ depended on the pressure and the temperature. The reduction factor of the diffusion coefficient $A_c$ at a pressure of 25 MPa proposed by Protopopov is given in the Table 7.3. as a function of the fluid density. Values in the Table 7.3. were obtained from the graph given in Protopopov et al.
Table 7.3. Correction of the diffusion coefficient of molecules in supercritical water at 25 MPa (Protopopov et al., 1994)

Table 7.3. illustrates that the most dramatic change of the diffusion coefficient happened around pseudocritical temperature. Given the fact that in this study the diffusion coefficient was estimated at the wall temperature which was much higher than the pseudocritical temperature, the reduction factor varied from 0.95 to 0.85 and did not have significant effect on diffusion coefficient calculation.

With the expressions (7.9), (7.8), (7.7) and (7.6.), the mass transfer coefficient could be calculated. The next step was to specify mass transfer driving force $\Delta C$. The driving force was defined as a difference between bulk and wall concentrations of the dissolved salt.

$$\Delta C = C_b - C_w$$

(7.10)

The concentration at the wall was equal to the initial concentration for the wall temperature that was lower than $T_{tp}$ and to the solubility limit for the wall temperature that was greater than $T_{tp}$.

$$C_w = C_0 \quad \text{for} \quad T_w < T_{tp}$$

(7.11.)

$$C_w = C_{\text{wsat}}(T_w) \quad \text{for} \quad T_w \geq T_{tp}$$

(7.12)

The fact that the dense liquid phase existed in the bulk fluid had to be taken into account when calculating concentration $C_b$. Based on the estimate of the $C_b$, the following models were developed.
Model 1 for the LT region

The Model 1 provided a salt thickness calculation for one extreme case, assuming that there was no liquid phase nucleation (equivalent to assuming the same mass transfer coefficient from both vapor and liquid phases). This assumption was very crude but helpful because it gave a very simple model and valuable results for comparison with experimental data. In this model the concentration of the salt in the bulk fluid $C_b$ would decrease along the length due to the turbulent mass transfer.

$$\frac{\partial C_b}{\partial z} = -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_b - C_{sat}(T_w)) \tag{7.13.}$$

The $C_b$ was found as an average bulk concentration along the length step $dz$.

$$C_b = \frac{(C_{b1} + C_{b2})}{2} \tag{7.14}$$

Where,

$C_{b1}$ - the bulk concentration at the beginning of the length step [kg/kg]

$C_{b2}$ - the bulk concentration at the end of the length step [kg/kg]

From equation 7.13, the following equation for calculation of the bulk concentration at the end of the length step was derived\(^1\):

$$C_{b2} = \frac{C_{b1} (\alpha - 1) + 2C_{\text{sat}}}{1 + \alpha} \tag{7.15}$$

Where,

\(^1\) Effectively, a semi-implicit numerical scheme is used to integrate the differential equation.
\[ \alpha = \frac{\dot{m}}{h_m \cdot \rho \cdot r \cdot \pi \cdot dz} \]  

(7.16)

**Model 2 for the LT region**

*Model 2* provided the lower bound on deposition. At the point where \( T_w = T_{tp} \), the liquid concentration was assumed frozen, so deposition would result only from mass transfer of salt from the vapor to the wall. The concentrations of the dissolved salt in the vapor phase at the beginning and at the end of the step were given as \( C_{vb1} \) and \( C_{vb2} \) respectively (Figure 7.2.). The concentrations of salt in the liquid phase at the beginning and at the end of the step were given as \( C_{lb1} = C_{lb2} \). The total bulk concentration was then:

\[ C_b = C_{eb} + C_{lb} \]  

(7.17)

The concentration \( C_{vb} \) was calculated as the average vapor concentration along the length step.

\[ C_{vb} = \frac{(C_{vb1} + C_{vb2})}{2} \]  

(7.18)

The concentrations of the vapor and liquid phases in the bulk were determined from the vapor-liquid equilibrium curve for the length steps before mass transfer calculation started. When the mass transfer calculation started, the concentration of the dissolved salt in the bulk fluid would change along the length step due to the turbulent mass transfer of molecules from the vapor phase only. For the vapor phase concentration \( C_{vb} \) that was lower than or equal to the concentration \( C_{vsat} (T_b) \), the concentration of the salt in the vapor phase was only affected by mass transfer from the vapor phase and there was no change in the concentration of the salt in the liquid phase along the length step\(^2\):

\(^2\) The program also had routines for \( C_{vb} > C_{vsat} \) that would constrain \( C_{vb} \rightarrow C_{vsat} \). In fact mass transfer from vapor to the wall was always huge enough so \( C_{vb} \leq C_{vsat} \).
\[
\frac{\partial C_{vb}}{\partial z} = -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot \left( C_{vb} - C_{sat}(T_w) \right)
\]

\[C_{vb} \leq C_{v\text{sat}}(T_b)\]

\[
\frac{\partial C_{lb}}{\partial z} = 0 \quad (C_{Lb1} = C_{Lb2})
\]

(7.20)

**Figure 7.2.** Sodium-chloride deposition along the length step of the LT region due to the mass transfer from the vapor phase only (no mass transfer from the liquid to the vapor)- Model 2

**Model 3 for the LT region**

Model 3 assumed mass transfer from the vapor phase followed by the fast mass transfer between liquid and vapor phases (vapor concentration at vapor-liquid
equilibrium). This model was similar to Model 2. The total salt concentration $C_b = C_{vb} + C_{Lb}$ decreased again due to the mass transfer from the vapor phase only.

$$\frac{\partial C_b}{\partial z} = \frac{\partial C_{vb}}{\partial z} + \frac{\partial C_{Lb}}{\partial z} = -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} (C_{vb} - C_{sat}(T_w)) \quad (7.21)$$

For the total salt concentration $C_b$ greater than or equal to the concentration of salt in vapor phase at vapor-liquid equilibrium $C_{sat}(T_b)$, the change of the concentration along the length step in the vapor and liquid phases is given as follows:

$$\begin{align*}
\frac{\partial C_{vb}}{\partial z} &= \frac{\partial C_{sat}}{\partial z} \cdot \frac{\partial T_b}{\partial z} \\
\frac{\partial C_{Lb}}{\partial z} &= -\frac{\partial C_{sat}}{\partial T_b} \cdot \frac{\partial T_b}{\partial z} - \frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} (C_{sat}(T_b) - C_{sat}(T_w)) \\
\end{align*} \quad (7.22)$$

For the total salt concentration in the bulk $C_b$ lower than the concentration of salt in vapor phase at vapor-liquid equilibrium $C_{sat}(T_b)$, the following applies:

$$\begin{align*}
\frac{\partial C_{vb}}{\partial z} &= -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} (C_{vb} - C_{sat}(T_w)) \\
\frac{\partial C_{Lb}}{\partial z} &= 0 \quad (C_{Lb} = 0) \\
\end{align*} \quad (7.23)$$
7.3.2. Mass transfer modeling in the HT region

The salt solution was in the vapor-solid region when $T_{tp}$ was exceeded suggesting that salt particles would be formed in the bulk if the bulk concentration was above saturation. Our experiments showed that a deposit peak in the high temperature region had been formed at the location where the $T_{tp}$ had been exceeded in the bulk fluid. Given the above observations, it was assumed that the mass transfer mode in the HT region was a combination of particle deposition and turbulent mass transfer of molecules. It was assumed that there was no surface resistance to the attachment of molecules and particles. A simple model called "complete" taking into account deposition of particles and molecular mass transfer that was written by Teshima (1997) was used to model deposition in the HT region.

The salt mass flux in the high temperature region was calculated as follows:

$$Q_{sHT} = Q_{sm} + Q_{sp} = h_m \rho \Delta C + V_p \rho \Delta C_p$$  \hspace{1cm} (7.24.)

Where,

$Q_{sm}$ - salt mass flux due to the molecular mass transfer [kg/s / m^2-s]
$Q_{sp}$ - salt mass flux due to the deposition of particles [kg/s / m^2-s]
$h_m$ - mass transfer coefficient for molecular mass transfer [m/s]
$V_p$ - particle deposition velocity [m/s]
$C$ - concentration of dissolved salt [kg_s / kg]
$C_p$ - concentration of particles [kg_s / kg]

The mass transfer coefficient was obtained as described in 7.3.1. To obtain the particle deposition velocity, the results of Papavergos and Hedley (1984) were used as suggested in Teshima's work (1997). Papavergos and Hedley studied deposition of particles from turbulent flows by reviewing previous experimental work on deposition of
aerosol droplets from air streams. Analyzing experimental results, they determined the following expressions for dimensionless particle deposition velocity $V_{d}^{+}$ depending on the value of dimensionless particle relaxation time $\tau_{p}^{+}$.

\[
V_{d}^{+} = \begin{cases} 
0.065(Sc)^{-2/3} & \tau_{p}^{+} < 0.2 \\
3.5 \times 10^{-4}(\tau_{p}^{+})^{2} & 0.2 \leq \tau_{p}^{+} \leq 20 \\
0.13 & \tau_{p}^{+} > 20
\end{cases}
\]  \quad (7.25)

Where,

\[
\tau_{p}^{+} = \frac{\tau_{p}(u^{+})^{2}\rho}{\mu}
\]  \quad (7.26)

Where $\tau_{p}$ [s] was the particle relaxation time and $u^{+}$ was the wall friction velocity of the fluid [m/s]. The particle relaxation time was calculated as:

\[
\tau_{p} = \frac{\rho_{s} \cdot d_{p}^{2}}{18 \cdot \mu}
\]  \quad (7.27)

Where,

$\rho_{s}$ - salt density [kg/m$^3$]

$d_{p}$ - the diameter of the salt particle [m]
Armellini et al. (1994) in their study of sodium chloride precipitation concluded that liquid droplets formed in the vapor-liquid region were precursors for solid particles formation. Armellini et al. found that the size of particles nucleated from 0.5 wt % jet ranged from 5 to 25 μm. The larger particles appeared to be formed by agglomeration. In our model it was assumed that all particles had same diameter of 5 μm and that they grew to that size instantaneously. This was very crude assumption but it was decided to start with the simplest possible model due to the complexity of the topic.

The wall friction velocity $u^*$ of the fluid was determined from the following expression:

$$ u^* = \left( \frac{\tau_w}{\rho} \right)^{0.5} \quad (7.28.) $$

Where $\tau_w$ was the wall shear stress $[N/m^2]$:

$$ \tau_w = \frac{\rho \cdot u^2 \cdot f}{8} \quad (7.29.) $$

Where,

- $u$- bulk stream fluid velocity
- $f$- friction factor calculated from Haaland 1983 (Appendix C, Exp. C.14)

Once the dimensionless particle deposition velocity $V_d^+$ and the wall friction velocity $u^*$ were determined, the particle deposition velocity was calculated as follows:

$$ V_p = V_d^+ \cdot u^* \quad (7.30.) $$
When the mass transfer coefficient for the molecular mass transfer and particle deposition velocity were found, the next step was to determine driving forces $\Delta C$ and $\Delta C_p$. The driving force $\Delta C$ was again defined as the difference between the concentration of the dissolved salt in the bulk and the concentration of the dissolved salt at the wall. The driving force $\Delta C_p$ was defined as the difference between the concentration of the particles in the bulk and the concentration of the particles at the wall.

\[
\Delta C = C_{vb} - C_w \quad (7.31)
\]

\[
\Delta C_p = C_{pb} - C_{pw} \quad (7.32)
\]

The initial concentration $C_{0HT}$ of the salt solution for the HT region was equal to the concentration of the salt solution at the outlet of the LT region. Since there were three models developed in the low temperature region, there were also three initial concentrations $C_{0HT}$ for the HT region. If this initial concentration was higher than the solubility limit for the bulk temperature, it was assumed that solid particles were formed in the bulk. It was also assumed that there was no mass transfer from the particles to the vapor phase. The concentration of the dissolved salt at the wall $C_w$ was set to the saturation concentration for the wall temperature $C_{wsat}$. The concentration of particles at the wall was assumed to be zero.

\[
C_w = C_{sat} (T_w) \quad (7.33)
\]

\[
C_{pw} = 0 \quad (7.34)
\]

The concentration of the dissolved salt in the bulk at the beginning of the length step was given as $C_{vb1}$ and at the end of the length step as $C_{vb2}$ (Figure 7.3). The concentration of the particles in the bulk at the beginning of the length step was $C_{pb1}$ and at the end of the length step $C_{pb2}$. 
The change of the total concentration of salt along the length step was affected by mass transfer from vapor phase and the particle deposition:

\[
\frac{\partial C_v}{\partial z} = \frac{\partial C_{vb}}{\partial z} + \frac{\partial C_{pb}}{\partial z} = -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w)) - \frac{V_p \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} (C_{pb} - 0) \quad (7.35)
\]

Figure 7.3. Sodium-chloride deposition along the length step of the HT region due to the molecular mass transfer and particle deposition.

For concentrations of salt in the vapor phase lower than or equal to the saturation concentration at the bulk temperature, the concentration of the salt in the vapor phase changed due to molecular mass transfer and the concentration of particles was affected by particle deposition\(^3\).

---

\(^3\) The program also had routines for \(C_{vb} > C_{sat}\) that would constrain \(C_{vb} \rightarrow C_{sat}\). In fact mass transfer from vapor to the wall was always huge enough so \(C_{vb} < C_{sat}\).
\[
\frac{\partial C_{vb}}{\partial z} = -\frac{h_m \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} \cdot (C_{vb} - C_{sat}(T_w)) \\
\frac{\partial C_{pb}}{\partial z} = -\frac{V_p \cdot \rho \cdot 2 \cdot \pi \cdot r}{m} (C_{pb} - 0)
\] (7.37)

### 7.3.3. Salt thickness calculation

When the salt mass flux \(Q_y\) was calculated for the step \(dz\), the salt thickness was obtained with the known time of deposition, salt density and porosity of the salt layer.

\[
S_t = \frac{Q_s \cdot dt}{\rho_s \cdot (1 - \phi)}
\] (7.38)

Where,

- \(Q_s\) - salt mass flux (Eq. 7.1. for LT, Eq. 7.22 for HT)
- \(S_t\) - salt thickness [m]
- \(dt\) - time of deposition [s]
- \(\rho_s\) - salt density [kg s/m³]
- \(\phi\) - porosity (0.1 for LT region, 0.6 for HT region, except in the experiments 3, 5, and 12 where porosities tabulated in the Table 6.3 were used)
7.4. Comparison of the experimental salt thickness profiles to the modeled salt thickness profiles for the LTE

Models 1, 2, and 3 were run for times yielding a total salt flux of 10 g through the test section. The results for LTE are summarized in Appendix E and an illustration of the results is given in Figure 7.4. for a low concentration experiment and in Figure 7.5. for a high concentration experiment.

Figure 7.4. Comparison between experimental and modeled salt thickness profiles for a low concentration LTE.
The comparison was performed for all the LTE by looking at the shape of the deposit, and the location and height of the deposit peaks. The shape of the deposit was triangular for the experimental profiles, Model 1 and Model 2 predictions for all the LTE. Model 3 produced a trapezoidal shaped deposit.

The location of the peak was predicted sooner in all models. For the low concentration LTE, Model 1 over predicted the peak heights whereas Models 2 and 3 under predicted the peak heights with Model 3 giving better results. For the high

---

1If thermocouple error is taken into account, the location is shifted by 0.1 m typically.
concentration experiment 7 Model 1 gave close prediction whereas Models 2 and 3 calculated almost no deposit.

<table>
<thead>
<tr>
<th>LTE #</th>
<th>C₀ [wt %]</th>
<th>Zₚₑ [m]</th>
<th>Zₚₑ₁-Zₚₑ [m]</th>
<th>Zₚₑ₂-Zₚₑ [m]</th>
<th>Yₚₑ [mm]</th>
<th>Yₚₑ₁/Yₚₑ [mm]</th>
<th>Yₚₑ₂/Yₚₑ [mm]</th>
<th>Yₚₑ₃/Yₚₑ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.106</td>
<td>2.44</td>
<td>-0.12</td>
<td>-0.26</td>
<td>-0.25</td>
<td>0.32</td>
<td>2.88</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td>0.103</td>
<td>2.44</td>
<td>-0.1</td>
<td>-0.21</td>
<td>-0.19</td>
<td>0.49</td>
<td>1.82</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>2.3</td>
<td>-0.12</td>
<td>-0.2</td>
<td>-0.2</td>
<td>0.28</td>
<td>2.57</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>0.912</td>
<td>2.71</td>
<td>-0.29</td>
<td>-0.48</td>
<td>-0.48</td>
<td>0.95</td>
<td>1.11</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>2.49</td>
<td>-0.24</td>
<td>-0.37</td>
<td>-0.32</td>
<td>0.33</td>
<td>2.36</td>
<td>1.12</td>
</tr>
<tr>
<td>10</td>
<td>0.102</td>
<td>2.55</td>
<td>-0.28</td>
<td>-0.42</td>
<td>-0.4</td>
<td>0.57</td>
<td>1.32</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*Table 7.4. Location Zₚₑ and height Yₚₑ of the peaks in LT region of the LTE obtained from the experiments and from the Model 1 and Model 2.*

The concentration of the solution at the outlet of the test section Cₜₒᵤₜₑ that was measured in the LTE was found to be higher than the concentration of the salt in the vapor phase at the three phase equilibrium temperature Cᵥₚₑₜ (Tₚₑ). This concentration was compared to the outlet concentrations obtained from Model 1, Model 2, and Model 3 and the comparison is summarized in Table 7.5.

<table>
<thead>
<tr>
<th>LTE #</th>
<th>C₀</th>
<th>Cₜₒᵤₜₑ</th>
<th>Cₜₒᵤₜₑ₁</th>
<th>Cₜₒᵤₜₑ₂</th>
<th>Cₜₒᵤₜₑ₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1060</td>
<td>385</td>
<td>196</td>
<td>811</td>
<td>269</td>
</tr>
<tr>
<td>4</td>
<td>1030</td>
<td>433</td>
<td>228</td>
<td>759</td>
<td>251</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>403</td>
<td>220</td>
<td>703</td>
<td>231</td>
</tr>
<tr>
<td>7</td>
<td>9120</td>
<td>487</td>
<td>571</td>
<td>8768</td>
<td>8255</td>
</tr>
<tr>
<td>9</td>
<td>1000</td>
<td>N.M.</td>
<td>194</td>
<td>680</td>
<td>220</td>
</tr>
<tr>
<td>10</td>
<td>1020</td>
<td>N.M.</td>
<td>199</td>
<td>708</td>
<td>228</td>
</tr>
</tbody>
</table>

*Table 7.5. Concentrations at the outlet of the LT region of the LTE obtained experimentally (Cₜₒᵤₜₑ) and from Model 1 (Cₜₒᵤₜₑ₁), Model 2 (Cₜₒᵤₜₑ₂), and Model 3 (Cₜₒᵤₜₑ₃).*
This comparison showed that *Models 1* and 3 consistently calculated lower outlet concentrations than the measured ones for the low concentration experiments (over predicted mass transfer). The outlet concentrations calculated with *Models 1* and 3 were lower than the vapor concentration at $T_p$. That meant that the solution at the outlet temperature (which was slightly below $T_p$) was in the vapor phase only and that if the temperature was increased further, the salt would nucleate directly from the vapor phase. On the other hand, *Model 2* calculated higher outlet concentrations than the measured ones which showed the presence of the liquid phase at the outlet of the test section. In the high concentration experiment 7, *Model 1* calculated an outlet concentration that was slightly above the measured concentration. *Models 2 and 3* gave very high outlet concentrations which indicated almost no mass transfer. This concentration was above the vapor concentration at the three phase equilibrium temperature which suggested liquid phase existence.

The comparison of modeled to experimental results showed that Models 2 and 3 worked well for low concentration experiments and Model 1 gave good prediction for the high concentration experiment. That indicated that the mass transfer from the liquid phase to the wall had to be taken into account for the high concentration experiments.

### 7.5. Comparison of the experimental salt thickness profiles to the modeled salt thickness profiles for the HTE

The results for the *HTE* are summarized in Appendix E and an illustration of the results is given in Figure 7.6. for a low concentration HTE and in Figure 7.7. for a high concentration HTE.
The low temperature region of the HTE was analyzed first because the outlet concentration of the LT region affected the deposition in the HT region. The locations and the heights of the deposit peaks for the LT region of the HTE are summarized in Table 7.6.
Figure 7.6. Comparison between experimental and modeled salt thickness profiles for a high concentration HTE.

