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The Experimental Analysis of Aqueous Lithium Bromide Vertical Film Absorption

William A. Miller
University of Tennessee - Knoxville

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To the Graduate Council:

I am submitting herewith a dissertation written by William A. Miller entitled “The Experimental Analysis of Aqueous Lithium Bromide Vertical Film Absorption.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Mechanical Engineering.

Majid Keyhani, Major Professor

We have read this dissertation and recommend its acceptance:

R. V. Arimilli, Stan Johnson, F. E. Weber

Accepted for the Council:
Dixie L. Thompson
Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
To the Graduate Council:

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[Signature]
Dr. Majid Keyhani, Major Professor

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[Signature]
Dr. R. V. Arimilli

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Dr. F. E. Weber

Accepted for the Council:

[Signature]
Associate Vice Chancellor and Dean of the Graduate School
The Experimental Analysis of Aqueous Lithium Bromide

Vertical Falling Film Absorption

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

William A. Miller

May 1998
Dedication

This dissertation is dedicated to my parents, Mr. and Mrs. Anthony T. Miller of Tullahoma Tennessee. During the late 1940s, my father served as a master mechanic at Wright Patterson Air Force Base in Dayton, Ohio. He spent eight years in evening school at the University of Dayton trying to earn his Bachelor of Science degree in engineering. A loving wife fully supported him by caring for the family; however, job opportunities forced them to relocate first to Chicago and then to Tennessee. He did not earn a degree, but valued education and made it a primary goal for his five children to complete college. He instilled in us the desire to complete our work to the best of our abilities. He would say, “If you are going to do it, then do it right!”

This legacy continues with their progeny. Some nine years were required for me to complete the Ph.D. while being fully employed at ORNL. I must thank a loving wife for her support during the course of study. I pray that the example I set may instill in my own children—Joanna Kristen, Joshua Simeon and Jodie Beth Miller—the desire to learn. Mt. 25:29: “For everyone who has, will be given more, and he will have an abundance. Whoever does not have, even what he has will be taken from him.”
Acknowledgments

There are many people to whom I am grateful for supporting me during the course of this work. First and foremost, I am very grateful to my major professor, Dr. Majid Keyhani, for his support during the analysis of the experimental data. I often left his office encouraged and enthused by his novel and keen insights into the absorption problem. His rigor for analysis guided and greatly enhanced both the eloquence of the correlations and the simple, yet accurate character of the predictive algorithm published in this study.

Appreciation is expressed to Professor Morioka of Tokushima University and Masanori KIYOTA for their permission to use their photographs of the aqueous LiBr falling films. The photos speak a thousand words and complement the present study.

Thanks are given to Dr. A. T. Conlisk of Ohio State University, Dr. Vikas Patnaik of Trane Corporation and S. K. Fisher of ORNL for the solutions they provided for comparison against the predictive algorithm.

In 1989, as a novice to absorption technology, I was briefly tutored by both Dr. Horacio Perez-Blanco of Penn State University and Dr. Gershon Grossman of Technion University. The opportunity to learn from them was invaluable and helped me better understand the complexities of absorption. Both men are to be commended for their willingness to share their knowledge.
My supervisors, Phil Fairchild and Bob DeVault, are both thanked for their support. The blending of academic and job requirements is not an easy task. Rarely is an employee given the opportunity to complete his writing while at work. However, Phil Fairchild and Bob DeVault both directed me to focus and complete the writing. Their patience and confidence are greatly appreciated.

A special acknowledgment is given Gene Holt, who always arrived early at work and daily prepared the mini-absorber test stand. He helped maintain the system's vacuum and always participated in design modifications for improving the capabilities of the mini-absorber test stand.

Dr. Vikas Patnaik and Daoud Jandal are both commended for their help with collecting and reducing the hydrodynamic data of the falling films. Their individual efforts provided key information for substantiating the concepts of a conduction-dominated, thinning film for wavy-laminar falling film flow.

Leroy Gilliam edited the figures. His artistry enhanced the readability of the thesis and is very much respected and appreciated by the author. Having been stricken earlier in life with polio, Leroy is a witness of an individual's ability to compensate and be productive in life.

The research reported herein was part of a larger study sponsored by Dr. Bill Ryan of GRI under contract number 5089-243-1844. The test stand was developed under the sponsorship of Ron Fiskum of DOE's Office of Building Equipment.
Abstract

A heat and mass transfer test stand was fabricated and used to investigate non-isothermal falling film absorption of water vapor into a solution of aqueous lithium bromide. The absorber was made of borosilicate glass for visual inspection of the falling film. Experiments were conducted on an internally cooled smooth tube of about 0.019 m outside diameter and of 1.53 m length. Laboratory testing evaluated the tube's performance at varying falling film flow rates, pressures, temperatures, and concentrations. No heat and mass transfer additive was used during testing nor had it been previously added to the stand.

The coolant temperature profile was measured along the running length of the absorber. The interface temperature of the falling film was measured with a new technique using thermographic phosphors. Information gleaned from the coolant measurements led to the development of a predictive algorithm. The algorithm was validated against the experimental data from this study and also from data published in the open literature. The algorithm predicts the absorber load and the mass absorbed within ±10 and ±14 %, respectively.

The data, for testing of aqueous LiBr at 0.62 and 0.64 mass fraction of LiBr, were reduced to nondimensional parameters and were successfully correlated into both Nusselt and Sherwood formulations. The average absolute error in the Nusselt correlation is about ±3.5% of the Nu number reduced from the experimental data. The Sherwood correlation is about ±5% of the reduced Sh data. The data by
Grossman and Alefeld (1996) were reduced to the author’s Nu and Sh formulations, and were within 5% of the correlations developed in the present study.

The hydrodynamics of the falling film, the absorber load, the mass absorbed, transport coefficients, and pertinent absorption data are presented as functions of the Re, Pr, Sc, Ja and Ka numbers. The data will prove useful in establishing design guidelines for the improvement in combined heat and mass exchangers.
Absorption chillers are gaining acceptance in the global market as quality comfort cooling systems. The machines are regaining a significant share of the large-tonnage market because of energy and environmental concerns. The equipment predominantly uses aqueous lithium bromide as the working fluid. Water is the refrigerant. These chillers can be direct-fired with natural gas or can be fired indirectly with steam or some other waste heat stream. In many applications, the machines can simultaneously support both heating and comfort cooling.

The heart of the chiller is the absorber, where a process of simultaneous heat and mass transfer occurs as the refrigerant water vapor is absorbed into a falling film of aqueous lithium bromide. The more water vapor absorbed into the falling film, the larger the chiller’s capacity for supporting comfort cooling. Improving the performance of the absorber leads directly to efficiency gains for the chiller.

The design of an absorber is empirical and requires experimental data. However, design data and correlations are sparse in the open literature. A study of simultaneous heat and mass transfer was therefore conducted on a vertical falling film absorber to better understand the mechanisms driving the heat and mass transfer processes. Falling films are characteristically unstable, and a wavy-laminar flow was observed during the experimental study. Experiments were conducted at various flow rates of the falling film, at various absorber pressures and at various compositions of the binary salt solution. A series of experiments were also conducted to measure the
coolant and the liquid-vapor interface temperatures along the running length of the absorber.

The literature review of the present study addresses both the hydrodynamics and the coupling of heat and mass transfer observed in falling film absorbers. Key issues gleaned from the review pertain to the effective film thickness of a wavy-laminar falling film and the effect of the roll waves on the heat and mass transfer process. The experimental setups are described in Chapter 3, and supplemental data are included in the Appendices. The results of falling film hydrodynamic testing and absorption testing are presented in Chapter 4. Data were correlated into the Nusselt and the Sherwood formulations, and their predictive accuracy is evaluated. The local coolant and interface temperature measurements revealed that the local heat and mass transfer rates can be closely approximated using a constant flux boundary condition. These bulk coolant and the interface temperature profiles were used in a numerical data-reduction scheme to quantify the local heat and mass transfer rates. In Chapter 5 a predictive algorithm is formulated and validated against the experimental data from the present study and also against independent data. Open-literature solutions are compared to the algorithm in the conclusion of the dissertation.
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<tr>
<td>A</td>
<td>Surface Area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>a</td>
<td>Bias Term for a Linear Absorbent</td>
<td>g-mole $H_2O/\text{cc soln}$</td>
</tr>
<tr>
<td>b</td>
<td>Gain Term for a Linear Absorbent</td>
<td>g-mole $H_2O/(C \cdot \text{ cc soln})$</td>
</tr>
<tr>
<td>$C_a$</td>
<td>Concentration of Absorbate</td>
<td>g-mole $H_2O/\text{cc soln}$</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific Heat at Constant Pressure</td>
<td>kJ/kg$\cdot K$</td>
</tr>
<tr>
<td>D, d</td>
<td>Pipe Diameter</td>
<td>m</td>
</tr>
<tr>
<td>$D_{ab}$</td>
<td>Diffusivity of a through b</td>
<td>$m^3/s$</td>
</tr>
<tr>
<td>F</td>
<td>Wave Frequency</td>
<td>1/s</td>
</tr>
<tr>
<td>g</td>
<td>Gravity</td>
<td>9.81 m/s$^2$</td>
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<td>$H_m$</td>
<td>Overall Liquid-side Mass Transfer Coefficient</td>
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<tr>
<td>$h_m$</td>
<td>Local Liquid-side Mass Transfer Coefficient</td>
<td>m/s</td>
</tr>
<tr>
<td>H</td>
<td>Overall Heat Transfer Coefficient</td>
<td>J/m$^2 \cdot K \cdot s$</td>
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<td>h</td>
<td>Local Heat Transfer Coefficient</td>
<td>J/m$^2 \cdot K \cdot s$</td>
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<tr>
<td>$I_f$</td>
<td>Heat of Absorption</td>
<td>kJ/kg</td>
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<tr>
<td>i</td>
<td>Enthalpy</td>
<td>kJ/kg</td>
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<td>i$f$</td>
<td>Latent Heat of Water Vapor</td>
<td>kJ/Kg</td>
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<tr>
<td>k</td>
<td>Thermal Conductivity</td>
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<td>L</td>
<td>Length</td>
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<td>$\Gamma$</td>
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<tr>
<td>$m$</td>
<td>Mass Flow Rate</td>
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<td>Mass Absorbed per Unit of Perimeter</td>
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<td>$P$</td>
<td>Partial Pressure of Absorbate Vapor</td>
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<tr>
<td>q</td>
<td>Heat Transfer Rate</td>
<td>J/s</td>
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<td>q'</td>
<td>Heat Transfer per Unit of Perimeter</td>
<td>J/m $\cdot s$</td>
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<td>Pipe Radius</td>
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<tr>
<td>Res</td>
<td>Heat Transfer Resistance</td>
<td>($^\circ \text{C} \cdot s$) / J</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>$^\circ \text{C}$</td>
</tr>
<tr>
<td>$\bar{U}$</td>
<td>Average Falling Film Velocity</td>
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<tr>
<td>u</td>
<td>Local Streamwise Velocity, in x Direction</td>
<td>m/s</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Rate of Liquid Pick-up from Substrate</td>
<td>m$^3$/s</td>
</tr>
<tr>
<td>V</td>
<td>Volumetric Flow Rate</td>
<td>m$^3$/s</td>
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<tr>
<td>v</td>
<td>Local Transverse velocity, in y Direction</td>
<td>m/s</td>
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<tr>
<td>x</td>
<td>Coordinate in Direction of Flow</td>
<td>m</td>
</tr>
<tr>
<td>y</td>
<td>Coordinate Normal to Direction of Flow</td>
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### Greek Symbols

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<td>(\alpha)</td>
<td>Thermal Diffusivity</td>
<td>(m^2/s)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>Inclination of Falling Film</td>
<td>(^\circ)</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>Average Film Thickness</td>
<td>(m)</td>
</tr>
<tr>
<td>(\Delta h)</td>
<td>Heat of Solution</td>
<td>(kJ/kg)</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Film Thickness as Function of (t, x, y)</td>
<td>(m)</td>
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<tr>
<td>(\rho)</td>
<td>Density</td>
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<td>(\eta)</td>
<td>Molecular Weight of Water</td>
<td>(g/g)-moles</td>
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<tr>
<td>(\nu)</td>
<td>Kinematic Viscosity</td>
<td>(m^2/s)</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Dynamic Viscosity</td>
<td>(kg/m\cdot s)</td>
</tr>
<tr>
<td>(X)</td>
<td>Mass Fraction</td>
<td>(kg LiBr / kg soln)</td>
</tr>
<tr>
<td>(\tau)</td>
<td>Wall Shear Stress</td>
<td>(N/m^2)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Surface Tension</td>
<td>(N/m)</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Scaled Coordinate Normal to Flow Direction</td>
<td></td>
</tr>
<tr>
<td>(\xi)</td>
<td>Scaled Coordinate in Direction of Flow</td>
<td></td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Normalized Heat of Absorption</td>
<td></td>
</tr>
<tr>
<td>(\theta)</td>
<td>Normalized Temperature</td>
<td></td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Normalized Concentration</td>
<td></td>
</tr>
<tr>
<td>(\Phi)</td>
<td>Viscous Dissipation</td>
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AGCC</td>
<td>American Gas Cooling Center</td>
</tr>
<tr>
<td>A/D</td>
<td>Analog-to-Digital</td>
</tr>
<tr>
<td>A/C</td>
<td>Air-conditioning</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>DAS</td>
<td>Data Acquisition System</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>COP</td>
<td>Coefficient of Performance</td>
</tr>
<tr>
<td>GRI</td>
<td>Gas Research Institute</td>
</tr>
<tr>
<td>HVAC</td>
<td>Heating, Ventilation and Air-Conditioning</td>
</tr>
<tr>
<td>ID</td>
<td>Inside Diameter</td>
</tr>
<tr>
<td>JGA</td>
<td>Japan Gas Association</td>
</tr>
<tr>
<td>JRAIA</td>
<td>Japan Refrigeration and Air Conditioning Industry Association</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos National Laboratory</td>
</tr>
<tr>
<td>MKS</td>
<td>Meter Kilogram Second Instruments, Inc.</td>
</tr>
<tr>
<td>OD</td>
<td>Outside Diameter</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial Differential Equation</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>QUICK</td>
<td>Quadratic Upstream Interpolation for Convective Kinematics</td>
</tr>
<tr>
<td>RT</td>
<td>Refrigerant Ton</td>
</tr>
<tr>
<td>RTD</td>
<td>Resistance Temperature Detector</td>
</tr>
<tr>
<td>SIMPLER</td>
<td>Semi-Implicit Method for Pressure Linked Equations Revised</td>
</tr>
<tr>
<td>TV</td>
<td>Television Monitor</td>
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<tr>
<td>VCR</td>
<td>Video Cassette Recorder</td>
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</table>
### Subscripts

- **a**: Absorbate “Water Being Absorbed”
- **b**: Absorbent ‘LiBr Able to Absorb”
- **bl**: Boundary Layer
- **cl**: Coolant
- **corr**: Correlated Value
- **cyc**: Cylindrical
- **eq**: Equilibrium
- **ex**: Exit
- **exp**: Experimental
- **f**: Film
- **fr**: Wave Front
- **H**: Heat
- **hy**: Hydraulic Diameter
- **i**: Inside Diameter or Inside Radius
- **in**: Inlet
- **l**: Liquid Phase
- **m**: mass
- **max**: Maximum
- **o**: Outside Diameter or Outside Radius
- **p**: Pipe
- **pk**: Wave peak
- **s**: Wave Substrate
- **t**: Wave Tail
- **v**: Absorbate Vapor
- **w**: Wave
- **wall**: Tube Wall

### Superscripts

- **rate**: Rate
- **r**: Per Unit Area (Flux)
- **′**: Per Unit Length
- *****: Liquid - Vapor Interface
- **−**: Average or Bulk
### Dimensionless Groups

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Formula</th>
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</thead>
<tbody>
<tr>
<td>(\varepsilon)</td>
<td>Aspect Ratio</td>
<td>(\varepsilon = \frac{\delta}{x})</td>
</tr>
<tr>
<td>(\text{Eck})</td>
<td>Eckert number</td>
<td>(\text{Eck} = \frac{\overline{U}^2}{C_p(T_f - T)})</td>
</tr>
<tr>
<td>(\text{Fr})</td>
<td>Froude number</td>
<td>(\frac{\overline{U}^2}{g \Delta} = \frac{\text{Re}^2}{16 \text{Nt}})</td>
</tr>
<tr>
<td>(\text{Ja})</td>
<td>Jacobs number</td>
<td>(\frac{C_p(T_f - T)}{h_f g})</td>
</tr>
<tr>
<td>(\text{Ka})</td>
<td>Kapitza number</td>
<td>(\frac{\sigma t}{\rho (\nu g)^2} = \frac{\text{Re}^2}{16 \text{We} \cdot \text{Nt}})</td>
</tr>
<tr>
<td>(\text{Le})</td>
<td>Lewis number</td>
<td>(\frac{\alpha}{D_{ab}} = \frac{\text{Sc}}{\text{Pr}})</td>
</tr>
<tr>
<td>(\text{Nt})</td>
<td>Film number</td>
<td>(\frac{\Delta}{\left(\frac{\nu^2}{g}\right)^{1/2}})</td>
</tr>
<tr>
<td>(\text{Nu})</td>
<td>Nusselt number</td>
<td>(\frac{H D_o}{k_f})</td>
</tr>
<tr>
<td>(\text{Pe_H})</td>
<td>Peclet Heat</td>
<td>(\frac{4 \overline{U} \Delta}{\alpha} = \text{Re} \cdot \text{Pr})</td>
</tr>
<tr>
<td>(\text{Pe_M})</td>
<td>Peclet Mass</td>
<td>(\frac{4 \overline{U} \Delta}{D_{ab}} = \text{Re} \cdot \text{Sc})</td>
</tr>
<tr>
<td>(\text{Pr})</td>
<td>Prandtl number</td>
<td>(\frac{C_p \mu}{k} = \frac{v}{\alpha})</td>
</tr>
<tr>
<td>(\text{Re})</td>
<td>Reynolds number</td>
<td>(\frac{4 \overline{U} \Delta}{\nu} = \frac{4 m}{\pi D_{\mu}})</td>
</tr>
<tr>
<td>(\text{Sc})</td>
<td>Schmidt number</td>
<td>(\frac{\nu}{D_{ab}})</td>
</tr>
<tr>
<td>(\text{Sh})</td>
<td>Sherwood number</td>
<td>(\frac{H m D_o}{D_{ab}})</td>
</tr>
<tr>
<td>(\text{We})</td>
<td>Weber number</td>
<td>(\frac{\rho \overline{U}^2 \Delta}{\sigma} = \frac{\text{Re}^2}{16 \text{Ka} \cdot \text{Nt}})</td>
</tr>
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CHAPTER 1

INTRODUCTION

Falling film absorption has found wide acceptance in both the air-conditioning (A/C) and the chemical industries. Absorption chillers are the central chilling plants of many large commercial buildings and supply for comfort cooling. Absorption is also widely applied in industrial and in chemical unit applications for synthesis, separation and cleaning processes.

Absorption is the assimilation of one or more constituents of a gas into a liquid and involves the transfer of mass between the participating liquid and gas phases. Chillers use falling films of aqueous lithium bromide (LiBr) that absorb a mass of water vapor in an absorber. The absorbed water vapor releases heat, and the exothermic heat release affects the temperature, the pressure and the composition equilibrium at the interface of this non-ideal binary mixture. The partial pressure of vapor, in the liquid phase, increases, causing the driving force for mass transfer to drop. The more exothermic the heat release, the larger the temperature gradient through the liquid phase. Heat flows through the film and further influences the thermodynamic equilibrium, which, in turn, affects the mass transfer. The simultaneous heat and mass transfer has heat effects which are inversely proportional to the mass effects if one imposes equilibrium on the interface. The greater the heat effect achievable, the lower the concentration gradient available for mass transfer. This paradox
mathematically complicates the simultaneous heat and mass transfer process and makes closed-form analysis difficult without the assumption of interfacial equilibrium with the gas phase.

### 1.1 Historical Perspective on Absorption Cooling

Absorption refrigeration was discovered about the 18th century; however, the first U.S. patent for an absorption refrigeration system was not awarded until 1860 to Ferdinand Carre. Only within the last 40 years has absorption played a predominant role in A/C and refrigeration. In the 1960s, central absorption chiller plants had earned about a 40% share of the domestic market, (Katzel 1992). This market share was maintained for over a decade.

The “energy crisis” of the 1970s led the U.S. government to regulate the use of natural gas as a fuel. Electric utility rates were low and the efficiency of electric-driven centrifugal chillers was continually improving. Hence, both government and economic factors drove the U.S. absorption industry to a near halt. The declining market caused all U.S. companies to reassign staff and reallocate their development resources for roughly a 20-year period. The ramification of these events is graphically seen in Fig. 1.1 in the sales of U.S. vs. Japanese absorption chillers (Garland 1995).

Meanwhile, in Japan absorption A/C flourished simply because electric power was expensive; fuel had to be imported for electric power generation. Japan encouraged the use of natural gas and fostered an aggressive program to stimulate absorption
Figure 1.1. Worldwide sales of U.S. and Japanese absorption chillers for air-conditioning large commercial buildings (adapted from Garland 1995).
research. Gas-fired cooling showed two-digit growth from 1987 through 1994, and the share of gas-fired cooling as of March 1994 stood at 15.8% of Japan's nationwide commercial cooling market (JGA 1994). The Japanese installed absorption chillers in department stores, office complexes, amusement and assembly facilities, medical facilities, district cooling and schools. In Japan, the absorption chiller was quickly being appreciated as a quality A/C system capable of air-conditioning an entire commercial office complex. As result, Japanese manufacturers were the first to introduce direct-fired double-effect chillers, which now account for the majority of absorption chiller sales throughout the world.

Since about 1993, all the major U.S. A/C manufacturers have entered into agreements with Japanese manufacturers to license Japanese absorption technology. Why? The U.S. market is now favorable for absorption cooling. In fact, the Gas Research Institute (GRI 1997) has projected that the domestic demand for gas will exceed 30 quads by 2015, about a 30% increase from 1995. Besides the demand for gas, several other factors are also relevant: (1) electric utilities are burdened by the peak rate of electric demand, (2) electric service requirements for absorption chillers are less than those for vapor compression chillers, (3) the elimination of chlorofluorocarbon (CFC) emissions makes absorption chillers environmentally friendly, (4) gas utilities offer rebate programs for the purchase of absorption chillers, and (5) operating cost savings are dependent on the fuel costs (Sweetser 1997). All these factors have caused a resurgence in absorption chiller sales, and U.S. manufacturers are developing the next generation of double-effect and triple-effect absorption chillers.
1.2 Overview of LiBr-Water

Research has shown LiBr as one of the best absorption working fluids because it has a high affinity for water; because it releases water vapor at relatively low temperatures and because it has a boiling point much higher than water's boiling point. Water is the refrigerant, and therefore the temperature of the chilled liquid from the evaporator, supporting comfort cooling, is limited to about 5°C to protect against freeze-up. The fact that LiBr is nonvolatile provides the system with a key feature: there is no need for a rectifier downstream from the generator.

In its natural state, LiBr is a solid salt crystal; however, in the presence of water vapor it will absorb the vapor and become a homogeneous mixture. For a non-equilibrium condition, the thermodynamic state point of the mixture cannot be established by pressure and temperature alone; one must include the composition of the mixture. We will express this in terms of the mass fraction $X$, which is the mass of LiBr salt divided by the mass of the mixture.

The liquid solution, termed LiBr brine, therefore exerts a water-vapor pressure that is a function of both the solution temperature and the concentration. The Dühring plot (Fig. 1.2) is a temperature-pressure-concentration (P-T-X) diagram which shows these intrinsic property relationships. Solution temperature is the abscissa and water-vapor pressure is the ordinate. Lines of constant concentration, based on the mass fraction of LiBr, are plotted and show the saturated conditions where the solution is in equilibrium with water vapor. To best understand the LiBr brine's P-T-X relationships as applied to falling film absorption, consider two tanks, one tank
Figure 1.2. Pressure-temperature-concentration Dühring chart for LiBr-water (adapted from Herold et al. 1996).
containing LiBr brine and the other containing pure water, as illustrated in Fig. 1.3. Suppose the brine is at 0.62 mass fraction and 51°C. At saturation it would exert a vapor pressure of 1 kPa (Fig. 1.2). Let the pure water be saturated at 3.7°C and 0.8 kPa, a design operating condition in the evaporator of a chiller. If the two tanks are suddenly connected, water from the tank of LiBr brine desorbs and travels to the tank of pure water. This desorption is termed flash and occurs because the solution entering the absorption process is superheated at the lower pressure of 0.8 kPa. For the two tanks to be in equilibrium, the temperature of the brine must be lowered to about 47°C. In other words, at 0.8 kP and 0.62 mass fraction, the 51°C brine was initially 4°C superheated. Therefore, the absorption of water into the brine will occur if and only if the pressure of the water vapor exceeds that of the partial pressure of water in the brine. Hence, for this example, the LiBr brine must be cooled below 47°C for absorption to occur. This is exactly the sequence of processes occurring in the absorber of a commercial chiller. Solution enters an absorber slightly superheated, it flashes suddenly and adiabatically to equilibrium with the absorber pressure, and it begins to absorb water vapor as it is externally cooled.

Suppose we continued to cool the brine to below 29.4°C. We would exceed the solubility limit of the mixture, and LiBr would precipitate out of the solution. This is termed crystallization and its T-X limits are shown by the bold line drawn in the lower right quadrant of Fig. 1.2. The region to the right and below this line indicates a precipitation of the LiBr from the solution. Crystallization is of particular interest because all absorption equipment, when fully loaded, operates very near crystallization conditions. Dropping into the crystallization region will cause formation of slush and would disrupt the operation of an absorption chiller.
Figure 1.3. Strong solution entering an absorber flashes and is driven to the equilibrium pressure of the surrounding vapor in the absorber.
However, these concerns have been minimized with the introduction of microprocessor base control units which continuously monitor concentration in today’s machines.

Suppose (Fig. 1.4) that we have just one tank with the pure LiBr salt separated from the water by an impermeable membrane. Let us have \( x \) kg of LiBr and \( (1 - x) \) kg of water both at the same temperature \( (T_1) \). If we removed the membrane, we would observe that the final temperature \( (T_2) \) would be different from \( T_1 \). Depending on the salt and liquid, we could observe a warming effect; in other salts, we could observe a cooling effect. The effect is expressed in terms of the heat of solution \( \Delta i_s \). For LiBr and water, the reaction is exothermic, and the final temperature \( T_2 \) would exceed \( T_1 \). Because the mixing occurs at constant pressure, \( \Delta i_s \) can be directly related to the enthalpy of the mixture. Initially, for the tank with membrane, the enthalpy would be

\[
i_1 = x i_b + (1 - x) i_a.
\]  

(1.1)

However, after mixing we get

\[
i_2 = x i_b + (1 - x) i_a + \Delta i_s.
\]  

(1.2)

Hence, if the enthalpies of the pure components and the heat of solution are known, then we can calculate the specific enthalpy in kJ per kg of mixture for a solution of known concentration at some fixed temperature and pressure.
Figure 1.4. A heat of solution evolves when mixing LiBr and water.
1.3 Overview of Aqueous LiBr Chillers

Present-day absorption chillers have sizes ranging from 10 to 2000 tons of refrigeration capacity. And virtually all machines use LiBr and water as the absorption fluids. Systems come in a variety of single-effect and double-effect designs. Typical examples are shown in Fig. 1.5. The single-effect system can operate using 105-kPa steam or hot water at about 100°C; the double-effect machine, because of its second generator, requires a higher steam input of about 860 kPa or some other waste heat stream at about 500°C. The units can be steam-fired, direct-fired or exhaust gas-fired depending upon available services (Fallek 1985). The absorbers of these machines are designed for high mass transfer performance by adding small amounts (less than 500 ppm) of a heat and mass transfer additive. Carrier serendipitously discovered the usefulness of 2-ethyl 1-hexanol as a chemical additive for enhancing heat and mass transfer. They experimentally measured enhancements of almost 200% in mini-absorber test stands (Biermann 1980).

Absorption chillers can be further classified into two basic types: those having a vertical column absorber and those with a horizontal absorber. Chillers with horizontal absorbers predominate worldwide, although Burdukov et al. (1980) experimentally found similar performance for vertical and horizontal falling film absorbers. A comparison of the two types is difficult because each geometry is operated at different flow ranges of the falling film. Vertical absorbers were applied to air-cooled machines by Ogawa, Hoshida and Oda (1991) and have the distinct advantage of minimizing the unit’s footprint, (i.e., the unit requires a smaller
Figure 1.5. Commercially available direct-fired and indirect-fired absorption chillers (adapted from AGCC 1996).
installation space). Absorption heat transformers that are used in industrial applications can take advantage of the smaller footprint where space is a premium. Briefly, the heat transformer recovers waste heat and, in the absorber, boosts its temperature to levels useful for industrial applications. Ikeuchi et al. (1985) claimed development of a prototype heat transformer, having a COP of 0.29, that could be driven by a waste heat source of 90°C with 23°C coolant and boost the source to process heat up to 150°C. The vertical column absorber is also frequently encountered in many chemical engineering applications for unit processing of fluid streams. Typical examples are the synthesis of a pure chemical product such as sulfuric acid by absorbing SO₃ into a liquid; the separation of gaseous mixtures in coke-oven gas to isolate benzene, a valuable component; and cleaning an exhaust gas from harmful impurities such as SO₂ prior to expelling the exhaust to the atmosphere.

The basic single-effect absorption cycle, shown in Fig. 1.6, consists of a condenser, refrigerant throttle, evaporator, absorber, boiler, solution heat exchanger, solution throttle and solution pump. The absorption cycle is similar to the vapor compression cycle in that they both use a condenser, a refrigerant throttle and an evaporator. The main difference pertains to a LiBr-water circuit that transports water vapor from the low-pressure evaporator to the high-pressure condenser. This LiBr-water circuit substitutes for the compressor of a vapor compression cycle.

High-temperature heat drives the refrigerant water vapor from the brine. Vapor at approximately 120°C and 21 kPa rejects heat in the condenser, is throttled to about 0.8 kPa and is sprayed as a fine mist over tubes in the evaporator. Because the
Figure 1.6. Single-effect absorption chiller showing the integration of the mini-absorber test section.
pressure is only 0.8 kPa, some water is vaporized, creating a refrigeration effect, and cools the plant’s chilled water supply from about 13°C to 7°C. In turn, the chilled water supplies comfort cooling to the complex. Strong solution, high in the mass of LiBr, leaves the boiler, transfers heat in the solution heat exchanger and is throttled to the evaporator pressure. It enters the absorber at about 0.62 mass fraction and 51°C and is distributed as a falling film over tubes in the absorber. Saturated water vapor leaves the evaporator at about 3.7°C, and is absorbed into the falling film.

Usually, when first exposed to the vapor in the absorber, the strong solution is not in equilibrium with the vapor. If the strong solution is subcooled, then it will absorb and its temperature will rise. Conversely, if the strong solution is superheated, then it will flash and the interface temperature drops. Both situations will be driven to equilibrium based on the pressure in the absorber and the concentration of the strong solution entering the absorber. Note that equilibrium is achieved instantly once the absorber pressure is imposed on the strong solution. Absorption continues if the partial pressure of absorbate at the liquid-vapor interface is less than that of the vapor in the absorber. This is accomplished by cooling the falling film with water flowing inside the absorber tubes countercurrent to the flow of the falling film. If coolant was not provided, absorption would diminish, and the chiller would stop providing comfort cooling. The coolant takes the waste heat, termed the absorber load, from the absorber and rejects it through a cooling tower to the environment.

To complete the cycle, weak liquid (i.e., solution having absorbed water vapor from the absorber) is pumped to the higher pressure and delivered back to the boiler.
As this description of the single-effect machine makes clear, the absorber is the heart of the chiller. The more mass absorbed, the larger the evaporator capacity, and the better the performance of the unit. In pure heat transfer, the specifications of effectiveness, fluid properties and flows enable calculation of the heat exchanger area. In the case of falling film absorption, a simultaneous heat and mass transfer governs the performance of the absorber.

Historically, the absorber design was viewed as a heat transfer problem which was driven by mass transfer. Design was accomplished using a semi-empirical approach based on log-mean temperature difference. Experiments would be conducted, and an empirical relationship would be derived for the overall heat transfer coefficient and the absorber load. The results would be scaled to the desired machine capacity. Absorber design was based on the experimental data as well as on the experience of the designer. Changing the absorber configuration (such as the tube spacing, tube diameter, tube length, or tube material) or changing the operating conditions would alter the design. Costly experiments would have to be rerun to develop a new design.

At issue is the exchange of mass across the liquid-vapor interface which involves the generation of heat. Water has a large heat of absorption, about 2700 kJ/kg, and heat effects associated with the mass exchange increase the temperature, which affects the pressure and composition equilibrium state and in turn affects the mass transfer. Why? For one thing, the diffusivity of water in aqueous LiBr is extremely low, about $10^{-9}$ m$^2$/s, and the absorbed mass tends to stay on the interface with little diffusion into the bulk of the film. Secondly, the driving force for mass transfer is the difference in pressure between the water vapor surrounding the absorber tube and the
partial pressure of water in the solution just within the liquid-vapor interface.

Therefore, as heat is released to the interface, the partial pressure of vapor in the solution increases, causing the pressure gradient across the liquid-vapor interface to drop. The point to be made is that a pure heat transfer analysis does not capture the dynamic pressure-temperature-composition changes occurring at the absorber's liquid-vapor interface. Nor does a pure heat transfer analysis allow, a priori, a prediction of the weak liquid's temperature or concentration.

Conservation of energy and binary diffusion must be observed at the liquid-vapor interface; however, it is classically assumed that the interface temperature and concentration are in equilibrium with the absorber pressure along the entire length of the absorber. In the literature, this is refereed to as linear absorbent theory and was first introduced by Grigor'eva and Nakoryakov (1977). A linear absorbent implies that the absorber vapor pressure is imposed on the liquid-vapor interface and that the interface is in equilibrium with this imposed pressure. Increasing the surface temperature would, for a linear absorbent, result in a corresponding decrease in concentration. Therefore, a linear absorbent describes a heating effect which opposes the mass effect. The greater the heat transfer to the interface, the less the concentration gradient achievable for mass transfer. The concept poses a paradox because in actuality the greater the load transferred to the coolant, the greater the mass absorbed by the absorber. The linear absorbent holds for several common salts in static conditions. However, the dynamic environment of a falling film makes the linear absorbent model at best an approximation of the actual interface condition. The key, therefore, for computing the local variations in the heat and mass transfer rates are the actual film temperature and concentration at the liquid-vapor interface.
These measures continue to elude researchers, but are important for understanding on a local as well as a global scale the heat effects at the interface, the heat transfer from the interface and the mass transfer onto and through the interface.

1.4 Research Objective

The absorption of water vapor into a falling film of aqueous LiBr is affected by several factors. The magnitude of the thermal and mass diffusivities in part regulate the transfer of water from the vapor-liquid interface into the bulk of the film. Film flow rate coupled to the physical properties of kinematic viscosity and surface tension govern the flow regime of the falling film. Wavy-laminar, roll-wave laminar and turbulent flows will develop convective contributions which can enhance the transfer of mass into the film.

The magnitude of the heat release and the pressure-temperature-concentration relationship for aqueous LiBr govern the rate at which mass is absorbed into the film. Inert gases such as air can blanket the interface and will retard absorption by elevating the partial pressure at the interface.

The heat transfer rate to the coolant affects the film temperature and is probably the major player in controlling the absorption process.

The combined interaction of all these factors makes the process very difficult to analyze. Some experimental data are available; however, all literature data to date
have been derived at LiBr concentrations ranging from 0.30 to 0.60 mass fraction. No literature data are readily available at the design operating conditions of 0.62 and 0.64 mass fraction of LiBr and 0.7 and 1 kPa absorber pressure. Along the length of the absorber, little is known about the temperature and concentration profiles that describe the local heat and mass transfer.

Hence, work was planned to better understand the first-principle concepts of falling film absorption with no heat and mass transfer additive. The driving mechanism causing enhancement with heat and mass transfer additive is a study in itself. Further, the chemical mechanism is very difficult to determine because of the dynamic complexities and the dearth of experimental data. Thus, the objectives of this study were as follows:

- Design and set up a mini-absorber test stand and a flow visualization test stand. Setup requires the selection and calibration of instrumentation as well as the setup of data acquisition software and data reduction codes.

- Conduct experiments to measure the film thickness of a free-falling film of aqueous LiBr and correlate the data using parameters that best predict the variations of the film thickness.

- Conduct experiments on a smooth tube absorber and experimentally show the effect of temperature, pressure and concentration on the rate of absorption in ranges typical of commercial and industrial operating equipment.
• Correlate the absorption data using Nusselt and Sherwood formulations.

• Measure the local variations in concentration and temperature along the length of the absorber and formulate a better understanding of the processes occurring in simultaneous heat and mass transfer.

• Develop and validate a closed-form algorithm for predicting the absorber load and the mass absorbed for a vertical column absorber.
CHAPTER 2

LITERATURE REVIEW

A multiplicity of research on the hydrodynamics of gas and liquid flows is available in the open literature. Specifically, falling films in the presence of vapors have been studied to determine the effect of the film’s hydrodynamics on the absorption rate. Accurate analysis of the hydrodynamic effect requires a good prediction of the free surface of the falling film; however, modeling it is a formidable mathematical challenge. The effect of the wall shear stress on the shape of the film is not well understood. Yet, the location, shape and motion of the free surface determines the boundary conditions needed for modeling the flow. Therefore, without an a priori knowledge of the free surface, one cannot easily predict its effect on either heat or mass transfer.

2.1 Falling Film Hydrodynamics

Viscosity, gravity and surface tension are the driving forces dominating falling film flows. A dimensional analysis shows the independent groups of Reynolds number (Re) and Kapitza number (Ka) describe the characteristics of the flow. Below a certain critical Re number the film flow will be laminar; however, the transition from laminar to turbulent flow is not as noticeable as that of internal pipe flow. Nor can
the flow regime be uniquely defined as simply laminar or turbulent. The critical Re number for inception of wavy-laminar flow is largely influenced by surface tension. Brauer (1956) formulated a correlation using the Ka number to show the flow strength at which a film transitions into a wavy flow. He published the following empirical relationship:

\[ Re_{\text{Crit}} = 1.224(Ka^{0.3}) \]  \hspace{1cm} (2.1)

which agreed fairly well with the works of Grimley (1945), Kapitza (1948) and most recently the works of Ishigai et al. (1972). Ishigai's formulation is

\[ Re_{\text{Crit}} = 1.88(Ka^{0.3}) \]  \hspace{1cm} (2.2)

Benjamin (1957) used stability analysis and predicted that vertical falling film flows are unstable over all flow ranges. Solorio and Sen (1987) further showed cylindrical falling films unstable for all Re numbers, Weber numbers (We) and radius ratios. Their results imply that all vertical falling films are naturally wavy. Fulford (1964) did an excellent topical study on the flow of thin films. His compilation showed three general falling film flow regimes—laminar, wavy-laminar and turbulent flow. Ishigai et al. (1972) refined Fulford’s descriptive into the following regimes:

1. Laminar flow \hspace{1cm} Re \leq 1.88(Ka^{0.3})
2. First transient \hspace{1cm} 1.88(Ka^{0.3}) \leq Re \leq 8.8(Ka^{0.3})
3. Stable wavy-laminar \hspace{1cm} 8.8(Ka^{0.3}) \leq Re < 300
4. Second transient \hspace{1cm} 300 \leq Re \leq 1600
5. Fully turbulent \hspace{1cm} Re \geq 1600
An excellent illustration of these differing flow regimes was experimentally observed by Morioka, Kiyota and Nakao (1993) and is shown in Fig. 2.1. Morioka used 59 wt% LiBr flowing down a 0.028-m tube. He photographed the films at an angle of 40° from the vertical axis at about 200 to 300 mm from the bottom of the 1.4-m-long test section. No absorption occurred while photographing the films. Given Ishigai’s regimes, the 59 wt% brine would have these flow fields:

1. Laminar flow $\quad Re \leq 16$
2. First transient $\quad 16 \leq Re \leq 60$
3. Stable wavy-laminar $\quad 60 \leq Re < 300$
4. Second transient $\quad 300 \leq Re \leq 1600$

At a Re number of 15, Morioka observed a mirror-like laminar flow which was completely smooth and uniform. Increasing the Re number to 20 shows the formation of small, uniform and symmetrical waves. Fulford (1964) in his own study stated that the waves in this regime were straight and almost normal to the flow direction. Morioka observed that the flow entered smooth laminar and then began to transition into wavy flow at about 200 mm from the inlet.

Keen observation reveals a thin laminar sublayer which nearly covers the entire film (Fig. 2.1). Researchers have termed this laminar sublayer the *film substrate*. Because the film is partly laminar in the substrate and partly turbulent in the waves, the transition from laminar to turbulent flow cannot be defined by a single critical Re number. Fulford’s review of the open literature confirmed this issue; his collection of some 1013 data points, by different researchers, showed (1) that the transition to
Figure 2.1. Vertical falling films of 59 wt% LiBr brine were photographed on a 0.028-m OD test tube (adapted from Morioka et al. 1993).
turbulence in a thin film is gradual, and (2) that research values of the critical Re number for turbulence are scattered around about 1600.

Brauner (1989) classified the waves in the transient wavy regime as either capillary wavy-laminar or inertial wavy-laminar. The capillary waves are observed for Re number flows of 20 and 41 in Fig. 2.1, and the inertial laminar waves are observed for Re number flows of 61 and higher. They are commonly known as roll waves (Brauer 1956). Increasing the Re number causes the roll waves to develop a steep front. The increase in curvature increases surface tension forces, which, in turn, leads to the growth of smaller push waves just in front of the larger wave (Fulford 1964). These push waves are clearly seen in front of the larger roll waves of Fig. 2.1.

Morioka observed that the push waves collapse as they flow downward; however, the roll and push wave combination appears to persist after the collapse.

Increasing the Re number causes the wave interval to increase, and the wave fronts lose their ring-like symmetry (Fig. 2.1). The flow has become chaotic in the second transient regime, and the waves are starting to interfere with adjacent waves. Yet the wave substrate is still preserved. At Re numbers of 406 and 812, the wave becomes distorted and the flow becomes chaotic.

Continuing to increase the flow strength leads to a blending of the roll and push waves, and the surface becomes covered with small, jagged, turbulent waves. Belkin et al. (1959) show an excellent photograph of a fully turbulent falling film of water, reproduced as the lefthand photograph in Fig. 2.2. The wavy-laminar roll wave flow has transitioned into a turbulent free surface having rather small, chaotic waves. For
Figure 2.2. A turbulent falling film of water (a) is compared to a laminar falling film of LiBr brine containing heat and mass transfer additive (b). [(a) Adapted from Belkin et al. 1959 (b) adapted from Biermann 1980.]
comparison, 60 wt% LiBr brine with heat and mass transfer additive is depicted in the righthand picture of Fig. 2.2. The two flows are very distinct and vividly show the differences between mechanical and chemical enhancements. The addition of only 500 ppm of 2-ethyl-1-hexanol causes a chaotic, undulating movement which is transverse in direction to the falling film (righthand photo of Fig. 2.2). The additive agitates the solution at the vapor interface and induces a mixing within the film which researchers believe is due either to Marangoni convection proposed by Kashiwagi (1985) or to a chemical catalytic mechanism that reduces the interface activation energy required for absorption, proposed by Biermann (1997). A study of heat and mass transfer additive is outside the scope of intended work for this project; however, the interested reader can glean information from several sources (Herold 1995; Kim, Berman and Wood 1986; Cosenza and Vliet 1990; Reiner et al. 1991; Kashiwagi and Rie 1993; and Jung, Sgambati and Perez-Blanco 1994).

Morioka's photographs vividly show the hydrodynamic complexities occurring within the wavy-laminar flow regimes. Unfortunately for the design engineer, wavy flow has always been observed in absorption machines. These wavy flows have fascinated and frustrated both researchers and absorber designers. Emmert and Pigford (1954) and Henstock and Hanratty (1979) conducted studies in the wavy-laminar regime. Both observed increases in mass transfer over a smooth film; however, their measurement techniques could not detect whether the roll waves or the turbulence generated by shear layers near the wall were the controlling factors. How is the wall shear stress coupled to the free surface, and what effect does the wall shear stress have on the wave pattern? Because of these complexities, only recently have models been
formulated that satisfactorily predict the role of wavy films in the transport of heat, mass and momentum.

**2.1.1 Smooth Laminar Flow**

Hopf (1910) and Nusselt (1916) were the first to develop solutions for the falling film hydrodynamics on a vertical flat plate. For a steady, uniform, fully developed one-dimensional flow [Fig. 2.3(a)], the Navier-Stokes equations reduce to

\[
\frac{d^2 u}{dy^2} + \frac{g}{v} = 0, \quad (2.3)
\]

and

\[
\frac{dP}{dy} = 0. \quad (2.4)
\]

Hopf used the no-slip boundary condition at the wall and assumed that the shear at the liquid-vapor interface was negligible. He solved Eq. 2.3 and derived a parabolic velocity profile:

\[
u(y) = \frac{g\Delta^2}{v} \left[ \frac{y}{\Delta} - \frac{y^2}{2\Delta^2} \right], \quad (2.5)
\]

which he then integrated over the film thickness to obtain the average velocity:

\[
\bar{U} = \frac{g\Delta^2}{3v}, \quad (2.6)
\]

Usually, Eq. 2.6 is substituted into Eq. 2.5 to simplify the profile as

\[
u(y) = \frac{3}{2} \bar{U} \left[ 2 \frac{y}{\Delta} - \left( \frac{y}{\Delta} \right)^2 \right] \quad (2.7)
\]
Figure 2.3. Cartesian (a) and cylindrical (b) coordinate systems for laminar falling films.
The mass flow rate of the falling film is easily calculated using Eq. 2.6:

\[
m = \rho \Delta \overline{U} = \frac{g(\pi D_0)\rho \Delta^3}{3\nu},
\]

(2.8)

from which the film thickness becomes

\[
\Delta = \left\{ \frac{3mv}{(\pi D_0)\rho g} \right\}^{\frac{1}{3}} = \left\{ 0.75 \frac{v^2}{g} \frac{\nu}{\text{Re}} \right\}^{\frac{1}{3}}.
\]

(2.9)

Dukler (1959) rearranged Eq. 2.9 into a normalized form and termed the normalized film thickness as the Nt number. Hence Eq. 2.9 written in terms of the Nt thickness becomes

\[
Nt = \frac{\Delta}{\frac{1}{(\nu^2/g)^{\frac{1}{3}}}} = \left\{ 0.75 \frac{\nu}{\text{Re}} \right\}^{\frac{1}{3}}.
\]

(2.10)

Hopf’s and Nusselt’s analysis predicts steady flow of a smooth film falling down an infinitely wide plate. A question arises regarding the effects of curvature for laminar flows down a cylindrical tube. Grimley (1947), Jackson (1955) and Mudawar and Houpt (1993) approached the problem using cylindrical coordinates. Other researchers argue that curvature effects are minor for large-diameter tubes. To justify a Cartesian coordinate approach, the author also solved the Navier-Stokes equations in cylindrical form to investigate the effects of curvature. In cylindrical coordinates [Fig. 2.3(b)], the momentum equation for laminar flow reduces to

\[
\frac{d^2u}{dr^2} + \frac{1}{r} \frac{du}{dr} + \frac{g}{\nu} = 0,
\]

(2.11)

and is solved using the following boundary conditions: \( u = 0 \) at \( r = R_O \) no slip at the wall, and
\[
\frac{du}{dr} = 0 \quad \text{at} \quad r = R_0 + \delta. \tag{2.12}
\]

By solving Eq. 2.11 subject to Eq. 2.12, we obtain the velocity profile:

\[
u(r) = \frac{g}{4v} (R_0^2 - r^2) - \frac{g}{2v} (R_0 + \delta)^2 \ln \left( \frac{R_0}{r} \right).	ag{2.13}\]

An expression for the mass flow rate can be derived in terms of the film thickness by integrating Eq. 2.12 from \( R_0 \) to \( (R_0 + \delta) \). The result follows:

\[
1 - 4\eta^2 + 3\eta^4 - 4\eta^4 \ln(\eta) + 4\text{Re} \left[ \left( \frac{v \sqrt{g}}{R_0} \right)^{1/3} \right]^3 = 0, \tag{2.14}\]

where \( \eta = (R_0 + \delta)/R_0 \) and the source term represents the Re number proportioned by the quotient of the transport property film thickness to pipe radius cubed. Equations 2.9 and 2.14 were solved for the respective film thickness in Cartesian and cylindrical coordinates. The results are plotted in Fig. 2.4 as a function of the source term in Eq. 2.14 to capture the combined effects of curvature, inertia and viscosity. The thickness based on planar coordinates is slightly larger than that based on cylindrical coordinates.

Reducing the tube diameter increases the effect of curvature. A tube of 0.0254 m in diameter would incur only 1% error, while a 0.00635-m-diameter tube would have upwards of 7% error in the calculated film thickness. Note for the given flow range displayed in Fig. 2.4, \( \Delta_{yc} \) is only about 2% less than \( \Delta_{ni} \) for all radius tubes. Therefore, Cartesian coordinates can satisfactorily predict the film thickness for laminar flow down cylindrical absorber tubes.
Figure 2.4. The error in calculated film thickness that occurs using Cartesian as opposed to cylindrical coordinates. The outside tube diameter is 0.01905 m.
2.1.2 Wavy-Laminar Flow

Falling films are well suited to interphase heat transfer processes because of the small thermal resistance through the film and the large contact surface achievable at small flow rates. Therefore, a number of studies have been conducted to measure and correlate the film thickness of wavy-laminar flows. However, literature data can be easily misread, and the film thickness must be carefully defined for wavy-laminar flows. The thickest and thinnest portions of the film represent respectively the wave crest and the film substrate. The reported average, however, is either a volume-averaged or a time-averaged film thickness, depending on the measurement technique. For example, some researchers used a stop-flow method where the flow of the liquid on the wetted surface was stopped abruptly and all the remaining liquid was measured. A volume-averaged film thickness was reduced from the volume of drained liquid and the wetted surface area. The volume-average measurement represents the entire flow field. Other more advanced schemes such as high-speed video recording, capacitance and especially the photometric technique are capable of detecting small changes in the film thickness over timed intervals. Several waves pass a detection point over time, and a time-averaged thickness is reduced from the data. For pure laminar flow the two measures are identical; however, for wavy-laminar flow, the time-averaged method yields the better measure because of the wave hydrodynamics. Greenberg (1956) observed that the larger the amplitude of the wave, the faster it moves past the measuring station, and the less its effect on the film thickness as compared to a volume-averaged measure. In light of the findings by Greenberg and also by Chu and Dukler (1974), the time-averaged film thickness
measurements would be less than the volume-averaged measurements made by Portalski (1960). Therefore, the time-averaged method more accurately predicts the transfer of heat through the film.

Fulford (1964) reviewed the open literature through 1959 and gleaned some 1013 data for film thickness. As examples, experiments by Hopf (1910); Chwang (1928); Cooper, Drew and McAdams (1934); Friedman and Miller (1941); Grimley (1945); Brauer (1956), and Zhivaikin (1962) all showed data similar to those predicted by Nusselt's theory for flows upwards of 1600 Re number. The film measurements were made using either a stop-flow, shadow photograph or micrometer needle technique. Portalski (1960) gives detailed criticism of these methods and concluded that the data were suspect for accurate comparison to Nusselt's theory.

Kapitza and Kapitza (1949) pioneered both experimental and theoretical analysis of sinusoidal wavy film flows. Kapitza was the first to recognize the importance of capillary forces on thin films having an appreciable curvature of the free surface. Allen (1962), Levich (1962) and Portalski (1960) present excellent reviews of the Kapitzas' work. Briefly, Kapitza and Kapitza scaled the momentum equations and reduced them to the familiar boundary layer form, where

\[
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \frac{\partial^2 u}{\partial x^2} + g, \quad (2.15)
\]

\[
\frac{\partial p}{\partial y} = 0, \quad (2.16)
\]

which are subject to the following boundary conditions:
capillary forces
\[ p \equiv -\sigma \frac{d^2 \delta}{dx^2}, \quad (2.17) \]
zero interfacial shear
\[ \mu \frac{\partial u}{\partial y} = 0, \quad (2.18) \]
no slip at the wall
\[ u = v = 0. \quad (2.19) \]
Eq. 2.16 shows that the pressure gradient is independent of the transverse \( y \) coordinate; this justifies substituting Eq. 2.17 into Eq. 2.15. Substituting the parabolic velocity profile expressed by Eq 2.7 into Eq. 2.15 and then averaging Eq. 2.15 by integrating over the film thickness and dividing by \( \delta \) leads to the equation
\[ \frac{\partial \bar{U}}{\partial t} + 0.9 U \frac{\partial \bar{U}}{\partial x} = \frac{\sigma}{\rho} \frac{\partial^3 \delta}{\partial x^3} - \frac{3v \bar{U}}{\delta^2} + g. \quad (2.20) \]
Kapitza, and later, Portalski (1960) and Levich (1962), recast Eq. 2.20 into an ordinary differential equation using the new variable \( x - U_w t \). Here \( U_w \) is the wave velocity. The waves are assumed to be long, periodic and sinusoidal, and are characteristic of the first transition wavy flows depicted in Fig. 2.1. Kapitza (1948) formulated a force balance equating the gravity force against the energy dissipated by the viscous force. This led Kapitza to the hypothesis that a steady and stable flow occurs when the film thickness attains a minimum with which the balance between energy dissipated and the work done by gravity can be maintained. He believed that a minimum film thickness corresponded to the minimum potential energy of the film and to the most stable flow. Kapitza’s theory yielded the following solution applicable only to wavy-laminar flows having a wavelength \( \geq 14\Delta \):
\[ Nt = \left\{ 0.599 \text{ Re} \right\}^{\frac{1}{3}}, \quad (2.21) \]
which is about 7% less than Nusselt's solution for smooth laminar film flow. Kapitza concluded that the most stable system had the least potential energy and that sinusoidal wavy flow was not necessarily the most stable flow pattern. He believed other flow regimes may lead to solutions describing wavy flows with a smaller film thickness and consequently a greater stability.

The solution methodology for the boundary layer analysis is not included because of the considerable detail and graph-type solutions used by Kapitza (1948). However, an excellent review of the setup and solution for Eq. 2.20 is presented by Portalski (1960), and Levich (1962) for the interested reader. Most important, Kapitza's results encouraged continued research. With improvements in measurement techniques, Jackson (1955), Greenberg (1956), Charvonia (1959), Portalski (1960), Allen (1962), Clegg (1969), and Chu and Dukler (1974) discovered appreciable reductions (upwards of 20 to 25%) of Nusselt's laminar flow theory. Even more important, they observed reductions to Kapitza's film thickness, Eq. 2.21, for wavy-laminar flow.

Jackson (1955) used a radioactive material dissolved in a liquid to measure the average film thickness in a wavy-laminar flow. He was one of the first to show that liquids more viscous than water had a film thickness which deviated from Nusselt's laminar flow theory. Portalski (1960) pointed out that Jackson used water to calibrate his system against Nusselt's theory and therefore biased his data. Fiend (as cited by Fulford 1964, pp. 180) used an improved stop-flow drainage technique; he tested liquids with kinematic viscosities ranging from 1 to 20 centistokes. In the laminar flow regime, his data closely matched laminar flow theory. Once waves appeared, his
data deviated from the \( N_t \) number, and as the \( Re \) number increased towards 1600, Feind’s data transitions back toward the \( N_t \) number. Feind did not discriminate similar flow regimes, as did Ishigai et al. (1972); however, his empirical correlation based on volume-averaged measurements are

\[
N_t = 1.442 \left( \frac{\nu}{\nu_R} \right)^{0.025} \left[ \frac{Re}{4} \right]^{0.11},
\]

for the region \( 2.9 \times 10^3 < Re \leq 5.4 \times 10^3 \),

\[
N_t = 1.442 \left( \frac{\nu}{\nu_R} \right)^{-0.055} \left[ \frac{Re}{4} \right]^{-0.03} \left( \frac{1}{3} \right)^{0.025},
\]

for the region \( 5.4 \times 10^3 < Re \leq 24 \times 10^3 \), and

\[
N_t = 1.442 \left( \frac{\nu}{\nu_R} \right)^{-0.055} \left[ \frac{Re}{4} \right]^{-0.03} \left( \frac{1}{3} \right)^{0.025},
\]

for the region \( 24 \times 10^3 < Re \leq 1600 \).

Feind used a relative viscosity term \( \nu/\nu_R \), where \( \nu_R \) was set to \( 0.6 \times 10^{-6} \) m\(^2\)/s.

Dukler and Bergelin (1952) proposed using Prandtl and von Kármán’s concept of a universal velocity profile for internal turbulent pipe flow to directly calculate the thickness of a falling film. The equations for the universal velocity profile are due mainly to the experimental work of Nikuradse. Prandtl and von Kármán’s contributions are discussed in White (1986); Nikuradse’s experimental work is found in Robertson and Crowe (1975). Nikuradse’s data on pipe flow revealed the existence of a universal velocity profile in terms of two parameters, \( u^+ \) and \( y^+ \). Dukler and
Bergelin (1952) applied these two parameters to falling films and developed the following definitions for von Kármán’s parameters:

\[ u^+ = \frac{u}{u^*} = \frac{u}{(\sqrt{\frac{\tau_{Wall}}{\rho}})} = \frac{u}{(\sqrt{\Delta g})}, \quad (2.25) \]

and

\[ y^+ = \frac{u^* \rho y}{\mu} = \frac{\left(\sqrt{\frac{\tau_{Wall}}{\rho}}\right) \rho \Delta}{\mu} = \frac{(\Delta)^{3/2} g^{1/2}}{v} = \frac{Re(Fr)^{1/2}}{4}. \quad (2.26) \]

Portalski (1963) was encouraged by Dukler and Bergelin’s work; he concluded that von Kármán’s velocity profile for pipe flow was, at that time, the best available theory for predicting the average film thickness. Later, Portalski (1977) modified von Kármán’s velocity profile to best describe all the regimes of thin film flow. The resulting profiles by Portalski (1977) are

\[ u^+ = y^+, \quad \text{for } 0 < y^+ \leq 2 \quad (2.27) \]

\[ u^+ = 0.3 + 0.85 y^+, \quad \text{for } 2 < y^+ \leq 10 \quad (2.28) \]

\[ u^+ = 1.7 + 0.85 \ln(y^+), \quad \text{for } 10 < y^+ \leq 30 \quad (2.29) \]

\[ u^+ = 5.1 + 2.1 \ln(y^+), \quad \text{for } 30 < y^+ \leq \Delta^+ \quad (2.30) \]

The weight rate of liquid flow per unit of perimeter can be defined in terms of \( u^+ \) and \( y^+ \) as:

\[ \Gamma = \mu \int_{0}^{\Delta^+} u^+ dy^+ \quad (2.31) \]

Portalski (1977) divided Eq. 2.31 into separate integrals and substituted the velocity profiles pertinent to the respective regions of flow. The integrals are delineated by the
respective boundary conditions (Eqs. 2.27 through 2.30). For example, for a flow
whose strength is bounded by $10 < y^+ \leq 30$, Eq. 2.31 becomes

$$\frac{\Gamma}{\mu} = \frac{\text{Re}}{4} = \frac{2}{0} y^+ dy^+ + \int_{2}^{10} \left(0.3 + 0.85y^+\right) dy^+ + \int_{10}^{\Delta^+} \left(1.7 + 0.85 \ln(y^+)\right) dy^+, \tag{2.32}$$

where $\Delta^+$ is a dummy variable representing the magnitude of $y^+$ at the given flow
rate. After integrating and collecting terms Eq. 2.32 becomes

$$\frac{\text{Re}}{4} = 0.128 + 0.85y^+ + 0.85y^+ \left[\ln(y^+)\right]. \tag{2.33}$$

Eq 2.33 is solved iteratively for $y^+$, and the mean film thickness is then directly
determined using Eq. 2.26. The author has found Portalski's correlation very accurate
when compared to literature data for film thickness. The only important caveats to
mention here are (1) the correlation neglects capillary forces, which can affect falling
film hydrodynamics, and (2) Portalski's formulation is based on volume-averaged
rather than time-averaged data. The implications of the type of film average are best
seen by the works of Greenberg (1956), Charvonia (1959), Allen (1962), Clegg and
Portalski (1972), and Chu and Duldler (1974).

Greenberg (1956), Charvonia (1959) and Allen (1962) all used a photometric light
absorption technique to measure the rapidly fluctuating film thickness of a wavy
flow. Greenberg (1956) as well as Portalski (1960) measured the falling film
characteristics for liquids having a wide range of density, viscosity and surface
tension. Each researcher observed findings similar to those of Morioka, Kiyota and
Nakao (1993), again illustrated in Fig. 2.1. The film enters smooth, becomes
unstable, and transitions into small-amplitude but fast-moving waves which then
grow into longer and much-larger-amplitude roll waves.
Increasing the viscosity increased the deviation between Greenberg's time-averaged film thickness and Nusselt's thickness (Eq. 2.9). Increasing the surface tension had similar effects and caused an increased thinning of the film. However, increasing the density caused an increase in body forces which then decreased the deviation from Nusselt's theory. Greenberg (1956) had also measured the film thickness at several locations along the running length of the film. He was surprised by the large starting lengths required for the flow to become fully developed. Using the film thickness as a characteristic dimension, he determined that the starting length for fully developed flow was between 960 and 1380 characteristic lengths. Ishigai et al. (1972) experimentally found, for water with Re numbers greater than 320, that the wave crests grow almost linearly, and do not fully develop even after 2 m. However, Ishigai et al. also observed that, for 50% ethylene glycol with a Re number less than 260, the crests reached a finite limit after about 0.5 m.

Allen (1962) showed from recorded film profiles a roll wave, push wave pattern which traveled over a thin laminar sublayer, termed the film substrate. He observed the film substrate to thin, and showed through an approximate calculation that the total mass traveling in the roll waves increased along the length of the tube. This thinning of the film substrate was later experimentally verified in independent studies by Clegg and Portaliski (1972) and by Chu and Dukler (1974) (Fig. 2.5). Clegg and Portaliski mapped the instantaneous film profile along the flow direction. A gradual reduction in the mean film thickness was measured upon the onset of wavy flow. Chu and Dukler calculated a mass flow in the large roll waves which was, surprisingly, 10 to 20 times greater than that flowing in the substrate (Fig. 2.5). At a Re number of 1000,
Figure 2.5. Re number of the flow in the substrate of a falling film compared to the Re number of the total liquid flow (adapted from Chu and Dukler 1974).
Chu and Dukler measured the Re number for the substrate to be only 70, or only 7% of the total flow.

Dukler’s work proved that the major part of the falling film was carried downstream by the ever-increasing roll waves. Therefore, for an absorbing film, the hydrodynamic findings led Dukler and Chu (1974) to view the velocity, concentration and temperature gradients in the substrate differently from those in the large roll waves. Dukler, in his award-winning lecture (1976), described the falling film as composed of large liquid lumps flowing over a thin substrate. He hypothesized that the large wave swept up liquid from the front-running push waves and deposited a freshly churned film behind. Brauner and Maron (1982) substantiated Dukler’s concepts and experimentally proved that mass transfers from within the substrate to the front of the wave in a mixing eddy. They made simultaneous measurements of the mass transfer and the film thickness: mass transfer was measured using an electrochemical technique (Mizushina 1971); film thickness was measured using a capacitance technique (Dukler and Bergelin 1952). Note that the mass transfer defined by Brauner and Maron’s experiments describes the redistribution of mass that occurs within the film; it is not the transfer of absorbate mass onto a liquid-vapor interface. The results in Fig. 2.6 show a fluctuation in the mass transfer within the film, which is directly related to the fluctuations in the wavy flow. The more intense the waves, the greater the fluctuations in mass transfer for Re numbers increasing from 85 to 280. Brauner and Maron also noted that the recordings of local film thickness and mass transfer rate revealed a sharp rise in mass transfer just ahead of the moving wave front. Because of the deep penetration of the large roll waves into the substrate, the slower velocity liquid in the thin substrate is continuously picked up and mixed into
Figure 2.6. Simultaneous measurements of the film thickness and the liquid pickup rate from the substrate of a falling film (adapted from Brauner and Maron 1982).
the wave front. Brauner and Maron (1983) stated: “The transfer rate continuously increases as the wave front is passing by, reaching a maximum value just beyond the wave peak. The major increase in transfer rate occurs in the wave front region. At the wave tail a decay in the transfer rate takes place which seems to end at the thin substrate film.”

The results of Allen (1962), Chu and Dukler (1974) and Brauner and Maron (1982) have helped better formulate the hydrodynamic concepts for wavy film flow. Brauner and Maron (1983) also gave helpful insight into the mechanism for the growth of the roll waves observed by Allen (1962) and Chu and Dukler (1974). The experimental results depict a film flow phenomena of isolated mass-carrying waves which sweep up fluid from the slower-moving substrate. The flow rate varies with time as the mass-carrying waves pass a given point. The pickup of mass is greatest at the wave’s front. The waves continue to grow and cause a thinning of the laminar substrate. Fully developed flow occurs only after about 0.5 m.