As in LTE modeling, Model 1 over predicted the heights of the LT deposit peaks and Models 2 and 3 under predicted the heights of the LT deposit peaks (except in the exp. 11 and 12 Table 7.5). The concentration at the end of the LT region of HTE was not measured. For the low concentration HTE, the calculated concentrations at the end of LT region from Model 1 and Model 3 were below vapor saturation concentration at the three phase equilibrium temperature. This concentration at the end of the LT region was the

---

1 Model 1 produced a saw-tooth profile because of the large time step.
initial concentration for the HT region. So, for Models 1 and 3 there were no particles forming because the bulk concentration stayed below the solubility limit and the deposition mechanism in the HT region was just molecular mass transfer. The exception was high temperature experiment 8 for which Model 3 predicted much higher concentration at the end of the LT region.

<table>
<thead>
<tr>
<th>HTE #</th>
<th>C_{0\text{HTE}} [wt %]</th>
<th>Z_{pe} [m]</th>
<th>Z_{p1-Z_{pe}} [m]</th>
<th>Z_{p2-Z_{pe}} [m]</th>
<th>Z_{p3-Z_{pe}} [m]</th>
<th>Y_{pe} [mm]</th>
<th>Y_{p1/Y_{pe}} [mm]</th>
<th>Y_{p2/Y_{pe}} [mm]</th>
<th>Y_{p3/Y_{pe}} [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.106</td>
<td>1.32</td>
<td>-0.2</td>
<td>-0.29</td>
<td>-0.26</td>
<td>0.46</td>
<td>1.59</td>
<td>0.63</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>0.062</td>
<td>0.57</td>
<td>-0.38</td>
<td>-0.51</td>
<td>-0.38</td>
<td>0.54</td>
<td>1.72</td>
<td>0.59</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>0.065</td>
<td>0.8</td>
<td>-0.36</td>
<td>-0.5</td>
<td>-0.37</td>
<td>0.72</td>
<td>1.57</td>
<td>0.59</td>
<td>1.13</td>
</tr>
<tr>
<td>8</td>
<td>0.461</td>
<td>1.58</td>
<td>-0.37</td>
<td>-0.5</td>
<td>-0.54</td>
<td>0.46</td>
<td>1.3</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>11</td>
<td>0.102</td>
<td>0.85</td>
<td>-0.16</td>
<td>-0.32</td>
<td>-0.25</td>
<td>0.32</td>
<td>2.56</td>
<td>0.91</td>
<td>1.2</td>
</tr>
<tr>
<td>12</td>
<td>0.102</td>
<td>1.41</td>
<td>-0.09</td>
<td>-0.1</td>
<td>0</td>
<td>0.18</td>
<td>9.1</td>
<td>4.05</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 7.6. Location Zp and height Yp of the peaks in LT region of the HTE obtained from the experiments and from the Model 1, Model 2 and Model 3

The calculated concentrations at the end of the LT region from Model 2 for all HTE and Model 3 for high concentration experiment 8 were higher than the vapor saturation concentration at Ttp (as it was calculated in the LT region of LTE). This indicated that liquid phase existed at the beginning of the HT region and that solid particles were formed when Ttp was exceeded in the bulk.

The locations and the heights of the HT peaks are given in the Table 7.7. Models 1, 2 and 3 calculated consistent locations. They predicted locations of the peaks sooner than it was experimentally determined. Model 1 and Model 3 under predicted the heights of the peaks and Model 2 over predicted the heights of the peaks in the HT region.
### Table 7.7. Location $Z_p$ and height $Y_p$ of the peaks in HT region of the HTE obtained from the experiments and from the Model 1, Model 2 and Model 3

<table>
<thead>
<tr>
<th>HTE #</th>
<th>$Z_{pe}$ [m]</th>
<th>$Z_{p1} - Z_{pe}$ [m]</th>
<th>$Z_{p2} - Z_{pe}$ [m]</th>
<th>$Z_{p3} - Z_{pe}$ [m]</th>
<th>$Y_{pe}$ [mm]</th>
<th>$Y_{p1}/Y_{pe}$ [mm]</th>
<th>$Y_{p2}/Y_{pe}$ [mm]</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.1</td>
<td>-0.11</td>
<td>-0.12</td>
<td>-0.11</td>
<td>0.55</td>
<td>0.07</td>
<td>3.02</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>1.32</td>
<td>-0.36</td>
<td>-0.37</td>
<td>-0.36</td>
<td>0.24</td>
<td>0.25</td>
<td>Plugged</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>1.58</td>
<td>-0.44</td>
<td>-0.47</td>
<td>-0.45</td>
<td>0.17</td>
<td>0.29</td>
<td>Plugged</td>
<td>0.29</td>
</tr>
<tr>
<td>8</td>
<td>No peak</td>
<td>$Z_{p1} = 2.08$</td>
<td>$Z_{p2} = 2.07$</td>
<td>$Z_{p3} = 2.1$</td>
<td>No peak</td>
<td>$Y_{p1} = 0.02$</td>
<td>Plugged</td>
<td>Plugged</td>
</tr>
<tr>
<td>11</td>
<td>1.41</td>
<td>-0.13</td>
<td>-0.14</td>
<td>-0.14</td>
<td>0.31</td>
<td>0.16</td>
<td>6.7</td>
<td>0.35</td>
</tr>
<tr>
<td>12</td>
<td>2.28</td>
<td>No peak</td>
<td>-0.14</td>
<td>No peak</td>
<td>0.59</td>
<td>No peak</td>
<td>1.83</td>
<td>No peak</td>
</tr>
</tbody>
</table>

### Table 7.8. Concentrations at the outlet of HT region of the HTE obtained experimentally and from Model 1 ($C_{out1}$), Model 2 ($C_{out2}$) and Model 3 ($C_{out3}$)

<table>
<thead>
<tr>
<th>HTE #</th>
<th>$C_{out}$</th>
<th>$C_{out1}$</th>
<th>$C_{out2}$</th>
<th>$C_{out3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>157</td>
<td>131</td>
<td>136</td>
<td>131</td>
</tr>
<tr>
<td>3</td>
<td>217</td>
<td>140</td>
<td>193</td>
<td>140</td>
</tr>
<tr>
<td>5</td>
<td>215</td>
<td>164</td>
<td>215</td>
<td>164</td>
</tr>
<tr>
<td>8</td>
<td>N.M.</td>
<td>122</td>
<td>165</td>
<td>3780</td>
</tr>
<tr>
<td>11</td>
<td>104</td>
<td>98</td>
<td>99</td>
<td>97</td>
</tr>
<tr>
<td>12</td>
<td>108</td>
<td>95</td>
<td>96</td>
<td>96</td>
</tr>
</tbody>
</table>

The measured and the calculated concentrations of the solution at the end of the test section are listed in the Table 7.8. The measured and the calculated concentrations were pretty close to each other and close to the solubility limit at the bulk outlet temperature.
The above results showed again how important the $LT$ deposition was for the $HT$ region modeling. It was shown that deposition of particles was happening in the $HT$ region of the low concentration experiments. To show the importance of the concentration at the end of the $LT$ region on the $HT$ model results, the concentration measured at the end of the $LT$ region in the $LTE$ was used as the initial concentration for the $HT$ region. The results are plotted for experiment 2 in Figure 7.7.

![Figure 7.7](image)

**Figure 7.7.** Modeled $HT$ region with different initial concentrations obtained from $LT$ region $C_{LTout}$ (e-experimental, 1-Model 1, 2-Model 2) compared to the experiment
Figure 7.7 showed that with the adequate initial concentration for the HT region, the HT region model (taking into account particle deposition and molecular mass transfer) calculated peak thickness close to the experimentally obtained one.

The above comparison showed that Models 1 and 3 were too extreme in calculating mass transfer from the liquid phase in the LT region (Model 1: liquid phase to wall, Model 2: liquid phase to vapor phase to wall) of low concentration HTE. Model 2, on the other hand underestimated the participation of the liquid phase in mass transfer and predicted a too high inlet concentration for the HT region deposition. For the high concentration HTE, Model 1 again produced best agreement.
8. CONCLUSIONS

This study of sodium chloride deposition from SCW turbulent flow in a horizontal electrically heated tube led to the following conclusions:

1) The solubility of sodium chloride in supercritical water was measured on UBC/NORAM SCWO plant at constant pressures of 24.1, 24.45 and 25.67 MPa with temperatures ranging from 461 to 559.5 °C. The solubility decreased with temperature increase and increased with pressure. No hydrolysis was observed. The simple semi-empirical solubility model developed by Martynova (1964), Styrikovich (1969), Galobardes et al. (1981) and Armellini (1993) that assumes that equilibrium between solid and vapor exists as a solvation type reaction agreed with our data and was used in our deposition modeling.

2) Deposition experiments were performed with various temperatures, pressures, flow rates, heat fluxes and times of deposition. The first group of experiments was Low Temperature Experiments (LTE) for which the temperature in the bulk fluid was below the three phase equilibrium temperature $T_{tp}$ (vapor-liquid region) and the wall temperature was above $T_{tp}$. These LTE examined the effect of the vapor-liquid region on deposition. The second group was the High Temperature Experiments (HTE) for which the bulk fluid was in both the vapor-liquid region (Low Temperature Region) and the vapor-solid region (High Temperature Region). The HTE reinforced findings of the LTE in the vapor-liquid region and examined deposition in the vapor-solid region. Deposition experiments involved fouling of the horizontal, electrically heated tube for a period of time and recording the consequent tube outer surface temperature change. The analysis of the measured temperature profiles showed that heat transfer coefficient increased by 1-6 kW/m²-K (20 -75 %) when the salt solution was introduced to the test section. There were two distinct regions of heat transfer inferred that corresponded to vapor-liquid and vapor-solid regions. The deposition rates did not change with time.
3). The salt thickness profiles were inferred from the outer surface temperature measurements. Buoyancy was not taken into account in this calculation. To obtain salt thickness profiles, the porosity of the salt layer was needed. The porosity was calculated from the outer surface temperatures and the mass of deposited salt at different deposition times. It was found that the average porosity of the salt layer in the LT region was 0.1 and in the HT region 0.6 (possible uncertainty ±50%). The calculated salt thickness profiles revealed that the first deposit peak was located in the LT region where $T_{tp}$ was reached at the fluid-salt interface. The second deposit peak was located in the HT region where $T_{tp}$ was reached in the bulk. For the high concentration HTE, only one peak located in the LT region was observed. The change of the growth rate of the peak with time showed that the deposit was more unstable in the LT region than in the HT region. There was no obvious effect of flow rate and heat flux on the heights of the deposit peaks.

4). The comparison of the model results to the salt thickness profiles in the LT region showed that the LT region deposition was affected by molecular mass transfer from the bulk to the wall and by mass transfer from the liquid phase. Direct participation of the liquid phase in the mass transfer to the wall was pronounced for high concentration solutions. The deposition in high temperature region was affected by particle deposition and molecular mass transfer and depended on the deposition in the LT region (on the amount of liquid phase carried from the low temperature to the high temperature region).
9. RECOMMENDATIONS

It would be interesting to perform experiments that would simulate conditions needed for sodium chloride removal in preheaters prior to the reactor. In the present study, the salt deposit in the low temperature region (bulk below $T_{tp}$, wall above $T_{tp}$) was formed over a relatively short length of the tube. It would be helpful to perform an experiment where the wall temperature gradient is rather small, bulk temperature is below $T_{tp}$ and the deposit is formed in Preheater 2, over the whole length of the test section and if needed in the Reactor. To make this possible, Preheater 2 should be equipped with surface temperature measurements to monitor unavoidable deposition. Also, the sample port before the test section should be rotated for 180° (facing upwards) to provide better measurements of the test section inlet concentration. I speculate that the length of time before tube plugging would be increased significantly by doing so. However, I am not certain to what extent the salt will be removed when entering the reactor.

The uncertainties related to the porosity calculation and change with time, buoyancy, as well as mass balance inaccuracies affect the results of the indirect method of the salt layer thickness measurement that was used in this study. The best way to obtain the salt layer thickness is to directly measure its location and thickness and the amount of salt deposited in the tube. In that way, the exact porosity of the salt layer could be obtained and compared to the results of the present work. If the results are verified, the uncertainties can be eliminated and the indirect method used with more confidence. The problem in direct measurement method is how to prevent salt from going back into solution during the cool-down. For direct measurements, preservation of the salt deposit in the tube is essential and for that purpose nitrogen purging was used in previous studies. Since our system has the means to introduce nitrogen into the test section, it is just the matter of the designing a direct measurement experiment. Nitrogen can be introduced into the system through the port constructed for oxygen experiments that is located in front of the heaters. To prevent re-dissolving of the salt deposit till nitrogen reaches the test section, the salt solution should be first switched to the distilled water and when salt
solution exits the system the heat flux to the test section should be increased (if we keep the same heat flux when we introduce nitrogen, the temperature in the test section can go down due to the different properties of nitrogen-water mixture). After that, nitrogen can be slowly introduced to the system with the slow closing of the valve for the water supply. One suggestion is to use tube insert in the test section that can be easily removed and cut after experiment is over. Another solution would be to use a medical probe that is used for measurements of the thickness of the arterial walls. After the location and thickness of the salt layer are determined, water purging of the segments of the test section could be used to measure the mass of deposited salt.

The indirect method of the NaCl thickness measurement could be also improved by taking into account possible porous structure of the HT deposit when modeling the conductivity of the salt layer in the high temperature region.

Since liquid droplets play a significant role in deposition in the low temperature region and affect deposition in the high temperature region, it would be useful to measure their concentration with the optical test cell (if possible) that was built at UBC. The concentration of the solid particles could be measured as well. In that way, the present deposition models can be improved.

The information on the actual concentration of sodium chloride in wastes that can be processed by SCWO as well as on concentrations of other salts would be very useful to have.

Since the investigation of the fouling from a binary salt-water system is the simplest step in the deposition study, the natural continuation of the work would be to examine deposition from more complex ternary sodium chloride-sodium sulfate-water system or sodium chloride-water-oxygen system.
10. REFERENCES


Armellini, F. J., Tester, J. W., and Hong, G. T.; "Precipitation of sodium chloride and sodium sulfate in water from sub- to supercritical conditions: 150 to 550°C, 100 to 300 bar", J. of Supercritical Fluids, 7, 147 (1994).


Clifford T. and Bartle K., “Chemical reactions in supercritical fluids”, Chem. and Ind., 17, 449 (June 1996)


Appendix A

Thermocouple Positions on the Heated Part of the Test Section

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>Location [m]</th>
<th>Thermocouple</th>
<th>Location [m]</th>
<th>Thermocouple</th>
<th>Location [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>0</td>
<td>S6</td>
<td>0.722</td>
<td>S12*</td>
<td>1.738</td>
</tr>
<tr>
<td>S1</td>
<td>0.073</td>
<td>SB6</td>
<td>0.797</td>
<td>S13*</td>
<td>1.922</td>
</tr>
<tr>
<td>SB1</td>
<td>0.145</td>
<td>S7</td>
<td>0.86</td>
<td>S14*</td>
<td>2.097</td>
</tr>
<tr>
<td>S2</td>
<td>0.218</td>
<td>SB7</td>
<td>0.953</td>
<td>S15*</td>
<td>2.216</td>
</tr>
<tr>
<td>SB2</td>
<td>0.296</td>
<td>S8</td>
<td>1.03</td>
<td>S16*</td>
<td>2.3</td>
</tr>
<tr>
<td>S3</td>
<td>0.359</td>
<td>SB8</td>
<td>1.131</td>
<td>S17*</td>
<td>2.437</td>
</tr>
<tr>
<td>SB3</td>
<td>0.442</td>
<td>S9</td>
<td>1.223</td>
<td>S18*</td>
<td>2.572</td>
</tr>
<tr>
<td>S4</td>
<td>0.505</td>
<td>SB9</td>
<td>1.323</td>
<td>S19*</td>
<td>2.714</td>
</tr>
<tr>
<td>SB4</td>
<td>0.571</td>
<td>S10</td>
<td>1.412</td>
<td>S20</td>
<td>2.874</td>
</tr>
<tr>
<td>S5</td>
<td>0.636</td>
<td>B3</td>
<td>1.473</td>
<td>B4</td>
<td>2.946</td>
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<tr>
<td>SB5</td>
<td>0.666</td>
<td>S11*</td>
<td>1.575</td>
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<td></td>
</tr>
</tbody>
</table>

*Table A1: Thermocouples positions on the heated part of the test section*
Appendix B

Calibration Charts and Tabulated Data
B.1. Pressure Calibration

*Differential Pressure Transducer*

Calibration charts for DP427- and DP 429- can be found in Teshima (1997).

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Pressure kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0069</td>
<td>500</td>
</tr>
<tr>
<td>1.8056</td>
<td>450</td>
</tr>
<tr>
<td>1.6021</td>
<td>400</td>
</tr>
<tr>
<td>1.4024</td>
<td>350</td>
</tr>
<tr>
<td>1.202</td>
<td>300</td>
</tr>
<tr>
<td>1.003</td>
<td>250</td>
</tr>
<tr>
<td>0.8003</td>
<td>200</td>
</tr>
<tr>
<td>0.59</td>
<td>150</td>
</tr>
<tr>
<td>0.39</td>
<td>100</td>
</tr>
<tr>
<td>0.19</td>
<td>50</td>
</tr>
<tr>
<td>0.09</td>
<td>25</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Table B.1:* Calibration data for differential pressure transducer DPT 429-5-56

*Figure B.1.* Calibration data and data fit for DPT 429-5-56
Absolute Pressure Transducer

<table>
<thead>
<tr>
<th>Measured voltage V</th>
<th>Measured pressure psi</th>
<th>Measured pressure MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.261</td>
<td>494</td>
<td>3.406031</td>
</tr>
<tr>
<td>2.254</td>
<td>994</td>
<td>6.853431</td>
</tr>
<tr>
<td>3.253</td>
<td>1494</td>
<td>10.30083</td>
</tr>
<tr>
<td>4.25</td>
<td>1994</td>
<td>13.74823</td>
</tr>
<tr>
<td>5.24</td>
<td>2494</td>
<td>17.19563</td>
</tr>
<tr>
<td>6.24</td>
<td>2994</td>
<td>20.64303</td>
</tr>
<tr>
<td>7.22</td>
<td>3494</td>
<td>24.09043</td>
</tr>
</tbody>
</table>

Table B.2: Calibration data for absolute pressure transducer APT

![Figure B.2: Calibration of the absolute pressure transducer](image)
B.2. Heat Flux Calibration

The heat flux supplied to the fluid Q can be calculated from the known power supplied to the test section Qt and heat loss Qloss on one hand and from energy balance on the other hand. To calculate the power supplied to the test section, RMS voltage across the test section Vrms and resistance of the tube are needed. AC voltage on our test section is not perfect sinusoidal signal (except for the maximum power supplied from the SCR panel) and hence RMS voltage (Vrms) could not be measured directly throughout our experiments. The only measurement available to us is measurement of RMS voltage prior to secondary transformers that is displayed on SCR panel (Vscr), (Chapter 3). To correlate the available SCR voltage reading to the power that is actually supplied to the test section, the RMS voltage and current supplied to the first segment of the test section were measured as described in the SCWO manual. It was found that the secondary transformer ratio Vscr/Vrms was close to 11 instead of 10 as specified by manufacturer. From the measured RMS voltage and current, the power supplied to the test section was calculated and plotted over SCR reading (Figure B.3.). The heat flux supplied to the fluid Q was calculated from the bulk enthalpies as described in the Appendix C, section C.2. and also plotted over SCR reading (Figure B.3). The expression obtained from the data fit that correlated the total power generated in the test section Qt to the SCR reading is given as follows:

\[ Qt = 0.00010683794 \times (V_{scr})^2 - 0.0108 \times V_{scr} + 0.57175 \]  \hspace{1cm} (B.1)

The expression correlating heat flux supplied to the fluid to SCR voltage was derived as follows:

\[ Q_{data\ fit} = 0.00010683794 \times (V_{scr})^2 - 0.01355 \times V_{scr} + 0.57175 \] \hspace{1cm} (B.2)

The heat loss from the test section was then expressed as:

\[ Q_{loss} = Qt - Q_f = 0.00275 \times V_{scr} \] \hspace{1cm} (B.3)
The heat loss is a function of the surface temperature and the temperature of the surrounding air and it was not reliable to use the expression B.3. for heat loss calculation. To find heat flux that was supplied to the fluid, bulk enthalpies were used as described in the section C.2.

**Figure B.3. Heat flux calibration for the test section**
Appendix C
Heat Transfer Calculations

C.0. Heat transfer model

The heat transfer model provided bulk temperature, inner wall and outer wall temperature profiles along the horizontal, electrically heated test section (constant heat flux) for turbulent, fully developed flow of sodium chloride-water solution. The model included obtaining thermodynamic and transport properties of the fluid, an energy balance for bulk temperature calculation, calculation of heat transfer coefficient to obtain inner surface temperatures, and radial conduction through the tube wall to obtain outer surface temperatures. The buoyancy effects were neglected as discussed in the Appendix C.2.

C.1. Transport and thermodynamic properties

The transport and thermodynamic properties of salt solution were taken as properties of pure water because of the low concentration of salt that was used in this study.