2.1.3 Wavy-Laminar Models

Dukler (1976) laid a groundwork for modeling wavy flows which academia readily accepted for this nonlinear and non-steady-state problem. He viewed the large roll wave as a literal reservoir for the film and pictured a plate drawn upward at a velocity equivalent to but in opposite direction of the wave. He then calculated the substrate film thickness using White and Tallmadge’s (1965) theory for laminar flow withdrawal. Except for turbulent flow, excellent agreement was seen between the
withdrawal theory and Dukler's data. Dukler’s concept also simplified the non-
steady-state problem by transforming the governing equations into a traveling
coordinate system. The transform reduced the wave model to a set of ordinary
differential equations with inclusion of an additional parameter, the wave velocity.

The approaches used to model wavy-laminar flows incorporate the physics first
offered by Dukler (1976). Brauner modeled wavy flow using an integral approach
that required experimental data. Li-Qun Yu (1995) reduced the momentum equations
into boundary layer form, transformed them using the stream functions, and applied
the method of weighted residuals for solving the resulting wave equations. Wasden
and Dukler (1989) solved the momentum equations using numerical techniques and
studied the effects of the hydrodynamics on a gas-absorbing interface. The three
approaches are discussed below to reveal the complexities of wavy laminar flows
having free surface boundary conditions.

2.1.3.1 Integral Approach
Brauner and Maron (1983) used the moving-coordinate concept, and in light of the
non-steady mass flow characteristics of the film, divided the wave into a series of
zones (Fig. 2.7). Conservation of mass was applied to the zones of the substrate, the
wave tail, the wave and the wave front by formulating a balance of the mass passing a
plane normal to the flow direction during the time interval of $1/F$ (the period of the
wave). Brauner and Maron (1983) defined $F$ as the wave frequency. The total mass
flow rate, per unit of wetted perimeter, was equated to the mass carried by each of
Figure 2.7. The wave and coordinates for Brauner's integral model (adapted from Brauner and Maron 1983).
these zones. A local film thickness, $\delta$, and local average velocity, $\bar{u}$, were used in each zone. Brauner expressed continuity as

$$\frac{\Gamma}{F} = \rho \int_{0}^{t_f} (\bar{u}\delta)_{fr} dt + \rho \int_{0}^{t_w} (\bar{u}\delta)_{w} dt + \rho \int_{0}^{t_t} (\bar{u}\delta)_{t} dt + \rho \int_{0}^{t_s} (\bar{u}\delta)_{s} dt.$$  \hspace{1cm} (2.34)

The times $t_f$, $t_w$, $t_t$ and $t_s$ were defined as the time duration required for the different wave zones to pass a fixed plane. The time scale was eliminated by introducing a constant wave velocity whereby $dt = dl/\bar{u}_w$, which transformed the continuity equation into the following form:

$$\frac{U_w \Gamma}{F} = \rho \int_{0}^{L_F} (\bar{u}\delta)_{fr} dl + \rho \int_{0}^{L_w} (\bar{u}\delta)_{w} dl + \rho \int_{0}^{L_t} (\bar{u}\delta)_{t} dl + \rho \int_{0}^{L_s} (\bar{u}\delta)_{s} dl.$$  \hspace{1cm} (2.35)

where $L_F$, $L_w$, $L_t$ and $L_s$ are the lengths of the wave front, the wave, the wave tail and the substrate, respectively. Given Brauner's experimental discovery, the liquid pickup in the wave front was expressed in a moving coordinate frame as $\psi = \delta(U_w - \bar{u})$, where $\psi$ is the rate of liquid picked up from the substrate. It is constant when viewed in a moving coordinate; however, Brauner noted that for a fixed coordinate, the actual pickup rate varies. Solving for $\bar{u}$ and substituting into Eq. 2.35, Brauner derived the following continuity relation:

$$\frac{U_w \Gamma}{F} = \rho U_w \left\{ \int_{0}^{L_F} (\delta)_{fr} dl + \int_{0}^{L_w} (\delta)_{w} dl + \int_{0}^{L_t} (\delta)_{t} dl + \int_{0}^{L_s} (\delta)_{s} dl - \frac{\psi}{F} \right\}.$$  \hspace{1cm} (2.36)

The expression describes the continuity of the wave passing a fixed plane during the time interval $1/F$. It states that the inlet mass flow rate equals the total wave mass flow rate (i.e., front, wave, substrate and tail) less the mass of liquid picked up from the substrate by a successive wave front.
Momentum balances were also solved for each zone, and the solutions were matched at the common boundaries. For example, one of Brauner’s momentum balances in a coordinate system moving with the wave velocity yields for the wave front

\[ \rho \frac{d}{dx} \left[ \delta (u - U_w)^2 \right] = \rho \delta g \{ \sin(a) \} - \tau_{wall} - \rho \delta g \{ \cos(a) \} \frac{d\delta}{dx}, \]  

(2.37)

with the conditions at the front boundaries being

\[ L = 0 \quad \delta = \delta_{pk} \quad \bar{u} = \bar{u}_{pk}, \]

and

\[ L = L_{fr} \quad \delta = \delta_s \quad \bar{u} = \bar{u}_s \]  

(2.38)

Brauner’s formulation included thirteen unknowns, four unknowns of length (i.e., \(L_{fr}, L_w, L_t\) and \(L_s\)), thickness and average velocity per zone, and an additional three unknowns of velocity, wave frequency and liquid pick-up rate for the whole wave. Her model included twelve independent equations and therefore required information on one variable to solve for the twelve unknowns. She selected either wave frequency or wave velocity for closure of the problem. Documentation of Brauner’s twelve independent equations is found in Brauner and Maron (1983) and in Brauner (1989). Her formulation requires input for an interface velocity parameter \(\phi_0 = 1 - u_{inf}/U_w\), which represents the deviation from stagnation for a moving coordinate system. Hence, Brauner’s model is empirical but supports the prediction of wave characteristics without the rigors of a numerical approach. Patnaik (1994) used the salient features of Brauner’s model as input to a heat and mass transfer numerical code for solving the temperature and concentration distribution in an aqueous LiBr film. His work is discussed in Sect. 2.2.4.
Brauner checked the model against data obtained from Chu and Dukler (1974), Webb and Hewitt (1975) and Zabaras (1985) for water on vertical surfaces. The predicted wave velocity, substrate thickness and wave peak showed satisfactory agreement with experiment, provided $c_0$ was confined to about 0.2. Brauner and Maron (1983) was also able to successfully predict the fraction of liquid flowing in the substrate of a wavy-laminar flow. Surprisingly, the fraction ranged between only 4 to 20% of the total flow rate, which substantiated Dukler’s work.

2.1.3.2 Method of Weighted Residuals

Linear stability analysis has been used by Benjamin (1957); Benney (1966); Rushton and Davies (1971); Pierson and Whitaker (1977); Alekseenko, Nakoryakov and Pokusaev (1985); Barrdahl (1986); Brauner, Maron, and Zijl (1987); Solorio and Sen (1987); Chang (1989); and others to analyze both the behavior and the onset of wavy film flows. Their approach uses flow disturbances that are either time- or space-dependent. The flow disturbances are imposed on the momentum equations and lead to equations of the Orr-Sommerfeld type (Benjamin 1957). Perturbation, power series or iterative finite difference techniques are used to solve for the velocity and amplitude of the most dominant waves. The approach, however, is only good for low Re number flows where the presence of nonlinear effects are small. Pierson and Whitaker (1977) extended the validity of the solution to a Re number of 375, although, their procedure required a tedious and time-consuming direct numerical integration of the governing equations.
As a simple alternative, Yang and Wood (1991) and Yu (1995) reduced the momentum equations to boundary layer form and manipulated them to deduce an equation of motion in terms of the free interface and interfacial velocity. Yang and Wood followed Kapitza’s and Levich’s techniques and derived a nonlinear third-order ordinary differential equation in terms of the free surface. They assumed a periodic wave profile. Collocation methods were used to develop approximate solutions of the wavy surface. Yang and Wood’s solution were, however, coupled to Pierson and Whitaker’s data, and Yang stated the results as good for Re numbers less than 150. Nonlinear wave effects and deviations from a parabolic velocity profile made Yang and Wood suspect the accuracy of solutions for Re numbers exceeding 150.

Li-Qun Yu (1995), under the guidance of the Dr. Abe Dukler and Dr. Vemuri Balakotaiah, modeled the nonlinear evolution of waves on thin films for Re numbers exceeding 300. Yu’s model, mathematically describing the two-dimensional wavy film flow, contains the conservation of x-momentum as

\[ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + g + v \left( \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial x^2} \right), \]  

the conservation of y-momentum as

\[ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + g + v \left( \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial x^2} \right), \]  

and the conservation of mass as

\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \]

with the boundary conditions of no slip at the wall given by \( u = v = 0 \) at \( y = 0 \), the kinematic condition of the free surface given by

50
\[ v = \frac{\partial \phi}{\partial t} + u \frac{\partial \phi}{\partial x} \text{ at } y = \delta. \] (2.41)

the tangential shear stress condition given by

\[
\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \left[ \frac{\partial v}{\partial y} - \frac{\partial u}{\partial x} \right] \frac{2(\partial \delta / \partial x)}{1 - (\partial \delta / \partial x)^2} = 0 \text{ at } y = \delta, \] (2.42)

and the normal stress condition at the free surface given by

\[ P - P_0 + \frac{2\mu}{1 + (\partial \delta / \partial x)^2} \left\{ \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \frac{\partial \delta}{\partial x} - \frac{\partial u}{\partial x} \left( \frac{\partial \delta}{\partial x} \right)^2 - \frac{\partial v}{\partial y} \right\} + \frac{\sigma (\partial^2 \delta / \partial x^2)}{1 + (\partial \delta / \partial x)^2} = 0. \] (2.43)

Yu scaled Eqs. 2.39 through 2.43 and formulated two different boundary layer models. The first model parallels Kapitza’s work and is mathematically described by Eqs. 2.15 through 2.19 with inclusion of Eq. 2.41 for the free surface condition. Yu found that Kapitza’s model could not predict large amplitude waves; he therefore formulated the following second-order model:

\[
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = - \frac{1}{\rho} \frac{\partial p}{\partial x} + g + \nu \left( \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial x^2} \right), \] (2.44)

\[ \frac{\partial \rho}{\partial y} = \rho \left( \frac{\partial^2 \delta}{\partial x^2} \right) u^2 \] (2.45)

Yu approximated the normal pressure gradient using a singular perturbation method devised by Schlichting (1979); he replaced Eq. 2.40 with Eq. 2.45, where the term \( \partial^2 \delta / \partial x^2 \) approximates the curvature of the free surface. Continuity and the kinematic condition for the surface are as before:

\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \]
\[
v = \frac{\partial \delta}{\partial t} + u \frac{\partial \delta}{\partial x} \ \ \text{at} \ \ y = \delta(x, t).
\] (2.46)

Yu used a scaling analysis to reduce the free surface shear stress condition to

\[
\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + 4 \frac{\partial \delta}{\partial x} \left[ \frac{\partial v}{\partial y} \right] = 0 \ \ \text{at} \ \ y = \delta(x, t),
\] (2.47)

and the normal stress condition to

\[
P - P_Y - 2\mu \left[ \frac{\partial v}{\partial y} \left( \frac{\partial u}{\partial y} \right) \frac{\partial \delta}{\partial x} \right] + \sigma \frac{\partial^2 \delta}{\partial x^2} = 0 \ \ \text{at} \ \ y = \delta(x, t)
\] (2.48)

Yu solved Eqs. 2.44 through 2.48 using the method of weighted residuals. The method assumes a solution composed of specified trial functions which have adjustable constants for satisfying the governing equation and boundary conditions. He selected the stream function to include streamwise variations in acceleration, its formulation being

\[
\Psi(x, y, t) = a_0(x, t) + a_1(x, t)y + \sum_{i=2}^{5} a_i(x, t)b_i(y),
\]

where

\[
b_i(y) = \left( y^i - \frac{(2i - 3)y^{i+1}}{(2i - 1)(2i)} \right).
\] (2.49)

Prokopiou, Cheng and Chang (1991) showed that a parabolic velocity profile did not adequately represent the effect of wall-shear stress on the wave shape. Yu therefore included six terms in Eq. 2.49, and he calculated the \(a_i\) coefficients using both boundary and integral conditions. Details of his derivations are found in Yu (1995) and also in Yu et al. (1995).
Yu studied the falling film profiles for pure water having a Ka number of 3371 and a Re number of 600. He mapped the streamlines for two large waves having peak to substrate ratios of 2.8 and 3.6 (Fig. 2.8). Yu showed that the normal inertia force, near the front of the wave, was ten times that of gravity's force. The fluid in the recirculation zone is nearly acceleration-free; however, Yu found significant deceleration just below the recirculation zone. Levich (1962) had shown that a transverse velocity of only 1% of the streamwise velocity yielded a 15% increase in mass transfer to the interface. Yu's data shows, for the example in Fig. 2.8, a transverse velocity which is 30% of the streamwise velocity. Yu therefore strongly inferred that the large waves are the driver for enhanced mass transfer.

As final caveats, Yu (1995) found that the Kapitza boundary layer model and the second-order boundary layer model both predicted similar trends. However, the secondary boundary layer model yielded a slightly larger film thickness and better predicted the wall-shear stress at the front of the large roll waves. It is also very interesting to note that Yu was unable to obtain solutions for certain wave velocities. As the wave velocity decreased, the wave amplitude increased until the wave profile became chaotic. Yu conducted a stability analysis of his secondary boundary layer equations and discovered the presence of a Hopf bifurcation for certain nonlinear waves.¹ Studies conducted near this bifurcation value showed chaotic nonlinear waves as the wave velocity drops below the value associated with the Hopf bifurcation.

¹ Hopf bifurcation is a stability analysis used to find any branching points where one point yields a stable solution and the other yields no solution due to instability. Subsequently, new solutions are constructed with continuous variations of the stability parameter.
Figure 2.8. Solution of Yu's stream function expansions showing the streamline contours for two different roll waves (adapted from Yu 1995).
2.1.3.3 Numerical Approach

Wasden and Dukler (1989) conducted numerical simulations of the different wave shapes observed on a falling film. They also experimentally measured the film thickness and the wall-shear stress. Measurements were made in a 50.8-mm ID vertical test tube for a Re number of 880; the measurement station was located 3.1 m below the injection point (Zabaras, Dukler and Maron 1986). Wasden and Dukler used the experimental data in a novel simulation approach for solving for the free surface flow phenomena.

Wasden and Dukler found that a direct solution of the Navier-Stokes equations had convergence problems because of the stress-free interface. An approach was needed for solving the governing equations and for determining the wave shape. They used their measured film thickness data for the wave shape, and given a measured δ(x), devised a scheme to find the streamwise location, x, that resulted in a shape and flow field that satisfied the free interface boundary conditions. Hence, they did not predict the shape of the interface; rather, the numerical solution corresponds to a given case of film flow, provided the interface assumed the shape input by these researchers. Wasden incorporated Dukler’s hydrodynamic concepts and transformed both the wave profile and the governing equations into a moving coordinate system. The system has the wave remaining fixed, and the wall moves upward at a constant speed, \( U_w \). The new streamwise velocity becomes \( u(x, y) = -u'(x, y, t) + U_w \), where \( u'(x,y,t) \) is the streamwise velocity in a coordinate system fixed on the wall.
Roll waves evolve rapidly over the streamwise coordinate and can change from solitary to interactive waves which encounter small front-running push waves. Wasden and Dukler modeled the effect by transforming the wave into a locally variable parameter \( x_i = x_o + U_{w,i}(t_i - t_o) \), where \( x_i \) is the streamwise coordinate fixed on the wave front, and \( U_{w,i} = U_w(1 + e(x_i)) \). The wave profile, \( U_{w,i} \), was specified, and they changed \( e(x_i) \) to adjust for an evolving wave shape. They compared the measured wall-shear stress to that computed for a given iterative wave profile and iterated on \( e(x_i) \) until the deviation between the computed and the measured wall-shear stress was small. For a solitary wave, similar in shape to that observed at a Re number of 141 in Fig 2.1, Wasden and Dukler set \( e(x_i) = 0 \); here, the wave shape does not deform.

The transformations used by Wasden and Dukler supported locally variable mass and momentum sources for the x-momentum and continuity equations. The approach simulated the deforming of the wave shape as it fell down the tube, as well as the chaotic wave interactions observed at a Re number of 812 (Fig. 2.1). Given these transformations, their formulation of the governing equations are as follows:

for the x-momentum equation

\[
\frac{\partial u}{\partial x} + \frac{dU_w}{dx} + \frac{\partial u}{\partial y} = \frac{-1}{\rho} \frac{\partial p}{\partial x} - g + \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} - \frac{d^2 U_w}{dx^2} \right);
\]  

(2.50)

for the y-momentum equation

\[
\frac{u}{\partial x} + \frac{v}{\partial y} = \frac{-1}{\rho} \frac{\partial p}{\partial y} + \nu \left( \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial x^2} \right);
\]

(2.51)
and for the continuity equation

\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} - \frac{dU_w}{dx} = 0. \tag{2.52} \]

Equations 2.50 through 2.52 are subject to the stress free interface conditions. The tangential shear stress condition becomes

\[ \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \left[ 1 - \left( \frac{d\delta}{dx} \right)^2 \right] - 2\left( \frac{d\delta}{dx} \right) \left( \frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} - \frac{dU_w}{dx} \right) = 0 \text{ at } y = \delta(x), \tag{2.53} \]

and the normal stress condition becomes

\[ P = \frac{\sigma \left( \frac{d^2\delta}{dx^2} \right) }{1 + \left( \frac{d\delta}{dx} \right)^2} + \frac{2\mu}{1 + \left( \frac{d\delta}{dx} \right)^2} \left[ \left( \frac{\partial u}{\partial x} \right) \frac{d\delta}{dx} - \left( \frac{\partial u}{\partial y} + \frac{\partial \delta}{\partial x} \right) \frac{d\delta}{dy} + \frac{\partial v}{\partial y} \right]. \tag{2.54} \]

The kinematic condition in moving coordinates reduces to \( \nu = u \left( \frac{d\delta}{dx} \right) \) at \( y = \delta(x) \), and at the wall \( u = U_w, \nu = 0 \). Wasden and Dukler discretized Eqs. 2.50 through 2.54 using a fully implicit finite-difference scheme and coded the model in FORTRAN-77 programming language. A nonuniform finite-difference grid was constructed having about 1200 control volumes in the y-direction and about 100 control volumes in the x-direction. The convective momentum terms were discretized using the QUICK scheme developed by Pollard and Siu (1992). They solved for the pressure and velocity distribution using Patankar’s (1980) SIMPLER algorithm. Wasden and Dukler input a \( U_w \), initialized the \( u \)-velocity field using a parabolic profile and set the \( v \)-velocity field to zero. Iterations continued until the sum of residuals of the mass and momentum over the flow domain were less than \( 10^{-3} \).
Wasden and Dukler (1989) stated that the procedure for solitary waves required 300 iterations for a converged velocity and pressure field. For interacting or evolving waves this increased to about 500 iterations, and the adjustment of the variable wave velocity required upwards of 40 iterations to match wall-shear-stress data. Execution times for convergence of the velocity and pressure fields for a given wave shape were of about 5 hours of processing time on a VAX 11-750 platform.

Selected results from Wasden and Dukler’s works are shown in Fig. 2.9 for an evolving wave emanating from a falling film having a Re number of 880. The wave is similar to flow observed by Morioka, Kiyota and Nakao (1993) at Re number 812 (Fig. 2.1); it has a peak-to-substrate thickness ratio of about 3. Wasden and Dukler numerically simulated the evolving wave by adjusting the code’s e(x) parameter until the difference between the computed and the measured wall-shear stress converged along the wave. Note that the streamlines are very similar to those computed by Li-Qun Yu (1995), and based on streamline continuity, imply that the wave travels as a lump of mass over a slower-moving substrate. Secondary flows are seen within the wave [Fig. 2.9(a)], with large normal velocities observed near the front and rear of the wave. The result showed them that a parabolic velocity profile, which yields a maximum inertial force at the interface, could not accurately predict the wall-shear stress under the wave as well as the wave’s surface velocity. They discovered that a cubic velocity profile accurately matched the simulation’s velocity data over all regions of the wave structure.

Wasden and Dukler calculated large surface accelerations particularly near the front and rear of the recirculation zone [Fig. 2.9(a) and (c)]. At the wave front, the inertial
Figure 2.9. Numerical simulations for an evolving wave having a peak-to-substrate thickness ratio of 3 and flowing at Re number 880 (adapted from Wasden and Dukler 1989, 1990).
forces were 2.3 times that of gravity; larger acceleration effects occurred nearer the surface than the wall [Fig. 2.9(c)]. Fluid in the wave front accelerates into the mass of the slower substrate, mixes under the wave, and then decelerates beyond the wave. The recirculation process, inferred from their inertial map in moving coordinates [Fig. 2.9(c)] may account for the enhanced rates of heat and mass transfer reported for wavy film flows. The mass enhancements are further reviewed in Fig. 2.9(b) and (d).

Wasden and Dukler (1990) adapted the numerical code to solve the diffusion equation for gas absorption through the wavy interface. The code solved for the velocity and pressure field, and used the velocity field for solving the diffusion equation. For a moving coordinate system, Wasden discretized the diffusion equation

\[
(u - U_w) \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D_{ab} \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right),
\]

subject to the initial condition that a pure solution enters as \(c(0, y) = 0\), for all \(y\) with the boundary conditions of \(c(x, \delta) = c_{sat}\), for all \(x\) and \(\partial c/\partial y = 0\) for \(y = 0\) and for all \(x\). The concentration field for Wasden's evolving wave, Re number 880, is shown in Fig. 2.9(b) for Schmidt numbers of 500 and 1000, respectively. The field is mapped in intervals of 0.1 units of saturated isoconcentration lines. The Sc number represents the penetrating strength of the absorbate; the higher the Sc number the less the penetration into the film, as observed in Fig. 2.9(b). Wasden observed that the transverse \(v\) velocities cause the observed deformation of the isoconcentration lines near the front and rear of the wave. These normal velocities, adjacent the recirculation zone, drove the absorbate from the surface into the wave substrate and
caused the mass flux to increase sharply near the wave front [Fig. 2.9(d)]. The flux then drops because of the drop in the normal velocities near the interface stagnation points (remember, Wasden is using a moving coordinate system, and the stagnation points correspond to the zero curvature of the streamwise velocity). As the wave evolves in time, mass transfer is enhanced by the convective motion. Wasden and Dukler calculated mass enhancements ranging from 1.7 to 3.5 times those expected for smooth laminar flow.

2.2 Simultaneous Heat and Mass Transfer

The simultaneous release of heat further complicates the analysis of mass transfer in wavy films. The heat effects at the interface, the heat transfer from the interface and the mass transfer onto and through the interface are all affected by variations of the roll waves. The wavy film is very thin, on the order of 0.5 mm, and it is difficult to accurately measure the surface temperature and calculate the local heat flux. To further exacerbate matters, the composition of a binary mixture cannot be determined solely on temperature. No one has successfully measured the surface concentration in a falling film absorber. These measurements continue to elude researchers but are key to better understanding the local dynamics of the coupled heat and mass transfer process. Therefore, while both experimental and analytical studies have well established the fact of enhancements caused by the presence of wavy flow, the mechanism describing why and how this happens is not clear. Some hypothesized the wavy flow increased the interfacial area; this concept was discounted by Clegg and Portalski (1971). Wasden and Dukler (1990) simulated the
waves as lumps of mass riding a thinning substrate. They and Brauner, Maron and Hewitt (1989) believed the waves would increase mixing of the film while thinning the substrate, leading to transport enhancements. Jayanti and Hewitt (1997) analytically investigated the hydrodynamic effect of the waves on just the heat transfer aspects. They proposed a conduction-dominant mechanism whereby the waves effected heat transfer by simply thinning the film.

Evidently, few studies have addressed both the heat and the mass transfer aspects of the absorption problem, and experimental data are sparse in the open literature. Approximate closed-form and numerical solutions will be reviewed to show the evolution of the methodologies used to approach the problem of simultaneous heat and mass transfer.

2.2.1 Static Pool

The penetration theory was one of the earliest proposed mechanism for mass transfer from a gas-liquid interface into a film. The basic model was proposed by Higbie (as cited by Bennett and Myers 1982, pp. 569), who applied the concept to industrial mass contacting equipment. He pictured a stagnant pool (Fig. 2.10) being brought into contact with a gas phase boundary for a short time, t. The pool is assumed at a uniform concentration, $C_f$, and uniform temperature, $T_f$. The concentration at the gas-liquid interface remains constant at $C^*$, while mass moves by molecular diffusion from the interface into the bulk.
Figure 2.10. Penetration theory applied to a stagnant pool of 62 wt% LiBr.
The process is both time- and distance-dependent and is described by the following partial differential equation:

$$\frac{\partial C}{\partial t} = D_{ab} \frac{\partial^2 C}{\partial y^2}, \quad (2.56)$$

where the initial condition and boundary conditions are as follows:

$$C = C_f \quad \text{at} \quad t = 0$$

$$C = C^* \quad \text{at} \quad t > 0, \ y = 0$$

$$C = C_f \quad \text{at} \quad y = \infty$$

The interface concentration, $C^*$, is assumed to be in equilibrium with the gas concentration and is determined from the saturated gas pressure and film temperature, $T_f$. No heat release occurs, and therefore $T_f$ remains constant. If heat rather than mass were diffusing, the model would be analogous to the problem of transient heat conduction into a semi-infinite wall. The boundary conditions are the same, and the solution proceeds in a similar manner by defining a similarity variable, $\eta$, where

$$\eta = \frac{y}{\sqrt{4D_{ab}t}}. \quad (2.57)$$

Substituting Eq. 2.57 into Eq. 2.56 yields the following ordinary differential equation:

$$\frac{\partial^2 C}{\partial \eta^2} + 2\eta \frac{\partial C}{\partial \eta} = 0, \quad (2.58)$$

which when solved results in the following solution for the concentration profile:

$$\frac{C - C_f}{C^* - C_f} = 1 - \text{Erf} \left[ \frac{y^2}{4D_{ab}t} \right]^{1/2}. \quad (2.59)$$
This solution is known in the open literature as the penetration theory by Higbie (1935). It contains the Gauss error integral and implies a nonlinear rate of diffusion which diminishes with time (Fig. 2.10).

### 2.2.2 Laminar Boundary Layer Analysis

Higbie next applied penetration theory to packed towers. Laminar films, entering at concentration $C_{in}$, would flow over packing elements and be briefly exposed to a gas. Higbie stated that the interfacial concentration remained constant, that convection effects were negligible, and that the absorbate did not release heat. The model also assumes a very thick film which is continuously generated by flow. The solution proceeds as before; however, the short contact time variable, $x/U_{max}$, substitutes for the time variable $t$. The solution for the penetration theory in a laminar film then becomes

\[
\frac{C - C_{in}}{C^* - C_{in}} = 1 - \text{Erf}\left[\frac{y^2}{4D_{ab}(x/U_{max})}\right]^{1/2}
\]  

(2.60)

Surprisingly, Higbie's theory is often in reasonable agreement with many experimental results, whether laminar or wavy-laminar. Its usefulness is easily seen by the solutions generated from Eq. 2.60, which are plotted in Fig. 2.10 for a film of LiBr brine at 62 wt%. Diffusivity of the brine is about $10^{-9}$ m$^2$/s, and mass diffusion is therefore slow. After 10 s of exposure time the mass has penetrated only 0.4 mm. In perspective, the author's test section is 1.524 m long, and a film with a Re number of about 280 would be exposed to absorbate vapor for about 2.5 s. Also for a Re
number of 280, the calculated film thickness is about 0.58 mm. Hence, by penetration theory, the absorbate has diffused only about a third of the way through the thickness of the film (seen by the 2.5-s time line in Fig. 2.10).

The approach used by Higbie was later applied to the case of an absorbate having a large latent heat release. Theoretical treatment required a formulation for the temperature, concentration and partial pressure at the surface, which was not mathematically described until the late '70s when Grigor’yeva and Nakoryakov (1977) introduced the concept of a linear absorbent. This concept implies that the liquid at the interface is in equilibrium with the vapor. Further, Grigor’yeva and Nakoryakov (1977) assumed that the vapor pressure of the gas phase is imposed on the liquid-vapor interface and that the interface temperature and concentration are linearly related by the following formulation:

\[ C^* = aT^* + b. \] (2.61)

The vapor pressure of the absorbate is fixed, and the constants a and b are correlated from the temperature and the concentration thermodynamic data at the imposed pressure. The linear equilibrium relation holds for a number of common absorbents, including aqueous solutions of LiBr, LiCl and CaCl₂.

The novel formulation for the interface condition allowed Nakoryakov and Grigor’yeva (1980) to approach the falling film problem using the boundary layer techniques of Schlichting (1979) (Fig. 2.11).
Figure 2.11. Laminar falling film showing the developing boundary layers.

\[ \eta = \frac{y}{\delta} \]

\[ \xi = \frac{1}{\text{Re Pr}} \frac{x}{\Delta} \]
They defined the problem mathematically using the energy and diffusion equations as:

\[ u \frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial y^2}, \quad (2.62) \]
\[ u \frac{\partial C}{\partial x} = D_{ab} \frac{\partial^2 C}{\partial y^2}. \quad (2.63) \]

Diffusion and temperature gradients in the flow direction are much smaller than those normal to the flow, y-direction, and have been neglected from the right side of Eqs. 2.62 and 2.63. Nakoryakov and Grigor’yeva (1980) understood that the interfacial concentration and temperature are both unknown functions of x. However, they solved the problem for short contact times, similarly to Higbie, and assumed the interface temperature and concentration as unknown but fixed for a short distance. The interface conditions were described by linear absorbent theory, Eq. 2.61, and by a first-principles energy balance, which they formulated as

\[ k \frac{\partial T}{\partial y} = \mathcal{I}_f \rho D_{ab} \frac{\partial C}{\partial y}. \quad (2.64) \]

The remaining boundary conditions used by Nakoryakov and Grigor’yeva to complete the mathematical descriptive are

\[ T = T_{in}, \quad C = C_{in} \quad x = 0, \]
\[ T = T_{wall} = \text{const}, \quad \frac{\partial C}{\partial y} = 0 \quad y = 0. \quad (2.65) \]

Their solutions follow as

\[ \frac{T - T^*}{T^* - T_{in}} = \text{Erf} \left[ \frac{1}{2} \left( \frac{U}{\alpha} \right)^{1/2} \left( \frac{\delta - y}{\eta^{1/2}} \right) \right]. \]
To find the interface temperature and concentration, Nakoryakov and Grigor'yeva substituted the solutions into Eqs. 2.62 and 2.64.


\[
\xi = \frac{1}{\text{Pe}_H} \frac{x}{\delta}; \quad \eta = \frac{y}{\delta}; \quad \frac{\mu(y)}{U} = \frac{3}{2} \left[ 2\eta - \eta^2 \right],
\]

\[
\theta = \frac{T - T_{\text{in}}}{T_{\text{eq}} - T_{\text{in}}}; \quad \gamma = \frac{C - C_{\text{in}}}{C_{\text{eq}} - C_{\text{in}}}.
\]

He scaled the heat and mass transfer terms based on unique temperature and concentration limits. He employed a temperature, \(T_{\text{eq}}\), which he specified as being the equilibrium temperature for the entering solute, \(C_{\text{in}}\), at the imposed vapor pressure. Similarly, a concentration, \(C_{\text{eq}}\), was specified at the entering temperature, \(T_{\text{in}}\), which was also in equilibrium with the vapor pressure. Both \(T_{\text{eq}}\) and \(C_{\text{eq}}\) have physical significance for short contact time analysis. Grossman (1982) stated: "\(T_{\text{eq}}\) is the temperature which would be reached in the film if thermodynamic equilibrium could be achieved without change in concentration. \(C_{\text{eq}}\) is the concentration that would be reached if thermodynamic equilibrium could be achieved without change in temperature."

\[
\frac{C - C^*}{C^* - C_{\text{in}}} = \text{Erf} \left[ \frac{1}{2} \left( \frac{U}{D_{ab}} \right)^{1/2} \left( \frac{\delta - y}{x^{1/2}} \right) \right].
\]
Using these dimensionless variables, Grossman’s formulation becomes

\[
\frac{3}{2} \left[ 2\eta - \eta^2 \right] \frac{\partial^2 \theta}{\partial \xi^2} = \frac{\partial^2 \theta}{\partial \eta^2}, \quad (2.69)
\]

and

\[
\frac{3}{2} \left[ 2\eta - \eta^2 \right] \frac{\partial^2 \gamma}{\partial \xi^2} = \text{Le} \frac{\partial^2 \gamma}{\partial \eta^2}. \quad (2.70)
\]

Grossman (1983) showed that the solution to Eqs. 2.69 and 2.70 depended on two parameters, the Le number and the dimensionless heat of absorption, which he derived from Eq. 2.64 as

\[
\lambda = \frac{f_{D_{ab}} \eta' (C_{eq} - C_{in})}{k(T_{eq} - T_{in})}. \quad (2.71)
\]

The linear absorbent model when scaled using Grossman’s variables becomes:

\[
\theta^* + \gamma^* = 1. \quad (2.72)
\]

Grossman solved Eqs. 2.69 and 2.70 subject to conditions 2.65, 2.71 and 2.72. His normalized temperature and concentration expressions are

\[
\theta = \frac{\lambda}{\lambda + \sqrt{\text{Le}}} \left\{ 1 - \text{Erf} \left[ \frac{3(1 - \eta)^2}{8 \xi} \right]^{1/2} \right\}, \quad (2.73)
\]

and

\[
\gamma = \frac{\sqrt{\text{Le}}}{\lambda + \sqrt{\text{Le}}} \left\{ 1 - \text{Erf} \left[ \frac{3(1 - \eta)^2}{8 \text{Le} \xi} \right]^{1/2} \right\}. \quad (2.74)
\]

Note that he defines \( \text{Le} = D_{ab}/\alpha \), which is the reciprocal of that used by the author (see Table of Nomenclature). As previously stated, Grossman’s solutions are for short
exposure times. They are applicable only for small $\xi$ where the heating effect is well within the developing boundary layer and has not penetrated to the constant temperature wall. Within these developing layers, the velocity is assumed to be uniform, and equal to $\overline{U}$ (by Eq. 2.9). If the dimensionless heat of absorption $\lambda \rightarrow 0$, then the problem would reduce to Higbie’s solution for isothermal mass transfer, Eq. 2.60. If by Eq. 2.74 $\lambda \rightarrow \infty$, then the mass effect $\gamma \rightarrow 0$ and the concentration $C$ would tend toward $C_{in}$, while $T$ would tend to $T_{eq}$. Plainly, the thermal and mass diffusivities control the transfer at the liquid-vapor interface. The greater the heat effect (i.e., latent heat released at the interface), the smaller the concentration change achievable, as described by Eq. 2.74.

An increasing heat effect also increases the surface temperature. Now for a linear absorbent (Fig. 2.12), this in turn causes the interface concentration of absorbate to drop, thereby reducing the maximum possible concentration gradient. However, does the concept of a linear absorbent apply over the full length of the absorber, or should it be restricted to short exposure times where equilibrium at the interface is assured? A linear absorbent is based on static equilibrium, not on the dynamics seen in wavy-laminar films. At issue is the concept of imposing the ambient vapor pressure on the liquid-vapor interface and assuming equilibrium. In other words, is the partial pressure of absorbate in the interface the same as the pressure in the gas phase, especially over the surface of a roll wave and substrate? Past the entrance region, absorption proceeds only as the coolant cools the interface (i.e., cooling lowers the partial pressure at the interface below the vapor pressure, therefore enabling mass transfer). The linear absorbent model poses a paradox, because it describes an increase in temperature (heating effect), which opposes a decrease in concentration
Fig. 2.12 Linear absorbent theory for aqueous LiBr.
(mass effect). The linear absorbent holds for several common salts in static conditions. However, the dynamic environment of a falling film, especially the variation in film thickness with each successive wave, makes the linear absorbent model at best an approximation of the actual interface condition.

As a final caveat, all analytical studies use the linear absorbent theory in order to bring closure to their mathematical descriptive.

### 2.2.3 Laminar Flow

If the mass and/or the heat effects penetrate to the wall (i.e., \( \xi \) is not small), then the velocity profile must be included in the model. Emmert and Pigford (1954) used a parabolic velocity profile and developed an approximate solution for isothermal mass transfer where mass penetrates to the wall. Grigor’yeva and Nakoryakov (1977) and later Grossman (1983) solved Eqs. 2.69 and 2.70 using the Fourier method where trial solutions are expressed as expansions in series of eigenfunctions. Their solutions, however, were limited to moderate and large values of \( \xi \). For small \( \xi \) a large number of terms were required, and the stability of the series made it difficult to obtain convergence for the eigenfunctions. For example, Nakoryakov and Grigor’yeva used more than 50 terms for the Fourier series.

Wekken and Wassenaar (1988), Habib and Wood (1990), and Yang and Wood (1992) completed numerical studies which either complemented or furthered the numerical work of Grossman (1983), who also numerically solved the Gratz-Nusselt
style formulation of Eqs. 2.69 and 2.70. Grossman used the boundary layer solutions of Eqs. 2.73 and 2.74 to overcome the singularity at the corner point \( \xi = 0, \eta = 1 \), which occurs due to the discontinuity in the temperature and concentration between the interface and the inlet of the film. Grossman checked his numerical results against the eigenvalue solution. His analyses are considered a landmark in absorption research.

The temperature and concentration profiles for an isothermal wall, shown in Fig. 2.13, were taken from Grossman (1982). Near the inlet for small \( \xi \), both the temperature and concentration gradients are severe and confined to the interface, especially the concentration gradient. As \( \xi \) increases, heat is seen to penetrate faster than mass, and the interface temperature is affected by the isothermal wall. For a \( \xi \) of about 0.01 (i.e., given a Re number of 280, a Pr number of 25, \( \Delta = 0.58 \text{ mm} \), and therefore \( x \equiv 0.04 \text{ m} \)) the temperature profile is more moderate than its counterpart, the concentration profile, which still has severe gradients that are confined near the interface. The wall's isothermal effect on the interface is clearly seen at a \( \xi \) of about 0.1 (i.e., 0.41 m from the inlet), and the temperature profile has now become linear. Boundary layers are developing, with the one for temperature leading the concentration layer, because of the strength of the two respective diffusivities, which is well described by the Le number. A Le number \( >> 1 \) would indicate the temperature boundary established well before the concentration boundary (i.e., the Le number for aqueous LiBr is about 100). Therefore, Grossman's results for smooth laminar flow show a mass transfer which is well confined to the interface even after 4.0 m of travel from the inlet. On the other hand, heat transfers rapidly across the film, and from the linear profiles it can be inferred to be conduction-dominated.
Figure 2.13. Numerical simulations of the normalized temperature and concentration across a laminar falling film having a constant temperature wall (adapted from Grossman 1982).
2.2.4 Wavy-Laminar Flow

Modern day absorption chillers operate in the wavy-laminar flow regime; however, because of its complexity, research has been limited until recently, with the advent of powerful computational tools. As discussed in Sect. 2.1.3, the wavy-laminar flow regime is considerably more dynamic than is smooth laminar flow and requires either considerable computational effort or excellent physical insight to simplify and solve.

Morioka and Kiyota (1991), Yang and Jou (1993), and Patnaik (1994) each numerically solved the wavy-laminar flow problem for absorption of water vapor into a film of aqueous LiBr. In all three studies, the velocity profile was assumed a priori and was used as input for solving the energy and diffusion equations. Morioka and Kiyota assumed a parabolic velocity profile and solved the energy and diffusion equations for periodic, sinusoidal wave motion. Their results showed that the average mass flux increases 1.7 to 2.4 times that of laminar flow. Temperature and concentration profiles were generated for various distances down the absorber, and their results showed the mass transfer to penetrate to the wall after only 0.03 m of travel as compared to 4 m of travel for Grossman's laminar simulations. The temperature profile became linear in the wave substrate, while in the thicker wave structure the interface temperature was hottest. As result, Morioka and Kiyota found the local mass flux was largest in the substrate and smallest in the wave.

Yang and Jou (1993) approached the problem using the velocity profiles developed by Yang and Wood (1991). Here, collocation techniques were used on a modified
momentum equation describing the wave shape based on Kapitza’s model (i.e., similar to Eq. 2.20). Their results concurred with those of Morioka and Kiyota, and showed the waves had a strong effect on absorption.

Patnaik (1994) selected the integral model proposed by Brauner (1989) (Sect. 2.1.3) and used the author’s hydrodynamic data to formulate the streamwise and normal velocity fields. He input the derived velocity field into a discretization of the time-dependent energy and diffusion equations and conducted numerical simulations as a function of time, film position and the Re number for a film of aqueous LiBr. He simulated a Re number flow of 400 and studied the growth of the temperature and concentration boundary layers over the length of a 0.35-m tube for exposure times of 0.15, 0.3 and 0.47 s. Simulations showed that the effects of absorption had not penetrated to the wall for the short exposure of 0.15 s. At 0.3 s, Patnaik found that mass penetrated to the wall at about 0.13 m from the inlet; this is quite different from the 0.03 m observed by Morioka and Kiyota at the lower Re number of 50. Patnaik observed periodic steady-state concentration profiles to develop around 0.47 s, and he concluded that the normal velocity components were the main drivers for mass penetration.

Jayanti and Hewitt (1997) conducted a numerical study very similar in content and approach to that of Wasden and Dukler (1990). Where Wasden and Dukler studied the effect of roll waves on mass transfer, Jayanti and Hewitt studied the effect of roll waves on heat transfer. Jayanti and Hewitt used the CFD code, Harwell-FLOW3D, to simulate a constant heat flux imposed on a wavy flow regime. Constant property data for water were assumed for the simulations.
The finite volume discretization code modeled solitary roll waves similar to those made by Wasden and Dukler (1989) (see Sect. 2.1.3). Jaynati and Hewitt numerically solved for the streamlines and corresponding isotherms for waves with peak-to-substrate ratios of 2, 4 and 6, respectively. The streamfunction contours, similar to Wasden and Dukler's, are shown in Fig. 2.14(a) for a roll wave with a peak-to-substrate ratio of 4. The isotherms within the wave were definitely affected by convection effects [Fig. 2.14(b)]; however, the extent of the convection effects was surprisingly small. Jaynati and Hewitt compared the heat transfer coefficient, defined as the local flux divided by the local gradient from the interface to the wall, to a conduction-dominant coefficient, defined by the thermal conductivity divided by the local film thickness. They found that the heat transfer coefficient in the wave was much less than that in the thin film outside the wave. This implies that the heat transfer process in the wave is dominated by thermal conduction [Fig. 2.14(c)]. The effect of recirculation in the wave enhances heat transfer near the tail of the wave; however, in the front, convection is not as strong as conduction [Fig. 2.14(c)]. Jaynati and Hewitt averaged the heat transfer over the wave and found enhancements of only a few percentage points. When averaged over the wave and substrate, the overall heat transfer rate was not enhanced by the recirculation within the waves.

Jaynati and Hewitt concluded that the substrate thins by the action of the roll waves, and this action causes the effective heat transfer coefficient to increase by conduction not convection. Hence, Jaynati and Hewitt concluded that the effect of waves on heat transfer in thin films is not directly related to convection effects. Rather, its effect is indirect and due to the effective thinning of the film. Their observations agree with those of Clegg and Portalski (1972), who had experimentally proven that roll waves thinned the film in wavy flow.
Figure 2.14. Numerical simulations for an evolving wave of water having a peak-to-substrate thickness ratio of 4 and a Re number of 140 (adapted from Jayanti and Hewitt 1997).
Conlisk (1994) believed the thin falling film to be conduction-dominated, as was recently proven by Jaynati and Hewitt (1997). Conlisk developed a design procedure based on analytical closed-form solutions that he validated against heat and mass transfer data of Miller and Perez-Blanco (1994). Given the premise of a conduction-dominated heat flow, Conlisk simply derived a linear temperature distribution:

\[ \theta(\eta, \mathbf{x}) = (\theta^* - \theta_{\text{wall}}) \eta + \theta_{\text{wall}}. \]  

(2.75)

where

\[ \theta = \frac{T - T_{\text{wall in}}}{T_{\text{in}} - T_{\text{wall in}}} \]

He normalized the diffusion equation and identified a small parameter which multiplied the highest-order derivative. He therefore used singular perturbation technique to solve the diffusion equation for the inner solution of the boundary layer. Wavy-laminar flow hydrodynamics were ignored; Conlisk believed the mass transfer was driven more by heat effects than by mixing effects in the waves. He assumed to leading order that the film thickness remained constant and used laminar flow theory to describe the velocity profile. His solution to leading order is:

\[ \gamma = \frac{\rho_{\text{H}_2\text{O}}}{\rho_S} \sqrt{2} \frac{x}{\pi} \int_0^x \text{Im}_y e^{- \left[ \epsilon \text{Re} \text{Sc}(1-\eta)^2 \right]} \frac{dt}{(x-t)^{1/2}}. \]  

(2.76)

where

\[ \gamma = \frac{\gamma - \tilde{\gamma}}{\gamma_{\text{in}} - \tilde{\gamma}}. \]

To develop his expression for dimensionless concentration, Conlisk used the interface boundary conditions of energy conservation and a linear absorbent (Eqs. 2.61
and 2.63). His design procedure also requires a specification of the wall temperature, which he assumes varies streamwise by

$$\theta_{wall} = \frac{\Delta T_{wall}}{\Delta T} x^{1/2} .$$  \hspace{1cm} (2.77)

The term $\Delta T_{wall}$ must be specified and is the overall temperature difference between the inlet and the outlet at the wall. Given this specification, Conlisk's procedure predicts well the effects of simultaneous heat and mass transfer (Conlisk 1992, 1995).
The experimental facility consisted of a falling film flow loop, a heat and mass transfer test stand and a data acquisition system (DAS). The flow loop was used to characterize the different flow regimes of a falling film and to measure the salient features of the flow. The heat and mass transfer test stand was used for testing a single stainless steel absorber tube of 0.01905 m OD and 1.524 m length. A unique feature of this stand is its ability to operate continuously and support testing of LiBr brine at a mass fraction of 0.62, the design conditions for absorption chillers. Most heat and mass transfer test stands support testing only in batch mode and cannot easily operate without crystallizing the brine at 0.62 mass fraction. Both test stands and the DAS are discussed in more detail in the following paragraphs.

3.1 Falling Film Flow Loop

A flow loop was constructed for measuring the thickness, wave amplitude and frequency of a film during hydrodynamic flow down a test pipe of 0.7 m length. The configuration of the loop is shown conceptually in Fig. 3.1. A liquid dispenser was attached directly to the test tube, and the dispenser could be adapted to tubes with ODs of 0.01905, 0.0127 or 0.009525 m. This vessel consisted of a small stainless
Figure 3.1. Flow loop used to measure the hydrodynamics of a falling film.
steel cup and a nozzle (Fig. 3.2). The cup was line-bored after fabrication, and a centering collar was used to center the nozzle and provide a uniform flow of liquid between the inner wall of the nozzle and the outer wall of the test section. Glass beads of 6-mm diameter were used to break up any vortex which might form as liquid flowed into the cup. Bubble-in-tube levels were used to check the alignment of the test section. This same dispenser configuration was also used in the heat and mass transfer test stand.

The lower portion of the test tube was placed into the open mouth of a 50-L carboy. A variable-speed liquid pump directed the flow of liquid from the carboy through a mass flow meter and then to the dispenser of the test section. Mass flow rate was checked by observing the timed change in weight of the carboy. Calibrations showed the measurements made by the mass flow meter were within 1% of the measurement made with a digital weigh scale.

A 35-mm camera, a VCR and a TV monitor were used to film flows of both water and 55 wt% LiBr brine. The falling film was viewed at different positions down the tube to observe the development stages of the flow field. Floodlights were used to illuminate the camera’s field of view; however, the nickel-plated pipe acted as a mirror and reflected the light, making it difficult to distinguish between the tube wall and the wavy flows on the TV monitor. Therefore, a thick but translucent white paper backdrop was positioned between the lighting and the test section. Opposite this backdrop, the camera viewed a darkened image of the test tube. The shadows produced by the lighting scheme better illuminated the wavy flow and showed a more defined border of the wave for measuring the film thickness.
Figure 3.2. The dispenser used in the flow loop and in the mini-absorber test section.
Data were recorded for mass flow rates ranging from a laminar to a turbulent regime. The flow rate was set using the variable speed pump, and the VCR was time-indexed for filming during a given flow rate. The shutter speed of the camera was 30 frames per second.

Image-processing software was used to capture the recorded data frame by frame. The video signal from the VCR was monitored by the TV and was also digitized by the imaging software and hardware. The video could be stopped and the still image acquired by digitizing and storing it pixel-by-pixel. The process image was viewed on the PC monitor (Fig. 3.1) and also on the TV to check for any distortion. In this manner, a sequence of grabbed frames were stored in the PC's memory, and measurements of the film substrate, the wave peak and average film thickness were made and recorded using the imaging software (Patnaik 1994).

### 3.2 Heat and Mass Transfer Test Stand

The heat and mass transfer test stand is shown schematically in Fig. 3.3. For testing purposes, the mini-absorber receives vapor directly from the boiler; however, if integrated into the mixing circuit of a single-effect machine (Fig. 1.5), the mini-absorber would otherwise receive vapor from an evaporator.

The boiler of the test stand is fired by resistance heaters of 2.5-kW capacity, and water is desorbed from the LiBr brine. The brine becomes stronger in LiBr salt, and the strong solution is used as the falling film in the absorber. A linear gate valve trims
Figure 3.3. Flow circuit for the heat and mass transfer test stand.
the flow of the vapor coming from the boiler to the absorber and helps to fine-tune the vapor pressure within the absorber. The strong solution is tempered by a tube-in-tube heat exchanger prior to entering the absorber. A coolant flows countercurrent to the falling film and supports the coupled heat and mass transfer process as the falling film of strong solution absorbs the water vapor from the boiler. Leaving the absorber, the brine is weaker in the concentration of the LiBr salt. The weak solution is gravity-fed from the absorber to a 1-L heated sump tank. The sump has a level indicator, which is manually set by adjusting the speed of the variable-speed pumps stationed upstream and downstream of the mini-absorber. During testing, the level control technique is a useful tool for balancing the flows entering and leaving the mini-absorber. The weak solution is pumped from the sump and is injected back into the boiler for continuous operation of the test stand.

The absorber test section is made of standard Pyrex glass pipe (7740 borosilicate glass). The glass pipe is 2.1 m long and has a 0.15 m ID (Fig. 3.4). Stainless steel end plates are bolted to the conical glass ends of the vessel using cast iron flanges. The gasket material, used for vacuum seal, is made of ethylene propylene terpolymer (EPDM), an elastomeric sheet compounded from a terpolymer of ethylene and propylene. It is suitable for gasket applications in steam at temperatures up to 121°C and has low permeability, minimal compression set, and excellent compatibility with LiBr brine. The dispenser and catch basin, seen in Fig. 3.2, are made of 304 L stainless steel and are both attached directly to the test tube.

A simple but crucial feature of the dispenser is its design, which allows the entering strong solution the opportunity to equilibrate. Holes were drilled atop the cup, and a
Figure 3.4. Mini-absorber test section.
screen was inserted into the entering strong solution line to help spray the solution into the cup. Exposing the strong solution as a spray caused it to equilibrate to the pressure of the ambient vapor within the absorber. Hence, the brine’s thermodynamic state point is known at the exact start of simultaneous heat and mass transfer process.

The catch basin is designed for test tubes with a maximum length of 1.53 m; however, it can be moved for testing at different absorber tube lengths. It is attached to the test tube 1.5 m from the inlet and is designed to quickly drain solution from the absorber. All line connections to the test absorber were fabricated from 304 L stainless steel.

The noncondensables in air, nitrogen, oxygen, and argon are known to literally stop the absorption process. The corrosion of stainless steel by LiBr will generate hydrogen gas, which also acts as a noncondensable and retards the absorption process. In their experimental studies, Battelle Columbus found that these noncondensables stratify in the lowest pressure zones of the absorber (Murray 1993). Little data are available to correlate the absorber’s performance as a function of the noncondensables. Rie and Kashiwagi (1991) studied the effect of noncondensables on absorption rates in aqueous LiBr. They found that small amounts of noncondensible air—about $10^7$ moles or 0.03 vol%—dropped the mass absorbed by roughly 50%. Its effect is significant and must be eliminated from the test stand if meaningful data are to be acquired for better understanding the absorption process.
Therefore, leak-checking was conducted using a mass spectrometer tuned for helium leak detection. The stand was certified to a leak rate of $10^{-7}$ atm-cc/s. As a check, the tightness of the stand was proven by observing the rate of pressure rise within the stand. If the stand was leak-tight, its internal pressure would initially increase because of the outgassing of water. In time, the pressure would level off as the vapor pressure corresponded to the ambient temperature within the stand. However, a continuous rise in pressure would show leakage into the stand. Data in Fig. 3.5 prove the stand leak tight.

Internal outgassing could also be a problem. The corrosive action of the LiBr brine on the stainless steel parts of the stand might generate hydrogen gas. To eliminate the gas, a purge tube was installed in the lower part of the absorber. The purge tube has ports spaced every 0.15 m to vacuum-pull any hydrogen gas from the absorber. We tested with and without a continuous purge to show whether hydrogen was outgassing during testing. No noticeable drop in absorber load or mass absorbed could be observed, from which we inferred that the confounding variable of noncondensables was minimized if not eliminated. The purge tube also serves another crucial function, that of increasing the concentration of the 8 liters of brine charged in the test stand. The technique is discussed in Sect. 3.4, "Startup Testing and Procedures." The technique successfully supported heat and mass transfer testing at brine concentrations of 62 and 64 wt% LiBr and enabled the acquisition of data which is not available in the open literature.
Figure 3.5. Outgassing of water from within the test stand.
3.3 Instrumentation

The test stand is instrumented at various locations for the measurement of temperature, pressure, density, flows, and boiler power. An instantaneous water heater of 24 kW capacity and a power controller temper cooling water directed to the absorber. Mass flow rate and density of solution entering and leaving the absorber are measured using Coriolis mass flow meters. The power of resistance heat input to the boiler is measured using a power transducer. Current draw is monitored with an analog current meter. A turbine meter is used to measure the cooling-water flow rate. Absolute pressure transducers, having a calibrated range of 0 to 30 kPa, measure vapor pressure in the boiler and the absorber. Two temperature controllers regulated heat to the inlet and exit solution lines of the absorber to guard against potential crystallization at concentrations exceeding 60 wt%. Specific instrumentation is discussed in more detail in the following paragraphs.

3.3.1 Thermocouples

Grounded-junction copper-constantan thermocouples, having 1.6-mm-diameter sheaths made of 316 stainless steel, were used to measure steam, solution, and cooling water temperatures throughout the loop. Compression fittings were welded into the pipelines at a given measurement point, and the sheathed thermocouple was inserted to directly sense the fluid temperature. The thermocouples were calibrated in
situ to minimize errors in the analog-to-digital (A/D) conversions made by the 16-bit A/D connection cards.

### 3.3.2 Pressure Transducers

Pressure measurements accurate to within ±0.014 kPa are crucial to successful interpretation of the absorption driving forces. Absolute pressures were measured in the absorber and in the generator. The sensors used incorporate an optical means of sensing the pressure on an elastic member. One side of the member is evacuated to zero pressure to compensate for absolute pressure measurement. A vane is attached to the elastic diaphragm, and the assembly moves in response to pressure. The movement is detected by a dual-element photodiode system consisting of a light-emitting diode and two light-measuring diodes. The vane position determines the intensity of light detected by each photodiode. Output from the photodiodes are converted to voltages that represent diaphragm displacement due to the applied pressure. Both photodiodes are affected similarly by temperature because of their monolithic structure; therefore, temperature drift of the sensor can be eliminated. The temperature compensation range is −40 to 82°C with 0.004% of span per °C over a temperature compensated range from 23°C. The pressure sensors were calibrated over a pressure range of 0 to 30 kPa using an MKS 270 Baratron sensor as the calibration standard. Calibrated accuracy was ±0.014 kPa of reading.
3.3.3 Flow Meters

A volume flow turbine meter having an operating range of 0 to 0.33 l/s was used to measure coolant flow rate. The turbine meter was calibrated by measuring the weight of water flowing through the meter over a timed duration. The calibration was conducted on two different occasions—at the start of the experiments and during the midstream of the testing—to check for any drift in calibration of the meter. The accuracy of the meter was judged to be ±1.0% of the reading.

Solution flows entering and exiting the mini-absorber were measured using Coriolis mass flow meters. The metered fluid flows through a U-shaped flow tube that vibrates as a tuning fork. The transducer detects from the flow a gyroscopic force that is directly proportional to the mass flow rate. Setup of the two Coriolis mass flow meters was altered to isolate the meters and eliminate any extraneous vibrations that could affect signal output (Fig. 3.6). Calibrations were conducted by measuring the weight of water flowing through the meter over a timed duration. Calibrated accuracy was ±0.4% of the reading.

3.3.4 Densitometers

The Coriolis flow meters were also used to measure the concentration of the brine entering and exiting the mini-absorber. Previous work by Ally et al. (1991) showed significant errors in density measurements as monitored by the Coriolis meter. A similar discrepancy was found in the model D-12 Coriolis meters used in this study.
Figure 3.6. Placement of the Coriolis mass flow meter.
The meters did not properly compensate for changes in the metered temperature. Therefore, in situ calibrations of the densitometers were conducted using various fluids of differing specific weights to verify proper density measurement. Under no-flow conditions, the accuracy of measurement was better than ±0.5% (i.e., ±0.005 g/cc) for the various fluids tested. The density of distilled water was then checked as a function of temperature for nominal flows of 0.017 kg/s through the densitometers. Again, results were similar to those of Ally and associates. The problem was corrected by substituting a 100-ohm resistance temperature detector (RTD) for the vendor's RTD, which had measured the tube wall temperature. The vendor stated that the very small diameter of the transducer's flow tube made it difficult to attach thermometry for accurate measurement. With the new RTD directly measuring the fluid temperature, the densitometer correctly trended the fluid density in the range of expected operating temperatures (Fig. 3.7). As compared to the density data for distilled water, gleaned from the International Critical Tables, measurements are about ±0.5% (i.e., ±0.005 g/cc) accurate.

Samples were taken to check the densitometer and the ρ-T-X calculation of wt% against measurement made using a refractometer (Zaltash and Ally 1992). The check was made at the start and midway through testing to verify results of the densitometer. Results showed the in-situ measurement made with the Coriolis meters was initially within 0.1 wt% of the sampling results. The second check showed it within 0.15 wt% of the sampling results. Consequently, heat balances calculated on the brine side and the water side were within about 10% agreement.
Figure 3.7. Densitometer calibration and temperature trending were checked using distilled water.
3.3.5 Data Acquisition System

The DAS consists of an IBM PC with an 80286 processor and analog data acquisition cards with 16-bit resolution differential analog inputs and digital input/outputs. The DAS monitors the temperatures, pressures, densities, flows, and boiler power. On command, data are scanned every 10 s over a 5-min test period. The instantaneous values, the running averages and the running standard deviations are then stored as ASCII data files. The ASCII files are numerically indexed automatically, making it convenient for a FORTRAN code to sequentially read and reduce all data files. Log sheets are generated for each test, and a worksheet of all the test data is also generated, which is then downloaded into an electronic spreadsheet for further plotting and analysis.

3.3.6 Profile Measuring Instruments

Measures of the temperature profiles of the coolant, wall and falling film were made along the running length of the absorber tube. The following discussion describes the instruments used for the coolant, wall and falling film temperature measurements.

3.3.6.1 Coolant Profile Thermometry

A probe of 1.8-m length and 6.35 mm OD was inserted inside the absorber test tube for measuring the local bulk temperature of the coolant along its flow path. The probe also helped enhance turbulent flow of the coolant. The probe has a stainless
steel sheath and is composed of 10 type T thermocouples spaced about 0.15 m apart. The thermocouple junctions are grounded to the sheath and are packed in a magnesium oxide powder. Response time for a 1.4°C step change in temperature is about 10 s, which is adequate for steady-state data collection. The probe’s thermocouples were calibrated in situ, and the maximum deviation observed was ±0.1°C from a NIST traceable standard thermometer.

3.3.6.2 Wall Profile

RTDs were selected for measuring wall temperatures because the sensor measures an average temperature over its exposed length. The falling film flow is not symmetric because of the wavy flow, and an average perimeter measurement would be more representative of the wall’s temperature than would a point measurement made with a thermocouple. Several grooves were knurled in the test tube, and the RTDs were attached within the grooves using an epoxy glue with a metal resin filler. The glue was selected to have a low vapor pressure. The epoxy was also applied atop the sensor and sanded down flush to the tube surface. Compatibility tests of the epoxy in 100°C LiBr brine showed no damage to the epoxy nor any contamination of the brine. The four-wire leads from each RTD were run through the inner diameter of the test tube and brought out from the coolant using a compression fitting having several ports for each RTD wire.

The selected RTD sensors are a flexible film type made of 70% Ni–30% Fe encased in a 1-mil Kapton plastic. The nickel-iron composite metal was used because of its nominally high resistance, about 200 ohms at 0°C. The high resistance helps
minimize measurement error and implies a metal with a high resistivity. The higher the resistivity, the less material required to make the sensor, an important consideration for this particular measurement application. The RTDs were calibrated in situ and checked by flowing only cooling water at 35°C through the tube. All RTDs read within 0.3°C of the cooling water temperature.

3.3.6.3 Temperature Profile of the Falling Film

A non-intrusive technique developed jointly at LANL and ORNL was used to measure the falling film temperature profile. This approach involves seeding the LiBr brine with thermographic phosphors and measuring the fluorescent decay rate of the phosphor when the solution is excited by a pulsed nitrogen laser. The phosphor—lanthanum oxysulfide doped with europium (La₂O₂S:Eu)—has an emission spectrum consisting of many sharply defined spectral lines, some of which are a strong function of temperature (Allison et al. 1989). The experimental setup is illustrated in Fig. 3.8. The nitrogen laser produced an excitation beam with a wavelength of 337 nm and a pulse duration of about 20 ns. The velocity of the falling film was about 0.5 m/s, and the phosphor particles were within the 6-mm excitation region on the film for about 0.02 s; the particles’ fluorescent decay was therefore easily detected during the 20-ns pulse. The excitation laser was mounted to give an incident angle of 54° with respect to the tube normal so that laser radiation reflected from the stainless steel would be directed away from the collection optics (Fig. 3.8). A helium neon laser beam was split into two parallel beams before being focused to an intersection precisely at the object plane of the collection optics. The focusing technique allowed for precise positioning of the excitation region, which was very
Figure 3.8. Nonintrusive film temperature measurements were made using thermographic phosphors.
important for pinpointing the interface of the thin film within the field of view of the collection system. A photomultiplier tube detects the radiation emitted from the phosphor and outputs to a programmable storage oscilloscope for data acquisition and measurement of the decay rate of the phosphors (Fig. 3.8).

The roll waves are a determining factor in assuming that the particles were dispersed more on the surface of the film than in its bulk. The hydrodynamic sweeping action of each successive roll wave kept the thermographic phosphor particles near the free surface of the falling film. In the substrate, Chu and Dulder (1974) measured a substrate thickness of about 100 µm for a Re number of 1000. The thermographic particles are about 10 µm thick. Therefore about one-tenth of the substrate is composed of the phosphors. Further, the thermographic phosphor data measured near the absorber inlet yielded a temperature very close to the equilibrium temperature reached by the absorbent when it is first exposed to the ambient vapor. The correspondence is very promising and helps substantiate the accuracy of the interface measurements. Further details of the non-intrusive measurement technique—including the theory, validation of measurement and calibrations used for aqueous LiBr testing are included in Appendix B.

### 3.4 Startup and Testing Procedures

Initially, the heat and mass transfer test stand was evacuated and vacuum-charged with about 8 L of distilled water. Steam condensation tests were conducted to formulate a coolant-side convective heat transfer correlation using Wilson's method.
of analysis (Bennett and Myers 1982). Data were reduced by Wilson’s technique, and the derived correlation was validated against literature data. See Appendix E for complete details of Wilson’s technique as applied to the coolant side of the mini-absorber.

Heat and mass transfer testing was conducted using commercially available brine for single-effect chillers. The brine is mixed with a LiNO₃ corrosion inhibitor, and has no heat and mass transfer additive. About 8 L of 55 wt% LiBr brine were pulled under vacuum into the generator of the test stand. Daily startup required a 15-min purge of the absorber and boiler to eliminate any internal outgassing of hydrogen. After purging, a valve between the cold trap and vacuum pump was closed, the vacuum pump was stopped, and the pressure rise on a thermocouple gage was observed for the rate of pressure rise in the absorber. The gage was located downstream of the cold trap but upstream of the vacuum valve and pump. Outgassing water from the absorber would freeze in the cold trap before the gage, and any in-leakage of air would be sensed by the thermocouple gage. The daily procedure was always followed to check for air leakage into the test stand.