To determine thermodynamic properties (specific enthalpy $H$, specific heat capacity $c_p$, etc.) the program IAPWS957.F (1995, Wagner) for pure water was used. In this program, it was necessary to specify either (T, p) or (T, $\rho$) point in order to obtain other thermodynamic properties. The transport properties (viscosity $\mu$ and thermal conductivity $k$) were calculated in the program TRSPTSUB.F. For the calculation of viscosity recommended interpolating equation issued in IAPS (1985) was used. For the calculation of conductivity recommended interpolating equation for scientific use (IAPS, 1985) was used.
C.2. Bulk temperature calculation

To obtain bulk temperature profile, it was necessary to first calculate heat flux per meter length of the tube \( q_L \) that was supplied to the fluid. The heat flux was calculated from the energy balance by first finding enthalpies at the inlet and the outlet of the test section from the program IAPWS957.F. The measured inlet and outlet bulk temperatures and pressure were used as inputs. With the known specific enthalpies \( H \) [kJ/kg], mass flow rate \( \dot{m} \) [kg/s] and the length of the tube \( L \) [m], the heat flux \( q_L \) [kW/m] was calculated as follows:

\[
q_L = \frac{\dot{m} \cdot (H_{out} - H_{in})}{L} \quad (C.1.)
\]

Once the heat flux was known, the next step was to calculate bulk temperatures along the tube at locations \( z_j \). In this calculation, the step size was determined as:

\[
\Delta z = z_j - z_{j-1} \quad (C.2.)
\]

With the known specific enthalpy at \( z_{j-1} \), the heat flux, the mass flow rate and the step size, the enthalpy at \( z_j \) was calculated as:

\[
H_j = H_{j-1} + \frac{q_L \cdot \Delta z}{\dot{m}} \quad (C.3.)
\]

With this enthalpy, bulk temperature \( T_{bj} \) was obtained from the IAPWS957.F program. With the known bulk temperature \( T_b \) [K] and pressure \( p \) [MPa] at \( z_j \), viscosity \( \mu_j \) [kg / m-s] and thermal conductivity \( k_j \) [kW/m-K] were obtained from TRSPTSUB.F, specific heat capacity \( c_p \) [kJ/kg-K] was found from IAPWS957.F, and the Reynolds \( Re \) and the Prandtl \( Pr \) numbers were calculated as follows:
\[ Re_j = \frac{4 \cdot \dot{m}}{d \cdot \pi \cdot \mu_{by}} \] (C.4.)

\[ Pr_j = \frac{c_{phy} \cdot \mu_{by}}{k_{by}} \] (C.5.)

where subscript \( b \) refers to bulk properties.

C.3. The inner surface temperature calculation (\( T_{w0} \))

Once the bulk temperature \( T_b \) was calculated at the location \( z_j \), the next step was to determine inner surface temperature \( T_{w0} \). For this calculation, the heat transfer coefficient was needed. To obtain the heat transfer coefficient, an appropriate Nusselt number \( (Nu) \) correlation had to be used. It was important to use a \( Nu \) number correlation that would take into account dramatic properties variation from the bulk to the wall that was occurring around pseudo critical point. The classic \( Nu \) number correlations were not suitable because they did not take into account variation of the properties. The classic correlations had following form:

\[ Nu = a \cdot (Re)^b \cdot (Pr)^c \] (C.6)

where \( Re \) and \( Pr \) numbers were evaluated with bulk properties.

There were several \( Nu \) number correlations that were tested by UBC/SCWO heat-transfer research group: Gnielinsky (1976), Shitsman-Miropolskii (1957), Jackson-Fewster (Ghajar and Asadi 1986), Yamagata et al. (1971), Swenson et al. (1965), and Petukhov et al (1962). All these correlations (except Gnielinsky, and Shitsman-Mirapolskii) took into account pseudo-critical region by adding extra terms to the classic correlation. These terms were typically ratios of bulk and wall properties.

The same correlations were tested at all experimental conditions encountered in this study with the program NUSLTB3.f written by M. Bazargan (UBC/SCWO heat...
transfer research group). The input into program included bulk temperature, pressure, flow rate and heat flux. The bulk temperatures and heat flux were obtained for each experiment as described in the section C.2. The illustrations of the results are given in the Appendix C1. The results were very sensitive to the variations in the heat flux.

The results showed that for conditions encountered in LTE Swenson et al. correlation predicted the heat transfer coefficient very well whereas the other tested correlations over predicted heat transfer coefficient. In HTE, Swenson et al. under predicted heat transfer coefficient whereas Shitsman-Miropolskii, Yamagata et al. and Gnielinsky over predicted heat transfer coefficient. The best agreement with experimental results for HTE was achieved with Jackson-Fewster and Petukhov et al.

In this study, the heat transfer coefficient was calculated with Swenson et al. Nusselt number correlation \((Nus, S\) stands for Swenson, C.7) for conditions encountered in LTE. In this correlation, Re number was calculated with viscosity of the fluid estimated at the wall temperature. Prandtl number was calculated with the average specific heat capacity \((\bar{c}_p)\). Viscosity \((\mu_w)\) and thermal conductivity \((k_w)\) were estimated at the wall. The property variation was also taken into account with the additional term given as the ratio between the wall density and bulk density raised to the power of 0.231.

\[
Nus = 0.00459(Re)^{0.233} (Pr)^{0.613} \left( \frac{\rho_w}{\rho_b} \right)^{0.231}
\]  \hspace{1cm} (C.7)

Where,

\[
Re = \frac{4 \cdot \dot{m}}{d \cdot \pi \cdot \mu_w} \hspace{1cm} \text{(C.8)}
\]

\[
Pr = \frac{\bar{c}_p \cdot \mu_w}{k_w} \hspace{1cm} \text{(C.9)}
\]
It was decided that Jackson –Fewster $Nu$ number correlation (C.10) be used for the conditions encountered in HTE. In comparison to classic $Nu$ number correlations, this correlation had two extra terms that took into account property variations. The first additional term considered variation of density from the wall to the bulk and the second term considered ratio of average specific heat capacity to bulk specific heat capacity. The second term was raised to the exponent $n$. The pseudo critical temperature $T_{pc}$ was used to set criteria for the exponent $n$ determination (C.11).

$$Nu_j = 0.0064 \, Re^{0.94} \, Pr^{0.48} \left( \frac{\rho_w}{\rho_b} \right)^{0.6} \left( \frac{C_p}{C_{pb}} \right)^n$$ \hspace{1cm} (C.10)

\[
\begin{align*}
    n &= 0.4 & \text{if} & \quad Tw \leq T_{pc} \text{ or } Tb \geq 1.2T_{pc} \\
    n &= 0.4 + 0.2 \left( \frac{Tw}{T_{pc}} - 1 \right) & \text{if} & \quad Tb \leq T_{pc} \text{ and } Tw > T_{pc} \\
    n &= 0.4 + 0.2 \left( \frac{Tw}{T_{pc}} - 1 \right) \left( 1 - 5 \left( \frac{Tb}{T_{pc}} - 1 \right) \right) & \text{if} & \quad T_{pc} \leq Tb \leq 1.2 T_{pc}
\end{align*}
\] \hspace{1cm} (C.11)

Where,

- $\rho$ – density of the fluid [kg/m$^3$]
- $c_p$ – specific heat capacity [kJ/kg-K]
- $w, b$ – subscripts referring to properties taken at inner wall temperature $Tw$ and bulk temperature $Tb$. 

The specific heat capacity \( \overline{c}_p \) was taken as integrated average specific heat from Petukhov et al. (1962).

\[
\overline{c}_p = \frac{1}{T_w - T_b} \int_{T_b}^{T_w} c_p \, dT = \frac{(H_w - H_b)}{(T_w - T_b)}
\]  
(C.12)

When calculating \( T_{w0} \), iterative procedure was used. This procedure was adopted from the program NUSLTB3.f that was developed by UBC/SCWO heat transfer research group. To obtain properties at the wall for the beginning of the iteration, classic \( Nu \) number correlation (Gnielinski) was applied to calculate initial \( T_{w0} \).

\[
Nu_{G} = \frac{f}{8} \frac{(Re-1000) \cdot Pr}{\left(1+12.7 \cdot \left(\frac{f}{8}\right)^{0.5} \cdot \left(Pr^{0.6667} - 1\right)\right)}
\]  
(C.13)

\[
f = \frac{1}{\left(1.8 \cdot \log\left(\frac{6.9}{Re} + \frac{\varepsilon}{3.7 \cdot d \cdot 1000}\right)\right)^{1.11}}
\]  
(C.14)

where,

- \( f \) - friction factor calculated from Haaland (1983)
- \( \varepsilon \) - surface roughness taken as 0.002 for drawn tubes [mm]

With the calculated \( Nu \) number, the heat transfer coefficient \( h_0 \) [kW/m\(^2\)-K] was determined as follows:

\[
h_{0j} = \frac{Nu_{cj} \cdot k_{bj}}{d}
\]  
(C.15)

\( k_b \) - the thermal conductivity of the bulk fluid [kW/m-K]
$d$ - the tube diameter [m]

With the known heat transfer coefficient $h_0$, bulk temperature $Tb$ [K] and heat flux $q$ [kW/m$^2$], the inner surface temperature at the location $z_j$ was then obtained as:

$$T_{w0j} = Tb + \frac{q}{h_{0j}} \quad (C.16)$$

With this wall temperature, the properties at the wall were evaluated and the new $Nu$ number calculated. The new Nusselt number was calculated with Swenson et al. ($Nu_s$, C.7) correlation for LTE and with Jackson-Fewster correlation ($Nu_f$, C.10) for HTE. With the new $Nu_f$ number, the new heat transfer coefficient was obtained from C.15 for HTE. For the low temperature experiments, the new heat transfer coefficient was calculated as follows:

$$h_{0j} = \frac{Nu_{sj} \cdot k_w}{d} \quad (C.17)$$

$k_w$ - the thermal conductivity of the fluid at the wall temperature [kW/m-K]

The new wall temperature was then calculated from C.16. This new wall temperature was compared to the old one. If they differed, the new temperature was set as the old one, the wall properties evaluated at this temperature and the new $Nu$ number, heat transfer coefficient and wall temperature calculated. The iteration was over when the old and the new wall temperatures differed by 0.1 °C. When the heat transfer coefficient was obtained for the clean tube, it was modified as described in 5.5 to account for the effect of the initial salt layer forming.
Appendix C1

Comparison Between Modeled Inner Surface Temperatures and Experimentally Obtained Ones

Nu number correlations:

1. - Gnielinsky (1976)
2. - Shitsman-Miropolskii (1957)
3. - Jackson –Fewster (Ghajar and Asadi 1986)
4. - Swenson et al. (1965)
5. - Yamagata et al. (1971)
6. - Petukhov et al. (1962)
Figure C1.1 Comparison between modeled and experimental surface temperatures for the experiment 1 (LTE)
Figure C1.2 Comparison between modeled and experimental surface temperatures for the experiment 2 (HTE)
Figure C1.3 Comparison between modeled and experimental surface temperatures for the experiment 3 (HTE)
Figure C1.4 Comparison between modeled and experimental surface temperatures for the experiment 4 (LTE)
Figure C1.6 Comparison between modeled and experimental surface temperatures for the experiment 6 (LTE)
Figure C1.7 Comparison between modeled and experimental surface temperatures for the experiment 7 (LTE)
Figure C1.8 Comparison between modeled and experimental surface temperatures for the experiment 8 (HTE)
Figure C1.9 Comparison between modeled and experimental surface temperatures for the experiment 9 (LTE)
Figure C1.10 Comparison between modeled and experimental surface temperatures for the experiment 10 (LTE)
Figure C1.11 Comparison between modeled and experimental surface temperatures for the experiment 11 (HTE)
Figure C1.12 Comparison between modeled and experimental surface temperatures for the experiment 12 (HTE)
Appendix C2
Buoyancy Effect

To determine buoyancy effect on heat transfer from one phase (Figure C2.1) and two-phase (vapor-liquid) solution (Figure C2.2.), a bottom surface temperature was measured throughout 6 experiments before and after solution was introduced to the test section (Exp. 1 through 6). At temperatures at which salt solution existed in one phase (temperatures close to pseudocritical temperature of pure water), no difference between bottom and top temperature measurements was observed (Figure C2.1). That implied that buoyancy could be neglected at these temperatures. The difference between top and bottom temperature measurements was observed at the initiation of deposition and disappeared with time in vapor-liquid region of the experiment 3 (Figure C2.2.). I assume that heavy liquid phase sank to the bottom and affected deposition rates. It is not clear why this effect disappeared with time. It was difficult to incorporate this behavior in salt thickness calculation and deposition models and hence it was completely neglected.
Surface temperature profile along the test section

Exp. 1

Axial distance [m]

Temperature [°C]

--- Outer surface temperature for the clean tube

- - - Outer surface temperature after 462.5 sec. of deposition

- X - Outer surface temperature after 1000 sec. of deposition

■ Control bottom surface temperature

Figure C2.1. Bottom and top surface temperature measurement as an indication of buoyancy in one phase region
Surface and bulk temperature profile along the test section

Exp. 3

Temperature [°C]

Axial distance [m]

- Outer surface temperature for the clean tube
- Outer surface temperature after 462.5 sec of deposition
- Outer surface temperature after 1000 sec. of deposition
- Surface temperature at the bottom - buoyancy control
- Outer surface temperature after 2000 sec. of deposition

Figure C2.2. Bottom and top surface temperature measurement as an indication of buoyancy in vapor-liquid region
Appendix D
Surface and Bulk Temperature Change with Time in Deposition Experiments

This appendix contains graphs of surface and bulk temperatures and conductivity change with time that were obtained from deposition experiments. This change is plotted in Figures D.1. to D.6. for Low Temperature Experiments. Plots for High Temperature Experiments are given in Figures D.7. to D.12.
Exp. #1, LTE, FLOW = 1.16 l/min, 
Tin=397 C, Tout= 443.3 C 
INIT. CONC.=1060 ppm

Figure D. 1. Change of temperatures and concentration with time for Exp. 1
Exp#4, LTE, FLOW = 0.62 L/min, Tin = 400.4 C, Tout = 450.1 C, INIT. CONC. = 1030 ppm

Figure D. 2. Change of temperatures and concentration with time for Exp. 4
Exp.#6, LTE, FLOW = 1.9 l/min,
Tin = 396.4 C, Tout = 449.7 C
INIT. CONC. = 1000 ppm

Figure D. 3. Change of temperatures and concentration with time for Exp. 6
Figure D. 4. Change of temperatures and concentration with time for Exp. 7
Exp. # 9, LTE, FLOW = 1.23 l/min, 
Tin = 386 C, Tout = 441 C 
INIT. CONC. = 1000 ppm

Figure D. 5. Change of temperatures and concentration with time for Exp. 9
Figure D. 6. Change of temperatures and concentration with time for Exp. 10
Exper. #2, HTE, FLOW = 1.15 l/min
Tin = 399.6 C, Tout = 493 C
INIT. CONC. = 1060 ppm

Figure D. 7. Change of temperatures and concentration with time for Exp.2
Exp. #3, HTE, FLOW = 1.12 l/min
Tin = 437.7 C, Tout = 484 C
INIT. CONC. = 620 ppm

Figure D. 8. Change of temperatures and concentration with time for Exp. 3
Exp. # 5, HTE, FLOW = 0.65 l/min,
Tin = 441.1 C Tout = 481.8 C
INIT. CONC. = unknown

Figure D. 9. Change of temperatures and concentration with time for Exp. 5
Exp. # 8, HTE, FLOW = 1.18 l/min, Tin = 395.5 °C, Tout = 480.6 °C, INIT. CONC. = 4610 ppm

Figure D. 10. Change of temperatures and concentration with time for Exp. 8
Exp. #11, HTE, FLOW = 1.23 l/min, Tin = 402.9 C, Tout = 507 C, INIT. CONC. = 1020 ppm

Figure D. 11. Change of temperatures and concentration with time for Exp. 11
Exp. #12, HTE, FLOW = 0.63 l/min
Tin = 387.3 C, Tout = 484 C,
INIT. CONC. = 1020 ppm

Figure D. 12. Change of temperatures and concentration with time for Exp. 12
Appendix E

Comparison of the Modeled and Experimental Salt Thickness Profiles

Results for the low temperature experiments LTE are given in the Figures E1 - E6 and for the high temperature experiments in the Figure E7-E12.
Figure E.1. Comparison between model and experimental data for Experiment 1

Figure E.2. Comparison between model and experimental data for Experiment 4
Figure E.3. Comparison between model and experimental data for Experiment 6

Figure E.4. Comparison between model and experimental data for Experiment 7
Figure E.5. Comparison between model and experimental data for Experiment 9

Figure E.6. Comparison between model and experimental data for Experiment 10
Figure E.7. Comparison between model and experimental data for Experiment 2

Figure E.8. Comparison between model and experimental data for Experiment 3
Figure E.9. Comparison between model and experimental data for Experiment 5

Figure E.10. Comparison between model and experimental data for Experiment 8
Figure E.11. Comparison between model and experimental data for Experiment 11

Figure E.12. Comparison between model and experimental data for Experiment 12
Appendix F

Source Code for the Computer Programs

This Appendix contains Fortran programs for calculation of salt layer thickness (SaltThick.f) and modeling of sodium-chloride deposition (SaltDep4.f).
F0. SaltThick.f

C *****************************************
C PROGRAM SALTTHICK
C *****************************************
C Converting outside surface tube temperatures to salt thicknesses-
C MODIFICATION OF PAUL TESHIMA'S PROGRAM PERFORMED BY
C FILIPOVIC DANIJELA
C *****************************************
C This program calculates salt thickness profiles from the measured
C outer surface temperatures for LTE and HTE NaCl experiments.
C The program also calculates porosity of the salt layer from the
C measured mass of deposited salt obtained from mass balance. For the
C given porosity, program calculates thickness and mass of deposited salt
C *****************************************
C Declaration of Variables
C *****************************************
C C = the concentration of the salt in the fluid [wt%]
C CP = specific heat [kJ/kg-K]
C CPW = using wall temp. properties [kJ/kg-K]
C D = density of flow [kg/m^3]
C DENACL = density of NaCl [kg/m^3]
C DH = difference in enthalpies between step sizes [kJ/kg]
C DIA = diameter of the tube [m]
C DIFTE = difference between measured and calculated
C outside wall temperature [K]
C DTE = difference between TE and TE2 [K]
C DW = density of fluid at inside wall temperature [kg/m^3]
C DZ = step size along the tube length [m]
C FLOW = mass flow [kg/s]
C FLOW2 = mass flow [kg/min]
C H1 = enthalpy of previous step [kJ/kg]
C H2 = enthalpy of present step [kJ/kg]
C HW = enthalpy at wall temperature [kJ/kg]
C ICOUNT = counter for axial location [-]
C ICOUNT2 = counter for inputing outside temperatures [-]
C IFLAG = tracks if there is a no thermocouple reading
C inside wall temperature
C SK = thermal conductivity [mW/K-m]
C SK625 = thermal conductivity of Inconel 625 at TK [W/K-m]
C SKH20 = thermal conductivity of water in pores
C in salt layer [W/K-m]
C SKSALT = thermal conductivity of NaCl [W/K-m]
C SKLAYER = effective thermal conductivity of NaCl
C layer [W/K-m]
C PHI = the porosity value for the salt layer [%]
C PR = Prandtl number [-]
C PRW = using wall temp. properties [-]
C Q1 = heat input per unit length of tube [kW/m]
C Q2 = heat input per unit area of tube [kW/m^2]
C RE = the Reynolds number of the flow [-]
C REW = using wall temp. properties [-]
C RI = inside radius of the tube [m]
C RO = outside radius of the tube [m]
RS = inside radius of the salt deposition [m]
T = temperature [K]
TCHECK = used to find T2 with H2 [K]
TE = external wall temperature [K]
TE2 = recalculation of external wall temperature [K]
TNU = Nusselt number [-]
TNUW = using wall temp. properties [-]
TS = surface temperature under the layer of salt [K]
TTP = three phase temperature for NaCl [K]
TW = inside wall temperature [K]
TW2 = calculated using TWTB2 (using wall temp. property variations) [K]
TWB = TW - TB, difference between wall and bulk temp. [K]
TWB2 = using wall temp. property variations [K]
VISC = viscosity [mg/s-m]
VISCW = using wall temp. properties [mg/s-m]
YSALT = thickness of salt deposition on tube walls [m]
YSALT2 = thickness of salt deposit [mm]
Z = distance along the tube length [m]

*********
Functions
*********
CRITICAL(P)
ENTHALPY(H1,Q1,DX,FLOW)
PRAN(VISC,CP,SK)
REYN(FLOW,DIA,VISC)
TGNIEL(T,R,RE,RA,PR,SKB,QW)
TRANSPORT(T,P,VISC,THK)
TINCONEL(K)
TLEWIS(SK,D,CP,DIFF)
TNUS1(RE,PR,DBB,DW)
TSALT(TS,Q1,SKLAYER,RS)
salt layer
TWO(TW,Q2,SK625,RI,RO)
outside wall temperature

IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER (I-N)
DIMENSION TE(30)
DIMENSION Z(30)
CHARACTER*40 OUTNAMEJNNAME

The following 'COMMON' statements were included from the IAPWS957.F main program

COMMON/CCPEQ/TCEQ,PCEQ,DCEQ
COMMON/CSUB2/R,XMOL,TC,PC,DC
COMMON/CNORM/TNORM,DNORM
COMMON/CSUB3/TTR,PTD,DLTR,DVTR,TBOYL,PBOYL,DLB,DVB
COMMON/COUT/NIN,NOUT

INPUT /OUTPUT ON PC:
NIN = 2
NOUT = 6

*************
INPUT DATA
*************

WRITE (*,*) 'INPUT FILE NAME?'
READ (*,*) INNAME
OPEN (UNIT=4, FILE=INNAME, STATUS='OLD')
READ(4,*),OUTNAME

C Input inlet and outlet bulk temperatures [K]
READ(4,*),TIN
READ(4,*),TOUT

C Input flow rate [l/min], pressure [MPa] and number of thermocouples
READ(4,*),FLOW2
READ(4,*),P
READ(4,*),NT

C Input measured surface temperatures [C]
DO 1000 I=1,NT
READ (4,*),TE(I)
TE(I)=TE(I)+273.15
1000 CONTINUE

C Input porosity [fraction], deposited mass [kg] and length of the tube [m]
C If you know porosity and want to calculate deposited mass input
C SMASS=0 (mass in LTE), SMASS1=0 (mass in HTE)
C If you want to find porosity for LTE input SMASS1=0 and phi=0.0
C If you want to find porosity for the second peak in HTE
C input PHI for the LTE, SMASS=0, and total obtained dep. mass SMASS1
READ (4,*),PHI
READ (4,*),SMASS
READ (4,*),SMASS1
READ (4,*),TLENGTH

C Input experimental setup: new [NSETUP=0], old [NSETUP=1]
READ (4,*),NSETUP

C Input type of the experiment: LTE [NETP=0], HTE [NETP=1]
READ (4,*),NETP

C NDFLAG1=0 for heat transfer coeff. correct, NDFLAG1=1 no correction
READ (4,*),NDFLAG1

C Nusselt correlation 1=Jackson-Fewster, 2=Swenson)
READ (4,*),NUSS

***************
HEAT FLUX CALCULATION
***************

FLOW = FLOW2/60
DS=BDENS(TIN,P,0)
D=DENS(P,TIN,DS,1.D-6)
HIN=HB(TIN,D)
DS=BDENS(TOUT,P,0)
D=DENS(P,TOUT,DS,1.D-6)
HOUT=HB(TOUT,D)
Q=FLOW*(HOUT-HIN)
Q1=Q/TLENGTH
DIA = 0.006272
Q2 = Q1/(3.14159265359*DIA)
Q2=126.9
Q1=Q2*DIA*3.14159265359
C
C ****************************
C Opening File for Data Storage
C ****************************
C
OPEN (UNIT=3, FILE=OUTNAME, STATUS='NEW')
C
C ****************************
C Constants and Counters
C ****************************
IF(NSETUP.EQ.0)THEN
  Z(1) = 0
  Z(2) = 0.296
  Z(3) = 0.571
  Z(4) = 0.797
  Z(5) = 0.953
  Z(6) = 1.131
  Z(7) = 1.323
  Z(8) = 1.575
  Z(9) = 1.738
  Z(10) = 1.922
  Z(11) = 2.097
  Z(12) = 2.216
  Z(13) = 2.3
  Z(14) = 2.437
  Z(15) = 2.572
  Z(16) = 2.714
  Z(17) = 2.874
ENDIF
IF(NSETUP.EQ.1)THEN
  Z(1) = 0
  Z(2) = 0.35
  Z(3) = 0.496
  Z(4) = 0.625
  Z(5) = 0.715
  Z(6) = 0.853
  Z(7) = 1.024
  Z(8) = 1.218
  Z(9) = 1.407
  Z(10) = 1.724
  Z(11) = 2.057
  Z(12) = 2.278
  Z(13) = 2.551
  Z(14) = 2.822
ENDIF
IF(NSETUP.EQ.3)THEN
  Z(1) = 0
  Z(2) = 0.063
  Z(3) = 0.204
  Z(4) = 0.35
  Z(5) = 0.496
  Z(6) = 0.715
  Z(7) = 0.853
  Z(8) = 1.024
  Z(9) = 1.218
  Z(10) = 1.485
Z(11) = 1.831
Z(12) = 2.212
Z(13) = 2.3
Z(14) = 2.485
Z(15) = 2.624
Z(16) = 2.751

ENDIF

C Critical temp.
TPC = CRITICALT(P)

C Heat flux
QW = Q2 * 1000.

C Density of NaCl
DENACL = 2170.0
PI = 3.1415926535
NT = NT + 1
ICOUNT1 = 2
T1 = TIN

C Three phase temperature for NaCl
TTP = 0.1136 * P * P + 0.9077 * P + 356.16
TTP = TTP + 273.15
SALTMASS1 = 0
PHIOLD = PHI
NFLAG = 0

C *********************************************
C INITIAL CONDITIONS
C *****************************************************************
14 CONTINUE
NDFLAG = NDFLAG1
YSALT = 0
SALTMASS = SALTMASS1
ICOUNT = ICOUNT1
IFLAG = 1
T = T1
TOLD = T1
DO WHILE (ICOUNT .LE. NT)
DS = BDENS(T, P, 0)
D = DENS(P, T, DS, 1, D-6)
H1 = HB(T, D)
CALL TRANSPORT(T, P, VISC, THK)
VIS = VISC * 1000000
SK = THK * 1000
CP = CPB(T, D)
RE = REYN(FLOW, DIA, VIS)
PR = PRAN(VIS, CP, SK)
DZ = Z(ICOUNT) - Z(ICOUNT1)
H2 = ENTHALPY(H1, Q1, DZ, FLOW)
CP = CPB(T, D)
DH = H2 - H1
DH2 = DH
TCHECK = T

C Loop to iterate to find the temperature at the new enthalpy
C *****************************************************************
C
15 CONTINUE
DO WHILE (DH2 .GT. 0.001)
TCHECK = TCHECK + DH/CP
DS = BDENS(TCHECK,P,0)
D = DENS(P,TCHECK,DS,1.D-6)
CP = CPB(TCHECK,D)
H1 = HB(TCHECK,D)
DH = H2 - H1
DH2 = ((DH)**2)**0.5
END DO
T = TCHECK
CT = T - 273.15
H1 = H2

C************************************************
C Recalculation of properties at new T
C************************************************

DW = D
CALL TRANSPORT(T,P,VISC,THK)
VIS=VISC*1000000
SK=THK*1000
SKB=THK
TNEW=T

C************************************************
C Change the initial conditions for HTE
C************************************************

IF(NETP.EQ.1)THEN
IF(NFLAG.EQ.0)THEN
IF(ICOTJNT.GT.3)THEN
IF(TE(ICOUNT-l).GT.TE(ICOUNT-2))THEN
IF(TE(ICOUNT-2).LT.TEaCOUNT-3))THEN
IF(TNEW.GE.TTP)THEN
IF(TOLD.LE.TTP)THEN
ICOUNT1=ICOUNT
SMSASS2=SMASS 1-SALTMASS
SALTMASS 1=SALTMASS
T1=TOLD
PHI=0.0
NFLAG=1
ENDIF
ENDIF
ENDIF
ENDIF
ENDIF
30 CONTINUE
DIA = 0.006272 - 2*YSALT
RE = REYN(FLOW,DIA,VIS)
PR = PRAN(VIS,CP,SK)
RA=DIA/2.
Gnielinski correlat. used to calculate initial TW
TWG=TGNIEL(T,RE,RA,PR,SKB,QW)
Jackson Fewster Nu number correl.
IF(NUSS.EQ.1)THEN
TW = TWG
19 DSW = BDENS(TW,P,0)
DW = DENS(P,TW,DSW,1.D-6)
HW = HB(TW,DW)
IF(TW.EQ.T) THEN
CPBAR=CP
ELSE
CPBAR=(HW-H2)/(TW-T)
ENDIF

TLIM=1.2*TPC
IF(TW.LE.TPC OR T.GE.TLIM)THEN
CN=0.4
ELSE IF(T.LE.TPC.AND.TPC.LT.TW)THEN
CN=0.4+0.2*((TW/TPC)-1)
ELSE IF(TPC.LE.T.AND.T.LE.TLIM)THEN
CN=0.4+0.2*((TW/TPC)-1)*(1-5*((T/TPC)-1))
ENDIF

NU=0.0064*(RE**0.91)*(PR**0.48)*((DW/D)**.6)*((CPBAR/CP)**CN)
HHEAT=NU*SKB/2./RA

TWNEXT = T + QW/HHEAT
DELTW=TWNEXT-TW
IF (ABS(DELTW) .GT. 0.1) THEN
TW = TW + (DELTW/10)
ENDIF
END IF
ENDIF

C Swenson Nu number correlation
IF(NUSS.EQ.2)THEN
TWS = TWG
DSW = BDENS(TWS,P,0)
DW = DENS(P,TWS,DSW,1.D-6)
HW = HB(TWS,DW)
call transport(TWS,P,VISC,THK)
VISCW=VISC*1000000
THERMKW=THK*1000
REW = REYN(FLOW,DIA,VISCW)
IF(TWS.EQ.T)THEN
PRW=CP*VISCW/THERMKW
ELSE
PRW = (HW - H2)/(TWS-T) * VISCW/THERMKW
ENDIF
TNU1 = 0.00459*(REW)**0.923*(PRW)**0.613*(DW/D)**0.231
HTCS=TNU1*THERMKW/(DIA*1000)
HHEAT=HTCS
TWTB=QW/HTCS
TWNEXT = T + TWTB
DELTW=TWNEXT-TWS
IF (ABS(DELTW).GE. 0.1) THEN
TWS = TWS + (DELTW/10.)
ENDIF
TW=TWS
ENDIF

C
C ********************************************************************************
C cALCULATION OF THE INNER AND OUTSIDE Wall Temperature
C ********************************************************************************
C
X = TW - TTP
TS = TW
IF (NDFLAG.EQ.0) THEN
  IF (T.LT.TTP) THEN
    IF (X.GE.10.0) THEN
      DELH = 0.1*X - 1
      HHEAT = HHEAT + DELH
    ENDIF
  ENDIF
  IF (T.GE.TTP) THEN
    IF (NETP.EQ.1) THEN
      HHEAT = HHEAT + DELH
    ENDIF
  ENDIF
  TW = T + QW/HHEAT
  TS = TW
ENDIF
CTS = TS - 273.15
RI = 0.0031
RO = 0.0048
CALL TRANSPORT(TS, P, VISC, THK)
SKH2O = THK
TSN = TW

C ********************
C CONDUCTIVITY OF NaCl
C ********************
C
17  TSOLD = TSN
PKSALT = 1.4622051 - 1.0700459*LOG10(TSN)
SKSALT = 100*(10**PKSALT)

C ********************
C CONDUCTIVITY OF POROUS SALT LAYER
C ********************
C
SKLAYER = (PHI)*SKH2O + (1-PHI)*SKSALT
Q2B = Q1/((3.14159265359*2*RO)

C ******************
C Inner Wall Temperature
C ******************
C
IF (IFLAG .EQ. 2) THEN
  RS = DIA/2
  TW = TSALT(TS, Q1, SKLAYER, RS)
  TSN = (TW + T)/2
  DTW = TSN - TSOLD
  DTW1 = (DTW)**2/0.5
  IF (DTW1.GT.0.1) THEN
    GO TO 17
  END IF
ENDIF

C ********************
C Outside Wall Temperature
C ****************************************************
C
SK625 = TINCONELK(TW)
TE2(ICOUNT-1) = TOUT(TW,Q2B,SK625,RI,RO)
CTW = TW - 273.15
C
C ****************************************************
C Outside Wall Temperature Comparison
C ****************************************************
C
IF (TE(ICOUNT-1) .LT. 274) THEN
   CTS = CTS
   CTW = 0
   CTE = TE2(ICOUNT-1) - 273.15
   GOTO 20
END IF
DIFTE = TE(ICOUNT-1) - TE2(ICOUNT-1)
DIFTE2 = ((TE(ICOUNT-1) - TE2(ICOUNT-1))**2)**0.5
IF (TS .GE. TTP) THEN
   GOTO 21
ELSE
   CTE = TE2(ICOUNT-1) - 273.15
   GOTO 20
ENDIF
YSALTOLD = YSALT
21 IF (DIFTE2 .GT. 0.1) THEN
   IFLAG = 2
   YSALT = YSALT + DIFTE / 1000000
   IF (YSALT .GE. 0) THEN
      GOTO 30
   ELSE
      YSALT = YSALTOLD
   ENDIF
ENDIF
C
C ****************************************************
C Calculation of the mass of salt deposited on the length dz
C ****************************************************
C
ZSALTMASS = (RI**2 - (RI - YSALT)**2) * PI * DZ * DENACL * (1 - PHI)
SALTMASS = SALTMASS + ZSALTMASS
20 CONTINUE
C
C Write Data To File
C *******************
C
IF (ICOUNT .EQ. 2) THEN
   WRITE(3,100)
100 FORMAT("Z", "TBULK [C]", "TSALT [C]", "TWALLin [C]", "TWALLout"
+ , "SALT THICKNESS [mm]", "SALT COND. [W/mK]", "LAYER COND. [W/mK]", "HEAT FLUX [kW/m2]","H2O COND. [W/mK]"
}
C Counters and Resets
C *****************************************************
ICOUNT = ICOUNT + 1
IFLAG = 1
TOLD = T
END DO
C *****************************************************
C No porosity adjustment
C *****************************************************
IF(SMASS.EQ.0)THEN
IF(SMASS.EQ.0)THEN
DSALTMASS = 0
GOTO 401
ENDIF
ELSE
IF(NETP.EQ.1)THEN
SMASS = SMASS1
ENDIF
ENDIF
C *****************************************************
C Porosity (phi) adjustment from the mass balance
C *****************************************************
C
DSALTMASS = ((SALTMASS - SMASS)**2)**0.5
401 CONTINUE
WRITE(3,300)
300 FORMAT (" SALTMASStKG", "SMASS[KG]", "POROSITY", "MASS DIFFERENCE"
   + )
WRITE(3,400) SALTMASS, SMASS, PHI, DSALTMASS
400 FORMAT(F8.4, ',', F8.4, ', ', F8.4, ' ', F8.4)
IF (DSALTMASS.GT.0.0005)THEN
PHI = PHI + 0.01
ENDIF
ENDIF
END
C
C*********************************************************************
REAL*8 FUNCTION REYN(FLOW,DIA,VIS)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
PI = 3.14159265359
RE = 4*FLOW/(PI*DIA*VIS)*1000000
REYN = RE
RETURN
END
C*********************************************************************
REAL*8 FUNCTION PRAN(VIS,CP,SK)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
PR = CP*VIS/SK
PRAN = PR
RETURN
END
C*********************************************************************
REAL*8 FUNCTION ENTHALPY(H1,Q1,DX,FLOW)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
H2 = H1 + Q1*DX/FLOW
ENTHALPY = H2
RETURN
END
C*********************************************************************
REAL*8 FUNCTION TWOUT(TW,Q2,SK625,RI,RO)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
A = RI/RO
TE = TW + Q2*1000*RI/(2*SK625)*((A**2-LOG(A**2)-1)/(1-A**2))
TWOUT = TE
RETURN
END
C*********************************************************************
REAL*8 FUNCTION TSALT(TW,Q1,SKLAYER,RS)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
PI = 3.14159265359
RI = 0.003136
TS = TW + Q1*1000/(2*PI*SKLAYER)*LOG(RI/RS)
TSALT = TS
RETURN
END
C*********************************************************************
REAL*8 FUNCTION TINCONELK(TK)
C*********************************************************************
IMPLICIT REAL*8 (A-Z)
TK2 = TK - 273.15
IF (TK2 .LT. 100) THEN
  THERMK625 = (TK2-23)/(100-23)*(11.4-9.8)+9.8
ELSE IF (TK2 .LT. 200) THEN
  THERMK625 = (TK2-100)/(200-100)*(13.4-11.4)+11.4
ELSE IF (TK2 .LT. 300) THEN
  THERMK625 = (TK2-200)/(300-200)*(15.5-13.4)+13.4
ELSE
  THERMK625 = (TK2-300)/(400-300)*(17.6-15.5)+15.5
ENDIF
ELSE IF (TK2 .LT. 400) THEN
  THERMK625 = (TK2-300)/(400-300)*(17.6-15.5)+15.5
ELSE IF (TK2 .LT. 500) THEN
  THERMK625 = (TK2-400)/(500-400)*(19.6-17.6)+17.6
ELSE IF (TK2 .LT. 600) THEN
  THERMK625 = (TK2-500)/(600-500)*(21.3-19.6)+19.6
ELSE IF (TK2 .GE. 600) THEN
  THERMK625 = (TK2-600)/100*(21.3-19.6)+21.3
ENDIF
TINCONELK = THERMK625
RETURN
END

REAL*8 FUNCTION TGNIEL(T,RE,RA,PR,SKB,QW)

C*****************************************************************************
IMPLICIT REAL*8 (A-Z)
EPS=0.002

F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*RA*1000))**1.11))**(-2)
TNU=(F/8)*(RE-1000)*PR/(1+12.7*((F/8)**(0.5))*(PR**(0.66667)-1))
HTCG=TNU*SKB/2./RA
TWB = QW/HTCG
TWG = T + TWB
TGNIEL=TWG
RETURN
END

C*****************************************************************************
REAL*8 FUNCTION CRITICALT(P)

C*****************************************************************************
IMPLICIT REAL*8 (A-Z)
TPC1=647
DELTPC=1
DSC=BDENS(TPC1,P,0)
DPC=DENS(P,TPC1,DSC,1.D-6)
CP1=CPB(TPC1,DPC)
15 TPC2 = TPC1 + DELTPC

   DS = BDENS(TPC2, P, 0)
   DPC = DENS(P, TPC2, DS, 1.D-6)
   CP2 = CPB(TPC2, DPC)
   CPDEL = ABS(CP2 - CP1)

   IF (CPDEL.GT.0.001) THEN
      IF (CP2.GT.CP1) THEN
         TPC1 = TPC2
         CP1 = CP2
      ELSE
         DELTPC = DELTPC/10
      ENDIF
   ENDIF
   GOTO 15

ENDIF

TPC = (TPC1 + TPC2)/2
CRITICALT = TPC
RETURN
END
Input file for SaltThick.f program:

two.o  calculate salt thicknesses for exp. 2
672.8  Inlet bulk temp. [K], Tin
766.2  Outlet bulk temp. [K], Tout
1.15   Flow rate [l/min], FLOW2
25.04  pressure MPa
16     Number of thermocouples
443    s1 Measured outer surface temp.[C], TE
445    s2
449.9  s3
454.5  s4
460.4  s5
510.9  s6
481.3  s7
498.6  s8
529.2  s9
606.6  s10
598.3  s11
589.8  s12
575.4  s13
571.1  s14
564    s15
560.5  s16
0.1    Porosity [fraction], phi
0.0    Deposited mass from mass balance LTE(if 0
       program calculates it),[kg] SMASS
0.008  Deposited mass [KG] from mass balance for HTE
2.946  length of the tube [m]
0      Thermocouple setup (0=new setup, 1=old setup)
1      Type of the experiment(0=LTE, 1=HTE)
0      Temperature decrease (0=yes, 1=no)
1      Type of Nu correlation (1=Jackson, 2=Swenson)
PROGRAM SaltDep4

C Program 1-D model of heat and mass transfer in a tubular SCWO system. Based on SCheat.f by Paul Teshima, rewritten Jan. 98 by Steven Rogak. Models 1, 2 and 3 for NaCl deposition incorporated by Filipovic Danijela in April '99 and new thermodynamic and transport properties added to the program.

C*************************************************************************
C Functions/subroutines
C
C STEP -main algorithm for stepping along reactor, considering heat, mass transfer
C
C DISCRETE interpolates T, H on an evenly spaced longitudinal grid.