A single absorber tube of 0.01905 m OD and 1.524 m length was tested over a range of falling film flow rates, a range of LiBr brine concentrations, a range of absorber pressures, and at two different coolant temperatures. Coolant flow rate was set at 3.785 L/min for all testing. The ranges of flow rate, concentration and pressure were established based on field operating conditions for air-cooled and water-cooled chillers (DeVuono et al. 1990). Water-cooled chillers operate at pressures of about 0.87 kPa to produce 7.2°C chilled water. Air-cooled machines operate at higher load
rejection temperatures, forcing the machine to approach concentration-temperature limits near the crystallization curve for LiBr brine. To avoid crystallization, the air-cooled machine operates at a higher evaporating temperature of about 10°C and therefore at a higher absorber pressure of about 1.3kPa.

Problems with crystallization of the brine did occur during startup testing of the rig. These problems were resolved, and testing was successfully conducted at 62 and 64 wt% LiBr. To increase the concentration, the loop was initially started at a safe concentration of about 60 wt% LiBr. The loop was heated using the boiler, solution heat exchanger, and heat tapes on the solution lines. The cooling water in the absorber was also heated to about 80°C. Heating was increased until all areas of concern were at least 15°C above the crystallization temperature. With the coolant at 80°C, water flashed from the falling film. The flashed vapor and vapor from the generator were pumped through the purge tube in the absorber into a nitrogen cold trap. The trap froze the vapor and protected the vacuum pump from any contaminating water. The density of brine leaving the absorber was monitored to determine when the brine had increased to the desired wt%. The cooling water to the absorber was then gradually cooled, and after about 1 hour of fine-tuning, testing would begin. To lower the concentration, a line connected between the generator and a carboy of distilled water was first vacuumed and then opened to pull distilled water into the generator (Fig. 3.9). The charge of brine was usually diluted to about 59 wt% LiBr, and the loop was operated for an additional hour to equilibrate the brine concentration throughout the loop for protection against crystallization.
Figure 3.9. Setup used to dilute the charge of LiBr brine.
3.5 Thermodynamic and Property Data for Aqueous LiBr

Aqueous LiBr- is a homogeneous mixture; however, it is not an ideal solution because it manifests a variation in volume and temperature when formed from the pure LiBr salt and water. The salt ionizes in water and occupies more volume than it would as a solid. Mixing LiBr and water also causes an exothermic heat release. The activity coefficient for aqueous LiBr—which naturally depends on the temperature, pressure and composition of the LiBr mixture—has been estimated at about 20 by Bahe (1975). To account for these variations, the LiBr brine is treated as an ideal mixture, and terms such as the volume change in mixing and the heat of solution are added to adjust for the real mixture properties of the brine.

Therefore for LiBr brine, the thermodynamic state relating the pressure, volume, temperature and composition requires empirical data to quantify these real mixture effects. Empirical data are available from the works of Uemura and Hasaba (1964), McNeely (1979), and most recently Jeter et al. (1990a, b). Patterson, Crosswhite and Perez-Blanco (1990) had developed FORTRAN routines from the work of Uemura and Hasaba (1964) and McNeely (1979). The routines use empirical curve fits to calculate the thermodynamic and transport properties of aqueous LiBr solutions. The author modified these routines to include the empirical fits by Jeter et al. (1990a, b). The viscosity, density, and thermal conductivity routines by Jeter et al. (1990a, b) were used for reducing data having mass fractions exceeding 0.60.
Diffusivity data are sparse; however, some empirical data measured during heat and mass transfer testing at a temperature of 25°C and concentrations ranging from 10 to 60 wt% LiBr were extracted from the work of Kashiwagi, Kurosaki, and Nikai (1984). These 1984 data are very significant, because they are the only known data which include the effects of simultaneous heat and mass transfer for high salt concentrations. Aqueous LiBr is a strong electrolyte solution, and diffusivity will decrease as concentration increases. The theory of the diffusion of salts at high concentrations in aqueous solutions is not well developed and requires empirical data.

A correlation was developed for predicting the effect of temperature and concentration, and it accounts for the effects of heat and mass transfer that occur within the absorber. Details can be found in Appendix A. The viscosity, thermal conductivity, surface tension and density for aqueous LiBr are plotted as function of the temperature and the mass fraction for review of their trending with temperature and concentration in Appendix A.

### 3.6 Data Reduction Procedures

The measured brine temperature entering and exiting the absorber was compared to the saturated temperature to determine the brine's thermodynamic state point. The saturated temperature was based on the absorber pressure and the measured brine concentration. If the measured temperature is less than the saturated temperature, then the solution will be subcooled. A superheated state point is possible only at the
absorber inlet; at the exit, the absorbent is either saturated or, in most cases, subcooled.

Conventional design has superheated brine sprayed over an absorber tube bundle, causing the brine to adiabatically flash to equilibrium with the absorber pressure. In the heat and mass transfer test stand, solution entered the absorber, either slightly superheated or slightly subcooled. An iterative algorithm was developed to calculate the equilibrium temperature and concentration at the start of the falling film. The algorithm corrects for either flashing from the film, if the solution is superheated, or for the rapid mass transfer to the film, if the solution is subcooled. Using the energy equation, continuity equations, and P-T-X empirical relationships, a balance is conducted from within the dispenser to the nozzle. Using continuity and noting that the mass of LiBr salt remains constant yields these two relationships:

\[ \dot{m}_{\text{in}} + \dot{m}_v = \dot{m}_{\text{eq}}, \text{ and} \]
\[ \dot{m}_{\text{eq}} = \dot{m}_i \left( \frac{X_i}{X_{\text{eq}}} \right). \]  

The strong solution will drive to equilibrium almost instantly. If the strong solution is sprayed, the process could be considered adiabatic. However, in the cup of the mini-absorber, some heat transfer to the coolant occurred while the strong solution equilibrated within the cup. An energy balance yields an expression for the mass flow rate of solution at the equilibrium point as follows:

\[ \dot{m}_{\text{eq}} = \frac{\dot{m}_{\text{in}}(i_{\text{in}} - i_{fg}) - q_{\text{cup}}}{(i_{\text{eq}} - i_{fg})}. \]
On command, the algorithm guesses an equilibrium temperature $T_{eq}$ and calculates an equilibrium concentration $X_{eq}$ based on P-T-X relationships. The solution enthalpy $i_{eq}$ is calculated from $X_{eq}$ and $P_v$. The mass flow rate at the equilibrium point is calculated based on the conservation of energy (Eq. 3.3) and is also calculated based on the conservation of the solute mass (Eq. 3.2). Values of the mass flow rate from Eqs. 3.2 and 3.3 are compared for convergence. The equilibrium temperature is incremented, and iteration continues until the error between the two calculations is less than ±0.1%.

The derived algorithm is very important because it ties the effect of absorber pressure to the heat transfer aspects of the problem. This temperature, $T_{eq'}$, is actually a very accurate measure of the interface temperature at the start of the absorption process. It is also the maximum film temperature the absorber will see as the film falls down the test tube.

Heat balances were calculated to check that the heat transferred to the coolant equivalence to the heat transferred from the solution-side. Solution-side and coolant-side balances were within about ±10%. The solution-side heat balance for calculating the absorber load takes the form of

$$ q = m_{eq}i_{eq} + m_{v fg} - m_{ex}i_{ex}. $$  \hspace{2cm} (3.4)

while the coolant-side heat load is simply

$$ q = \left(mC_P\right)_{cl}[T_{ex} - T_{in}]_{cl}. $$  \hspace{2cm} (3.5)

The coolant temperatures in Eq. 3.5 were measured by the temperature probe inserted inside the test tube. The exit coolant temperature is measured at the same
vertical position where the falling film leaves the dispenser. Therefore, its measurement position is very useful for viewing the heat transfer driving forces from the film interface, $T_{eq}$, to the bulk of the coolant, $T_{ex}$.

The mass absorbed into the falling film was calculated from the densitometer instruments and was also back-calculated by using Eqs. 3.4 and 3.5. The mass of solute, LiBr, remains constant during absorption, and the conservation of mass coupled to the conservation of solute yields the following:

$$m_v = m_{eq} \left( \frac{X_{eq}}{X_{ex}} - 1 \right). \quad (3.6)$$

Solving Eq. 3.4 for the mass absorbed and substituting for $q$ from Eq. 3.5 yields

$$m_v = \frac{q - m_{eq}(i_{eq} - i_{ex})}{i_{fg} - i_{ex}}. \quad (3.7)$$

The solution enthalpy is a strong function of the concentration and the temperature. Therefore, to decouple the mass absorbed from errors in the densitometers, an iterative scheme was devised for correcting for the overall concentration gradient. As a first guess, the exit density and temperature measurements were used in calculating the enthalpy of solution leaving the absorber. A mass absorbed was calculated from Eq. 3.6, and substituted into Eq. 3.8 to calculate a new concentration:

$$X_{ex} = X_{eq} \left( \frac{m_{eq}}{m_v + m_{eq}} \right). \quad (3.8)$$

Then, given the new concentration and measured exit temperature, the mass absorbed was back-calculated from Eq. 3.7. Note that the enthalpy of solution leaving the absorber was corrected for the effect of subcooling. The procedure was repeated, and the previous calculated value of the mass absorbed from Eq. 3.7 was compared to
most recent value. Iteration stopped once the mass absorbed converged to within 0.01% of its previous value.

An uncertainty analysis was conducted to determine the maximum error for each reduction approach of the absorbed mass. Since the true value of a given measurement is not directly known, it is more accurate to speak of experimental uncertainty than of experimental error. The uncertainty analysis should account for both the random error and the systematic error. Random error is due to the lack of repeatability and therefore describes the precision of measurement. Statistics are applied to the random error to establish measurement bands within which replication of measurement is assured to a given confidence interval. Systematic error is the bias from the true measurement and describes the inaccuracy of a calibration procedure. Details for the derivation and calculation of the uncertainty in absorber load and the mass absorbed are given in Appendix D

For testing at 60 wt%, the average uncertainty in the mass absorbed as measured directly by densitometry was about ±60% for a 95% confidence interval. Compared to the approach of back-calculating the mass from the absorber load, the uncertainty was only ±12% at 95% confidence. As might be expected the major contributing error was due to the density measurement. It contributed about 60% to the total uncertainty despite the meticulous calibrations conducted on the densitometers. In fact, if the densitometer were an order of magnitude more accurate (i.e., ±0.0005 g/cc vs the measured ±0.005 g/cc), the uncertainty would improve to only ±23%. The uncertainty in the absorber load measured on the coolant side was ±7.0% at 95% confidence. The major error in the load was due to the temperature gain of the
coolant, which was 3.5°C for the Appendix D test results. If the coolant gain dropped to 1.5°C, then the uncertainty would increase to upwards of ±50% of the absorber load.

The uncertainty analysis helped justify eliminating data having too low a coolant temperature gain, and also justified using the procedure of back-calculating the mass absorbed from the absorber load. The analysis showed two strong results: (1) the densitometers should be at least ±0.0005 g/cc for confident measurement accuracy of the mass absorbed; and (2) the temperature gain of the coolant should be at least 2°C. Post priori, these finding seem obvious. However, industry designs have the coolant flowing in the absorber at Re of about 40,000. These flows would cause a large error in the load measured in the mini-absorber test section. This, in part, was the reasoning for the coolant temperature probe, which, when inserted in the absorber tube, helped enhance turbulence in the annular gap.
CHAPTER 4

EXPERIMENTAL RESULTS

The experimental approach included three phases of study. The hydrodynamics of a falling film of water and 55 wt% LiBr were measured to better understand its effect on the heat and mass transfer process. Heat and mass transfer testing was conducted on a single vertical tube to measure the temperature profile of the falling film in the streamwise direction. These data were useful for describing the physics of local heat and mass transfer as function of length. A parametric study then followed to map the performance of the absorber as function of the vapor pressure, the entering absorbent concentration, the falling film mass flow rate, and the entering coolant temperature.

4.1 Film Hydrodynamics

Video films were recorded of a falling film observed on three different OD tubes; each tube was 0.7 m long. Measurements of the film thickness were made at different stations along the length of each tube to observe the developing flow. Patnaik (1994), in a parallel study by Miller, Perez-Blanco and Patnaik (1992), reduced the data with image-processing software and generated approximate wave profiles over a 1.5-s time domain (Fig. 4.1). The trace was taken from data for 55 wt% LiBr having a mass flow rate of 0.022 kg/s (i.e., Re number of 270). The random nature of the film profile
Fig. 4.1. The time trace of the film thickness for a falling film of aqueous LiBr flowing at 0.022 kg/s (Re number of 270).
clearly shows the peaks and troughs of the individual waves and gives good indication of the penetration of the waves into the film substrate. The shape is indicative of the waves observed in Fig. 2.1 for stable wavy-laminar flow. Patnaik (1994) subjected the time trace to a fast Fourier transform and found a dominant wave frequency of about 13 Hz. Similar findings were observed by Brauner and Maron (1982), who found the wave frequency between 14 and 16 Hz for a falling film Re number of 220.

4.1.1 Film Thickness

The mean film thickness, the wave peak and wave tail were measured on tubes having ODs of 0.01905, 0.0127 and 0.009525 m. Increasing the falling film flow rate caused the amplitude of the waves to increase on the largest-diameter tube. However, as seen in Fig. 4.2, the wave amplitude on the smaller-diameter tubes is much less than that observed on the larger tube. Wave inception was observed 0.125 m down from the inlet on the 0.01905-m tube. On the 0.009525-m tube, the flow was smooth laminar, and waves were not visible to the observer until after 0.5 m. For a fixed flow, decreasing the tube diameter results in a thicker film. The mean film thickness was 0.48 mm on the 0.01905-m tube and 0.61 mm on the 0.009252-m tube for a flow of 0.021 kg/s. Brauer (1956) had shown that waves begin to form once the momentum boundary layer reaches the surface of the film. Applying the momentum integral for a boundary layer flow of 0.021 kg/s on the smallest-diameter tube shows that only 0.03 m are required for the layer to reach the surface. Hence, the momentum boundary

---

1 The wave amplitude is defined as the difference between the peak and the tail thickness.
Fig. 4.2 The peak, the mean and the tail thickness of roll waves measured 0.40 m from the inlet for different OD tubes.
layer is established well above the start of wavy flow, it being observed at 0.5 m for the smallest tube. Therefore, the differences in wave amplitude seen in Fig. 4.2 must be caused by curvature effects. The thicker film on the smaller-diameter tube may require a greater vorticity at the liquid surface to initiate the instabilities for wave inception.

If one just touched the film, it would break down at the lowest flows and would no longer wet the entire surface. We visually observed a thin film layer which appeared to adhere to the tube, while a faster moving bulk traveled atop the thin layer. We also noticed that the waves were more pronounced (i.e., larger) near the bottom of the 0.01905- and 0.0127-m OD tubes. This observation of a traveling wave reservoir which grows in the streamwise direction is consistent with the physics formulated by Allen (1962), Portalski (1960), Dukler (1976) and Brauner and Maron (1983). Even more interesting are the trends in mean film thickness observed at three different streamwise locations for the 0.01905-m tube (Fig. 4.3). Increasing the falling film flow rate increases the mean film thickness; however, as the flow exceeded 0.010 kg/s (i.e., a Re number of about 120), the mean film thickness at the 0.4-m measuring station deviated below that observed at either the 0.13- or the 0.23-m station located below the dispenser. These results show a thinning of the film due to the physics, proposed by Kapitza (1948) and later by Dukler (1976).
Fig. 4.3. The mean thickness of an aqueous LiBr falling film decreases as the film fully develops in the streamwise direction. Tube OD is 0.01905 m.
4.1.2 Comparison to Literature Data

Several techniques for correlating the film thickness have been mentioned in Sects. 2.1.1 and 2.1.2. The most widely accepted technique was developed by Dukler (1959), who cast the film thickness by Nusselt (1916) into the scaled format of Eq. 2.10. The Nt formulation was therefore selected, and the data of Greenberg (1956), Charvonia (1959), Portalski (1960), Allen (1962), and the author's data were reduced and plotted (Fig. 4.4). Results clearly show a deviation due to the presence of roll waves. For Re numbers less than 20, the data are close to laminar theory. However, the data deviates from the Nusselt curve as the wave amplitude increases, with the largest deviations observed at Re numbers ranging from 60 to 400. Heat and mass transfer equipment operates in this nebulous range of Re number flows. Yet interestingly, most researchers use the Nusselt film thickness in their approach for solving the coupled heat and mass transfer problem. As the Re number further increases towards 1600, turbulent flow occurs, and the data transitions back toward the Nt curve.

Fiend (1960) and Brauer (1956) correlated their data into discrete regions of the Ka number; see Eqs. 2.22 through 2.24. Inspection of the data of Greenberg and Portalski shows a trending of the film thickness with the Ka number. As the Ka number increases, a monatomic decrease is observed in the film thickness. Greenberg had observed that increasing the surface tension also increased wave amplitude. By Kapitza's theory, an increase in amplitude corresponds to a reduction in the film thickness and in part explains the deviation between the measured data of Fig. 4.4
Fig. 4.4. Data are included for hydrodynamic tests conducted with water, 55 wt% LiBr, glycerin, carbon tetrachloride, ethyl alcohol and isopropyl alcohol.
and Nusselt’s laminar theory. By definition, an increase in surface tension results in an increase in Ka number. Therefore, the Re number and the Ka number were selected to correlate data within the ranges used in heat and mass transfer testing. The Re number ranged from 100 to 500, while for 64 through 60 wt% LiBr, the Ka number requires a range of 400 through 850, respectively. The author’s 55 wt% LiBr data, observed on a 0.01905-m tube, and Greenberg’s data for glycerin and ethyl alcohol were used in the correlation. The water data of Allen (1962) and Charvonin (1959) were excluded since they were outside the range of experimental values. Portalski’s (1960) data was also excluded because of the volume-averaged measurement technique used in his study. The Nt correlation for the range of heat and mass transfer test conditions studied therefore becomes

\[
Nt = \frac{\Delta}{\left(\frac{v^2}{g}\right)^{3/4}} = 1.4 \text{Re}^a \text{Ka}^b, \quad (4.1)
\]

where

\[
a = 0.4715829, \\
b = -0.2078418.
\]

The regression equation explains 95.7% of the total variation in the data about the average (i.e., \(R^2\) of 0.957). Increasing the Re number increases the film thickness; increasing the Ka number decreases the film thickness. Hence, the correlation is consistent with the data in Fig. 4.4 and with the observation made by Greenberg (1956) and Portalski (1960) concerning the effects of surface tension. The error in the experimental and correlated Nt is shown in Fig. 4.5. A maximum error is seen for Greenberg’s ethyl alcohol datum at a Re number of about 370; however, at a Re number of 550, Greenberg’s datum for ethyl alcohol is only 1.5% in error. All other
Fig. 4.5. The error incurred between the experiment and the correlation for $N_t$ (Eq. 4.1).
data have errors of less than 10\% with the average deviation for all the data being only 4.0\% of experiment. The average error was calculated using the formula

\[
\text{Error} = \frac{\sum_{j=1}^{N} \text{ABS} \left( 1 - \frac{N_{t,\text{corr},j}}{N_{t,\text{exp},j}} \right)}{N}
\]  

(4.2)

4.2 Bulk Temperature and Concentration Profiles

Absorption theory predicts that the transport coefficients are high near the inlet where thermal and absorbate concentration profiles in the falling film are not fully developed. In addition, the driving potential for absorption may vary along the length of the tube and result in a variation in the rate of absorption. Computing these local variations in heat and mass transfer rates requires a determination of the film temperature and concentration. Conventional film temperature sensors would disrupt the normal flow patterns in a thin falling film. Nakoryakov, Bufetov and Grigor'yeva (1982) used a traversing sampler to measure the local concentrations and temperatures. Researchers such as Wood et al. (1993) and Grossman and Alefeld (1996) fitted their mini-absorber test section with a moveable solution collector cup so that its position on the tube could be varied. A disadvantage of this feature is that moving the cup requires that the test section be opened up, reassembled and vacuum-sealed for each adjustment. Several studies have been conducted in Germany, the most notable being that of Riede (1985), who developed a unique absorption test stand for measuring the profiles of the tube wall temperature and the concentration over the last 0.4 m of the falling film. Testing was conducted during adiabatic operation at an absorber pressure of 9.3 kPa and a concentration of 48 wt\% LiBr.
Work was continued by Yueksel and Schluender (1988), who made interface
temperature measurements using optical pyrometry. However, both of these studies
were conducted for the limiting case of adiabatic absorption at conditions atypical of
absorption machines. Typically, the absorber operates at about 1.0 kPa, and the
concentration is controlled to about 62 through 64 wt%. The studies of Burdukov et
al., Yueksel and Schluender, Wood et al., and Grossman and Alefeld are the only
ones of the variations of either temperature or concentration along the film flow.

Since the inception of this project, a means of nonintrusively sensing film surface
temperature was introduced by LANL personnel. It involves doping the solution with
a very light amount of a phosphor. Phosphorescence is induced by a pulsed laser, and
the rate of decay of phosphorescence can be correlated with temperature. The
technique is well developed, and ORNL scientists skilled in its use assisted the author
in making interface temperature measurements. The main uncertainty is related to
the degree of spatial resolution that can be obtained by focusing the emission sensor
on the thin wavy film. A description of a preliminary evaluation of the
phosphorescent thermographic technique for this application is presented in
Appendix B.

4.2.1 Thermographic Phosphor Temperature Data

The test tube was instrumented internally to measure the axial temperature profile of
the coolant (refer to Sect. 3.3.6). The charge of LiBr brine was doped with a
lanthanum oxysulfide phosphor to support the non-intrusive measure of the interface
temperature. Testing was conducted at an entering solution concentration of 60 wt%. The Re number of the falling film was fixed at about 290, and the coolant temperature was controlled to 35°C. Absorber pressure was controlled throughout all testing at 1.3 kPa. For these operating conditions, the measures of the coolant and interface temperatures are plotted in Fig. 4.6. The symbols in Fig. 4.6 represent the measured data, and the lines are exponential curve fits. The vertical bars represent the error in the data. The coolant probe was calibrated and checked in situ; its measurement error was ±0.15°C. Preliminary testing with thermographic phosphors showed an error of about ±0.5°C; however, in the mini-absorber, we repeated several measurements at a given station to better estimate the actual error. Results showed the interface temperatures to be about ±1.5°C accurate. Despite this large error, the trends are very useful for understanding on an overall scale the coupled heat and mass transfer processes.

The strong solution had an entering interface temperature of 50.4°C in equilibrium with the vapor pressure in the absorber. This temperature is closely matched by the curve fit to the thermographic phosphor data when extrapolated to \( x = 0 \) (the start of absorption). The saturated temperature of brine leaving the absorber is 49°C; it is based on the absorber pressure and the bulk concentration leaving the absorber. Also, the subcooling at the absorber exit was about 6°C. If the brine had left the absorber at 49°C, it would have absorbed the maximum possible amount of water for the given operating conditions. The thermographic phosphor data show that the interface temperature along the length of the absorber is less than the saturated temperature at the absorber exit. However, whether the interface is subcooled or in equilibrium with the vapor pressure requires information about the interface concentration.
Fig. 4.6. Thermographic phosphor and coolant temperature profiles measured along the running length of the falling film.
Surprisingly, the curve fit through the coolant data shows a near linear temperature gain over the full length of the absorber. This result was also discovered by Grossman and Alefeld (1996). Grossman inserted a helically wound wire into the bore of a stainless steel test tube. The tube had 10 thermocouples for measuring temperature distribution. Unfortunately, the thermocouples were delicate and malfunctioned after a few tests. Yet, while operable, Grossman observed the profile to be slightly exponential but rather flat and approximately linear. In fact, the bolder coolant curve in Fig. 4.6 is exponential in form, while the dashed curve is a linear fit to the measured data. Close inspection of Fig. 4.6 shows a similar slight exponential deviation for the last three coolant temperatures (i.e., stations near the inlet of the falling film). What is surprising, however, is the minimal effect seen on the coolant profile near the film inlet, where absorption heat flows are largest.

The total resistance to heat transfer is composed of the resistance through the film, the tube wall and the coolant. These resistances can be derived from energy balances, since the heat transfer through the film, the tube wall and the coolant remain constant at any cross section of the tube. They are derived as

\[
\sum \text{Res}_{\text{Total}} = \frac{1}{h_{CL} A_I} + \frac{\ln \left( \frac{D_O}{D_I} \right)}{2 \pi k_p L} + \frac{1}{h_f A_O}.
\] (4.3)

The film-side resistance is the largest resistance, being about 70% of the total resistance. However, the coolant resistance is only 20% of the total and for the present study, is based on a coolant Re number of 6000. In practice, the coolant Re number can exceed 40,000. Hence, the coolant-side resistance is very small, and any
heat transfer due to absorption is readily swept away by the coolant, especially for the absorbers of single- and double-effect chillers. This helps to explain the strongly linear coolant profiles seen in Fig. 4.6. For chillers, the gradient of the coolant temperature profile will then be less than that measured in the mini-absorber simply because of the stronger coolant capacitance at which the chiller operates.

4.2.2 Reduction Procedure for Local Absorbed Mass

A reduction scheme was formulated to quantify the local concentration and mass absorbed along the length of the absorber. The coolant and interface temperature data (Fig. 4.6) were fit to exponential profiles of the form

\[ T(x) = a + be^{\left(-\frac{x}{c}\right)} , \]  

(4.4)

with the coefficients shown in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1. Regression constants for the temperature profiles, Eq. 4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Coolant</td>
</tr>
<tr>
<td>Film Interface</td>
</tr>
</tbody>
</table>

An energy balance is set up for the control volume shown in Fig. 4.7. The local heat flow from the film to the coolant can be expressed by the water-side balance:

\[ dq' = \left( m C_p \right)_{CL} \frac{dT_{CL}}{dx} . \]  

(4.5)
Fig. 4.7. Differential element for the vertical falling film absorber with counterflow coolant.
The differential heat flow is expressed in units of (kJ/m·s). It is calculated from the coolant side measurements by taking the gradient of Eq. 4.4 at a given x location. Starting at the solution inlet, the local balance is incremented by $\Delta x$, and the gradient $d\bar{T}_{cl}/dx$, is substituted into Eq. 4.5 for the local heat flow. Then, given the water-side convective coefficient, the inside-wall temperature profile is calculated from a first-law balance:

$$T_{wall_i} = \bar{T}_{CL} + \frac{dq'}{(2\pi R_i)h_{CL}}.$$ (4.6)

The profile on the outer wall, based on conduction through the tube material, becomes

$$T_{wall_o} = T_{wall_i} + \left[\frac{\text{Ln}(R_o/R_i)}{2\pi k_p}\right]dq'.$$ (4.7)

These calculated wall temperatures are shown in Fig. 4.6 along with measured RTD wall temperatures. The calculated and measured RTD temperatures are within 0.3°C, which substantiates the accuracy of the calculated wall profiles. By including both the coolant and the film in the control volume of Fig. 4.7, the energy balance for the small element $\Delta x$ becomes

$$\left(\bar{m}C_pT\right)_x + \dot{m}_f i_{fg} \Delta x = \left(\bar{m}C_pT\right)_{x+\Delta x} + dq' \Delta x.$$ (4.8)

Taking the limit of Eq. 4.8 as $\Delta x \to 0$ and substituting Eq. 4.5 for $dq'$ yields an expression for the local mass absorbed per unit length:

$$\dot{m}_f = \left[\frac{(mC_p)}{i_{fg}}\right]d\bar{T}_f \frac{dq'}{dx} + \frac{dq'}{i_{fg}}.$$ (4.9)
A water balance for the absorbate within the film side control volume of Fig. 4.7 yields

\[
\left( \frac{m}{\rho} \right)_f \eta^* \frac{\partial}{\partial x} C_a + \frac{m_f}{\rho} \Delta x = \left( \frac{m}{\rho} \right)_f \eta^* \frac{\partial C_a}{\partial x} \Delta x. \tag{4.10}
\]

Again taking the limit of Eq. 4.10 as \( \Delta x \to 0 \) yields the continuity expression:

\[
m_f = \left( \frac{m}{\rho} \right)_f \eta^* \frac{dC_a}{dx}. \tag{4.11}
\]

The concentration is derived from Eq. 4.11 and can be used to march down the tube for calculation of the local bulk profile. This can be expressed as a bulk water concentration:

\[
\bar{C}_a = \frac{m_f' \Delta x}{\eta \left( \frac{m}{\rho} \right)} \, , \tag{4.12}
\]

or, it can be expressed in terms of the solute:

\[
\bar{X}_f = 1 - \frac{m_f' \Delta x}{m_f} \, . \tag{4.13}
\]

The differential mass absorbed is expressed in units of (kg/m·s). The energy balance of Eq. 4.9 is dependent on the gradient of the bulk temperature in the film with respect to the tube length. Thermographic phosphor measurements are considered interface temperatures, and a local bulk temperature was needed as input to Eq. 4.9. By using the definition for bulk temperature,

\[
m C_p \bar{T}_f = \int_0^\Delta \rho C_p u(y) T(y) 2 \pi R_o dy \, , \tag{4.14}
\]

a parabolic velocity profile (Eq. 2.5), and a linear temperature profile were substituted into Eq. 4.14 to derive an expression for the local bulk temperature. The
film is very thin, about 0.48 mm, and is assumed to be conduction-dominated. The linear temperature profile through the film thickness is therefore

\[ T(y) = T_{\text{wall}} + \left( \frac{T^* - T_{\text{wall}}}{\Delta} \right) y, \]  

(4.15)

which then yields the following simple relation for the bulk temperature:

\[ \bar{T}_f = \frac{5}{8} T^* + \frac{3}{8} T_{\text{wall}}. \]  

(4.16)

To start the calculation procedure, the concentration and temperature are initialized to the equilibrium condition observed at the absorber inlet. The local heat flow per unit length is calculated by Eq. 4.5, and the wall temperature profiles are evaluated using Eqs. 4.6 and 4.7. The bulk temperature profile is then calculated and used in Eq. 4.9 to calculate the local mass absorbed per unit length of the absorber. The absorbate water balance of Eqs. 4.12 and 4.13 is used to determine the bulk concentration within the \( \Delta x \) increment. Data calculated in a \( \Delta x \) increment is stored, \( x \) is incremented by \( \Delta x \), and the previous values are used as entering conditions for the next increment. The procedure marches forward until the \( x \) location matches the absorber length of 1.524 m. Local values are summed to determine an overall calculated load and mass absorbed. The summation for mass is simply

\[ \dot{m}_v = \sum_{j=0}^{N} \dot{m}_{v_j}(\Delta x_j), \]  

(4.17)

while for the absorber load the summation becomes

\[ q = \sum_{j=0}^{N} dq_j(\Delta x_j) \]  

(4.18)
Results, including the calculated bulk concentration and temperature, were compared to the experimental data measured at the absorber exit to validate the numerical procedure.

The procedure validates well, as seen in Table 4.2, with the mass absorbed within 8.5% of experiment (Table 4.2). The numerical values of load and of mass absorbed slightly overpredict experiment and are physically consistent because they are directly proportional. The bulk mass fraction, $X_{ex}$, is in excellent agreement, while the error in temperature is in part attributed to the error in the interface temperature measurement.

Table 4.2. Accuracy of the numerical data reduction procedure

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Numerical</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (W) coolant side</td>
<td>936.5</td>
<td>956.3</td>
<td>2.12</td>
</tr>
<tr>
<td>Load (W) film side</td>
<td>1087.7</td>
<td>1124.4</td>
<td>3.37</td>
</tr>
<tr>
<td>$m_v$, kg/s</td>
<td>$2.64 \times 10^{-4}$</td>
<td>$2.866 \times 10^{-4}$</td>
<td>8.54</td>
</tr>
<tr>
<td>$X_{ex}$, wt% LiBr</td>
<td>59.052</td>
<td>58.996</td>
<td>-0.09</td>
</tr>
<tr>
<td>$T_{ex}$, °C</td>
<td>43.4</td>
<td>41.0</td>
<td>-5.5</td>
</tr>
</tbody>
</table>

4.2.3 Concentration Profile and Local Transfer Rates

The bulk concentration profile, in units of wt% LiBr, is plotted in Fig. 4.8 for the present study. Also included in Fig. 4.8 are the independent data by Burdukov et al. (1980) and Grossman and Alefeld (1996). Table 4.3 shows the test conditions for
Fig. 4.8. The bulk concentration of the falling film for the present study is compared to the independent data of Burdukov et al. (1980) and of Grossman and Alefeld (1996).
each of the three studies. Grossman and Alefeld inserted a helically wound wire into
the bore of the absorber tube to promote turbulence in the coolant although the Re
number for the coolant was low, at 4500. Burdukov et al. tested at a Re number of
about 60,000 to study the absorption problem with constant wall temperature.
Burdukov et al. used a traversing sampler to measure the local bulk concentration of
LiBr. Grossman and Alefeld had a moveable cup. Hence, both of these data sets,
plotted in Fig. 4.8, are actual measures of the local bulk concentration.

Table 4.3. Testing conditions for the present study and two comparison studies

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present study</th>
<th>Burdukov et al. 1980</th>
<th>Grossman and Alefeld 1996</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube dimensions, m</td>
<td>1.524 m long, 0.01905 m OD</td>
<td>1.0 m long, 0.0245 m OD</td>
<td>1.3 m long, 0.01905 m OD</td>
</tr>
<tr>
<td>LiBr concentration, wt%</td>
<td>60</td>
<td>60</td>
<td>56</td>
</tr>
<tr>
<td>Vapor pressure, kPa</td>
<td>1.3</td>
<td>2.03</td>
<td>4.0</td>
</tr>
<tr>
<td>Coolant temperature, °C</td>
<td>35</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>Re number, falling film</td>
<td>290</td>
<td>250</td>
<td>280</td>
</tr>
<tr>
<td>Re number, coolant</td>
<td>6,000</td>
<td>60,000</td>
<td>4,500</td>
</tr>
</tbody>
</table>

The author’s results and the results of these two studies are very eye-opening because
they all display linear trends with tube length. The slope of the trends in bulk
concentration vary between studies because of the strength of the coolant Re number.
Burdukov et al. tested at a coolant Re number of 60,000; however, Grossman and
Alefeld tested at a Re numbers of 4500. The mass absorbed is a direct function of the
bulk concentration gradient, $\frac{dC_a}{dx}$, which is seen in Fig. 4.8 to be nearly constant
for the independent studies. Therefore the mass absorbed is inferred constant by
Eq. 4.12 because \( \frac{d\bar{C}_a}{dx} \) is constant. Burdukov et al. noted that the experimental observation of a constant mass flux contradicted their analytical boundary layer model (see Sect. 2.2.2). They concluded that the theory of combined heat and mass transfer developed by Naroryakov and Grigor'yeva (1977) needed to be refined to possibly include the mixing effect of the waves. Brauner (1983) had alluded to a reestablishment of boundary layers with each successive wave front. Burdukov et al. applied their boundary layer model over the wavelength of a respective wave and iterated over each wavelength by using the previous zone to march forward into the next wavelength zone. Their numerical prediction was then found to be in satisfactory agreement with experiment. A difficulty with this approach, however, pertains to the chaotic wave flow at Re numbers exceeding 300. The wavelength is not necessarily constant (see Fig. 2.1). Nakoryakov, Bufetov and Grigor'yeva (1982) studied Re numbers of the falling film ranging only from 30 to 250; beyond a Re number of 200 the flow transitions into an unstable flow regime, making it difficult to predict wavelength.

In falling film absorption, the driving force for mass transfer is described by the concentration gradient from the interface to the bulk of the film. The bulk concentration profile, in units of g-moles \( \text{H}_2\text{O} \) per cc of solution, is plotted in Fig. 4.9 for the numerical result obtained from Eq. 4.12. As observed, the bulk concentration profile is approximately linear. Its trend must be tied to the effect of the coolant, whose temperature profile is also linear because of its dominant capacitance, which readily absorbs any heat from the film. If the interface is saturated at the ambient vapor pressure, then the interface concentration can be described by the linear absorbent in Fig. 4.9. Data from the thermographic phosphors were used for
Fig. 4.9. The driving force for mass diffusion is described by the gradient from the interface to the bulk.
calculating the interface concentration. The driving force is seen to increase with tube length and is due to the effect of the coolant; however, because the thermal diffusivity is about two orders of magnitude greater than the mass diffusivity, heat is transferred readily across the film, while absorbate tends to remain on the surface. Hence, while the concentration gradient across the film increases with length, the liquid-side diffusion resistance forces the bulk concentration profile to follow the trend of the coolant.

The local heat and mass flows are plotted in Fig. 4.10 to observe their variations as a function of tube length. The horizontal dashed lines represent the measured load and the mass absorbed per unit of length, each being divided by the absorber length of 1.524 m. Both load and mass are highest near the inlet, where the temperature gradient from the interface to the coolant is largest. The interface-to-coolant temperature gradient was a measured 11.5°C at the film inlet, and dropped to about 6.8°C at the exit. The load per unit length (Eq. 4.5) decreases in a near-linear fashion, as does the mass absorbed (Fig. 4.10). Integrating each of these curves over the absorber length leads to the total load and mass absorbed, which was shown in Table 4.2 to be within 2% and 8%, respectively, of the experiment. The results reveal two very important findings: (1) on a macro scale, bulk film temperature and concentration profiles are roughly linear, and therefore the load and mass absorbed can be calculated using a constant flux approximation; (2) the mass transfer is driven more by the temperature gradient across the film than by the normal convective forces for Re numbers not exceeding about 400. For the present study, the Re number of the falling film was 290. Wasden and Dukler (1990) studied wavy flow for a Re number of 880 and reported strong convective effects across the film, as did
Fig. 4.10. The local heat and mass transfer is calculated for test conditions of 60 wt% LiBr, 1.3 kPa vapor pressure, 35°C coolant and falling film Re number of 290.
Patnaik (1994) who studied a Re number of 400. Jayanti and Hewitt (1997) studied wavy flow for a Re number of 140 and reported the heat transfer as being conduction-dominated. Apparently, the steeper the temperature gradient across the film, the greater the cooling effect and the greater the mass absorbed. The convective effect within the waves does not significantly affect the process until the falling film transitions into the second transient turbulent-laminar regime at a Re number of about 400 (Fig. 2.1). Hence, the results are consistent with the findings of Patnaik (1994), Wasden and Dukler (1990), and Jayanti and Hewitt (1997).

The coupled heat and mass transfer process therefore becomes one which is mass-transfer-driven at the absorber inlet, where the solution drives to equilibrium with the vapor. The process then becomes heat-transfer-driven. As waves develop along the tube, they cause the film substrate to thin (Fig. 4.3), which causes the temperature gradient across the film to become steeper. Hence, more mass is absorbed into the thin tail section than is absorbed into the thicker wave. Possibly, the interface along the wave tail is subcooled while the thicker wave is saturated at the pressure of the absorber. The thermographic phosphor data could not distinguish this subtle difference. Therefore, assuming a saturated interface, the concentration gradient across the film increases along the tube (Fig. 4.9); however, the mass transfer along the tube drops because of the high diffusion resistance of the brine. Here, the mass transfer is driven by the heat transfer; otherwise, little if any absorption would occur. Local heat and mass transfer coefficients were calculated to substantiate the proposed concepts. The local heat transfer coefficient was calculated as follows:

\[
h = \frac{dq'}{2\pi R_o \left( T^* - T_{wall} \right)},
\]

(4.19)
and the local mass transfer coefficient follows as

\[ h_m = \frac{m_i}{2\pi R_0 \eta (C^* - \bar{C})}. \] (4.20)

The local mass transfer coefficient was plotted against Higbie's coefficient based on penetration

\[ \frac{h_m}{D_{ab}} = \sqrt{Re Sc \epsilon}. \] (4.21)

The results in Fig. 4.11 show that the mass transfer coefficient for the present study exceeds that of Higbie's penetration theory. However, as the axial flow length increases and fully developed flow is achieved, the two coefficients begin to converge after about 1 m. Near the top, the flow is smooth with no waves. Yet the mass transfer coefficient is higher for the coupled heat and mass transfer of this study. The interface-to-coolant temperature gradient enhances the mass transfer over penetration theory, and as waves develop, the normal convective forces become more dominant. However, in this wavy-laminar region, mass is absorbed by the effect of the coolant, and enhancements by the roll waves are due to the indirect effect of thinning the film as the waves fully develop down the tube. On the other hand, the local heat transfer coefficient is seen to increase along the length of the tube, which is consistent with a thinning film. Because the film is thin, about 0.48 mm, the heat transfer can be considered conduction-dominated, as alluded to by Jayanti and Hewitt (1997). Hence, the heat transfer coefficient can be approximated as \( h \approx k_f / \delta \). An increasing heat transfer coefficient therefore yields a decreasing local film thickness. For the data in Fig. 4.11 this yields roughly a 28% reduction in the mean film thickness, which, when compared to Fig. 4.3 is reasonable, since at 0.0194 kg/s (i.e., a Re number of 290) the film thins roughly 25% due to hydrodynamics of the roll waves.
Fig. 4.11. Local heat and mass transport coefficients calculated for test conditions of 60 wt% LiBr, 1.3 kPa vapor pressure, 35°C coolant and falling film Re number of 290.
4.3 Absorption Test Results

A single absorber tube of 0.01905 m OD and of 1.524 m length was tested to obtain baseline data for the purposes of formulating correlations of heat and mass transfer. Testing was conducted over a range of operating conditions that included near-field conditions for industrial and commercial systems. In air-cooled applications the operating conditions would be about 62 wt% LiBr, an absorber pressure of about 1.5 kPa, and an inlet cooling water temperature of about 46°C. Testing was also conducted at 35°C cooling water temperature to simulate load rejection to a cooling tower. In commercial equipment, some of the solution leaving the absorber is circulated back and mixed with strong solution to improve wetting of the absorber tubes. Thus, the net concentration entering the absorber is about 60 to 62 wt%. Testing was therefore conducted at 60, 62, and 64 wt%, for absorber pressures of 1.5, 1.3, and 1.0 kPa, to characterize operating conditions for commercial application. Appendix C lists data for testing at 62 wt% LiBr and 35°C coolant.

4.3.1 Absorber Performance

Tests were run by establishing the independent parameters of flow, temperature, concentration and pressure. Flow rate was the easiest variable to change, and therefore the effects of the other variables were tested one parameter at a time for falling film mass flows ranging from 0.014 to 0.026 kg/s (i.e., Re numbers of 100 to 400). The load is defined as the heat removed from the absorber by the coolant; it is plotted in Fig. 4.12. The increase in load is directly related to the mass of vapor.
Fig. 4.12. The absorber load is affected by the concentration, the pressure, the coolant temperature and the falling film mass flow rate.
absorbed into the falling film. The more vapor that is absorbed, the greater the
capacity of a chiller’s evaporator. The absorber load, then, is a good indicator of the
system performance although the important variable is the mass absorbed (Fig. 4.13),
which was back-calculated from the load (see Appendix D, Fig. D.3).

The effects of mass flow rate, coolant temperature, absorber pressure, and
concentration are all described by the variations of the load and mass absorbed
(Figs. 4.12 and 4.13, respectively). The load is not strongly affected by the falling
film mass flow rate. Stable wavy-laminar roll-waves and, at the highest flows, second-
transition turbulent laminar roll waves were observed during testing. The inception of
the waves appeared to be influenced by the solution flow rate. At the lowest flow, of
0.014 kg/s, the inception of short waves of small amplitude were seen about 0.2 m
from the inlet. The short waves transition into longer roll-waves whose length and
amplitude were at least double that of the short waves. Similar observations are
described in Fig. 4.13 for the mass absorbed. Increasing the mass flow rate of the
falling film shows an effect only at the lowest flow rates. The data are relatively flat
and differed from the results of Grossman And Alefeld (1996). The latter tested at a
higher absorber pressure of 4 kPa and introduced the solution into the absorber with
about 15 to 20°C of subcooling. For the present study, the solution entered the
absorber saturated at about the operating pressure for chiller equipment.

The data are separated and plotted in Fig. 4.14 to better view the effects of absorber
pressure, concentration, and coolant temperature. Pressure and concentration both
have strong effects on the mass absorbed. Testing at 64 wt% LiBr and 46°C coolant
showed the mass absorbed to increase by almost 200% as the pressure was increased
Fig. 4.13. The mass absorbed is affected by the concentration, the pressure, the coolant temperature and the falling film mass flow rate.
Fig. 4.14. The independent variables of pressure, concentration and coolant temperature are described to show the effect of each one on the mass absorbed.
from 1 to 1.5 kPa [Fig. 4.14(a)]. Similar boosts in mass absorbed were observed by increasing the concentration from 60 to 64 wt% LiBr for a coolant temperature of 46°C and pressure of 1.5 kPa [Fig. 4.14(b)]. For testing at 62 wt% and 1.3 kPa pressure, decreasing the coolant temperature from 46 to 35°C also caused the mass absorbed to nearly double [Fig. 4.14(c)].

In the absence of noncondensables, the resistance in the vapor phase is negligible, allowing the vapor pressure to be imposed on the interface. The driving force for absorbing the water vapor into the falling film is then the difference between the pressure of the absorber vapor on the interface and the partial pressure of the absorbate water in the liquid-vapor interface. Obviously, the driving force increases with an increase in the absorber pressure. The driving force would also increase as the concentration of LiBr increases. The higher the wt% LiBr the lower the partial pressure of water in the brine, and therefore the greater the driving force for mass transfer. Lowering the cooling water temperature causes a steeper approach temperature for the falling film. The interface temperature drops, lowering the partial pressure of water vapor within the interface. The driving potential then increases, which in turn increases the mass absorbed and the load. Hence, the observations in Fig. 4.14 are consistent with absorption theory. However, once the vapor has been absorbed, the driving force is liquid-side controlled because of the high resistance to mass diffusion. Once absorbed, the mass transfer driving force is defined in terms of the difference in concentration between the interface and the bulk of the film. The higher the bulk concentration of LiBr, the larger is this liquid-side driving force and the more mass absorbed into the bulk although the absorbate tends to lay on the interface, and continued mass transfer requires a cooling of the interface. The results
show the coupling between mass transfer and heat transfer that is tied to the composition of the interface, the diffusion of absorbate from the interface, and most important, the transfer of heat from the interface.

### 4.3.2 Formulation of Nu and Sh Numbers

Naroryakov and Grigor’yeva (1977), Seban and Faghri (1978) and Grossman (1982) developed heat and mass transfer correlations by solving the energy and diffusion equations using the classical Gratz-Nusselt approach. Diffusion and conduction are neglected in the direction of flow (see Eqs. 2.62 and 2.63). Their correlations typically take the form

\[
\text{Nu} = f\{\text{Re}, \text{Pr}, \varepsilon\}
\]

and

\[
\text{Sh} = f\{\text{Re}, \text{Sc}, \varepsilon\}.
\]  
(4.22)

The Nu and Sh equations account for the effects of viscosity, diffusivity and inertia; but the coupled heat and mass transfer process has very strong pressure, concentration and temperature effects, as seen in Fig. 4.14. The formulations in Eq. 4.22 do not explicitly account for these independent parameters. Therefore, to accurately correlate simultaneous heat and mass transfer data, a judicious selection of the temperature and concentration driving forces is needed.
4.3.2.1 Heat Transfer

In conventional equipment, superheated brine is sprayed over an absorber tube bundle. As a spray, the brine flashes and is driven to equilibrium with the absorber pressure; it is saturated when it hits the first absorber tubes. In the mini-absorber, brine entered either slightly superheated or slightly subcooled. To simulate conventional operation, the dispenser was fabricated with vapor ports to allow the brine opportunity to equilibrate before being introduced to coupled heat and mass transfer. Therefore, the driving force is well defined at the top of the absorber tube, because the brine is initially saturated. An algorithm (described in Sect. 3.6) was used to calculate the entering interface temperature and concentration based on saturation with the absorber pressure. The interface temperature is, at that instant, the maximum temperature observed on the interface of the falling film; it is defined as $T_{f,max}$. The corresponding concentration is, at that instant, the lowest water concentration; it is defined as $C_{eq}$. Hence, both variables are useful for describing the overall driving forces for heat and mass transfer.

$T_{f,max}$ is dependent on the entering concentration, temperature and pressure of the absorber and would account for their independent effects. The entering coolant temperature is the lowest temperature that the film could ideally achieve. Therefore, an overall heat transfer coefficient was defined in terms of the load and this maximum achievable temperature gradient; it is

$$\frac{q}{A_{o}} = q_{wall} = H(T_{f,max} - T_{cl}) \quad (4.23)$$

The load can also be defined in terms of the temperature gradient along the wall as
\[ q''_{\text{wall}} = -k \frac{dT}{dy} \bigg|_{y=0} \quad (4.24) \]

Using the scales of \( \bar{T} = T/(T_f - T_{cl,i}) \) and \( \bar{y} = y/D_o \), and then substituting for the overall heat transfer coefficient from Eq. 4.23 yields the following overall Nu number:

\[ \text{Nu} = \frac{HD_o}{k_f} = \frac{(q''_{\text{wall}})D_o}{k_f(T_{f_{\text{max}}} - T_{cl_{i,n}})} \quad (4.25) \]

Inspection of Eq. 4.25 shows that the effects of coolant temperature, absorber pressure and solution concentration are supported implicitly through the defined overall temperature gradient.

### 4.3.2.2 Mass Transfer

Care was taken to ensure that the test section operated under vacuum pressure with only trace amounts of noncondensable. Therefore, the gas-film resistance was negligible, and the absorber pressure was imposed on the liquid-vapor interface. The absorption process is therefore liquid-side controlled, and the liquid-side coefficient expresses the driving force for mass transfer. At the top of the absorber the concentration is \( C_{eq} \). The mass diffusivity of aqueous LiBr is very low, on the order of \( 10^{-9} \text{ m}^2/\text{s} \), and any absorbed mass will lay on the interface unless mixed into the bulk of the film. The tube wall is impervious to mass diffusion, and the very high diffusion resistance through the bulk of the film would keep mass from contacting the wall, unless it is mixed by the roll waves. Yet, it is assumed that the waves ride over a thin substrate, and that the equilibrium concentration therefore prevails along the wall.
over the entire length of the absorber because of the distance needed to establish the concentration boundary layer. The maximum water concentration would be observed at the absorber exit, tied to the film temperature. An overall concentration driving force could then be viewed as (1) the continuity of absorbate from inlet to exit of the absorber or as (2) the maximum driving force from the bulk of the film to the wall, being defined at the exit of the absorber. Hence, from either perspective, we define an overall liquid-side mass transfer coefficient as

\[ \frac{m_v}{A_o} = \dot{m}_v'' = H_m \left( C_{a_{ex}} - C_{a_{eq}} \right). \]  \hspace{1cm} (4.26)

The mass flux can also be defined in terms of the concentration gradient along the interface as

\[ \dot{m}_v'' = -D_{ab} \eta' \left. \frac{dC_a}{dy} \right|_{y=\Delta}. \]  \hspace{1cm} (4.27)

The scales of \( \bar{C}_a = C_a/(C_{a_{ex}} - C_{a_{eq}}) \) and \( \bar{y} = y/D_o \) are substituted into Eq. 4.27, and the overall mass transfer coefficient from Eq. 4.26 is used to yield the following overall Sh number:

\[ Sh = \frac{H_mD_o}{D_{ab}} = \frac{\dot{m}_v''D_o}{\eta'(C_{a_{ex}} - C_{a_{eq}})D_{ab}}. \]  \hspace{1cm} (4.28)

We defined the overall liquid-side Sh number according to Eq. 4.28 to avoid use of the equilibrium condition along the interface. Neither the interface temperature nor concentration are known, and they cannot be determined unless equilibrium is assumed with the absorber pressure. Reductions of liquid coefficients based on Eq. 4.26 showed excellent trending of data, whereas an arithmetic or log-mean concentration difference yielded too much scatter because they require interface
measurements. Eq. 4.26 has two unknowns—the mass absorbed and the exit concentration. The concentration of water leaving the absorber can be related to the continuity of the solute and to the continuity of mass as follows:

\[
C_{a_{ex}} = \frac{\rho}{\eta'} \left[ \frac{\dot{m}_{eq}(1 - X_{ex}) + \dot{m}_V}{\dot{m}_{eq} + \dot{m}_V} \right].
\]  

(4.29)

Given the two equations for the mass absorbed and the exit concentration, both unknowns can be determined if a suitable correlation for the Sh number is formulated from the data.

Diffusivity data for LiBr brine is reported in Appendix A, and it is strongly recommended that the correlation for diffusivity given in Appendix A be used for calculating the Sh number.

\subsection*{4.3.3 Heat and Mass Transfer Correlations}

The data described in Fig. 4.12 for the load and in Fig. 4.13 for the mass absorbed were reduced to Nu and Sh numbers, and the results are depicted in Fig. 4.15. All data collapse into a tight trend with the exception of Nu data for testing at 60 wt% and 35°C coolant. Sh data for 60 wt% testing fell within the bulk of the data; however, Nu data for 60 wt% testing appears as an outlier [Fig. 4.15(a)]. We checked the data by repeating some testing at 60 wt%, and results are shown in Fig. 4.15 by the + symbols. In fact, these later data represent testing conducted with the thermographic phosphors. Both 60 wt% data sets are similar in magnitude and prove that the earlier data are not spurious. All attempts using regression analysis to
Fig. 4.15. Overall Nu and Sh numbers were reduced from tests conducted at different pressures, concentrations, coolant temperatures and falling film mass flow rates.
collapse Nu data for 60 wt% testing failed, and therefore, it was decided to exclude these data. Only the 62 and 64 wt% data were included in the regression analysis, and the 60 wt% data were then compared to the correlations of Nu and Sh numbers.

Regression analysis was conducted using Statistical Application Software (SAS), and the results for both the Nu and the Sh numbers are listed in Table 4.4. The Nu number was correlated as function of the Pr, Ka and the Ja numbers; the Sh number was correlated as function of the Sc and the Ka numbers.

The results of correlating the data are also depicted in Fig. 4.16. Here, the Nu and Sh data are scaled by the regression parameters listed in Table 4.4. The curve fit, $C_1Re^a$, is then superimposed onto the scaled data to compare the correlation to the reduced experimental data. Both correlation and experiment are in excellent agreement, as seen in Fig. 4.16. Analysis showed that the Ka number significantly improved the correlation, and its trends were consistent with the regression equation for the Nt number (Eq. 4.1). Increasing the Ka number resulted in a decrease in Nt number (i.e., thinner film), which, in turn, leads to an increase in both the heat and mass transfer.

Hence, the Ka exponent in the Nt number is negative (i.e., a larger Ka yielding a thinner film), while regression yielded positive exponents for the Ka number in the formulations for the Nu and Sh correlations (i.e., a larger Ka, thinner film, and increased load and mass absorbed). If the 60 wt% data were included
Table 4.4. Heat and mass transfer regression analysis

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Nu number</th>
<th>Sh number</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (mass fraction LiBr)</td>
<td>0.62 - 0.64</td>
<td>0.62 - 0.64</td>
</tr>
<tr>
<td>P (kPa)</td>
<td>1.0 - 1.5</td>
<td>1.0 - 1.5</td>
</tr>
<tr>
<td>T (°C)</td>
<td>35 - 47</td>
<td>35 - 47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Range of Regression Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re number</td>
</tr>
<tr>
<td>Sc</td>
</tr>
<tr>
<td>Pr</td>
</tr>
<tr>
<td>Ka</td>
</tr>
<tr>
<td>Ja</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regression Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Nu = C_1 Re^{\alpha_1} Pr^{\alpha_2} Ka^{\alpha_3} Ja^{\alpha_4} )</td>
</tr>
<tr>
<td>( Sh = C_1 Re^{\alpha_1} Sc^{\alpha_2} Ka^{\alpha_3} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 = 0.8429 )</td>
</tr>
<tr>
<td>( \alpha_1 = 0.145664 )</td>
</tr>
<tr>
<td>( \alpha_2 = 0.048053 )</td>
</tr>
<tr>
<td>( \alpha_3 = 0.330440 )</td>
</tr>
<tr>
<td>( \alpha_4 = -0.071242 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of Data Points</th>
<th>86</th>
<th>86</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Absolute Deviation</td>
<td>3.45%</td>
<td>4.28%</td>
</tr>
<tr>
<td>Maximum Error</td>
<td>9.00%</td>
<td>14.1%</td>
</tr>
</tbody>
</table>
(a) The Nu correlation is compared to experiment.

(b) The Sh correlation is compared to experiment.

Fig. 4.16. Nu and Sh numbers were correlated from 62 and 64 wt% LiBr data and account for the effects of absorber pressure, concentration and coolant temperature.
in the regression, then the correlation parameter for the Ka number was too strong, and it made the Nu and Sh correlations somewhat biased by increasing the exponent of Ka to about 0.8. The SAS routines showed that the Nu correlation also improved with inclusion of the Ja number. Although its regression coefficient is small; it supports the Nu number by helping to account for film-to-coolant temperature effects. The negative coefficient for the Ja number reflects a decrease in the Nu number, which again is consistent with the defined heat transfer coefficient in Eq. 4.23 (i.e., \( H = \frac{q''}{\Delta T} \), an increasing Ja number, implies an increasing \( \Delta T \), which in turn implies a drop in Nu). The Gratz-Nusselt approach would formulate the Nu and Sh correlations in terms of \( \text{Pe}_H \) and \( \text{Pe}_M \) numbers, which cancels the effect of viscosity. However, regression for the Nu number showed the coefficient for the Pr number to be significantly different from the coefficient for the Re number, while for the Sh number, it was found that the regression yielded similar coefficients for the Re and Sc numbers. Apparently, the effect of viscosity is more pronounced in the Nu formulation than in the Sh (see Fig. 4.15). Also, the thermal boundary layer easily develops within 0.2 m of the inlet, while the concentration boundary layer requires about 4 m (Sect. 2.2.4). Hence, the Sh formulation is dominated more by the diffusion effects of mass penetration than by the effects of viscosity, which for the Sh number are accounted for in the Ka number.

A point-by-point review is shown in Fig. 4.17 for both the Nu and Sh numbers for all experimental data. The ordinate in both 4.17(a) and 4.17(b) is the correlation, listed in Table 4.4, divided by the reduced experimental data. The results prove that the data are well described by the correlations for Nu and Sh numbers. The average
Fig. 4.17. A point-by-point review of the error observed in the heat and mass transfer correlations.
overall deviation in Nu number is only 3.45% for the fitted data. The 60 wt% data for the Nu number is about 17% less than the experimental value. The Sh correlation has an average overall deviation of only 4.3% for the fitted data. Inclusion of 60 wt% Sh data causes the average error to increase to 6.7%, with the error for the 60 wt% Sh data being about 15% below the experimental value. The average error was calculated using the formula

\[
\text{Error} = \frac{\sum_{j=1}^{N} \text{ABS}\left[1 - \frac{\text{Nu}_{corr,j}}{\text{Nu}_{exp,j}}\right]}{N}.
\]

Runs conducted at 60 wt% and 35°C coolant had the thinnest film of all the data, yet the mass absorbed was comparable to testing at 62 wt% and 35°C coolant (see Fig. 4.13). It was therefore believed that viscosity and possibly surface tension effects caused the 60 wt% data to behave differently from the bulk of the data. To demonstrate the effect, we evaluated the transport properties for testing at 60 wt% LiBr at concentrations of 50, 55 and 56.5 wt% LiBr (i.e., we assumed that the mass absorbed had some variable property effect and caused a local decrease in both viscosity and surface tension). If the transport properties of viscosity and surface tension were evaluated at about 55 wt% LiBr rather than at 60 wt%, then the data closely matched the Nu correlation curve [Fig. 4.18(a)]. The results affected both the Nu and Sh correlations; however, the effect was more pronounced for the Nu correlation [Fig. 4.18(a) and 4.18(b)].

Wasden and Dukler (1990) had shown that the convective motion of the waves accelerated fluid in the wave front into the mass of the slower substrate (Sect. 2.1.3). For a hot absorbate, this would force a hotter fluid from the surface into the cooler
(a) The Nu number for 60 wt% data correlates best using transport data evaluated at 55 wt% LiBr.

(b) The Sh number for 60 wt% data correlates best using transport data evaluated at 56.5 wt% LiBr.

Fig. 4.18. Decreasing the viscosity and surface tension improves the agreement between 60 wt% data and the correlations for the Nu and the Sh numbers.
substrate, thereby creating anomalous temperature gradients (see Fig. 2.9). Liquid viscosity, being a strong function of temperature, would drop at the wave front. The less viscous absorbate would be mixed into the substrate and would reduce the viscous shear effect on the wave. Shair (1971) modeled a variable-viscosity laminar film and showed that the flow characteristics could be greatly affected by a change in the transport properties within the film. Further, the composition and diffusivity would also be affected by the heat inversion near the wave front. Yih and Seagrave (1980) analyzed gas absorption into liquid films with accompanying chemical reactions. They modeled a linear temperature drop across the film and varied the viscosity, diffusivity, kinetic rate, and gas solubility. They concluded that the heat transfer had a profound effect on the mass transfer and found that an exponential representation was more accurate than an assumed linear profile. Their study is a useful guide and helps explain the anomalous behavior for testing at 60 wt%.

Observations of the wave structure during testing in the mini-absorber differed from those made during the hydrodynamic study of the falling film. Differences were due to the effects of absorption. During testing in the mini-absorber at 64 wt% LiBr, the solution flow was reduced to a point that it would just wet the entire tube surface. A further decrease to 0.013 kg/s caused the film to break down, and the flow did not wet the entire tube. If the steam valve was closed, the entire surface would re-wet within 30 s. Once again opening the steam valve caused dry out to occur within 30 s. The process was successfully repeated several times. Each time the steam valve was opened, dry out would occur, not instantaneously, but within about 30 s. The results show the strong influence of the absorbate on the hydrodynamics of the falling film. Unfortunately, we did not measure hydrodynamic data during simultaneous heat and
mass transfer testing. However, visual observations indicated a larger wave structure
during absorption than was observed during the hydrodynamic study. Coupling this
observation with the results by Wasden and Dukler (1990) leads to the conclusion
that the viscosity of falling film varies nonuniformly through the thickness of the film
and causes the waves to slide along a less viscous substrate because of the hot
absorbate that is forced from the surface of the wave front into the bulk of the film.
The proposed dynamics would further accelerate the waves and yield peak-to-
substrate ratios larger than those observed during hydrodynamic testing.
CHAPTER 5

PREDICTIVE ALGORITHM

The profiles of local coolant temperature and bulk concentration led the author to approach the coupled heat and mass transfer problem from a macro point of view. Rather than rigorously solving the momentum equations for the velocity flow field, as did Wasden and Dukler (1989) and Yu et al. (1995), we ignored the convective effects of the roll waves. The experimental results of Sect. 4.2 imply that the heat transfer to the coolant is approximately a constant flux because of the near-linear coolant temperature profile. We therefore assumed the heat flux to be constant, and further assumed that the thin film is conduction-dominated, as supported by Jaynati and Hewitt (1997). The approach simplifies the energy equation and allows a direct calculation of the load and the mass absorbed.

5.1 Scaling of the Energy and the Diffusion Equations

The governing energy and binary diffusion equations in two dimensions are

\[
\rho C_p \left\{ \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right\} = \kappa \left\{ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right\} + \mu \Phi \tag{5.1}
\]

and
\[
\frac{\partial C_a}{\partial t} + u \frac{\partial C_a}{\partial x} + v \frac{\partial C_a}{\partial y} = D_{ab} \left( \frac{\partial^2 C_a}{\partial x^2} + \frac{\partial^2 C_a}{\partial y^2} \right). \tag{5.2}
\]

The transport properties of diffusivity, specific heat, density and thermal conductivity are assumed to be constant. Experimental data, measured at the inlet and the exit of the mini-absorber, showed that variations in specific heat, density and thermal conductivity did not exceed 5% of inlet conditions. The mass diffusivity is also assumed to be constant because of the moderate change in film temperature and because the concentration gradient from inlet to exit was usually less that 0.75 wt% LiBr. Normalizing yields the following scaled equations:

\[
\left\{ \begin{array}{c}
\frac{\partial T}{\partial t} + \bar{u} \frac{\partial T}{\partial x} + \bar{v} \frac{\partial T}{\partial y} = \frac{1}{\varepsilon \text{Pe}_H} \left\{ \varepsilon \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right\} + \frac{\varepsilon \text{Pe}_M}{\varepsilon \text{Re}} \frac{\varepsilon \text{Eck}}{\varepsilon \text{Re}} \\
\bar{C}_a = \frac{\bar{u}}{\bar{u}} \frac{\partial C_a}{\partial x} + \frac{\bar{v}}{\varepsilon \text{Pe}_M} \frac{\partial C_a}{\partial y} = \frac{1}{\varepsilon \text{Pe}_M} \left\{ \varepsilon \frac{\partial^2 C_a}{\partial x^2} + \frac{\partial^2 C_a}{\partial y^2} \right\}, \tag{5.3}
\end{array} \right.
\]

Viscous dissipation can be neglected, since the parameter \( \varepsilon \text{Eck}/(\varepsilon \text{Re}) \) is of the order of \( 10^{-5} \). Eqs. 5.3 and 5.4 are changed into a conservative form, and convective terms are moved to the right side, thereby casting the energy and binary diffusion equations into the following format:

\[
\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{\varepsilon}{\varepsilon \text{Pe}_H} \frac{\partial T}{\partial x} - \bar{u} T \right\} + \frac{\partial}{\partial y} \left\{ \frac{1}{\varepsilon \text{Pe}_H} \frac{\partial T}{\partial y} - \bar{v} T \right\}, \tag{5.5}
\]
All of the convective terms are of order 1, while the diffusion terms are multiplied by the reciprocal of the product of the Pe number and \( \varepsilon \), the aspect ratio. The key issue in the balance of these scales is the film thickness through which heat flows. Going back to Fig. 2.1, the test tube is seen covered more by the substrate film than by the thicker roll waves for Re numbers ranging from 60 through 203; even at Re 406, most of the tube appears to be covered by a thinner substrate. Given the magnitude of the scales, the key player is in the energy equation, in the balance between conduction and convection in the direction normal to the film flow. Balancing these two modes of heat transfer leads to

\[
\varepsilon \approx \frac{1}{\text{Pe}_H},
\]

which for a test tube 1.524-m long and a PeH number of about 1820 requires a film thickness of about 0.8 mm. However, the measured mean thickness is on the order of 0.5 mm. Further, Chu and Dukler (1974) had measured substrate film thickness data on the order of 0.15 mm for a Re number of 1000 (i.e., a factor of 5 less than that required in Eq. 5.7). The range of the present study is about 100 to 400 in Re number and is more in the range studied by Jaynati and Hewitt (1997). Wasden and Dukler (1990) studied isothermal mass absorption for a Re number of 880. Given these results, the problem for the present study can be assumed to be conduction-dominated because the thin film causes the conduction effects to be more pronounced than the convection effects as seen by the balance in Eq. 5.7. Further, Jaynati and Hewitt (1997) showed that even over the wave, the mode of heat transfer was due more to conduction than to convection.
5.2 Formulation of the Algorithm

The two classical problems of forced-convection internal flow are those having an isothermal wall and those having a constant heat flux at the wall. If one assumes a uniform wall heat flux, then $q''$ is not a function of $x$, because $\frac{\partial T}{\partial x}$ is a constant proportional to $q''$. The coolant profile was observed in Fig. 4.6 to be almost linear, and therefore $\frac{\partial T}{\partial x}$ is constant. The discovery implies that the temperature everywhere in the cross section varies linearly in $x$ and that the slope of the temperature profiles are proportional to $q''$. The temperature gradient from the coolant to the film interface would remain constant along the length of the tube. In Fig. 4.6, the coolant-to-film interface gradient varies from about 11°C at the inlet to about 7°C at the outlet. Yet, the interface temperatures are about ±1.5°C accurate. More heat is absorbed at the top of the test tube; however, the flux is linear (Fig. 4.10) and on an overall basis can be approximated as constant.