INTEGER NIN,NOUT,NSEGMENT,I,IREF,i,NJ,NTIME,PARFLAG,NM
INTEGER NMASS,NRAD,NLEN,IMASS,IRAD,ILEN,MODEL,IONUM
REAL*8 RADIUS,RFLOW,c1,c2,c0,c11,LENGTH,DZ,P,diamol,SIGMA
REAL*8 DTIME,SALTDENS,POROS,REFF,TAU,Dpart,POROS1,POROS2
REAL*8 RADIUS0,LENGTH0,FLOW0,DZ0,CT1,SMALL

REAL*8 ZSEG(20),QSEG(20),QSEG0(20),TIME(20),vseg0(20),QSEG0(20)
REAL*8 TBULK(2000),Q(2000),CSAT,CLD1,CLD2,CVAPOR2,CWALL,CP1,CP2
REAL*8 Y(2000)
REAL*8 QMASS,YPEAK,ZPEAK
REAL*8 LENFACT,MASSFACT,RADFACT,TOLERR
REAL*8 TW,TB1,TB2,THICK,PI,TTP
REAL*8 NPART,MOM1,APART, VOLPART
PARAMETER (PI = 3.14159265359,SMALL=1.e-40)
CHARACTER*40 OUTNAME,INNAME,OUTPROF,OUTDETA11
CHARACTER*10 SPECIES

C Input routine

C Input/output unit numbers must be passed to the eqtest.f routines
COMMON/COUT/NIN,NOUT
NIN = 2
NOUT = 6
WRITE(*,*) 'INPUT FILE NAME?'
READ(*,*) INNAME

C
C THIS IS THE FILE WITH THE MAIN RUN SUMMARY INFORMATION
DOCUMENT OUTNAME
READ(4,*), OUTNAME
C
C THIS IS THE REACTOR PROFILE INFORMATION AS A FUNCTION OF Z
C THIS IS A FILE FOR DUMPING DETAILS FROM SUBROUTINES
C
REAL*8 RADIUS in m, P in MPa, massflow G in kg/s, number of tube segments
C and the desired length step (usually 0.01 m)
READ(4,*), RADIUS
READ(4,*) P
READ(4,*) MFLOW
READ(4,*) NSEGMENT
read(4,*) IREF
READ(4,*) DZ
C Now read in the segment starting z coordinate and heat flux kW/m for that
c segment and starting bulk temperature.
c If the heat flux is to be used, enter a negative temperature.
c The segment IREF contains the most reliable temperature for the modelling
c run.
DO 5 I=1,NSEGMENT+1
  READ(4,*) ZSEG(I),QSEG(I),TSEG(I)
5 CONTINUE
LENGTH=ZSEG(NSEGMENT+1)
C Salt initial mass fraction, species name, density kg/m^3, porosity
c, hydrodynamic diameter (M), and surface tension SIGMA. If SIGMA
c <0, then the moment model will not be called.
READ(4,*) C0
READ(4,6) SPECIES
6 FORMAT(A10)
C options are 'NACL or NA2SO4 or SHARP (a custom salt)'
READ(4,*) SALTDENS
C for NaCl porosl is porosity in LT region and poros2 is porosity
C in HT region
READ(4,*) POROS1
READ(4,*) POROS2
READ(4,*) DIAMOL
READ(4,*) SIGMA
READ(4,*) TOLERR
C IN METERS, SIMULATION TIMES:
READ (4,*) NTIME
DO 7 I=1,NTIME
  READ(4,*) TIME(I)
7 CONTINUE
C Now allow for parametric studies. If Parflag>1 then we can input ranges
C of variables, resulting in multiple runs.
C Input number of mass flows. The massflow read above will be
C the minimum; the higher mass flows will be scaled up by factor
C massfact.
READ(4,*) NMASS,MASSFACT
READ(4,*) NRAD,RADFACT
READ(4,*) NLEN, LENFACT
PARFLAG=NMASS*NRAD*NLEN
READ(4,*) MODEL
  READ(4,*) NM
READ(4,*) NDEC
C "MODEL" controls the salt deposition model used in STEP, NM specifies
correlation used for mass transfer coefficient calculation NM=1-based on
C Swenson, for NDEC n.e. 1 correction of heat transfer coefficient for salt
C (NaCl) effect is calculated
C Echoe input data
OPEN(UNIT=3,FILE=OUTNAME,STATUS='NEW')
IONUM=8
OPEN(UNIT=IONUM,FILE=OUTDETAIL,STATUS='NEW')
OPEN(UNIT=7,FILE=OUTPROF,STATUS='NEW')
WRITE(3,9) INNAME,OUTPROF,OUTDETAIL,MODEL
     ' Model number used:',I3)
WRITE(3,10) RADIUS*1000.,P,MFLOW*60.,C0,SPECIES,saltdens,porosl,
     poros2,SIGMA,TOLERR,parflag,LENGTH/DZ
10 FORMAT('R(mm)=',F5.1, ' P(MPa)=',F5.1, ' FLOW kg/min =',F6.2,
     ' initial wt fraction',F6.5, 
     ' salt density kg/m^3 =',F6.0, ' porosity1=',F5.3,
     ' porosity2=',F5.3, ' Surface Tension n/m^2 =',F12.4, '/ time step
     factor',F4.0/
     ' Number of Parametric Runs=',I5, ' Number of steps=',F5.1/)

This is calculation of three phase equilibrium temperature for NaCl-H2O
solution-curve fit to data from Bischoff 1991

TTP=0.1136*P*P+0.9077*P+356.16
TTP=TTP+273.15

--- End of Input Section --------------------------------------------------
c --- Convert the segmented reactor into a continuous one with varying bulk
c temperature, discretized to DZ resolution.
NJ=LENGTH/DZ+1
IF(NJ.GE.2000) THEN
   STOP ' DZ IS TOO SMALL'
ELSE
   CALL DISCRETE(P,NSEGMENT,ZSEG,QSEG,TSEG,IONUM,
c ,IREF, DZ,mflow,RADIUS,TBULK,Q,TAU)
END IF
DO 100 J=1,NJ
   Y(J)=0.0
100 CONTINUE
IF(PARFL AG. GT. 1) THEN
   NTIME=2
   DTIME=TAU
   C for parametric studies, fix output time to one residence
c time, and give results only for this time
END IF
C-----------------------
C ---START TIME LOOP HERE-------------------------------
C-----------------------------------------------
DO 2000 I=2,NTIME
   IF(PARFLAG.EQ.1) THEN
      DTIME=TIME(I)-TIME(I-1)
      WRITE(7,34) TIME(I)
      WRITE(*,34) TIME(I)
34   FORMAT(//'TIME: ',F6.1,' s',/
            'Z(m) TB(K) TW(K) kW/m^2 ppmsat ppmbulk',
            ' PPMTOT Y(mm) part(#/m^3) Dp(microns)')
   END IF
C//   INTEGRATE ALONG LENGTH //////////////////////////////////////////////////////////////////////////////////
   YPEAK=0
   ZPEAK=0
   C Setting initial concentrations
   C C1,C2 concentration of dissolved salt at the beginning and the
c end of the step,
c CLD1,CLD2 conc. of salt in liquid phase at teh beg. and the end
c of the step
c CP1, CP2 conc. of salt in particles
   C1=C0
      C2=C0
      CLD1=0
      CLD2=0
      CP1=0
      CP2=0
      NPART=0
      APART=0
      MOM1=0
      VOLPART=0
   DO 1000 J=1,NJ-1
REFF=RADIUS-Y(J)
c Setting ndec to 1 excludes heat transfer coefficient correction when
c fouling starts
IF(REFF.NE.RADIUS)THEN
  NDEC=1
ENDIF
IF(REFF.LE.0.) THEN
  WRITE(7,*) 'TUBE PLUGGED HERE'
  STOP
ENDIF
TB1=TBULK(J)
TB2=TBULK(J+1)
CALL STEP(P,TB1,TB2,REFF,MFLOW,SALTDENS,DIAMOL,SPECIES,
  SIGMA,C1,C0,NM,NDEC,TTP,mom1,APART,volPART,MODEL,IONUM,TOLERR,C1,C2,QMASS,TW
  CLD1,CLD2,CVAPOR2,CWALL,CP1,CP2,C11)
C
C Setting porosity of LT and HT regions
IF(TB1.GE.TTP)THEN
  POROS=POROS2
ELSE
  POROS=POROS1
ENDIF
C Salt thickness calculation
THICK=QMASS*dTIME/SALTDENS/(1.-Poros)
Y(J)=Y(J)+THICK
Dpart=1.6e6*(6.*volpart/(npart+SMALL)/Pi)**0.3333333
CTB1=TB1-273.15
  CTW=TW-273.15
write(*,40)(j-l)*dz,CTB1,CTW,Q(J),
  Csat*1e6,C1*1e6,ctl*1e6,Y(J)*1000.,NPART,Dpart,CLD2*1e6,
C  CVAPOR2*1e6,CWALL*1E6,CP2*1E6,C11*1E6
write(7,40) (j-l)*dz,CTB1,CTW,Q(J),
  Csat*1e6,C1*1e6,ctl*1e6,Y(J)*1000.,NPART,dpart,clrd2*1e6,
C  cvapor2*1e6,CWALL*1E6,CP2*1E6,C11*1E6
40 FORMAT(F6.2,2F7.1,F6.1,3F9.1,F8.4,2G10.2,5F9.1)
C
C ============ END LOO
C -------END TIME LOOP HERE--------------------------------------
C
C ============ END LOOP FOR PARAMETRIC STUDIES HERE ===========
CLOSE (3)
CLOSE (4)
CLOSE (7)
CLOSE (IONUM)
stop

END

SUBROUTINE STEP(P,TB1,TB2,DZ,R,MFLOW,SALTDENS,DIAMOL,SPECIES,
   SIGMA, C1,C0,NM,NDEC,TTP,NPART, mom1, APART,
   volPART, MODEL,IONUM,TOLERR,CT1, Csat1, C2,QMASS,TW,
   CLD1,CLD2,CVAPOR2,CWALL,CP1,CP2,C11)
C This routine marches 1 distance step down the reactor.

C ON INPUT:
   REAL*8 P,TB1,TB2,DZ,R,MFLOW,SALTDENS,DIAMOL,SIGMA,TTP
   P is the pressure in MPa
c Tb1 and Tb2 are the initial and final bulk temperatures,
c dz is the distance increment.
   C R is the effective tube radius (with fouling)
   C MFLOW mass flow in kg/s
   C SALTDENS - salt density in kg/m^3
   C DIAMOL - molecular effective hydrodynamic diameter
   C SIGMA - surface tension
   CHARACTER*10 SPECIES
   C SPECIES specifies the salt species considered
   REAL*8 C1,C0,NPART,MOM1,APART,VOLPART,TOLERR
   C C1 dissolved salt wt. fraction initially
   C NPART,MOM1,APART,VOLPART - particle number, 1st moment, area, and volume per m^3
   C (these are updated at the end)
   C TOLERR tolerance parameter for the particle formation model
   INTEGER MODEL,IONUM
   C flag specifying model type;
   C IONUM is the unit number for the detailed output from this subroutine

C ON OUTPUT:
   REAL*8 C2,QMASS,TW,Csat1,CLD2,CLD1,CWALL,CSAT2,CVAPOR1,CVAPOR2,
   C VCONC,C11
   C C2 - dissolved salt concentration at end of the step
   C Csat1 - saturated salt wt fraction at beginning of the step
   C QMASS - Salt mass deposited over this length, per unit time
   C TW - wall temperature midway along the interval

C PARAMETERS OF PROP. ROUTINE CALLED BELOW
   REAL*8 DB1,HB1,CPB1,VISB1,KB1,PRB1,DB2,HB2,CPB2,VISB2,KB2,PRB2
   C PROPERTIES AT MID-STEP POSITION
   REAL*8 TB,DB,HB,CPB,VISB,KB,PRB
   C Properties at the wall:
   REAL*8 DW,HW,CPW,VISW,KW,PRW
   C ADDITIONAL HEAT/MASS TRANSFER PARAMETERS
   REAL*8 QW,HHEAT,RE,HMASS
   real*8 DELTIME,CT1,CT2,ALPHA,CBULK,CDEP,PDEP,T
c time derivatives:
real*8 dTdt, dDdt
REAL*8 PI,SAT

REAL*8 CBP2,CP1,VISKIN,DIFFW,SC,VEL,EPS,F,DIAP,TAUW,USTAR,TAUP
REAL*8 TAUPPLUS,**STAR,**CPARTW,CP2,QMASSM,QMASSP

INTEGER IPHASE,NM,NDEC

PARAMETER (PI = 3.14159265359)

c write(ionum,10) TB1,TB2,DZ,R,MFLOW,SALTDENS,DIAMOL,SPECIES
c 10 FORMAT(7G10.2,A10)

CALL PROP(TB1,P,DB1,HB1,CPB1,VISB1,KB1,PRB1)
CALL PROP(TB2,P,DB2,HB2,CPB2,VISB2,KB2,PRB2)
QW=MFLOW*(HB2-HB1)/(DZ*PI*2*R)
TB=(TB1+TB2)/2.
DB=(DB1+DB2)/2.
HB=(HB1+HB2)/2.
CPB=(CPB1+CPB2)/2.
VISB=(VISB1+VISB2)/2.
KB=(KB1+KB2)/2.
PRB=(PRB1+PRB2)/2.
CALL HEAT(QW,TB,P,DB,HB,VISB,KB,PRB,MFLOW,R,
C TW,DW,HW,CPW,KW,PW,HHEAT,RE,NDEC,TTP)
CALL MASSTRAN(HHEAT,T,TW,DIAMOL,HMASS,
C DB,VISB,DW,VISW,CPB,HB,HW,kb,KW,NM,CPW)
C Calculating saturation in the bulk and at the wall for vapor-solid
C region
CSAT1=SAT(SPECIES,TTP,TB1,P)
CSAT2=SAT(SPECIES,TTP,TB2,P)
CWALL=SAT(SPECIES,TTP,TW,P)
C Calculating saturation of vapor phase in teh bulk for vapor-liquid
C region using interpolation of Bischoff's data(1991)
IF(TW.GE.TTP)THEN
CVAPOR1=VCONC(TB1,P)
CVAPOR2=VCONC(TB2,P)
ELSE
CVAPOR1=C0
CVAPOR2=C0
ENDIF
IF(CWALL.GT.C1) THEN
CWALL=C1
ENDIF

C-------------------------------------------------------------------
C Model 1 assumes molecular mass transfer from both phases with the same
C mass transfer coefficient in LT region (bulk below TTP) and
C combination of molecular and particle mass transfer with no mass transfer
C between phases in HT region (bulk above TTP)

IF(MODEL.EQ.1) THEN
For wall temperature lower than three phase temperature there is no mass transfer

\[
\text{IF}(T_{W} \lt T_{TP}) \text{THEN} \\
\quad Q_{\text{MASS}} = 0. \\
\text{ELSE} \\
\text{ Calculation of mass flux } Q_{\text{MASS}}, \text{ molecular mass transfer from both phases with the same mass transfer coefficient in LT region. } C \text{ is total salt concentration} \\
\text{IF}(T_{B} \lt T_{TP}) \text{THEN} \\
\quad \alpha = \frac{H_{\text{MASS}} \pi R DZ DB}{M_{\text{FLOW}}} \\
\text{use semi-implicit forward marching. This can be derived by assuming that the diffusional mass transfer is driven by the average concentration over the interval and that this must balance the reduction in salt mass flux.} \\
\quad C_{2} = \frac{(C_{1} \ast (1 - \alpha) + 2 \ast \alpha \ast C_{\text{WALL}})}{(1 + \alpha)} \\
\quad Q_{\text{MASS}} = H_{\text{MASS}} DB \left( \frac{(C_{2} + C_{1})}{2} - C_{\text{WALL}} \right) \\
\text{ENDIF} \\
\text{This is calculation of mass flux } Q_{\text{MASS}} = Q_{\text{MASSM}} + Q_{\text{MASSP}} \text{ in HT region} \\
\text{molecular mass transfer from vapor phase } Q_{\text{MASSM}} \\
\text{plus particle deposition } Q_{\text{MASSP}} \text{ (no mass transfer between phases).} \\
\text{IF}(T_{B} \geq T_{TP}) \text{THEN} \\
\text{If concentration of salt carried from LT region } C_{11} \text{ is higher than solubility limit at bulk temp. } C_{\text{sat2}}, \text{ particles are formed.} \\
\text{Concentration of salt in particles is affected only by particle deposition-there is no mass transfer between particles and vapor phase} \\
\text{IF}(C_{\text{SAT2}} \leq C_{11}) \text{THEN} \\
\quad \text{Molecular mass transfer} \\
\quad Q_{\text{MASSM}} = H_{\text{MASS}} DB \left( \frac{(C_{\text{SAT2}} + C_{\text{SAT1}})}{2} - C_{\text{WALL}} \right) \\
\quad C_{2} = \frac{(C_{\text{SAT2}} + C_{\text{SAT1}})}{2} - Q_{\text{MASSM}} \frac{\pi 2 \ast R DZ}{M_{\text{FLOW}}} \\
\text{Particle deposition Calculation of deposition velocity as given in Papavergos et al. (1984). } CBP_{2} \text{ is concentration of salt in particles at the end of the step} \\
\text{CBP}_{2} = CP_{1} + C_{11} - C_{\text{SAT2}} \\
\text{Calculation of Schmidt number} \\
\quad \text{VISKIN} = \frac{\text{VISW}}{\text{DW}} \\
\quad \text{DIFFW} = 1.38E-23 \ast \frac{\text{TW}}{(3 \ast \pi \ast \text{VISW} \ast \text{DIAMOL})} \\
\quad SC = \frac{\text{VISKIN}}{\text{DIFFW}} \\
\text{Flow velocity} \\
\quad VEL = \frac{\text{MFLOW}}{(DB \ast \pi \ast R \ast \ast 2)} \\
\text{roughness of the tube [mm]} \\
\quad EPS = 0.002 \\
\text{friction factor calculated from Haaland 1983} \\
\quad F = (1.8 \ast \log_{10}(6.9 / \text{RE} + (\text{EPS} / (3.7 \ast 2 \ast R \ast 1000)))^{1.11})^{(-2)} \\
\text{NaCl particle diameter [m] taken from Armellini (1993)} \\
\text{DIAP = 5E-6} \\
\text{The wall shear stress [N/m2]} \\
\quad \text{TAUW} = DB \ast \text{VEL} \ast \ast 2 \ast F / 8
The wall friction velocity [m/s]
USTAR=(TAUW/DW)**0.5
The particle relaxation time [s]
TAUP=SALTDENS*DIAP**2/(18*VISKN*DW)
Dimensionless particle relaxation time:
TAUPPLUS=TAUP*USTAR**2/VISKIN

IF(TAUPPLUS.GT.20)THEN
  Dimensionless particle deposition velocity
  VDSTAR=0.13
ELSE IF(TAUPPLUS.LT.0.2)THEN
  VDSTAR=0.065*(SC)**(-0.6667)
ELSE
  VDSTAR=3.5E-4*TAUPPLUS**2
ENDIF
Particle deposition velocity [m/s]
VD=VDSTAR*USTAR
CPARTW=0
QMASSP=VD*DB*(CBP2-CPARTW)
CP2=CBP2-QMASSP*PI*2.*R*DZ/MFLOW
QMASS=QMASSM+QMASSP
C11=C2
ENDIF

If concentration of salt carried from LT region or of the dissolved salt
C11 is lower than
solubility limit at bulk temp. csat2, there is no new particle formation.
Concentration of salt in particles is affected only by particle
deposition—there is no mass transfer between particles and vapor phase.
Concentration of the dissolved salt is affected only by mass transfer from
the vapor phase

IF(CSAT2.GT.C11)THEN
  ALPHA=HMASS*PI*R*DZ*DB/MFLOW
  C2=(C11*(1-ALPHA)+2.*ALPHA*CWALL)/(1.+ALPHA)
  QMASSM=HMASS*DB*((C11+C2)/2.- CWALL)
  C11=C2
  VISKIN=VISW/DW
  DIFFW=1.38E-23*TW/(3*PI*VISW*DIAMOL)
  SC=VTSKm/DIFFW
  VEL=MFLOW/(DB*PI*R**2)
  EPS=0.002
  F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000))**1.11))**(-2)
  DIAP=5E-6
  TAUW=DB*VEL**2*F/8
  USTAR=(TAUW/DW)**0.5
  TAUP=SALTDENS*DIAP**2/(18*VISKN*DW)
  TAUPPLUS=TAUP*USTAR**2/VISKIN
ENDIF
VDSTAR=0.13
ELSE IF(TAUPPLUS.LT.0.2)THEN
  VDSTAR=0.065*(SC)**(-0.6667)
ELSE
  VDSTAR=3.5E-4*TAUPPLUS**2
ENDIF
VD=VDSTAR*USTAR
CPARTW=0
QMASSP=VD*DB*(CP2-CPARTW)
CP2=CP2-QMASSP*PI*2.*R*DZ/MFLOW
QMASS=QMASSM+QMASSP

ENDIF
ENDIF
END IF

C  
Model 2 for NaCl deposition assumes molecular mass transfer from vapor phase only
with liquid phase frozen (no mass transfer between phases) for LT region
(bulk below TTP) and
combination of molecular and particle mass transfer with no mass transfer
between phases in HT region (bulk above TTP)

IF(MODEL.EQ.2)THEN
For wall temperature lower than three phase temperature there is no mass
transfer

IF(TW.LT.TTP)THEN
QMASS=0
ELSE
This is calculation of mass flux QMASS in LT region, C1 is salt cone, in
vapor phase, C11 is the total salt cone (vapor+liquid) carried from the LT region
into HT region. CVAPOR is vapor solubility in vapor-liquid region

IF(TB.LT.TTP)THEN
For C1 greater than vapor solubility there is liquid phase formation. This liquid
phase does not participate in mass transfer
IF(CVAPOR2.LE.C1)THEN
CLD2=CLD1+C1-CVAPOR2
QMASS=HMASS*DB*((CVAPOR2+CVAPO1)/2-CWALL)
C2=(CVAPOR2+CVAPO1)/2-QMASS*PI*2.*R*DZ/MFLOW
ENDIF
For C1 below vapor solubility there is no new liquid phase formation
IF(CVAPOR2.GT.C1)THEN
ALPHA=HMASS*PI*R*DZ*DB/MFLOW
C2=(C1*(1-ALPHA)+2.*ALPHA*CWALL)/(1.+ALPHA)
QMASS=HMASS*DB*((C1+C2)/2.-CWALL)
ENDIF
C11=CLD2+C2
ENDIF
This is calculation of mass flux QMASS=QMASSM+QMASSP in HT region
molecular mass transfer from vapor phase QMASSM
plus particle deposition QMASSP (no mass transfer between phases).