The driving force for heat transfer is well defined at the top of the absorber. The entering solution is in equilibrium with the absorber pressure, and the interface temperature, $T_{f \text{ max}}$, is at that instant the maximum temperature seen on the film's interface. The thermal conductance of the test tube is known, and the cooling-water convective coefficient was correlated using Wilson's method (Appendix E). Knowing that the heat transfer at any cross section of the tube is constant, we can solve for the load using the following two first-law equations:

$$q = (mC_p)_{cl} \left( T_{cl_{ax}} - T_{cl_{in}} \right), \quad (5.8)$$

and
\[ q = \frac{\{T_{f_{\text{max}}} - T_{c_{\text{in}}}\}}{\sum \Re s_{\text{Total}}} \]  

where

\[ \sum \Re s_{\text{Total}} = \frac{1}{h_{\text{CLA}_1}} + \frac{\ln \left( \frac{D_o}{D_I} \right)}{2\pi k_p L} + \frac{\ln \left( \frac{D_o + 2\Delta}{D_o} \right)}{2\pi k_f L} \]  

Eqs. 5.8, 5.9 and 5.10 have three unknowns: the load, the coolant temperature at the exit of the absorber and the film thickness. Both Eqs. 5.8 and 5.9 are combined to solve for the coolant temperature at the absorber outlet:

\[ T_{c_{\text{in}}} = \frac{T_{f_{\text{max}}}}{1 + \left( m C_p \right)_{c_{\text{in}}} \sum \Re s_{\text{Total}}} + \frac{T_{c_{\text{in}}}}{1 + \left( \sum \Re s_{\text{Total}} (m C_p)_{c_{\text{in}}} \right)} \]  

The film thickness is calculated from the Nt correlation (Eq. 4.1), which was developed from film data in the Re and Ka range of the present study. Accuracy of the algorithm is strongly dependent on the measure of the film thickness. Thickness data are presented in Fig. 5.1 for the test-by-test experimental conditions measured during testing in the laboratory. Note that all transport properties are based on an average of the inlet temperatures of the respective fluids (i.e., \( T_{f_{\text{max}}} \) and \( T_{c_{\text{in}}} \)). Increasing the concentration or decreasing the coolant temperature increases the brine’s viscosity and results in a thicker film (Fig. 5.1). The Ka number accounts for the surface-tension-induced effects of the roll waves. The waves cause a thinning of the film as the flow proceeds down the tube. The Nt correlation does not account for axial effects. Rather, it predicts the mean film thickness for a fully developed wavy-
Fig. 5.1. The Nt correlation (Eq. 4.1) was used to calculate the film thickness from the operating conditions measured during laboratory testing.
laminar falling film, which has no heat and mass transfer effects. The study by Yu et al. (1995) has, to the author’s knowledge, the only user-friendly predictive model capable of calculating the velocity profile as well as the film-thinning effect caused by the waves. However, the falling film falls into regimes of flow instability (Yu 1995), and variable viscosity effects are induced by the coupled heat and mass transfer. Both issues make prediction of the film hydrodynamics very complicated if not impossible.

Once the coolant temperature is known, the load is easily found from Eq. 5.8. The constant flux assumption is again invoked to determine the interface temperature at the absorber exit. Assuming a constant gradient across the film yields

\[ T_{f_{\text{max}}} - T_{cl_{\text{x}}} = T'_{f_{\text{x}}} - T_{cl_{\text{a}}} \]  

With the load known, the wall temperature is calculated at the absorber exit by using the interface temperature in the following energy balance:

\[ T_{\text{wall}_{\text{x}}_{\text{ex}}} = T'_{f_{\text{x}}} - \frac{q}{2 \pi k_f L} \left( \ln \left( \frac{D_o + 2 \Delta}{D_o} \right) \right) . \]  

Given Eqs. 5.12 and 5.13, the bulk film temperature is determined as done previously in Sect. 4.2.2, using Eqs. 4.14, and 4.15. The bulk film temperature at the absorber exit becomes

\[ T'_{f_{\text{x}}} = \frac{5}{8} T' + \frac{3}{8} T_{\text{wall}_{\text{x}}_{\text{ex}}} . \]  

To complete the algorithm, we need to formulate a procedure for calculating the mass absorbed and the bulk concentration at the absorber exit. An iterative scheme was
developed where the bulk mass fraction of LiBr, $X_{ex}$, is estimated and the enthalpy of the brine calculated from the empirical relationship by McNeely (1979):

$$i_{r_{ex}} = f\left(\bar{X}_{f_{ex}}, \bar{T}_{f_{ex}}\right).$$

(5.15)

The absorber pressure is used with the estimated mass fraction to calculate the saturated temperature of brine leaving the absorber in the following empirical equation from Patterson, Crosswhite and Perez-Blanco (1990):

$$T_{f_{ex}, sat} = f\left(\bar{X}_{ex}, P_v\right).$$

(5.16)

The saturated film temperature is compared to the calculated bulk temperature, $T_{f_{ex}}$, and adjustments for subcooling are made to the enthalpy calculated in Eq. 5.15. An overall energy balance is formulated to account for the sensible and absorption heat flows. The balance is made on the film side and takes the form

$$\frac{q - m_{f_{in}}(i_{f_{in}} - i_{f_{ex}})}{(i_{fg} - i_{f_{ex}})} = \frac{m_{v,j}}{m_v,j + m_{f_{in}}^*}.$$

(5.17)

The mass flow leaving the absorber is by continuity $m_{ex,j} = m_{v,j} + m_{f_{in}}^*$, from which the bulk concentration is updated using the solute continuity as

$$\bar{X}_{ex,j} = \bar{X}_{eq} \left(\frac{m_{eq}}{m_{ex,j}}\right).$$

(5.18)

The new concentration is used to recalculate the saturation temperature and enthalpy at the absorber exit. Iteration continues using the load, $T_{f_{ex}}$, and the absorber pressure as fixed inputs while $X_{f_{ex}}$ and $m_{v,j}$ vary per iteration. The mass absorbed converges quickly, and iterations are stopped once the error becomes less than 0.01% of the previous value. Mathematically this is described by the inequality
\[ \text{ABS} \left( 1 - \frac{m_{v,j}}{m_{v,j+1}} \right) < 0.0001 \] \quad (5.19)

5.3 Validation of the Algorithm

Experimental data from the present study were used to validate the predictive algorithm. Independent data were also acquired and filtered for pertinent information in the Re and Ka range of the present study. An additional filter of the independent data were conducted to eliminate any data whose coolant-side versus film-side energy balance exceeded 20% error. Jianpin, Tianfu and Zhonghuao (1985) had studied only smooth laminar falling films. The data from the works of Burdukov et al. (1980) were useful for concentration profiles, Fig. 4.8. Nakroyakov, Bufetov and Grigor'yeva (1982) lists the data; however, the data are limited and do not include the exiting coolant temperature. For their data the experimental load had to be calculated on the film side of the absorber. Wood et al. (1993) had mentioned a noncondensable effect, and reducing his data showed the film-side versus the coolant-side energy balance exceeded an error of 20% for the bulk of his data. Grossman and Alefeld (1996) had the most consistent data useful for validation of the predictive algorithm and for correlation of heat and mass transfer.

5.3.1 Validation against the Present Study

The load and mass absorbed are shown in Fig. 5.2 for testing conducted at 60 through 64 wt% LiBr, 1.0 through 1.5 kPa absorber pressure and 35 and 47° coolant
Fig. 5.2. The load and mass absorbed are validated against the laboratory data for the present study. Testing was conducted at 60-64 wt% LiBr, 1.0-1.5 kPa pressure and coolant temperatures of 35 and 47°C.
temperatures. The ordinate represents the predicted value, while the abscissa is the experimental measure. If the prediction exceeds the experimental value, then a datum will fall above the diagonal in Fig. 5.2. An underprediction would fall below this dashed line. For testing at 62 and 64 wt%, the predicted load is well behaved and shows a very tight clustering along the diagonal in Fig. 5.2(a). The mass absorbed shows more scatter because of the errors incurred with its measurement [Fig. 5.2(b)]. Notice that as the load and the mass absorbed increase, the scatter in the data also increases. The deviation is better seen in Fig. 5.3 for the data plotted against the Re number of the falling film. Increasing the Re number increases the effects of convection and causes the algorithm to underpredict the experiment, especially for testing at 60 wt% and 35°C coolant. Referring again to Eq. 5.5, the interaction between convection and conduction is affecting the results because the algorithm neglects convection. A Re number flow of about 225 shows little error in load and mass absorbed (Fig. 5.3). Decreasing the Re number below 225 results in a slight overprediction, while increasing the Re number causes an underprediction. Yet despite the approximation, the average error in all the data is about 10% for the load and 14% for the mass absorbed. The error is largest for the 60 wt% data, which is underpredicted by about 30% of experiment (Fig. 5.3). Here, the error is believed to be due to the effect of a variable film viscosity induced by the absorption process. Tests conducted at 60 wt%, 35 °C coolant (refer back to Fig. 4.13) absorbed about the same mass as observed for testing at 62 wt%, 35 °C. By the Nt correlation, the 60 wt% tests had the thinner film. Also, Chu and Dukler (1974) had shown through statistical analysis of their data that the thin substrate is exposed to the absorbate vapor for up to 50% of the free fall time of the film. It is therefore very possible that the film for the thinner 60 wt% tests is actually at a lower viscosity and lower surface
Fig. 5.3. Increasing the Re number causes the algorithm to underpredict the experiment. The convection effects are more significant as the Re number increases.
tension, as demonstrated in Fig. 4.18 for the Nu and Sh numbers. The film is thinner than that predicted using viscosity and surface tension properties based on 60 wt%, and as a result the algorithm underpredicts the 60 wt% data. If we exclude the 60 wt% data, then the average error drops to 6.5% for the load and 9.5% for the mass absorbed.

The thermodynamic state of the brine leaving the absorber is of particular interest to designers because the degree of subcooling is a good indicator of the absorber’s performance. Too much subcooling shows poor performance. It also indicates the degree of possible improvement. The greater the subcooling, the larger the amount of mass that the absorber can support through improved tube design. The bulk film temperature, the bulk concentration and the subcooling are shown in Fig. 5.4 for all the experimental data. The algorithm predicts the bulk concentration with an average error of about 0.2% of experiment [Fig. 5.4(a)]. However, the bulk temperature is overpredicted by about 1.2°C [Fig. 5.4(b)]. Overprediction is believed to be caused by a continued thinning of the film, even after 1.5 m of falling film travel. The Nt correlation does not account for axial variation of the film thickness, and the predicted film is too thick (Clegg and Portalski 1972). Subcooling is therefore underpredicted by an average error of about 1.2°C [Fig. 5.4(c)]. Using Fig. 5.3(b) as a guide, data at 62 wt% and 35°C coolant shows about a 5% overprediction in the mass absorbed. This translates [Fig. 5.4(c)] into an underprediction of the subcooling. The more mass absorbed the less the subcooling leaving the absorber. Therefore, the predicted subcooling should be lower because the algorithm overpredicted the mass absorbed for data at 62 wt% and 35°C coolant. Increasing the coolant temperature from 35 to 47°C, for testing at 62 wt%, decreased the error because the amount of
Fig. 5.4. **The algorithm supports the prediction of bulk temperature, bulk concentration and the subcooling of the brine exiting the absorber.**

(a) The average error in the bulk concentration is 0.2% of experiment.

(b) The bulk temperature is overpredicted due to a thinning effect of the film in the axial direction. 60 wt% data is underpredicted.

(c) Subcooling is underpredicted by about 1°C. 60 wt% data is overpredicted.
load and mass absorbed that the absorber can support is also reduced. The subcooling, however, was still underpredicted, which again is caused by the film continuing to thin even at the absorber exit.

Chillers operate fully loaded at the design conditions of 62 and 64 wt% LiBr brine. When unloaded, they operate at 58 through 60 wt% LiBr. The algorithm is therefore reviewed for its accuracy and use at the design operating conditions for commercial equipment. Data for testing at 62 wt% LiBr and 35°C coolant are shown in Fig. 5.5 for absorber pressures of 1.0, 1.3 and 1.5 kPa. An uncertainty analysis was performed on the load and mass absorbed and is described in Appendix D. Briefly, the uncertainty analysis considered both the random and systematic error in measurement, and the error bars in Fig. 5.5 describe the uncertainty in the data for a 95% confidence interval. The lines describe the results of the predictive algorithm, and as seen in Fig. 5.5, the discrepancy between measurement and prediction is well within the tolerance of experimental uncertainty. The load was about ± 10% uncertain, and the mass absorbed was about ± 25%. The prediction for both the load and the mass absorbed decreases as the Re number increases because the thickness calculated from Eq. 4.1 increases as the Re number increases. This increase in \( \Delta \) would cause the load, and in turn, the mass absorbed, to decrease. However, the experimental load and the mass absorbed appears flat, with some decrease observed at the highest flows. Yet despite this discrepancy, the algorithm does an excellent job of predicting the load and mass absorbed for the design conditions of an absorber. The average error in load and the mass absorbed is only 4.3% and 8.2%, respectively. The results are quite amazing, especially when one considers all the complexities of the problem and the simplifications of the proposed algorithm.
(a) The experimental load has a measurement uncertainty of ± 10%.

(b) The experimental mass absorbed has an uncertainty of ± 25%.

**Fig. 5.5.** The accuracy of the algorithm is described for the full-load operating conditions of 62 wt% LiBr and 35°C coolant. The error bars are the uncertainty in the measurements; the lines represent the algorithm.
5.3.2 Validation against Independent Data

The salient operating conditions used during testing by Nakroyakov, Bufetov and Grigor’yeva (1982) and Grossman and Alefeld (1996) are given in Table 4.3. In the two independent studies, the brine was introduced into the mini-absorber with about 10 to 20 °C of subcooling. Therefore, the brine may not have had sufficient time to reach thermodynamic equilibrium with the vapor before being introduced to the test tube. When first exposed to absorbate, a subcooled brine will absorb rapidly; however, the brine at the surface may travel upwards of 0.1 m prior to reaching equilibrium. This is why it is important to introduce the brine as close to saturation as possible. Otherwise, the state point is not well defined at the start of absorption on the test tube. In commercial chillers the brine is sprayed into the absorber, and adiabatically equilibrates with the absorbate vapor prior to contacting the absorber tubes. Hence the mini-absorber should allow adequate time for the strong solution to equilibrate within the dispenser to (1) best simulate field conditions of chillers and to (2) best define the entering thermodynamic state point of the strong solution.

For the validations, we assumed that the interface temperature atop the absorber was in equilibrium with the absorbate vapor. Grossman and Alefeld (1996) and Nakroyakov, Bufetov and Grigor’yeva (1982) stated the temperature and concentration entering the mini-absorber, which we assumed as the bulk temperature and concentration introduced from the dispenser to the test tube.
The predictive algorithm validates very well against the two independent studies. The results in Fig. 5.6(a) show that the absolute average error in the predicted load is less than 13%. The mass absorbed in both studies is a direct measurement. Grossman and Alefeld (1996) used densitometry instruments at the inlet and the exit of their mini-absorber. Nakroyakov, Bufetov and Grigor'yeva (1982) pulled samples and used a gravimetric technique to measure the concentration of the brine. The absolute average error in the mass absorbed is about 21% of the experimental data from both studies. Three data points from Grossman and Alefeld (1996) appear as outliers (Fig. 5.6). Based on a vapor pressure of 4 kPa, the interface temperature atop the absorber is about 63°C, while the measured temperature entering the mini-absorber is 48°C. If $T_{f_{\text{max}}}$ is assumed to be 48°C, then the predicted and measured load and mass absorbed almost match. Possibly, there might have been a noncondensable effect for these three test points which would help explain the improved agreement using the lower temperature. Excluding the three outlier data, results in the load and mass absorbed being predicted within an absolute average error of 4.0 and 10.0%, respectively.

Grossman and Alefeld's data were reduced using Eq. 4.25 for the Nu number, and Eq. 4.28 for the Sh number. Their data were scaled using the correlation regressions, listed in Table 4.2, and they are plotted in Fig. 5.7 against the correlation for Nu and Sh. Grossman and Alefeld's data closely matches the Nu and Sh correlations which further substantiates the accuracy of the correlations formulated from the present study. The results are very promising.
Fig. 5.6. The algorithm was tested against data from the open literature.
Fig. 5.7. The correlation for Nu and Sh numbers are compared to independent data which were reduced using the Eq. 4.24 for the Nu number and Eq. 4.27 for the Sh number.
5.3.3 Heat and Mass Transfer Solutions in the Open Literature

Comparisons are made against the different solutions in the open literature. The boundary layer solution by Nakoryakov and Grigor’yeva (1980), the laminar flow model of Grossman (1982), the wavy-laminar model of Patnaik (1995) and the analytical closed-form solution by Conlisk (1996) are reviewed for their predictive accuracy as compared to algorithm of the present study. Nakoryakov and Grigor’yeva’s solutions for the overall heat and mass transfer are

$$q'' = \frac{6}{\pi} \left[ \frac{k_f(T_{eq} - T_w)}{\left( \frac{\sqrt{Le}}{Ha} + 1 \right)\Delta} \right] \left\{ \frac{Pe_H \cdot \varepsilon}{\varepsilon} \right\}^{1/2}, \quad (5.20)$$

$$\dot{m}'' = \frac{6}{\pi} \left[ \frac{D_{ab}(C_{eq} - C_{fn})}{\left( \frac{Ha}{\sqrt{Le}} + 1 \right)\Delta} \right] \left\{ \frac{Pe_M \cdot \varepsilon}{\varepsilon} \right\}^{1/2}, \quad (5.21)$$

where

$$Ha = \frac{|a| \overline{I_f}}{C_p}.$$ 

These solutions for heat and mass transfer are applicable only for short contact times where the boundary layer has not penetrated to the wall. Heat penetrates quicker than does the mass because of the strength of the Le number. An integral analysis for smooth laminar flow showed the heat penetrated to the wall within 0.2 m while mass required about 24 m for smooth laminar flow. Hence, the solution by Nakoryakov
and Grigor'yeva for the mass absorbed is included in Table 5.1 because the boundary layer may still be developing over the 1.524-m length of the test tube.

Grossman's (1982) smooth laminar flow model was not available for the simulation. S. K. Fisher of ORNL had coded a similar smooth laminar model which closely followed Grossman's algorithms. Fisher validated the parallel model against Grossman's (1982) published numerical simulations. The code uses Grossman's closed form solutions (Eqs. 2.73 and 2.74) for the temperature and concentration at the entrance of the absorber to avoid the singularity in the boundary layer. A central difference numerical discretization is then used outside the entrance region. The grid spacing for the discretization had to be very fine to avoid instabilities caused by the inertia convective effects. The author ran Fisher's code for Grossman's (1982) constant temperature wall condition. Patnaik and Conlisk supplied the outputs to their solutions at the request of the author.

The solution by Nakoryakov and Grigor'yeva underpredicts the experimental mass absorbed by about 86%. Grossman's numerical formulation, which accounts for a parabolic velocity profile, does no better: it underpredicts by about 82% the experimental values.

Patnaik (1995) used Patankar's (1980) numerical discretization scheme and input a priori a wavy-laminar velocity profile. He used the integral model by Brauner (1989) to formulate the streamwise and transverse velocity profile (see Sects. 2.1.3 and 2.2.4). His model therefore accounts for the normal convective effects, which he had stated as causing the enhancements in heat and mass transfer. His model is quite
### Table 5.1. Chronology and comparison of approximate analytical solutions

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Model</th>
<th>Load (W)</th>
<th>Error (%)</th>
<th>Mass Absorbed (kg/s)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakoryakov &amp; Grigor'yeva (1980)</td>
<td>Boundary layer approach (see Sect. 2.2.2)</td>
<td>NA</td>
<td>NA</td>
<td>3.467 E-05</td>
<td>-86.8</td>
</tr>
<tr>
<td>Grossman 1982)</td>
<td>Smooth laminar numerical approach (see Sect. 2.2.3)</td>
<td>89.4</td>
<td>-91.5</td>
<td>4.758 E-05</td>
<td>-81.9</td>
</tr>
<tr>
<td>Patnaik (1995)</td>
<td>Wavy-laminar numerical approach (see Sect. 2.2.4)</td>
<td>949.6</td>
<td>-9.5</td>
<td>2.430 E-04</td>
<td>-8.0</td>
</tr>
<tr>
<td>Conlisk (1995)</td>
<td>Boundary layer perturbation approach (see Sect. 2.2.4)</td>
<td>1377</td>
<td>+31.3</td>
<td>4.767 E-04</td>
<td>+80.6</td>
</tr>
<tr>
<td>Predictive Algorithm</td>
<td>Conduction-dominated, constant flux approx. (see Sect. 5.2)</td>
<td>971.9</td>
<td>-7.4</td>
<td>2.620 E-04</td>
<td>-0.76</td>
</tr>
<tr>
<td>Experiment Test 85 (see Appendix D)</td>
<td>$P_v = 1.516$ kPa $\bar{X}<em>f = 62.15$ wt% LiBr $\bar{T}<em>f = 58.35 , ^\circ C$ $\bar{T}</em>{cl} = 35.08 , ^\circ C$ $Re = 289$ $Re</em>{cl} = 5388$</td>
<td>1049.1</td>
<td></td>
<td>2.640 E-04</td>
<td></td>
</tr>
</tbody>
</table>


sensitive to the development length required for the concentration boundary layer, and he had to extrapolate this distance from previous simulation results of his model for Re number flows of 400 and an absorber length of 0.4 m. He calculated a development length of about 1.4 m, and his load and mass absorbed are both about 10% low of the experimental measurements. Patnaik stated that the code would require about 8 hours of processing time on a VAX 11-750 platform to yield a convergent solution for the author’s tube length of 1.524 m.

Conlisk (1995) approached the problem using perturbation theory on the binary diffusion equation (see Sect. 2.2.4). He assumed that the problem is conduction-dominated, which implies that all the absorption heat is transferred directly to the coolant. The interface was described by a linear absorbent, and he ignored the effects of the roll waves, as did Jayanti and Hewitt (1997). Conlisk overpredicted the load by 31% and overpredicted the mass absorbed by 80%. His latent load was about 1177 W, which is about 12% high of the total measured load.

The predictive algorithm underpredicted the load by 7.4% and was within 1% of the experimental measure of the mass absorbed. These results are very eye-opening. Despite the simplicity of the predictive algorithm as compared to the complex and intricate approaches used by the other investigators, its predictive capability is clearly demonstrated. The simultaneous heat and mass transfer process is extremely complicated and very difficult to describe mathematically because the interactions of heat and mass transfer coupled to wave hydrodynamics are not well understood. Yet, approximating the flux to the coolant as constant yields accurate predictions of the load and the mass absorbed. Results were also validated against the independent data.

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of Grossman and Alefeld (1996). Hence, the effect of the waves has been one of confounding the problem. Their effect is an indirect one in which the substrate is thinned along the length of the absorber. Mass transfer is enhanced because the thin substrate is cooler than the thicker wave.
CHAPTER 6

SUMMARY AND CONCLUSIONS

This study presents much-needed experimental data for both industry and academia on the heat- and mass-transfer processes in aqueous LiBr absorption cycle absorbers. The state of the art in absorber design is still maturing because of the strong market share gained by vapor compression technology in the early 1970s.

This study provides both correlations and a predictive algorithm for the complex heat- and mass-transfer process. Correlations and the algorithm were validated against extensive experimental data. Hence, this study contains useful information for the design of a vertical column absorber with no heat and mass transfer additive.

The design guidelines provided by Kays and London’s greatly benefited heat exchanger developments. Hopefully, the results of the present study will help advance the understanding of the simultaneous heat and mass transfer process, and foster a continued improvement in the design of an absorber, a key component of the absorption chiller.
6.1 Summary

The market for comfort cooling has been dominated for the last decade by electrically driven vapor compression equipment. The efficiency, low maintenance and ease of use of electric-driven machines, coupled with the low cost of electricity in the early 1970s, made vapor compression the exclusive cooling system. Electric utilities had to increase their capacity to support the increased user load; and this upsizing proved to be very expensive. The rapid growth in demand loading led to brownouts in some heavily populated industrial sectors. As result, charges for peak demand electricity increased sharply during the summer months. Threats of global warming and the depletion of the ozone layer are also significant forces shaping the future of the HVAC market for comfort cooling.

Absorption technology was cast aside during the energy crisis of the mid-1970s. However, forecasts of an abundant supply of natural gas and relatively low prices through 2050 have given absorption chillers a second chance, so that absorption chillers are regaining a significant share of the large-tonnage market because of both the energy and the environmental issues. Direct-fired and waste-heat-driven absorption chillers now have an energy consumption rate comparable to that of vapor-compression machines. Several case studies have proven the economic competitiveness of absorption technology [e.g., Sweetser (1996) and Lane and Huey (1995)]. Absorption chillers offer an alternative for reducing peak electric demand that benefits both gas and electric utilities. Large-tonnage absorption chillers use lithium bromide as the absorbent and water as the refrigerant. Chlorofluorocarbon (CFC) refrigerants are eliminated, making absorption chillers environmentally
attractive. Continued improvement in absorption technology is an important goal because advanced gas cooling and heating products would foster job growth in the United States and would improve our competitiveness in international markets.

The heart of a thermally activated chiller is the absorber. Its performance dictates the overall performance of the machine. The more refrigerant absorbed per unit of absorbent, the greater the refrigerant mass flow rate available for the evaporator; this, in turn, increases the comfort cooling capacity of the chiller. Hence, improvements in system performance are integrally tied to a fundamental understanding of the falling film hydrodynamics and the simultaneous heat and mass transfer processes occurring within the absorber. Historically, rules of thumb coupled to empirical data have led to extrapolations causing chiller equipment to be overdesigned, heavy and costly. HVAC manufacturers would use a small amount of heat and mass transfer additive to enhance performance. The manufacturers viewed the serendipitous discovery of the additive effect as a cost effective means of achieving a twofold boost in performance through chemical rather than mechanical enhancement. Hence, the issues of falling film hydrodynamics, thermodynamic and transport properties, the magnitude of the heat effects and composition at the vapor-liquid interface, heat transfer and mass transfer from the vapor-liquid interface and pressure drops through the tube bundle were of secondary concern until the recent resurgence of absorption technology. The advancement of design dictates a better understanding of the fundamental issues governing the absorption process.

Almost all chillers use a horizontal rather than a vertical tube bundle in their absorber. HVAC manufacturers strongly believe the horizontal configuration superior
to the vertical because of its ability to better mix the absorbate into the film. The droplets form at the bottom of a horizontal tube and splash onto the lower tubes within the bundle. The intimate contact between the droplets and the vapor and the subsequent splashing action is believed to enhance performance; however, Burdukov et al. (1980) experimentally proved similar performance for vertical and horizontal absorbers when tested with no heat and mass transfer additive. Biermann (1984) experimentally found identical performance for both configurations when tested with heat and mass transfer additives. The vertical column absorber is used in newly designed air-cooled machines as well as in industrial heat transformers for waste heat recovery. Absorbent, aqueous LiBr flows down along the cylindrical walls of a tube bundle in the form of thin films. The thin film, referred to as a falling film, is well suited to coupled heat and mass transfer because of the large contact surface achievable at small flow rates. The hydrodynamics of vertical tube absorbers is not clouded with questions regarding the effect of droplet formation and subsequent splashing onto the lower tubes, and is therefore better suited for both experimental and analytical studies of the effects of the falling film hydrodynamics on the coupled heat and mass transfer processes occurring within the absorber.

A review of the literature shows that cylindrical falling films are unstable for all Re numbers, We numbers and radius ratios (Solorio and Sen 1987). Ishigai et al. (1972) subdivided the falling film into five flow regimes, which Morioka, Kiyota and Nakao (1993) depicted in the excellent still photograph of Fig. 2.1. Kapitza and Kapitza (1949) analytically showed that wavy-laminar films were thinner than the classical smooth laminar theory presented by Hopf (1910) and Nusselt (1916). Kapitza hypothesized that flow regimes other than sinusoidal wavy flow could lead to
hydrodynamic solutions describing wavy flows with even smaller film thickness. The experimental studies by Brauer (1956), Greenberg (1956), Charvonia (1959), Fiend (1960), Portalski (1960), Allen (1962), Clegg (1969) and Chu and Dukler (1974) substantiated the Kapitzas’ theory. All of these studies found appreciable reductions to Nusselt’s theory for smooth laminar flow and also to the Kapitzas’ theory for sinusoidal wavy-laminar flow. Greenberg (1956) experimentally proved that increasing the surface tension caused a thinning of the film; increasing the density caused an increase in body forces which reduced the deviation from smooth laminar flow theory. Greenberg (1956) and Ishigai et al. (1972) observed the falling film to become fully developed after about 1000 Δ. Allen (1962) further showed, using recorded film profiles, a thinning of the film substrate along the length of the vertical falling film. His observations were later verified by Clegg and Portalski (1972) and also by Chu and Dukler (1974). Most surprising were the results observed by Chu and Dukler, which showed the mass flow in the roll waves to be 10 to 20 times greater than that flowing in the substrate. Dukler (1976) hypothesized that the wave front of the roll waves swept up liquid from the substrate which was then churned into the secondary flows within the wave. The wave grows in mass and the film substrate thins. His proposal is consistent with Greenberg’s observations for fully developed flow, and later Brauner and Maron (1982) experimentally proved Dukler’s concept of mass movement from the substrate to the wave.

Hence, the hydrodynamic findings of Chu and Dukler (1974) led Dukler (1976) to view the velocity, temperature and concentration gradients in the substrate differently from those in the large roll waves. For wavy-laminar falling film the assumption of a smooth film of constant thickness was in error. Wasden and Dukler
(1990) used experimentally measured film thickness data as input for the free surface and conducted numerical simulations of the mass transfer into wavy-laminar falling films flowing at a Re number of 880. They observed velocities normal to the flow direction that drove absorbate from the surface into the wave structure. The convective motion caused mass transfer enhancements ranging from 1.7 to 3.5 times those expected for smooth laminar flow. Similar observations were made by Patnaik (1994), who studied simultaneous heat and mass transfer for falling films flowing at a Re number of 400. However, Jayanti and Hewitt (1997), in a numerical study which closely parallels Wasden and Dukler’s numerical approach, observed very different results for Re numbers of about 140. Jayanti and Hewitt concluded that the effect of the waves on heat transfer in a thin film was not directly related to convection effects; rather, its effect is indirect and due to the thinning of the film. Further, the heat transfer from the liquid-vapor interface to the wall was dominated by conduction effects, even within the waves. A closer inspection of Fig. 2.1 is in order, given Jayanti and Hewitt’s results for a Re number of 140. At a Re number of 142 in Fig. 2.1, the film is predominantly covered by a thin substrate, with successive roll waves uniformly spaced about 0.1 m apart. Even for Re number flows of 203 and 406, most of the tube is covered by a thin substrate over which roll waves travel as lumps of mass, as proposed by Dukler (1976).