IF(TB.GE.TTP)THEN
If concentration of salt carried from LT region C11 is higher than
solubility limit at bulk temp. csat2, particles are formed.
Concentration of salt in particles is affected only by particle deposition-there is no mass transfer between particles and vapor phase.

IF(CSAT2.LE.C11) THEN
    Molecular mass transfer from vapor phase
    QMASSM=HMASS*DB*(CSAT2-CWALL)
    C2=CSAT2-QMASSM*PI*2.*R*DIAMOL/MFLOW

Particle deposition. Calculation of deposition velocity as given in Papavergos et al. (1984). CBP2 is concentration of salt in particles at the end of the step

    CBP2=CP1+C11-CSAT2
    VISKIN=VISW/DW
    DIFFW=1.38E-23*TW/(3*PI*VISW*DIAMOL)
    SC=VISKIN/DIFFW
    VEL=MFLOW/(DB*PI*R**2)
    EPS=0.002
    F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000))**1.11))**(-2)
    DIAP=5E-6
    TAUW=DB*VEL**2/F/8
    USTAR=(TAUW/DW)**0.5
    TAUP=SALTDENS*DIAP**2/(18*VISKIN*DW)
    TAUPPLUS=TAUP*USTAR**2/VISKIN
    IF(TAUPPLUS.GT.20) THEN
        VDSTAR=0.13
    ELSE IF(TAUPPLUS.LT.0.2) THEN
        VDSTAR=0.065*(SC)**(-0.6667)
    ELSE
        VDSTAR=3.5E-4*TAUPPLUS**2
    ENDIF
    VD=VDSTAR*USTAR
    CPARTW=0
    QMASSP=VD*DB*(CBP2-CPARTW)
    CP2=CBP2-QMASSP*PI*2.*R*DIAMOL/MFLOW
    QMASS=QMASSM+QMASSP
    C11=C2
ENDIF

If concentration of salt carried from LT region or of the dissolved salt C11 is lower than solubility limit at bulk temp. csat2, there is no new particle formation. Concentration of salt in particles is affected only by particle deposition-there is no mass transfer between particles and vapor phase. Concentration of the dissolved salt is affected only by mass transfer from the vapor phase.

IF(CSAT2.GT.C11) THEN
    ALPHA=HMASS*PI*R*DIAMOL*DB/MFLOW
    C2=(C11*(1-ALPHA)+2.*ALPHA*CWALL)/(1.+ALPHA)
    QMASSM=HMASS*DB*((C11+C2)/2.-CWALL)
    C11=C2
    VISKIN=VISW/DW
    DIFFW=1.38E-23*TW/(3*PI*VISW*DIAMOL)
    SC=VISKIN/DIFFW
    VEL=MFLOW/(DB*PI*R**2)
    EPS=0.002
    F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000))**1.11))**(-2)
DIAP=5E-6
TAUW=DB*VEL**2*F/8
USTAR=(TAUW/DW)**0.5
TAUP=SALTDENS*DIAP**2/(18*VISKIN*DW)
TAUPPLUS=TAUP*USTAR**2/VISKIN
IF(TAUPPLUS.GT.20)THEN
VDSTAR=0.13
ELSE IF(TAUPPLUS.LT.0.2)THEN
VDSTAR=0.065*(SC)**(-0.6667)
ELSE
VDSTAR=3.5E-4*TAUPPLUS**2
ENDIF
VD=VDSTAR*USTAR
CPARTW=0
QMASSP=VD*DB*(CP2-CPARTW)
CP2=CP2-QMASSP*PI*2.*R*DZ/MFLOW
QMASS=QMASSM+QMASSP
ENDIF
ENDIF
ENDIF
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ENDIF

C  Model 3 for NaCl deposition assumes mass transfer from vapor phase with vapor
C  and liquid phases in equilibrium for LT region (bulk below TTP) and
C  combination of molecular and particle mass transfer with no mass transfer
C  between phases in HT region (bulk above TTP)

IF(MODEL.EQ.3)THEN
C  For wall temperature lower than three phase temperature there is no mass
C  transfer
IF(TW.LT.TTP)THEN
QMASS=0
ELSE
C  This is calculation of mass flux QMASS in LT region, C1 is total salt conc. in
C  bulk fluid, C11 is the total salt conc (vapor+liquid) carried from the LT region
C  into HT region. CVAPOR1 is vapor solubility in vapor-liquid region

IF(TB.LT.TTP)THEN
IF(CVAPOR1.LE.C1)THEN
CLD1=C1-CVAPOR1
QMASS=HMASS*DB*((CVAPOR1+CVAPOR2)/2-CWALL)
C2=(CVAPOR1+CVAPOR2)/2-QMASS*PI*2.*R*DZ/MFLOW
C2=C2+CLD1
CLD2=CLD1
ENDIF
IF(CVAPOR1.GT.C1)THEN
ALPHA=HMASS*PI*R*DZ*DB/MFLOW
C2=(C1*(1-ALPHA)+2.*ALPHA*CWALL)/(1.+ALPHA)
QMASS=HMASS*DB*((C1+C2)/2.-CWALL)
ENDIF
C11=C2
ENDIF

C  This is calculation of mass flux QMASS=QMASSM+QMASSP in HT region
molecular mass transfer from vapor phase QMASSM
plus particle deposition QMASSP(no mass transfer between phases).

IF(TB.GE.TTP)THEN
If concentration of salt carried from LT region Cl 1 is higher than
solubility limit at bulk temp. csat2, particles are formed.
Concentration of salt in particles is affected only by particle
deposition—there is no mass transfer between particles and vapor phase
IF(CSAT2.LE.C11)THEN

Molecular mass transfer from vapor phase

QMASSM=HMASS*DB*((CSAT2+CSAT1)/2-CWALL)
C2=(CSAT2+CSAT1)/2-QMASSM*PI*2.*R*DZ/MFLOW
C11=C2

Particle deposition. Calculation of deposition velocity as given in
Papavergos et al. (1984). CBP2 is concentration of salt in particles
at the end of the step
CBP2=CP1+C11-CSAT2

VISKIN=VISW/DW
DIFFW=1.38E-23*TW/(3*PI*VISW*DIAMOL)
SC=VISKIN/DIFFW
VEL=MFLOW/(DB*PI*R**2)

Tube roughness
EPS=0.002
F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000)**1.11))**(-2)

Diameter of particles DIAP
DIAP=5E-6

TAUW=DB*VEL**2*F/8
USTAR=(TAUW/DW)**0.5
TAUP=SALTDENS*DIAP**2/(18*VISKIN*DWM)
TAUPPLUS=TAUP*USTAR**2/VISKIN
IF(TAUPPLUS.GT.20)THEN
VDSTAR=0.13
ELSE IF(TAUPPLUS.LT.0.2)THEN
VDSTAR=0.065*(SC)**(-0.6667)
ELSE
VDSTAR=3.5E-4*TAUPPLUS**2
ENDIF
VD=VDSTAR*USTAR
CPARTW=0
QMASSP=VD*DB*(CBP2-CPARTW)
CP2=CBP2-QMASSP*PI*2.*R*DZ/MFLOW
QMASS=QMASSM+QMASSP
ENDIF

If concentration of salt carried from LT region or of the dissolved salt
C11 is lower than
solubility limit at bulk temp. csat2, there is no new particle formation.
Concentration of salt in particles is affected only by particle
deposition—there is no mass transfer between particles and vapor phase.
Concentration of the dissolved salt is affected only by mass transfer from
the vapor phase
IF(CSAT2.GT.C11)THEN

   c Molecular mass transfer
   ALPHA=HMASS*PI*R*DZ*DB/MFLOW
   C2=(C11*(1.-ALPHA)+2.*ALPHA*CWALL)/(1.+ALPHA)
   QMASSM=HMASS*DB*((C11+C2)/2.-CWALL)
   C11=C2

c Particle deposition
   VISKIN=VISW/DW
   DIFFW=1.38E-23*TW/(3*PI*VISW*DIAMOL)
   SC=VISKIN/DIFFW
   VEL=MFLOW/(DB*PI*R**2)
   EPS=0.002
   F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000))**1.11))**(-2)
   DIAP=5E-6
   TAUW=DB*VEL**2*F/8
   USTAR=(TAUW/DW)**0.5
   TAUP=SALTDENS*DIAP**2/(18*VISKIN*DW)
   TAUPPLUS=TAUP*USTAR**2/VISKIN
   IF(TAUPPLUS.GT.20)THEN
      VDSTAR=0.13
   ELSE IF(TAUPPLUS.LT.0.2)THEN
      VDSTAR=0.065*(SC)**(-0.6667)
   ELSE
      VDSTAR=3.5E-4*TAUPPLUS**2
   ENDIF
   VD=VDSTAR*USTAR
   CPARTW=0
   QMASSP=VD*DB*(CP2-CPARTW)
   CP2=CP2-QMASSP*PI*2.*R*DZ/MFLOW
   QMASS=QMASSM+QMASSP

ENDIF

ENDIF

ENDIF

ENDIF

ENDIF

ENDIF

ENDIF

C~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

IF(MODEL.EQ.4) THEN

   c 4. MODEL WITH PARTICLE FORMATION AND MASS TRANSFER
   CBULK=C1
   CDEP=2.*HMASS/R
   PDEP=0.
   DELTIME=DZ*DB*PI*R**2./MFLOW
   T=TB1
   dTDT=(TB2-TB1)/DELTIME
   dddt=(DB2-DB1)/DELTIME
   IPhase=1
   CT1=C1+SALTDENS/DB1*VOLPART
   CALL moments(T,P,dTDT,visB,sigma,DIAMOL,SALTDENS,
                 CPARTW=0.
                 QMASSP=VD*DB*(CP2-CPARTW)
                 CP2=CP2-QMASSP*PI*2.*R*DZ/MFLOW
                 QMASS=QMASSM+QMASSP
                 ENDIF
                 ENDIF
                 ENDIF
                 ENDIF

C~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
IF(MODEL.EQ.5) THEN
  C5. MODEL WITHOUT MASS TRANSFER LIMITATIONS
  C  C2=CSAT2
  IF(C2.LT.C1) THEN
    QMASS=(C1-CSAT2)*MFLOW
  ELSE
    QMASS=0.
  END IF
ENDIF

WRITE(IONUM,200) TB,TW,HHEAT/1000.,HMASS*1000.,RE/1000.,
C2*1E6,T2*1E6,CSAT2*1E6
200 FORMAT(2F6.1,6F11.2)
RETURN
END
c THERMO.F IS A SUITE OF SUBROUTINES DEALING WITH THERMOPHYSICAL PROPERTIES
C AND HEAT TRANSFER IN SUPERCRITICAL WATER. THE ROUTINES IN THIS FILE INCLUDE:
c
C MASSTRAN - mass transfer coefficient
C HEAT - heat transfer coefficient
C TOFH - Temperature as a function OF H (enthalpy)
C PROP - calls the eqtest.f routines to return the most commonly
C used properties. It is a more convenient interface than
C calling the eqtest routines directly. Also gives K, visc
C TRANSPORT-gives conductivity and viscosity
C
C DIFFUSE - gives diffusivity by Stokes -Einstein and correction of
C Protopopov
C CORRECT - correction of the diffusivity as a funct of density
C given in Protopopov
C Sat - gives saturated wt. fraction for specified salt species.
C VCONC- gives saturation of vapor phase along vapor-liquid equilibrium
C curve for NaCl
C
C******************************************************************************
C SUBROUTINE MASSTRAN(HHEAT,TB,TW,DIA,HEMM,DC,VISB,
C DW,VISW,CPB,HB,HW,KB,KW,NM,CPBAR)
C calculates the masstransfer coefficient HMASS for a molecule of
C diameter DIA, given the heat transfer coefficient and the
C fluid properties
C The subroutine PROP calculates the relevant water properties at T,P
C Diffuse(T,visc,dia) calculates diffusion coeff. from Stokes-Einstein
C and uses correction factor of Protopopov
C******************************************************************************
REAI*8 HHEAT,TB,TW,DIA,HEMM
REAI*8 DB,HB,CPB,VISB
REAL*8 DW,HW,VISW,CPBAR,KB,KW
REAL*8 LEWIS,DIFFUSE
REAL*8 CPBAR,LEWIS
INTEGER NM

IF(TW.EQ.TB) THEN
  CPBAR=CPB
ELSE
  CPBAR=(HW-HB)/(TW-TB)
END IF

IF(NM.EQ.1) THEN
  LEWIS=KW/(DIFFUSE(TW,VISW,DW,DIA)*CPBAR*DW)
  HMASS=HHEAT/(DW*CPBAR*LEWIS**0.387)
ENDIF

IF(NM.EQ.2) THEN
  LEWIS=KB/(DIFFUSE(TB,VISB,DB,DIA)*CPBAR*DB)
  HMASS=HHEAT/(DB*CPBAR*LEWIS**0.52)
SUBROUTINE HEAT(QW,TB,P,DF,HB,VB,KB,PRB,DFLOW,R,
C TW,DF,HW,CPW,VBW,KW,PRW,HEAT,RE,NDEC,
C TTP)
C Routine that calculates the heat transfer coefficient HEAT, 
C wall temperature TW, and Reynolds number Re 
C and wall properties for a given bulk flow, and heat flux QW. 
C All units are SI, T in K 
C Correction of HEAT is given for NaCl deposition(ifNDEC.ne.1) 
C TTP is three phase equilib. temp. for NaCl 
C The subroutine PROP calculates the relevant water properties T,P 
C Swenson, Carver Karakia correlation is used here. 
C*****************************************************************************
REAL*8 QW,TB,P,MFLOW,R,TW,HEAT
REAL*8 DB,VB,KB,PRB,AREA
REAL*8 DF,HW,CPW,VBW,KW,PRW
REAL*8 RE,Nu
REAL*8 TTP,X,Y
INTEGER NDEC
TOL=0.1
C less than 0.1 deg. change in TW between iterations is required 
C for the final iteration.
AREA=3.14159*R**2
C*****************************************************************************
C Swenson & Carver correlation requires the wall density, so we will 
C have to iterate to get the Nusselt number 
DF=DB
PRBAR=PRB
K=KB
TWP=LST=TB
10 NU = 0.00459*(RE)**0.923*(PRBAR)**0.613*(DF/DB)**0.231
C NU=hD/k, where k is the wall conductivity 
HEAT=KW*NU/2./R
C wall properties: 
TW=TB+QW/HEAT
IF(ABS(TW-TWLAST).GT.TOL) THEN 
CALL PROP(TW,P,DF,HW,CPW,VBW,KW,PRW)
PRBAR=(HW-HB)/(TW-TB)*VISW/KW
RE=(RE+DFLOW*2.*R/(AREA*VISW))/2.
ENDIF
IF(NM.EQ.3)THEN
LEWIS=KW/(DIFFUSE(TW,VBW,DF,DIA)*CPW*DF)
HEAT=HEAT/(DF*CPW*LEWIS**0.52*(KB/KW)**0.52)*(VISW/VISB)**0.48
+(CPW/CPB)**0.48
ENDIF
RETURN
END
C*****************************************************************************
C*****************************************************************************
TWLAST=TW
GOTO 10
ENDIF

C Correction of heat transfer coefficient to account for the effect of salt
C (for NaCl)

X=TW-TTP

IF(NDEC.NE.1)THEN
  IF(TB.LT.TTP)THEN
    IF(X.GE.10.0)THEN
      Y=0.1*X-1
      HHEAT=HHEAT+Y
      TW=TB+QW/HHEAT
    ELSE
      HHEAT=HHEAT+Y
      TW=TB+QW/HHEAT
    ENDIF
  ELSE
    HHEAT=HHEAT+Y
    TW=TB+QW/HHEAT
  ENDIF
ENDIF
RETURN
END

REAL*8 FUNCTION TOFH(P,H,T)
C**************************************************************
C This function returns T(H,P) given an initial guess for T
C P in MPa, T in K, H in J/kg
C BDENS,DENS,HB are functions in the eqtest.f library
REAL*8 P,H,T
REAL*8 DS,D,HGUESS,BDENS,DENS,HB,CP,CPB,DT

10 DS = BDENS(T,P,0)
   D = DENS(P,T,DS,1.D-6)
   HGUESS=HB(T,D)*1000.
   CP=CPB(T,D)*1000.
   write(*,*) H,Hguess,T,CP
   DT=(H-Hguess)/CP
   T=T+DT
   IF(ABS(DT).GT.0.2) GOTO 10
   TOFH=T
RETURN
END

**********************************************************************
SUBROUTINE PROP(T,P,D,H,CP,VIS,K,PR)
**********************************************************************
C This routine calls the eqtest and other routines to get
the usual thermodynamic properties as a function of T and P
All are in SI, T IN K, P IN MPa
REAL*8 T,P,D,H,CP,VIS,K,PR,THK,VISC
REAL*8 DS
DOUBLE PRECISION BDENS, DENS, CPB, HB

DS = BDENS(T,P,0)
D = DENS(P,T,DS,1.D-6)
CALL TRANSPORT(T,P,VISC,THK)
VIS = VISC
K = THK
H = HB(T,D)*1000.
CP = CPB(T,D)*1000.
PR = vis*cp/K
RETURN
END

C***********************************************************************
REAL*8 FUNCTION DIFFUSE(T, VISC, DM, DIA)
c returns diffusion coefficient of a molecule using
  Stokes-Einstein, with all variables in SI.
C***********************************************************************
REAL*8 DM, DIFF, T, VISC, PI, BOLTZ, CORRECT, DIA
PARAMETER (PI = 3.14159265359, BOLTZ = 1.38E-23)

DIFF = BOLTZ*T/(3*PI*VISC*DIA)
DIFF = DIFF*CORRECT(DM)
DIFFUSE = DIFF
RETURN
END

C***********************************************************************
REAL*8 FUNCTION sat (SPECIES, TTP, T, P)
c returns wt FRACTION concentration at temp T(K), P (MPA)
C for several salt species.

Tc = T - 273
TTPl = TTP - 273
IF(SPECIES.EQ.'NA2SO4') THEN
  IF(Tc .LT. 385.8) THEN
    IF(TC.LT.339.) THEN
      TC=339.
      WRITE(*,*)' T TOO LOW IN CSAT; TC SET TO 339C'
    ENDIF
    A = log((Tc-337.70602)/49.11281)
    sat=-3.49612*A
  ELSE
    IF(Tc.LT. 388.5) THEN
      A = (Tc-385.645)*(log(1000*Tc**1.2))*32.19
      sat = 2.2/A
    ELSE
      sat=10.**(232.3458-.605186*Tc)
    END IF
  ENDIF
ELSE
  IF(Tc .LT. 388.5) THEN
    sat=10.**(232.3458-.605186*Tc)
  ELSE
    A = (Tc-385.645)*(log(1000*Tc**1.2))*32.19
    sat = 2.2/A
  END IF
ENDIF
sat = sat/100.
ELSE
IF (SPECIES.EQ.'NACl') THEN
ENDIF

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ETIME
RETURN
END

C********************************************************************
REAL*8 FUNCTION TINCONELK(TK)
C********************************************************************

IMPLICIT REAL*8 (A-Z)
TK2 = TK - 273.15
IF (TK2 .LT. 100) THEN
 THERMK625 = (TK2-23)/(100-23)*((11.4-9.8)+9.8
ELSE IF (TK2 .LT. 200) THEN
 THERMK625 = (TK2-100)/(200-100)*((13.4-11.4)+11.4
ELSE IF (TK2 .LT. 300) THEN
 THERMK625 = (TK2-200)/(300-200)*((15.5-13.4)+13.4
ELSE IF (TK2 .LT. 400) THEN
 THERMK625 = (TK2-300)/(400-300)*((17.6-15.5)+15.5
ELSE IF (TK2 .LT. 500) THEN
 THERMK625 = (TK2-400)/(500-400)*((19.6-17.6)+17.6
ELSE IF (TK2 .LT. 600) THEN

THERMK625 = (TK2-500)/(600-500)*(21.3-19.6)+19.6
ELSE IF (TK2 .GE. 600) THEN
THERMK625 = (TK2-600)/100*(21.3-19.6)+21.3
ENDIF
TINCONELK = THERMK625
RETURN
END

REAL*8 FUNCTION CRITICALT(P)
IMPLICIT REAL*8 (A-Z)
TPC1=647
DELTFC=1
DS=BDENS(TPC1,P,0)
DPC=DENS(P,TPC1,DS,1.D-6)
CP1=CPB(TPC1,DPC)

15 TPC2=TPC1+DELTFC
DS=BDENS(TPC2,P,0)
DPC=DENS(P,TPC2,DS,1.D-6)
CP2=CPB(TPC2,DPC)
CPDEL=ABS(CP2-CP1)
IF(CPDEL.GT.0.001)THEN
IF(CP2.GT.CP1)THEN
TPC1=TPC2
CP1=CP2
ELSE
DELTFC=DELTFC/10
ENDIF
ENDIF
GOTO 15
ENDIF
TPC=(TPC1+TPC2)/2
CRITICALT=TPC
RETURN
END

REAL*8 FUNCTION TGNTEL(TB,RE,R,PRB,KB,QW)
IMPLICIT REAL*8 (A-Z)
EPS=0.002
F = (1.8*LOG10(6.9/RE+(EPS/(3.7*2.*R*1000))**l.11))**(-2)
TNU=(F/8)*(RE-1000)*PRB/(1+12.7*((F/8)**(0.5))*(PP_3**(0.66667)-1))
HTCG=TNU*KB/2./R
TWTB = QW/HTCG
TWG = TB + TWTB
TGNTEL=TWG
RETURN
END

REAL*8 FUNCTION CORRECT(DM)
IMPLICIT REAL*8 (A-Z)
EF(DM.EQ.50.)THEN
C=l
ENDIF
IF(50.LT.DM. AND.DM.LE. 100)THEN
C=0.95+0.05/50.*(100-DM)
ENDIF
IF(100.LT.DM.AND.DM.LE.150)THEN
C=0.85+0.1/50.*(150-DM)
ENDIF
IF(150.LT.DM.AND.DM.LE.200)THEN
C=0.75+0.1/50.*(200-DM)
ENDIF
IF(200.LT.DM.AND.DM.LE.250)THEN
C=0.6+0.15/50.*(250-DM)
ENDIF
IF(250.LT.DM.AND.DM.LE.300)THEN
C=0.3+0.3/50.*(300-DM)
ENDIF
IF(300.LT.DM.AND.DM.LE.350)THEN
C=0.05+0.25/50.*(350-DM)
ENDIF
IF(350.LT.DM.AND.DM.LE.400)THEN
C=0.2-0.15/50.*(400-DM)
ENDIF
IF(400.LT.DM.AND.DM.LE.450)THEN
C=0.5-0.3/50.*(450-DM)
ENDIF
IF(450.LT.DM.AND.DM.LE.500)THEN
C=0.65-0.15/50.*(500-DM)
ENDIF
IF(500.LT.DM.AND.DM.LE.550)THEN
C=0.85-0.05/50.*(550-DM)
ENDIF
IF(550.LT.DM.AND.DM.LE.600)THEN
C=0.85-0.05/50.*(550-DM)
ENDIF
IF(600.LT.DM.AND.DM.LE.650)THEN
C=0.85-0.05/50.*(650-DM)
ENDIF
IF(650.LT.DM.AND.DM.LE.700)THEN
C=0.88-0.05/50.*(650-DM)
ENDIF
IF(700.LT.DM.AND.DM.LE.750)THEN
C=0.9-0.03/50.*(700-DM)
ENDIF
IF(750.LT.DM.AND.DM.LE.800)THEN
C=0.94-0.04/50.*(800-DM)
ENDIF
IF(DM.GT.800)THEN
C=1.
ENDIF
CORRECT=C
RETURN
END

REAL*8 FUNCTION VCONC(TB,P)
IMPLICIT REAL*8 (A-Z)
TBC=TJ3-273.15
TTP=0.1136*P*P+0.9077*P+356.16
PRESSURE HAS TO BE GREATER THAN 23.75 AND LOWER THAN 26.25 MPa

IF(ABS(P-24.)LE.0.25)THEN

IF(TBC.EQ.390)THEN
  VC=0.115
ENDIF

IF(390.LT.TBC.AND.TBC.LE.400)THEN
  VC=0.068+0.047/10.*((400-TBC)
ENDIF

IF(400.LT.TBC.AND.TBC.LE.410)THEN
  VC=0.05+0.018/10.*(400-TBC)
ENDIF

IF(410.LT.TBC.AND.TBC.LE.420)THEN
  VC=0.037+0.013/10.*(410-TBC)
ENDIF

IF(420.LT.TBC.AND.TBC.LE.430)THEN
  VC=0.03+0.007/10.*(420-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.TTP)THEN
  VC=0.025+0.005/(TTP-430)*(TTP-TBC)
ENDIF

ENDIF

IF(ABS(P-24.5).LE.0.25)THEN

IF(TBC.EQ.390)THEN
  VC=0.165
ENDIF

IF(390.LT.TBC.AND.TBC.LE.400)THEN
  VC=0.083+0.082/10.*((400-TBC)
ENDIF

IF(400.LT.TBC.AND.TBC.LE.410)THEN
  VC=0.06+0.023/10.*(410-TBC)
ENDIF

IF(410.LT.TBC.AND.TBC.LE.420)THEN
  VC=0.043+0.017/10.*(420-TBC)
ENDIF

IF(420.LT.TBC.AND.TBC.LE.430)THEN
  VC=0.035+0.008/10.*(430-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.TTP)THEN

...
VC=0.029+0.006/(TTP-430)*(TTP-TBC)
ENDIF

ENDIF

IF(ABS(P-25.).LE.0.25)THEN

IF(TBC.EQ.390)THEN
VC=0.24
ENDIF

IF(390.LT.TBC.AND.TBC.LE.400)THEN
VC=0.1+0.14/10.*(400-TBC)
ENDIF

IF(400.LT.TBC.AND.TBC.LE.410)THEN
VC=0.068+0.032/10.*(410-TBC)
ENDIF

IF(410.LT.TBC.AND.TBC.LE.420)THEN
VC=0.05+0.018/10.*(420-TBC)
ENDIF

IF(420.LT.TBC.AND.TBC.LE.430)THEN
VC=0.041+0.009/10.*(430-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.TTP)THEN
VC=0.03+.004/(TTP-440)*(TTP-TBC)
ENDIF

ENDIF

IF(ABS(P-25.5).LE.0.25)THEN

IF(TBC.EQ.390)THEN
VC=0.5
ENDIF

IF(390.LT.TBC.AND.TBC.LE.400)THEN
VC=0.128+0.372/10.*(400-TBC)
ENDIF

IF(400.LT.TBC.AND.TBC.LE.410)THEN
VC=0.084+0.044/10.*(410-TBC)
ENDIF

IF(410.LT.TBC.AND.TBC.LE.420)THEN
VC=0.06+0.024/10.*(420-TBC)
ENDIF

IF(420.LT.TBC.AND.TBC.LE.430)THEN
VC=0.041+0.009/10.*(430-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.TTP)THEN
VC=0.03+.004/(TTP-440)*(TTP-TBC)
ENDIF

ENDIF
VC=0.048+0.012/10.*(430-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.440)THEN
VC=0.039+0.009/10.*(440-TBC)
ENDIF

IF(440.LT.TBC.AND.TBC.LE.TTP)THEN
VC=0.035+0.004/(TTP-440)*(TTP-TBC)
ENDIF

ENDIF

IF(ABS(P-26.).LE.0.25)THEN

IF(400.LT.TBC.AND.TBC.LE.410)THEN
VC=0.1+0.07/10.*(410-TBC)
ENDIF

IF(410.LT.TBC.AND.TBC.LE.420)THEN
VC=0.068+0.032/10.*(420-TBC)
ENDIF

IF(420.LT.TBC.AND.TBC.LE.430)THEN
VC=0.055+0.013/10.*(430-TBC)
ENDIF

IF(430.LT.TBC.AND.TBC.LE.440)THEN
VC=0.046+0.009/10.*(440-TBC)
ENDIF

IF(440.LT.TBC.AND.TBC.LE.TTP)THEN
VC=0.04+0.006/(TTP-440)*(TTP-TBC)
ENDIF

ENDIF

VCONC=VC/100.

RETURN
END
SUBROUTINE DISCRETE(P,NSEGMENT,ZSEG,QSEG,TSEG,IONUM,
             IREF,DZ,MFLOW,RADIUS,TBULK,Q,TAU)

This routine interpolates heat transfer and temperatures to DZ resolution,
given information for a number (NSEGMENT) of segments of unequal length.
For each segment, you need the starting axial position ZSEG, the heat flux
per length kW/m Qseg and the temperature TSEG at ZSEG. This overspecifies
the problem, so the heat flux is only used if the starting or ending
temperature for a segment is unspecified (entered as a negative number).
P is the system pressure.
TAU is the system residence time
Q is the heat flux per unit area

REAL*8 ZSEG(20),QSEG(20),TSEG(20),DELTAH(20)
REAL*8 P,DZ,MFLOW,T1,T2,H1,H2,D,CP,VIS,K,PR,RADIUS
REAL*8 TOFH,L,DI,PI,TAU,Re
PARAMETER (PI = 3.14159265359)
INTEGER I,NSEGMENT,IREF,J,N,NI,IONUM

C examine reactor segment by segment and find enthalpy change relative to
z=0
DO 100 I=1,NSEGMENT
  L=ZSEG(I+1)-ZSEG(I)
  IF((TSEG(I).LT.0).OR.(TSEG(I+1).LT.0)) THEN
    C rely on the nominal heat flux to find enthalpy change
    DELTAH(I)=L*QSEG(I)/MFLOW
  ELSE
    T1=TSEG(I)
    T2=TSEG(I+1)
    CALL PROP(T1,P,D,H1,CP,VIS,K,PR)
    CALL PROP(T2,P,D,H2,CP,VIS,K,PR)
    DELTAH(I)=(H2-H1)/1000.
  END IF
  write(IONUM,20) I,zseg(i),L,qseg(i),tseg(i),deltah(i)
20   format(i3,5fl2.3)
100  CONTINUE
C Now use the reference temperature and position stored for segment IREF
II=ZSEG(IREF)/DZ+1.1
T1=TSEG(IREF)
TBULK(II)=T1
CALL PROP(T1,P,D,H1,CP,VIS,K,PR)
HBULK(II)=H1/1000.
C Work forward from the position with the known temperature
DO 200 I=IREF,NSEGMENT
  L=ZSEG(I+1)-ZSEG(I)
  NI=L/DZ+.1
  II=ZSEG(I)/DZ+1.1
  DH=DELTAH(I)/NI
  DO 150 J=II+1,II+NI
    HBULK(J)=HBULK(J-1)+DH
    H1=1000.*HBULK(J)
    T1=TOFH(P,H1,T1)
    TBULK(J)=T1
c work backward from the position of known temperature
DO 300 I=IREF,2,-1
   L=ZSEG(I)-ZSEG(I-1)
   NI=L/DZ+.5
   II=ZSEG(I)/DZ+.1
   DH=DELTAH(I-1)/NI
   DO 250 J=II,II-.NI,-1
      HBULK(J)=HBULK(J+1)-DH
      H1=1000*HBULK(J)
      T1=TOFH(P,H1,T1)
      TBULK(J)=T1
250 CONTINUE
300 CONTINUE

c Now go back over the whole length to find heat flux at each section
c and integrate to find the residence time TAU

TAU=0
NI=ZSEG(NSEGMENT+1)/DZ+.5
DO 400 J=1,NI
   Q(J)=(HBULK(J+1)-HBULK(J))*MFLOW/(DZ*PI*RADIUS*2)
   T1=(TBULK(J+1)+TBULK(J))/2.
   CALL PROP(T1,P,D,H1,CP,VIS,K,PR)
   TAU=TAU+PI*RADIUS**2.*DZ*D/MFLOW
   Re=Mflow*2.*Radius/(PI*Radius**2.)/vis
   write(IONUM,399) J,TBULK(J),HBULK(J),Q(J),D,Re/1000.
399 FORMAT(I4,F10.1,F11.1,F12.1,F12.1,F10.1)
400 continue
RETURN
END
subroutine TRANSPORT(T,P,VISC,THK)
C Written by Majid Bazargan
C GIVEN T AND P, THIS ROUTINE CALCULATES VISCOSITY AND
C THERMAL CONDUCTIVITY OF WATER. "EQTEST.F" MUST BE
C ATTACHED TO THE MAIN PROGRAM USED IN CONJUNCTION WITH
C ROUTINE.
C
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER (I-N)
REAL*8 ACOEF(4),BCOEF(6,7),ECOEF(4),FCOEF(5,6)
C
COMMON/CCPEQ/TCEQ,PCEQ,DCEQ
COMMON/CSUB2/R,XMOL,TC,PC,DC
COMMON/CNORM/TNORM,DNORM
COMMON/CSUB3/TTR,PTR,DLTR,DVTR,TBOYL,PBOYL,DLB,DVB
COMMON/COUT/NIN,NOUT
C
BRO=BDENS(T,P,0)
RO=DENS(P,T,BRO,1.D-6)
C
TSTAR = 647.27
ROSTAR= 317.763
PSTAR=22.115E06
VISTAR=55.071E-6
THKSTAR = 0.4945
C
TBAR = T/TSTAR
ROBAR = RO / ROSTAR
PBAR = P/PSTAR

DELP = 0.2
P0 = P
P1 = P + DELP
P2 = P + 2*DELP
P3 = P + 3*DELP
P4 = P + 4*DELP
RO0 = RO
BRO1=BDENS(T,P1,0)
RO1=DENS(P1,T,BRO1,1.D-6)
BRO2=BDENS(T,P2,0)
RO2=DENS(P2,T,BRO2,1.D-6)
BRO3=BDENS(T,P3,0)
RO3=DENS(P3,T,BRO3,1.D-6)
BRO4=BDENS(T,P4,0)
RO4=DENS(P4,T,BRO4,1.D-6)

DELRO0=RO1-RO0
DELRO1=RO2-RO1
DELRO2=RO3-RO2
DELRO3=RO4-RO3
C
DEL2RO0=DELRO1-DELRO0
\[ \text{DEL2RO1} = \text{DELRO2} - \text{DELRO1} \]
\[ \text{DEL2RO2} = \text{DELRO3} - \text{DELRO2} \]
\[ \text{C} \]
\[ \text{DEL3RO0} = \text{DEL2RO1} - \text{DEL2RO0} \]
\[ \text{DEL3RO1} = \text{DEL2RO2} - \text{DEL2RO1} \]
\[ \text{C} \]
\[ \text{DEL4RO0} = \text{DEL3RO1} - \text{DEL3RO0} \]
\[ \text{C} \]
\[ \text{DRODP} = (\text{DELRO0} - (0.5 \times \text{DEL2RO0}) + (\text{DEL3RO0}/3) - (\text{DEL4RO0}/4))/\text{DELP} \]
\[ \text{XTBAR} = \text{ROBAR} \times \text{PSTAR} \times \text{DRODP} / \text{ROSTAR} \]
\[ \text{C} \]
\[ \text{ACOEF(1)} = 1.000000 \]
\[ \text{ACOEF(2)} = 0.978197 \]
\[ \text{ACOEF(3)} = 0.579829 \]
\[ \text{ACOEF(4)} = -0.202354 \]
\[ \text{C} \]
\[ \text{BCOEF(1,1)} = 0.513204 \]
\[ \text{BCOEF(1,2)} = 0.215177 \]
\[ \text{BCOEF(1,3)} = -0.281810 \]
\[ \text{BCOEF(1,4)} = 0.177806 \]
\[ \text{BCOEF(1,5)} = -0.041766 \]
\[ \text{BCOEF(1,6)} = 0.000000 \]
\[ \text{BCOEF(1,7)} = 0.000000 \]
\[ \text{BCOEF(2,1)} = 0.320565 \]
\[ \text{BCOEF(2,2)} = 0.731788 \]
\[ \text{BCOEF(2,3)} = -1.070786 \]
\[ \text{BCOEF(2,4)} = 0.460504 \]
\[ \text{BCOEF(2,5)} = 0.000000 \]
\[ \text{BCOEF(2,6)} = -0.01578386 \]
\[ \text{BCOEF(2,7)} = 0.000000 \]
\[ \text{BCOEF(3,1)} = 0.000000 \]
\[ \text{BCOEF(3,2)} = 1.2410440 \]
\[ \text{BCOEF(3,3)} = -1.263184 \]
\[ \text{BCOEF(3,4)} = 0.2340379 \]
\[ \text{BCOEF(3,5)} = 0.000000 \]
\[ \text{BCOEF(3,6)} = 0.000000 \]
\[ \text{BCOEF(3,7)} = 0.000000 \]
\[ \text{BCOEF(4,1)} = 0.000000 \]
\[ \text{BCOEF(4,2)} = 1.476783 \]
\[ \text{BCOEF(4,3)} = 0.000000 \]
\[ \text{BCOEF(4,4)} = -0.4924179 \]
\[ \text{BCOEF(4,5)} = 0.1600435 \]
\[ \text{BCOEF(4,6)} = 0.000000 \]
\[ \text{BCOEF(4,7)} = -0.003629481 \]
\[ \text{BCOEF(5,1)} = -0.7782567 \]
\[ \text{BCOEF(5,2)} = 0.000000 \]
\[ \text{BCOEF(5,3)} = 0.000000 \]
\[ \text{BCOEF(5,4)} = 0.000000 \]
\[ \text{BCOEF(5,5)} = 0.000000 \]
\[ \text{BCOEF(5,6)} = 0.000000 \]
\[ \text{BCOEF(5,7)} = 0.000000 \]
\[ \text{BCOEF(6,1)} = 0.1885447 \]
\[ \text{BCOEF(6,2)} = 0.000000 \]
\[ \text{BCOEF(6,3)} = 0.000000 \]
\[ \text{BCOEF(6,4)} = 0.000000 \]
B(6,5) = 0.000000
B(6,6) = 0.000000
B(6,7) = 0.000000

EC(1) = 1.000000
EC(2) = 6.978267
EC(3) = 2.599096
EC(4) = 0.998254

FC(1,1) = 1.3293046
FC(1,2) = -0.40452437
FC(1,3) = 0.24409490
FC(1,4) = 0.018660751
FC(1,5) = -0.12961068
FC(1,6) = 0.044809953
FC(1,7) = 0.0000000
FC(2,1) = 1.7018363
FC(2,2) = -2.2156845
FC(2,3) = 1.6511057
FC(2,4) = -0.76736002
FC(2,5) = 0.37283344
FC(2,6) = -0.11203160
FC(2,7) = 0.0000000
FC(3,1) = 5.2246158
FC(3,2) = -10.124111
FC(3,3) = 4.9874687
FC(3,4) = -0.27297694
FC(3,5) = -0.43083393
FC(3,6) = 0.13338849
FC(3,7) = -8.7127675
FC(4,1) = -9.5000611
FC(4,2) = 4.3786666
FC(4,3) = -0.91783782
FC(4,4) = 0.0000000
FC(4,5) = 0.0000000
FC(4,6) = 0.0000000
FC(4,7) = -1.8525999
FC(5,1) = 0.93404690
FC(5,2) = 0.0000000
FC(5,3) = 0.0000000
FC(5,4) = 0.0000000
FC(5,5) = 0.0000000
FC(5,6) = 0.0000000

C

C CALCULATIONS FOR VISCOSITY; VISC=VISC0*VISC1*VISC2

V0 = 0.0
DO 21 K=1,4
KK=K-1
V0 = V0 + ACOEF(K)/(TBAR**KK)
21 CONTINUE
VISC0 = (SQRT(TBAR))/V0

V1 = 0.0
DO 23 I=1,6
II=I-1
DO 22 J=1,7
JJ=J-1
V1 = V1 + B(1,1)**II)**JJ)**((ROBAR-1)**JJ)
22 CONTINUE
22 CONTINUE
23 CONTINUE
VISC1 = EXP(ROBAR*V1)
C
VISC2 = 1
C
XBART = ROBAR*DRODP
C
IF((TBAR.GE.0.997.AND.TBAR.LE.1.0082).OR.
C  + (ROBAR.GE.0.775.AND.ROBAR.LE.1.290))THEN
C
IF(XBART.GE.21.93)THEN
C
VISC2 = 0.992*(XBART**0.0263)
C
ENDIF
C
ENDIF
C
VISC = VISTAR*VISC0*VISC1*VISC2
C
C CALCULATIONS FOR THERMAL CONDUCTIVITY; THK = THK0*THK1 + THK2
C
TH0 = 0.0
DO 31 L=1,4
LL = L - 1
TH0 = TH0 + ECOEF(L)/(TBAR**LL)
31 CONTINUE
THK0 = SQRT(TBAR)/TH0
C
TH1 = 0.0
DO 33 M=1,5
MM = M - 1
DO 32 N=1,6
NN = N - 1
TH1 = TH1 + FCOEF(M,N)*((1/TBAR - 1)**MM)*((ROBAR - 1)**NN)
32 CONTINUE
33 CONTINUE
THK1 = EXP(ROBAR*TH1)
C
TO CALCULATE THK2, del(P)/del(T) AT CONSTANT DENSITY IS REQUIRED
LIKEWISE del(RO)/del(P), NEWTON'S FORMULA IS USED:
C
DELT = 0.5
T0 = T
T1 = T+DELT
T2 = T+2*DELT
T3 = T+3*DELT
T4 = T+4*DELT
P0 = P
P1 = PB(T1,RO)
P2 = PB(T2,RO)
P3 = PB(T3,RO)
P4 = PB(T4,RO)
C
DELP0 = P1 - P0
DELP1 = P2 - P1
DELP2 = P3 - P2
DELP3 = P4 - P3
C
DELP2P0 = DELP1 - DELP0
DEL2P1 = DELP2 - DELP1
DEL2P2 = DELP3 - DELP2
C
DEL3P0 = DEL2P1 - DEL2P0
DEL3P1 = DEL2P2 - DEL2P1
C
DEL4P0 = DEL3P1 - DEL3P0
C
DPDT = (DELP0 - (0.5 * DEL2P0) + (DEL3P0 / 3) - (DEL4P0 / 4)) / DELT
C
ONE = (0.0013848 * SQRT(ROBAR)) / (VISC0 * VISC1)
C
TWO = ((TBAR / ROBAR) * (DPDT * TSTAR / PSTAR))**2
THREE = XTBAR**0.4678
FOUR = EXP((-18.66 * (TBAR - 1)**2) - (ROBAR - 1)**4)
THK2 = ONE * TWO * THREE * FOUR
C
THK = THKSTAR * (THK0 * THK1 + THK2)
C
RETURN
END
PROGRAM NUSLTB3
C Written by Majid Bazargan
C THIS PROGRAM CALCULATES HEAT TRANSFER COEFFICIENTS BASED ON FEW
C NUSSELT NUMBER CORRELATIONS.
C INPUT: Tb, P, flow and qflux, OUTPUT: Tw and HTC
C Tw MUST BE GREATER THAN Tb (HEATING).
C PETUKHOV ET AL.'S CORRELATION IS INCLUDED.
C SUBROUTINE TRANSPORT IS USED TO CALCULATE TRANSPORT PROPERTIES.
C
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER (I-N)
C
C THE FOLLOWING COMMON STATEMENTS ARE USED IN EQTEST PROGRAM WHICH
C CALCULATES THE THERMODYNAMIC PROPERTIES OF WATER.
C
COMMON/CCPEQ/TCEQ,PCEQ,DCEQ
COMMON/CSUB2/R,XMOL,TC,PC,DC
COMMON/CNORM/TNORM,DNORM
COMMON/CSUB3/TTR,PTR,DLTR,DVTR,TBOYL,PBOYL,DLB,DVB
COMMON/COUT/NIN,NOUT
C
C OUTPUT FILE IS:
C
OPEN(UNIT=9,FILE='nusbo58.TXT')
OPEN(UNIT=8,FILE='nusbin58.TXT')
C
C WRITE THE HEADER OF THE OUTPUT FILE:
C
WRITE(9,91)
91 FORMAT(9,91)

DIA=0.006272
PI=3.14159265359
RO=0.0048
RI=0.003136
A=RI/RO
AA=(A**2-LOG(A**2)-1)/(1-A**2)
C
C GEOMETRIC PARAMETERS. "AA" WILL BE USED IN CALCULATION OF INNER SURFACE
C TEMPERATURE FROM MEASURED OUTER SURFACE TEMPERATURE.
C
IF(T.LE.85)STOP
C
C READ P[MPa], T[degC], QFLUX[Kw/m2], FLOW[kG/s]
11 Read (8,*)T,P,QFLUX,FLOW
C
CHANGE OF UNITS
IF(T.LE.85)STOP
T = T + 273.15

C CALCULATE PSEUDOCRITICAL TEMPERATURE CORRESPONDING TO P. THIS
C INFORMATION WILL BE NEEDED LATER IN NUSSEL NUMBER CALCULATIONS.

IF(P.LT.22) THEN
WRITE(*,*) 'THIS IS NOT A CASE WITH SUPERCRITICAL PRESSURE'
WRITE(*,*) 'USE ANOTHER METHOD OF SOLUTION WHICH DOES NOT REQUIRE'
WRITE(*,*) 'CALCULATION OF PSEUDOCRITICAL TEMPERATURE.'
STOP
ENDIF

TPC1 = 647
DELTPC = 1
DS = BDENS(TPC1, P, 0)
DPC = DENS(P, TPC1, DS, 1.D-6)
CP1 = CPB(TPC1, DPC)

15 TPC2 = TPC1 + DELTPC
DS = BDENS(TPC2, P, 0)
DPC = DENS(P, TPC2, DS, 1.D-6)
CP2 = CPB(TPC2, DPC)
CPDEL = ABS(CP2 - CP1)
IF(CPDEL.GT.0.001) THEN
  IF(CP2.GT.CP1) THEN
    TPC1 = TPC2
    CP1 = CP2
  ELSE
    DELTPC = DELTPC / 10
  ENDIF
GOTO 15
ENDIF

C PROPERTIES AT Pseudo Critical (PC) TEMPERATURE:

TPC = (TPC1 + TPC2) / 2
CPPC = (CP1 + CP2) / 2
call transport(TPC, P, VISQTHK)
VISCPC = VISC * 1000000
THERMKPC = THK * 1000

C THERMKPC = VISCOSITY(TPC, P)
C PRPC = CPPC * VISCPC / THERMKPC

C BULK PROPERTIES AND NON-DIMENSIONALIZED NUMBERS

RHOS = BDENS(T, P, 0)
RHO = DENS(P, T, RHOS, 1.D-6)
H = HB(T, RHO)
call transport(t, p, visc, thk)
VISCb = VISC * 1000000
THERMKb = THK * 1000

C THERMKb = TCONDUCT(T, P)
C VISCb = VISCOSITY(T, P)
C CP = CPB(T, RHO)
C RE = REYN(FLOW, DIA, VISCb)
C PR = PRAN(VISCb, CP, THERMKb)
FEW NUSSELT NUMBER CALCULATION IS USED TO CALCULATE THE INNER WALL TEMPERATURE, TWG, AS WELL AS LOCAL HEAT TRANSFER COEFFICIENT

(A) GNIELINSKY

\[ F = FRICTION(RE,DIA) \]
\[ TNU5 = TNUSCLASSIC(RE,PR,F) \]
\[ HTCG = TNU5 \times \text{THERMKb} / (DIA \times 1000) \]
\[ TWTB = QFLUX \times 1000 / HTCG \]
\[ TWG = T + TWTB \]
\[ CTWG = TWG - 273.15 \]
\[ \text{WRITE}(*,*)CTWG \]

(B) shitsman-miropolski

\[ PRMIN = PR \]
\[ TNUK = 0.023 \times RE^{0.8} \times PRMIN^{0.8} \]
\[ HTCK = TNUK \times \text{THERMKb} / (DIA \times 1000) \]
\[ TWTB = QFLUX \times 1000 / HTCK \]
\[ TWK = T + TWTB \]
\[ BRHOK = BDENS(TWK,P,0) \]
\[ RHOK = DENS(P,TWK,BRHOK,1,D-6) \]
call transport(TWK,P,VISC,THK)
\[ VISCK = VISC \times 1000000 \]
\[ THERMKK = THK \times 1000 \]
\[ \text{C THERMKK = TCONDUCT(TWK,P)} \]
\[ \text{C VISCK = VISCOSITY(TWK,P)} \]
\[ CPK = CPB(TWK,RHK) \]
\[ PRK = VISCK \times CPK / THERMKK \]
\[ \text{IF(PRK.GE.PR)GOTO 14} \]
\[ PRMIN = PRK \]
\[ TNUK2 = 0.023 \times RE^{0.8} \times PRMIN^{0.8} \]
\[ HTCK2 = TNUK2 \times \text{THERMKb} / (DIA \times 1000) \]
\[ TWTB = QFLUX \times 1000 / HTCK2 \]
\[ TWK2 = T + TWTB \]
\[ TWDEF = TWK2 - TWK \]
\[ \text{IF(ABS(TWDEF).LT.0.1)THEN} \]
\[ \text{HTCK = HTCK2} \]
\[ \text{GOTO 14} \]
\[ \text{ENDIF} \]
\[ BRHOK2 = BDENS(TWK2,P,0) \]
\[ RHOK2 = DENS(P,TWK2,BRHOK2,1,D-6) \]
call transport(TWK2,P,VISC,THK)
\[ VISCK2 = VISC \times 1000000 \]
\[ THERMKK2 = THK \times 1000 \]
\[ \text{C THERMKK2 = TCONDUCT(TWK2,P)} \]
\[ \text{C VISCK2 = VISCOSITY(TWK2,P)} \]
\[ CPK2 = CPB(TWK2,RHK) \]
\[ PRK2 = VISCK2 \times CPK2 / THERMKK2 \]
\[ PRMIN = PRK2 \]
\[ TWK = TWK2 \]
\[ HTCK = HTCK2 \]
\[ \text{GOTO 12} \]
\[ CTWK = TWK - 273.15 \]
\[ \text{WRITE}(*,*)CTWK \]
C (C) JACKSON-FEWSTER
C IF(P,LT,22.1)GOTO 18
TWJ = TWG
17 DSW = BDENS(TWJ,P,0)
DW = DENS(P,TWJ,DSW,1.D-6)
HW = HB(TWJ,DW)
TNU4=TNUS4(TPC,HW,TWJ,T,RE,PR,DW,RHO,CP)
HTCJ=TNU4*THERMKb/(DIA*1000)
TWTB=QFLUX*1000/HTCJ
TWNEXT = T + TWTB
DELTW = TWNEXT-TWJ
IF (ABS(DELTW) .GT. 0.1) THEN
    TWJ = TWJ + (DELTW/10)
C    TWJ = TWNEXT
    GOTO 17
END IF
CTWJ = TWJ - 273.15
WRITE(*,*)CTWJ
C (D) SWENSON ET AL.
C TWS = TWG
18 DSW = BDENS(TWS,P,0)
DW = DENS(P,TWS,DSW,1.D-6)
HW = HB(TWS,DW)
call transport(TWS,P,VISC,THK)
VISCW=VISC*1000000
THERMKW=THK*1000
c THERMKW = TCONDUCT(TWS,P)
c VISCW = VISCOSITY(TWS,P)
REW = REYN(FLOW,DIA,VISCW)
PRW = (HW - H)/(TWS-T) * VISCW/THERMKW
TNU1 = 0.00459*(REW)**0.923*(PRW)**0.613*(DW/RHO)**0.231
HTCS=TNU1*THERMKW/(DIA*1000)
TWTB=QFLUX*1000/HTCS
TWNEXT = T + TWTB
DELTW = TWNEXT-TWS
IF (ABS(DELTW) .GT. 0.1) THEN
    TWS = TWS + (DELTW/10)
C    TWS = TWNEXT
    GOTO 18
END IF
CTWS = TWS - 273.15
WRITE(*,*)CTWS
C (E) YAMAGATA ET AL.
C NCHANGE=0
TWY = TWG
E = (TPC-T)/(TWY-T)
19 DSW = BDENS(TWY,P,0)
DW = DENS(P,TWY,DSW,1.D-6)
HW = HB(TWY,DW)
CPBAR = (HW-H)/(TWY-T)
TNU3 = TNUS3(RE,PR,E,CPBAR,CP,PRPC)
HTCY=TNU3*THERMKb/(DIA*1000)
TWTB=QFLUX*1000/HTCY
TWNEXT = T + TWTB
DELTW=TWNEXT-TWY

C SINCE NUSSELT NUMBER IS CALCULATED DIFFERENTLY AT VARIOUS RANGE
C OF TEMPERATURES, IT MAY HAPPEN THAT WALL TEMPERATURE ITERATION DOES
C NOT CONVERGE. IN SUCH CASES ITERATION IS CUT AFTER 10 TIMES. THEN,
C THE ESTIMATE FOR WALL TEMPERATURE SHOULD BE ACCEPTABLE, BUT THERE
C WILL BE SOME DOUBTS ON ACCURACY OF NUSSELT NUMBER CALCULATED THIS
C WAY.

C IF (ABS(DELTW) .LE. 0.05) THEN
   E2=(TPC-T)/(TWY-T)
   IF((E.GT.l.AND.E2.GT.l).OR.(E.LT.0.AND.E2.LT.0))GOTO 191
   IF((E.LE.l.AND.E.GE.0).AND.(E2.LE.l.AND.E2.GE.0))GOTO 191
   NCHANGE=NCHANGE+1
   IF(NCHANGE.GE.10)GOTO 191
   E=(E+E2)/2
   TWY=(TPC-T)/E + T
ELSE
   TWY = TWY + (DELTW/10)
   END IF
GOTO 19

191 CTWY = TWY-273.15
WRITE(*,*)CTWY

C (F) PETUKHOV ET AL.

TWP=TWG
20 DSW=BDENS(TWP,P,0)
   DW = DENS(P,TWP,DSW,1.D-6)
   HW = HB(TWP,DW)
call transport(TWP,P,VISC,THK)
   VISCW=VISC*1000000
   THERMKW=THK*1000
   THERMKW = TCONDUCT(TWP,P)
   VISCW = VISCOSITY(TWP,P)
   CPBAR = (HW - H)/(TWP-T)
   ZETA = 1/(1.82*LOG10(RE)-1.64)**2
   TERM1=(ZETA*RE*PR*)((VISCb/VISCW)**0.11)8
   TERM2=12.7*(SQRT(ZETA/8)*(PR**0.66667-1))+1.07
   TERM3=((THERMKW/THERMKb)**0.33)*((CPBAR/CP)**0.35)
   TNUP=TERM1*TERM3/TERM2
   HTCP=TNUP*THERMKb/(DIA*1000)
   TWTB=QFLUX*1000/HTCP
   TWNEXT = T + TWTB
   DELTW=TWNEXT-TWP
   IF (ABS(DELTW) .GT. 0.1) THEN
      TWP = TWP + (DELTW/10)
   END IF
CTWP = TWP - 273.15
WRITE(*,*)CTWP
WRITE(*,*)CCCCCCCCCCCCCCCCCC

C
C PREPARING DATA FOR OUTPUT FILE:
C
TB=T-273.15
WRITE(9,93)flow,qflux,p,H,TB,CTWG,HTCJ/1000,CTWS,HTCS/1000,CTWY,ITrCY/1000
CTWP,HTCP/1000
93 FORMAT(1X,F7.4,1X,3(F7.2,lX),F5.1,6(lX,F5.1,lX,F6.2))
GOTO 11
C
STOP
END

ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc

REAL*8 FUNCTION REYN(FLOW,DIA,VISC)
IMPLICIT REAL* 8 (A-H,0-Z)
PI = 3.14159265359
RE = 4*FLOW/(PI*DIA*VISC)*1000000
REYN = RE
RETURN
END

C******************************************
REAL*8 FUNCTION PRAN(VISC,CP,THERMK)
IMPLICIT REAL*8 (A-H,0-Z)
PR = CP*VISC/THERMK
PRAN = PR
RETURN
END

C***************************************
REAL*8 FUNCTION TNUS3(RE,PR,E,CPBAR,CP,PRPC)
IMPLICIT REAL*8 (A-H,O-Z)
CN1=-0.77*(1+1/PRPC)+1.49
CN2= 1.44*(1+1/PRPC)-0.53
IF(E.GT.1)THEN
FC=1
ELSE IF(E.GE.0.AND.E.LE.1)THEN
FC=0.67*(PRPC)**(-0.05)*(CPBAR/CP)**CN1
ELSE IF(E.LT.0)THEN
FC=(CPBAR/CP)**CN2
ENDIF
TNU = 0.0135*(RE)**0.85*(PR)**0.8*FC
TNUS3=TNU
RETURN
END

C****************************************
REAL*8 FUNCTION TNUS4(TPC,HW,H,TW,T,RE,PR,DW,D,CP)
IMPLICIT REAL*8 (A-H,O-Z)
CPBAR=(HW-H)/(TW-T)
TLIM=1.2*TPC
IF(TW.LE.TPC.OR.T.GE.TLIM)THEN
CN=0.4
ELSE IF(T.LE.TPC.AND.TPC.LT.TW)THEN
CN=0.4+0.2*((TW/TPC)-1)
ELSE IF(TPC.LE.T.AND.TX.E.TLIM)THEN
CN=0.4+0.2*((TW/TPC)-1)*(1-5*((T/TPC)-1))
ENDIF
TNU=0.0064*(RE**0.91)*(PR**0.48)*((DW/D)**6)*((CPBAR/CP)**CN)
TNUS4=TNU
RETURN
END

C*********************************************************************
REAL*8 FUNCTION TNUSCLASSIC(RE,PR,F)
C*********************************************************************
IMPLICIT REAL*8 (A-H,0-Z)

TNU = (F/8)*(T^-1000)*PR/(1+12.7*((F/8)**(0.5))*(PR**(0.66667)-1))
TNUSCLASSIC = TNU
RETURN
END

C*********************************************************************
REAL*8 FUNCTION FRICTION(RE,DIA)
C*********************************************************************
IMPLICIT REAL*8 (A-H,0-Z)

EPS = 0.002
F = (1.8*LOG10(6.9/RE+(EPS/(3.7*DIA*1000))**1.11))**(-2)
FRICTION = F
RETURN
END

C*********************************************************************
REAL*8 FUNCTION COMLIQENTH(T)
C*********************************************************************
IMPLICIT REAL*8 (A-H,0-Z)

IF (T.LT. 313.15) THEN
HI = (T-293.15)/20*(189.52-107.24)+107.24
ELSE IF (T .GE. 313.15) THEN
HI = (T-313.15)/60*(437.85-189.52)+189.52
ENDIF
COMLIQENTH = HI
RETURN
END

C*********************************************************************
REAL*8 FUNCTION COMLIQTEMP(H2)
C*********************************************************************
IMPLICIT REAL*8 (A-H,0-Z)

IF (H2 .LT. 189.52) THEN
T = (H2-107.24)/(189.52-107.24)*20+293.15
ELSE IF (T .GE. 189.52) THEN
T = (H2-189.52)/(437.85-189.52)*60+313.15
ENDIF
COMLIQTEMP = T
RETURN
END

C*********************************************************************
REAL*8 FUNCTION COMLIQDENS(T)
C*********************************************************************
IMPLICIT REAL*8 (A-H,0-Z)

IF (T .LT. 313.15) THEN
H1 = (T-293.15)/(189.52-107.24)+107.24
ELSE IF (T .GE. 313.15) THEN
H1 = (T-313.15)/(437.85-189.52)+189.52
ENDIF
IMPLICIT REAL*8 (A-H,O-Z)
IF (T .LT. 313.15) THEN
   V1 = (T-293.15)/20*(0.9971-0.9907)+0.9907
ELSE IF (T .GE. 313.15) THEN
   V1 = (T-313.15)/60*(1.0313-0.9971)+0.9971
ENDIF
D = 1/V1*1000
COMLIQDENS = D
RETURN
END

REAL*8 FUNCTION COMLIQCP(T)

C********************************************************************
IMPLICIT REAL*8 (A-H,O-Z)
IF (T .LT. 293.15) THEN
   CP = (T-273.15)/20*(4.112-4.109) + 4.109
ELSE IF (T .LT. 313.15) THEN
   CP = (T-293.15)/20*(4.126-4.112) + 4.112
ELSE IF (T .LT. 333.15) THEN
   CP = (T-313.15)/20*(4.131-4.126) + 4.126
ELSE IF (T .LT. 353.15) THEN
   CP = (T-333.15)/20*(4.143-4.131) + 4.131
ELSE IF (T .LT. 373.15) THEN
   CP = (T-353.15)/20*(4.163-4.143) + 4.143
ENDIF
COMLIQCP = CP
RETURN
END