Conlisk (1995) approached the simultaneous heat and mass transfer problem by assuming the thin film to be conduction-dominated. He solved the energy equation directly for a linear temperature profile and applied singular perturbation technique for developing an approximate solution for the binary diffusion equation. Conlisk used linear absorbent theory to complete his mathematical descriptive, as have all
other analysts. A linear absorbent implies that the absorber is vapor pressure is imposed on the liquid-vapor interface and that the interface is in equilibrium with this imposed pressure. Increasing the surface temperature would, for a linear absorbent, result in a corresponding decrease in concentration. Therefore, a linear absorbent describes a heating effect which opposes the mass effect. The greater the heat transfer to the interface, the less the concentration gradient achievable for mass transfer. The concept poses a paradox, because in actuality, the greater the load transferred to the coolant the greater the mass absorbed by the absorber. The linear absorbent holds for several common salts in static conditions. However, the dynamic environment of a falling film having variable film thickness with each successive wave, and therefore a variable temperature gradient from the interface to the coolant, makes the linear absorbent model at best an approximation of the actual interface condition. And unfortunately, falling film absorbers operate in this chaotic and dynamic wavy flow regime.

Thus, keys for computing the local variations in the heat and mass transfer rates are the actual film temperature and the concentration at the liquid-vapor interface. These measures continue to elude researchers but are important for understanding on a local as well as a global scale the heat effects at the interface, the heat transfer from the interface and the mass transfer onto and through the interface. Wood et al. (1993) and Burdukov et al. (1980) measured the bulk concentration down the running length of the falling film. Both researchers found the bulk concentration profile to be linear with axial length. Their results, coupled to the numerical studies by Wasden and Dukler (1990) and Jayanti and Hewitt (1997), have shed some light
on the mechanisms of why and how heat and mass transfer enhancements are caused by wavy-laminar flows.

Experimental data for falling film absorption is sparse. Nakoryakov, Bufetov and Grigor'yeva (1982) conducted some limited testing at about 60 wt% LiBr for Re numbers ranging from 80 to 250 and absorber pressures of 0.9–2.0 kPa. Wood et al. (1993) also conducted batch mode testing at about 50 and 60 wt% LiBr; he alluded to the presence of small amounts of noncondensables. Their effect can confound analysis. Jianpin, Tianfu and Zhongnghuao (1985) experimentally tested smooth laminar film absorption. Grossman and Alefeld (1996) conducted parametric testing to observed the independent effects of coolant temperature, falling film mass flow rate, and absorbent concentration. The testing by Grossman and Alefeld, however, was done at abnormally high absorber pressures of about 4.0 kPa, and the absorbent entered the mini-absorber with about 15 to 20 °C of subcooling.

The dearth of experimental data strongly suggested the need for a combined experimental and analytical approach to the absorption phenomena. The primary objective was to acquire much needed experimental data. The data had to be free of the confounding issue of noncondensables and had to provide information in the operating ranges of present-day equipment. No literature data is readily available at the design operating conditions of 62 and 64 wt% LiBr and 0.7 through 1.5 kPa absorber pressure.

Hence, the experimental approach for the present study included three phases. In phase one, the literature review revealed the need to study the hydrodynamics of a
wavy-laminar falling film to determine its effect on simultaneous heat and mass transfer. Second, heat and mass transfer data were needed to better understand the local variations in the heat and mass transfer rates along the running length of the absorber. The underlying mechanism driving absorption is not well defined by linear absorbent theory because of the dynamics of the wavy-laminar falling film. Finally, data were also needed over a parametric map to correlate the performance parameters of Nu and Sh numbers in the ranges of operating equipment. These three phases of work have been reported in this study. The conclusions are provided for a completion of the work.

6.2 Conclusions

6.2.1 Falling Film Hydrodynamics

Benjamin (1957) and Solorio and Sen (1987) analytically proved that falling films are unstable for all Re numbers, We numbers and radius ratios. Hydrodynamic data from the present study for aqueous LiBr were consistent with their findings. Decreasing the tube diameter to 0.009525 m caused the amplitude of the wavy flow to diminish, especially as the film transitions into the turbulent-laminar regime.

Measurements taken at 0.13-, 0.23- and 0.4-m stations along the 0.01905-m OD test tube showed a thinning of the average film thickness for mass flows of aqueous LiBr exceeding 0.1 kg/s (Fig. 4.3). Fully developed flow therefore requires a large starting length. Greenberg (1956) had measured the film thickness at several stations located
0.165, 0.292, 0.422, 0.54 and 0.670 m below the injection port. Allen (1962) did similar work and measured the film at 0.127, 0.305, 0.457 and 0.61 m below the film’s inlet. Both investigators’ data showed that the water film attained a constant thickness at about 0.3 m for a Re number flow of 1000. Aqueous LiBr has a kinematic viscosity roughly five times that of water; therefore, for a Re number of 200 and a measured film thickness of 0.00043 m, fully developed flow is attained within about 0.43 m.

The falling film enters as a smooth laminar flow, and within about 0.1 m is visually observed to be unstable and transitioning into small-amplitude wavy flow. The waves grow in length and amplitude and are identified as roll waves (see Fig. 2.1). Fluid is swept from the substrate into the secondary flows of the wave (Dukler 1976). Subsequently, the average film thickness thins as compared to laminar theory (Brauer 1956, Greenberg 1956, Charvonia 1959, Fiend 1960, Portalski 1960, Allen 1962, Clegg 1969 and Chu and Dukler 1974). The reduced Nt number decreases below Nusselt’s laminar theory as the Re number increases from 60 to 400. Further increasing the Re number to 1600 causes the film to transition into full turbulence, and the deviation between the Nt number for experimental data and Nusselt’s Nt number diminishes.

Heat and mass transfer equipment operate in the nebulous wavy-laminar flow regimes (Fig. 2.1). Therefore, the use of Nusselt’s theory is in error if applied to vertical column absorbers. Increasing the Re number increases the film thickness because of the increase in mass flow rate per unit of wetted perimeter. Increasing the Ka number causes a decrease in the film thickness (Greenberg 1956). Regression
analysis using SAS showed that the Re and Ka numbers described the data trends in wavy-laminar flow. Rather than correlating the Re number in strict ranges of the Ka number, as did Brauer (1956) and Fiend (1960), this study made the Ka number an independent regression variable along with Re number. The Nt correlation (Eq. 4.1) has an $R^2$ of 0.96 and predicts the correlation data within an average error of ±4.0%. The correlation supports the calculation of a fully developed film thickness and was used in the predictive algorithm.

6.2.2 Bulk Temperature and Concentration Profiles

The local data for heat and mass transfer revealed a physics unknown except in the work by Burdukov et al. (1980). The capacitance of the coolant dominates the heat flow across the thermal resistance network and strongly affects the bulk temperature and concentration profiles of the falling film. Wasden and Dukler (1990) had shown a sharply varying mass flux over a roll wave [Fig. 2.9(d)]; while Jayanti and Hewitt (1997) showed the heat transfer driven by conduction due to the thinness of the wavy-laminar falling film. For an absorber, mass transfer continues past the entrance effects by the action of the coolant. The greater the interface-to-coolant temperature gradient, the greater will be the mass absorbed. The wave tail is seen in Fig. 2.1 to predominate over the entire tube. Its thickness is almost one-fifth that of the wave peak. These insights led the author to view the substrate as the medium for most of the mass transfer. Therefore, a data-reduction scheme was developed to map the bulk temperature and concentration profiles over the length of the absorber in order to assess the strength of the coolant's capacitance on the film profiles. Results showed
the bulk concentration gradient, \( \frac{d\bar{C}_a}{dx} \), to be approximately constant. This trend was validated by the independent works of Burdukov et al. (1980) and Grossman and Alefeld (1996), who experimentally measured the bulk concentration profile. Hence, the results of the present study are strongly substantiated by these independent studies. And the results show that the local heat and mass transfer rates are nearly linear. The implication is that the absorber load, and therefore its mass flux, can be solved for using a constant flux approximation.

### 6.2.3 The Predictive Algorithm

An algorithm was developed and validated against the experimental data. Its formulation is simple and supports accurate prediction of the load, the mass absorbed and the absorbent’s temperature and concentration at the absorber exit. The algorithm assumes a constant flux and therefore assumes that the interface-to-coolant temperature gradient remains constant along the length of the tube. The average error in all the data is about \( \pm 10\% \) for the load and \( \pm 14\% \) for the mass absorbed. As the Re number of the falling film increases, the effects of convection within the roll waves become more prominent and the algorithm underpredicts the experiment. However, the algorithm does an excellent job for testing at the design operating conditions for absorption chillers, with the load predicted within an average error of \( \pm 4.3\% \) and the mass absorbed within \( \pm 8.2\% \).
6.2.4 The Absorber Parametric Study

The mini-absorber was proven void of any noncondensable (Fig. 3.5). Eliminating this confounding variable dropped the gas-side resistance and allowed us to assume that the ambient pressure of the absorber was imposed on the liquid-vapor interface of the falling film. Therefore, the transfer of mass is liquid-side controlled. In heat transfer, the interfacial temperature is identical for each phase, but in mass transfer there is a discontinuity in concentration at the liquid-vapor interface. This occurs because in mass transfer the driving potential within the liquid phase is concentration. Hence, because of the discontinuity, one can also view the driving force for mass transfer as the difference between the vapor pressure imposed on the interface and the partial pressure of absorbate just within the liquid-vapor interface.

Increasing the absorber pressure, increasing the absorbent concentration or decreasing the coolant temperature causes the load and mass absorbed to increase (Fig. 4.14). For each case, the pressure gradient across the liquid-vapor interface drives the process. The higher the mass fraction of LiBr, the lower the partial pressure of water in the brine, and therefore the greater is the driving force for mass transfer. Lowering the cooling water temperature causes the interface temperature to drop, and this drop lowers the partial pressure of absorbate just within the interface.

However, once vapor is absorbed onto the interface, it tends to stay there because of the high liquid-side mass transfer resistance (thermal diffusivity is on the order $10^9$ m$^2$/s). As a result, absorption continues only because of the effect of the coolant. Its heat-transfer capacitance is so dominating that it controls the bulk and interface
temperature and concentration profiles. Increasing the mass flow rate of the falling film has only marginal influence on the absorption rate. Hence, convection effects are small and conduction is more prominent in the Re number range tested in the present study. Falling film flows exceeding a Re number of about 400 (see Fig. 2.1 for Re ≥ 400) would have stronger convective forces and are in-part the cause of the underpredictions on the order of 20% observed in the predictive algorithm for a Re number ≥ 300 (Fig. 5.3).

6.2.5 Overall Heat and Mass Transfer Correlations

The correlation of Nu and Sh numbers provides a simple and direct calculation of the load and mass absorbed given the entering conditions for the absorber. The Sh correlation is coupled to the continuity of the solute, and the two independent equations yield the overall mass absorbed. Aqueous LiBr is a salt solution, and ions rather than molecules diffuse through the liquid. The theory of diffusion of salts at low concentrations is well developed; however, little is known about the behavior of more concentrated solutions, especially in the presence of heat and mass transfer. The Sh correlation accounts for these intermolecular forces by using the empirical data of Kashiwagi (1985); see Appendix A.

Simultaneous heat and mass transfer has strong pressure, concentration and temperature effects. The Nu and Sh correlations support these effects through the defined heat and mass transport coefficients. Regression analysis revealed the Ka number as a strong regression parameter; its inclusion significantly improved the
correlation of Nu and Sh numbers. Its formulation in Nu and Sh was consistent with 
the correlation for the Nt number. An increasing Ka number resulted in a thinner 
film for wavy-laminar flow, which in turn would increase load and mass absorbed. 
The exponent for the Ka number was negative in the Nt correlation, while in Nu and 
Sh correlations, the Ka power was positive and of the same magnitude as in the Nt 
correlation (see Eq. 4.1 and Table 4.2). The average error, excluding 60 wt% data, is 
±3.5% for the load and ±4.3% for the mass absorbed.

The 60 wt% data was an outlier as compared to data at 62 and 64 wt% LiBr because 
of the variable viscosity effects observed for the 60 wt% data having the thinnest 
falling films. Using viscosity and surface tension transport properties evaluated at a 
lower concentrations of LiBr (about 55.5 wt%) caused the data to better match the 
Nu and Sh correlation curves. If these properties are evaluated at the lower 
concentration of 55 wt% LiBr, the Re number for 60 wt% testing increased to a 
maximum value of about 450. Convective effects could be influencing the results; this 
would be consistent with findings from the predictive algorithm.
CHAPTER 7

RECOMMENDATIONS

The results of the present study lead to two very important questions: (1) Are the findings for the vertical absorber applicable to that of the horizontal absorber? (2) What is the effect of heat and mass transfer additives, since the industry commonly uses chemical enhancement to boost performance?

7.1 Horizontal Absorber

The author has conducted parallel studies on a single-row, horizontal bundle of six copper tubes, each tube being 0.305 m long with a 0.0159-m OD. We measured the coolant temperature profile in the bore of each tube, and the results for testing at the design operating conditions for commercial chillers are shown in Fig. 7.1. Testing with no heat and mass transfer additive shows the coolant temperature profile to be strongly linear. At issue is the effect of the droplet flow regime, which is common to all horizontal absorbers. The author strongly recommends continued study to determine whether a similar formulation of the predictive algorithm can be applied to the falling film flowing over the tubes with neglect of the droplet flow regime.
Fig. 7.1 Coolant temperature profile for a horizontal absorber with a six-tube single-row bundle. Tests were conducted at a pressure of 0.87 kPa and a concentration of 62 wt% LiBr.
The mini-absorber configured with the horizontal tube bundle was also tested with 500 ppm of 2-ethyl 1-hexanol. These data for testing at the design operating conditions of commercial chillers are also shown in Fig. 7.1. The results are quite surprising: the additive increased the slope, but the coolant profile remains fairly linear. Hence, the \( \frac{dT}{d\chi} \) is approximately constant. The discovery found for the vertical absorber is applicable to the horizontal absorber both with and without heat and mass transfer additive. Because \( \frac{dT}{d\chi} \) is about constant, the temperature everywhere in the cross section varies linearly in the flow direction of the coolant. Further, the slopes of the temperature profiles shown in Fig. 7.1 are directly proportional to \( q'' \). The chemical agitation induced by the additive boosts capacity, yet the flux remains constant. These findings strongly suggest the need for continued study of the problem with heat and mass transfer additives. One major issue is the effect of the additive on the film thickness. The additive reduces the surface tension at the interface and causes a chaotic, undulating, lateral movement of the falling film (see Fig. 2.2 for vertical absorber tube). If the film thickness can be quantified, then the approach using the predictive algorithm has a strong chance of accurately predicting the performance of an absorber configured with either a vertical or a horizontal tube bundle.

7.2 Falling Film Hydrodynamics

The predictive algorithm developed in the present study is relatively simple but effective in accurately predicting the load and mass absorbed. The author has strived to formulate a more eloquent scheme that includes the hydrodynamic effects of the
falling film on a local level but avoids the rigors of a full-blown numerical
discretization of the momentum, energy and binary diffusion equations. However,
the chaotic nature of the wavy-laminar flow complicates a more detailed analysis. The
effects of the wall shear stress on the free surface of the falling film, for Re numbers
ranging from about 100 to 400, are not well understood. Wasden and Dukler (1989)
and also Yu et al. (1995) proved that a cubic velocity profile better fitted their
numerical hydrodynamic results than did the parabolic profile of pure laminar flow.
The problem, however, still remains to mathematically describe the effects of the wall
shear on the free surface. Yu et al. present a predictive hydrodynamic model validated
for falling film Re numbers exceeding about 300. Whether this approach is useful for
the chaotic wave profiles observed for Re numbers of about 100 through about 400
(Fig. 2.1) is of keen interest. Wasden and Dukler (1990) had shown high mass
transfer rates near the front surface of the roll waves where strong accelerations of the
fluid particles were observed [Fig. 2.9(c)]. In simultaneous heat and mass transfer,
the hot absorbate on the wave surface may mix into the wave structure and reduce
the viscous shear effect on the wave. The proposed heat inversion near the wave front
could be causing variable viscosity effects that would enhance the growth of the
waves and increase the length needed to establish fully developed flow. Visual
observations during simultaneous heat and mass transfer testing showed a larger and
better-defined wave structure than was observed during hydrodynamic testing. To the
author's knowledge, no data are available that characterize the effect, and therefore,
hydrodynamic data are needed to better quantify the relational dependence of roll
wave hydrodynamics and simultaneous heat and mass transfer in vertical falling film
absorbers.
Absorption theory for aqueous LiBr falling films predicts that the thermal boundary layer will develop faster than the concentration boundary layer. The thermal diffusivity of the film is about two orders of magnitude greater than the mass diffusivity. Heat is therefore readily transferred across the film, while the absorbate water vapor will tend to remain at the surface, thus inhibiting absorption of additional water vapor. This is the reason mixing of the film is considered important by many researchers.

In smooth-tube tests conducted in the present study, the falling film has been wavy-laminar. The bulk of the film appears laminar (Fig. 2.1), with waves or ripples superimposed on the flow that were observed during testing to travel faster than the bulk of the film. The secondary flows within the roll waves induce some mixing of the film; however, as pointed out by Jaynati and Hewitt (1997), the effect of waves is not directly related to convection effects. The waves act upon the substrate and effectively thin the film along the direction of flow (Clegg and Portalski 1972). The heat transfer is film-side limited, and any reduction in the film thickness will directly result in greater heat transfer and, in turn, more mass transfer. This further substantiates the need for hydrodynamic data measured during coupled heat and mass transfer of the falling film.

7.3 An Approach to Simultaneous Heat and Mass Transfer

For wavy-laminar falling films with Re numbers not exceeding about 400, the coupled heat and mass transfer solution is complicated more by the mass transfer aspects of
the problem than by the heat transfer. The temperature distribution quickly becomes conduction-dominated once exposed to the test tube. An integral analysis shows that the heating effect is first sensed at the tube wall for $x/\delta \geq 0.025\text{Pe}_H$. Because of the thinness of the film, and because of the strength of the thermal diffusivity, the distribution quickly becomes linear, and is described by the simplified energy equation as

$$\frac{\partial^2 T}{\partial y^2} = 0. \quad (7.1)$$

Conlisk (1995) recognized this and solved Eq. 7.1 for a linear temperature profile. For small $\varepsilon$, the binary diffusion equation, Eq. 5.4, reduces to the following scaled form:

$$\bar{u} \frac{\partial \bar{C}_a}{\partial \bar{x}} + \bar{v} \frac{\partial \bar{C}_a}{\partial \bar{y}} = \frac{1}{\varepsilon \text{Pe}_M} \frac{\partial^2 \bar{C}_a}{\partial \bar{y}^2}. \quad (7.2)$$

A study of Eq. 7.2 shows the parameter $1/(\varepsilon \text{Pe}_M)$ is small, on the order of 0.001.

Hence, mass transfer is confined to a thin layer near the liquid-vapor interface. The small parameter multiplies the highest-order derivative and is typical of a singular perturbation problem. Hence, Eq. 7.2 could be solved using perturbation theory or by using either the method of weighted residuals or a numerical approach. Completing the mathematical descriptive requires a knowledge of the velocity profiles and the proper wall and interface boundary conditions that couple energy (Eq. 7.1) and binary diffusion (Eq. 7.2). The velocity profiles of Yu et al. (1995) are recommended as inputs to Eq. 7.2. The wall temperature is a function of the axial dimension, yet the wall flux is about constant. Hence, the wall boundary conditions can be described as follows:
\[ q''_{\text{wall}} = -k_f \left. \frac{dT}{dy} \right|_{y=0} = \text{Const} \tan t . \quad (7.3) \]

Substituting a linear temperature profile into Eq. 7.3 leads to the following relationship:
\[ q''_{\text{wall}} = -k_f \left. \frac{dT}{dy} \right|_{y=0} = \frac{T^*(x) - T_{\text{wall}}(x)}{\delta(x)} = \text{Const} \tan t . \quad (7.4) \]

Now, as \( \delta(x) \) thins by the action of the roll waves, the temperature gradient must drop proportionately for Eq. 7.4 to hold. It would be of keen interest to determine whether the approach used by Yu et al. (1995) could predict the variation of the film thickness. Accurate prediction of \( \delta(x) \) is crucial and would bring closure to the problem. For consideration of the concentration, the wall is impervious to mass penetration, and the concentration gradient at the wall would be
\[ \left. \frac{dC_a}{dy} \right|_{y=0} = 0 . \quad (7.5) \]

Continuity of energy is observed at the interface and is described by the following balance:
\[ k_f \left. \frac{dT}{dy} \right|_{y=\Delta} = \bar{I}_f D_{ab} \left. \frac{dC_a}{dy} \right|_{y=\Delta} . \quad (7.6) \]

Given the linear temperature profile, the left side of Eq. 7.6 is known, and therefore the concentration gradient is known at the interface. The linear temperature profile implies that all heat from the interface is directly transmitted to the coolant and that there is no sensible effect on the falling film. However, the film does transfer sensible heat to the coolant in order for absorption to occur past the inlet effects. In fact, test results showed that sensible cooling accounts for about 20 to 30\% of the load. This
being the case, a better formulation of the interface boundary condition (Eq. 7.6) would require an energy balance for a differential element of the falling film:

\[
\dot{m}_v' = \frac{1}{l_{fg}} \left[ \frac{d}{dx} (\dot{m}_i)_f + q' \right].
\]  \hspace{1cm} (7.7)

The axial temperature profile of the film should be assumed to be linear and of the same slope as the coolant profile because of the constant flux approximation. Therefore, \( \dot{m}_v' \) can be found from Eq. 7.7, and because the diffusion resistance is so high, it can be substituted into the following boundary condition to determine the concentration gradient at the interface:

\[
\dot{m}_v' = (\pi D_o)D_{ab} \frac{dC_a}{dy} \bigg|_{y=\Delta}.
\]  \hspace{1cm} (7.8)

Historically, researchers have used the linear absorbent concept to mathematically describe the interface. The concept implies that as temperature increases, the concentration decreases, which limits the mass absorption. The results of the present study indicate that a constant flux at the wall would better describe the dynamics occurring at the interface. In other words, the temperature gradient from the coolant to the interface is about constant along the length of the absorber. This is not exactly correct because the film thins by the action of the roll waves (Dukler 1976). For a good approximation, though, the interface can be modeled as

\[
\Delta T = \left( T^* - \bar{T}_{cl} \right) = \text{Constant}.
\]  \hspace{1cm} (7.9)

This completes the author’s recommended mathematical descriptive. At the top of the absorber, the interface temperature is known because the absorbent will drive immediately to equilibrium with the absorbate vapor pressure. The coolant temperature is an unknown at the absorber exit; however, if we assume fully
developed flow, then the $N_t$ correlation (Eq. 4.1) and the predictive algorithm can be used to calculate an accurate value of the coolant temperature. Assuming the functional relationship $\delta(x)$ is unknown, then an iterative scheme can be formulated where the temperature of the coolant exiting the absorber is initialized from the predictive algorithm, and the solutions to Eq. 7.1 and 7.2 marched down the tube. At the top of the tube, the film thickness, $\delta(x)$, would be described by laminar flow theory, and its thinning should be assumed to be a linear function of $x$, as observed by Clegg and Portalski (1972). If the measured and calculated values for the temperature of the entering coolant are in error, then the iterative scheme would correct and update the exit coolant temperature and again proceed from the top until convergent on the inlet coolant temperature.
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APPENDICES
Appendix A

DIFFUSIVITY AND PROPERTY ROUTINES
FOR AQUEOUS LiBr

The mass diffusivity of aqueous LiBr is on the order of $10^{-9}$ m$^2$/s, and is about two orders of magnitude less than the thermal diffusivity. Heat is readily transferred directly across the film, while the mass is restricted to the interface. The effect of diffusivity is very significant because it directly limits the efficiency of an absorber. In addition, diffusivity is used in the definition of the SH number. Hence, the correlation of diffusivity used in the present study is included for use with the SH correlation.

The thermodynamic and transport properties relating the pressure, density, temperature and composition for LiBr brine need empirical data to quantify the real mixture effects. Empirical data are available from the works of Uemura and Hasaba (1964), McNeely (1979), and most recently Jeter et al. (1990a, b).

A.1 Diffusivity

The theory of the diffusion of salts at low concentrations in aqueous solutions is well developed; however, strong salt solutions, such as those used in absorption chillers, are in fact strong electrolytes. The theory for predicting the variation of diffusivity with concentration is not as well developed for strong electrolytes. Mass diffusivity is
represented by the diffusion coefficient $D_{ab}$ and is defined by Fick's law for unidirectional binary diffusion as

$$n_a = -D_{ab} \frac{dc}{dy}. \quad (A.1)$$

Diffusivity is the ratio of the molar flux density to the negative of the concentration gradient, and is analogous to thermal conductivity as defined by Fourier's law of conduction. The symbolism $D_{ab}$ implies the diffusion of $a$, the absorbate water vapor, into the liquid medium $b$, which is the absorbent aqueous LiBr. Note that Eq. A.1 neglects the electrical effect caused by ion mobility, ionic charge and electrostatic potential. These intermolecular effects are not well described at high concentrations of the salt.

The diffusion is treated as molecular diffusion in the absence of any applied electrical potential. At low concentrations, diffusivity is commonly estimated using the Stokes-Einstein equation:

$$D_{ab} = \frac{k_b T}{6\pi \mu_f R_o}, \quad (A.2)$$

where

- $R_o = \text{the radius of the solute, LiBr},$
- $k_b = \text{the Boltzmann constant}.$
The Stokes-Einstein equation is in fact limited to infinitely dilute solutions. Yet, the diffusivity varies with both the concentration and the temperature of the LiBr brine. We therefore needed experimental data to supplement the Stokes-Einstein equation. Literature data for aqueous LiBr is sparse; however, two useful sources were found in the open literature. Schönh (1986) measured the diffusivity of aqueous LiBr using the diaphragm cell method. This method uses two solutions of different concentrations held in separate compartments of the cell. The diaphragm, a porous glass plate, allows the solutions to diffuse into each other. The concentration of each compartment is monitored, and Eq. A.1 is used to calculate the diffusivity. Kashiwagi, Kurosaki and Nikai (1984) published measurements of the diffusivity of aqueous LiBr for concentrations ranging from 10 through 60 wt%. Measurements were made during static pool steam absorption. Kashiwagi, Kurosaki and Nikai photographed the interference lines that were created when light was deflected through a refractive index gradient. Each line was connected to a respective refractive index gradient, and from this gradient the diffusivity was accurately calculated. The resulting data are very significant, because this is the only known data set that includes the effects of simultaneous heat and mass transfer for high salt concentrations.

Jernqvist and Gierow (1994) measured the diffusivity using a holographic interferometer within a diffusion cell. No heat and mass transfer occurred during their measurements. They compared the data of Kashiwagi and colleagues against their own measurements and found good agreement if the concentration was less than 20 wt% LiBr. Increasing the concentration showed the 1984 data to drop roughly 15 to 20% below the 1994 data. The aqueous LiBr is a strong electrolyte.
solution, and it is the ions of Li\(^+\) and Br\(^-\) that diffuse. Each Li\(^+\) ion becomes hydrated with four water molecules. The molecular motion within the liquid then becomes more complicated. For example, a potassium ion diffuses faster than a lithium ion does, which suggests that the potassium ion is smaller than the lithium ion (Cussler 1994). Yet, in the solid state, the potassium ion is larger. However, in solution the potassium ion is less hydrated than is the lithium ion. Franks (1975) proposed a water structure concept whereby the lithium ions enhance the tetrahedral bonding with water. The ions are surrounded by water molecules that are more structured than pure water. The more organized water structure has a higher apparent viscosity, and the ions diffuse more slowly (Cussler 1994). Therefore, diffusivity will decrease as concentration increases. Hence, the data of Kashiwagi, Kurosaki and Nikai are deemed more suitable for correlating the diffusivity for absorber applications.

We assumed, according to the Eyring theory, that the molecules of the liquid formed a quasi-crystalline lattice structure similar to that of a pure solid. The effects of the concentration and the temperature were represented by the empirical equation

\[ D_{ab} = D_0 e^{\frac{E}{RT}}, \]

where \( R = \) the universal gas constant, \( E = \) the activation energy, and \( D_0 = \) the diffusivity at infinite dilution. A. Zaltash, a colleague of the author, and M. R. Ally used the data at 45 wt% LiBr from Schön (1986) and from Kashiwagi, Kurosaki and Nikai (1984) to determine the diffusivity at infinite dilution (i.e., \( D_0 \)) (Zaltash and Ally 1992). These data were measured at different temperatures and were substituted in Eq. A.3, yielding the following two relationships:
The diffusivity at infinite dilution is independent of the concentration and the temperature and can be eliminated when Eqs. A.4 and A.5 are solved:

\[
D_{ab_1} = D_o e^{\frac{E}{RT_1}}, \quad \text{(A.4)}
\]

\[
D_{ab_2} = D_o e^{\frac{E}{RT_2}}, \quad \text{(A.5)}
\]

The term \( \frac{E}{R} \) was solved and substituted back into Eq. A.3 to empirically determine \( D_o \) from Schön's data. Zaltash and Ally then used Kashiwagi's data to solve for \( \frac{E}{R} \) at different mass fractions. A functional relationship of \( \frac{E}{R} = f(X_f) \) was correlated to yield the following formulation of the diffusivity for concentrations of LiBr brine:

\[
D_{ab} = D_o e^{\left[ \frac{1}{(T+273)} \left( \frac{E}{R} (X_f) \right) \right]}, \quad \text{(A.7)}
\]

where \( D_o = 7.1317 \times 10^{-8} \text{ (m}^2/\text{s}) \), \( T = \) the bulk fluid temperature, and

\[
\frac{E}{R} (X_f) = -1179.7591 + 5.9558(100 \cdot X_f) - 0.13624(100 \cdot X_f)^2. \quad \text{(A.8)}
\]

The correlation was fit for mass fractions ranging from 0.10 through 0.60 LiBr and for temperatures ranging from 25 to 50°C. The average error—calculated from the 21 data points of Schön (1986) and Kashiwagi, Kurosaki and Nikai (1984)—was within 5%. Diffusivity data calculated at mass fractions exceeding 50 wt% all had less than 4% error as compared to the experimental data. The diffusivity correlation is shown
in Fig. A.1. The data reaches a maximum at about 20 wt% LiBr; it then begins to
decrease as more of the Li$^+$ ions hydrate with the water molecules. The diffusivity is a
monatomic decreasing function as the mass fraction exceeds 50 wt% LiBr. The trend
is encouraging because the correlation was extrapolated from the 60 wt% fit range to
obtain diffusivity estimates at 62 and 64 wt% LiBr. No diffusivity data exists at these
high concentration levels. Hence, the correlation is very useful for predicting the
effect of temperature and concentration, and it accounts for the effects of heat and
mass transfer that occur within the absorber. It is strongly recommended that it be
used in conjunction with the SH correlation.

A.2 Transport Property Routines

The FORTRAN routines from Patterson, Crosswhite and Perez-Blanco (1990) were
modified to include the routines by Jeter et al. (1990). The routines by Patterson and
colleagues were used to reduce data with $X_f \leq 0.60$ LiBr. The viscosity, density, and
thermal conductivity routines by Jeter were used for reducing data having mass
fractions of 0.62 and 0.64 LiBr.

The kinematic viscosity is shown in Fig. A.2 as a function of the temperature and
concentration of the LiBr brine. Viscosity data for saturated liquid water is included
as a base of reference and is about five times less than the viscosity of 62 wt% LiBr.
Increasing the mass fraction of LiBr increases the viscosity. Increasing temperature
causes the viscosity to drop. The Pr number, defined as $\nu/\alpha$, is directly proportional
to $\nu$ and increases as the mass fraction increases; it drops as temperature drops. The
conductivity of the brine is shown in Fig. A.3. The thermal diffusivity, \( \alpha \), is inversely proportional to the Pr number. Increasing the mass fraction decreases the thermal conductivity, increases the density and causes slight decreases in the specific heat, which, in turn, causes the Pr number to increase. Similar trending is seen for the Sc number, defined as \( \nu/D_{ab} \). Increasing the mass fraction increases viscosity, which increases the Sc number. The diffusivity drops (Fig. A.1) but also causes the Sc number to increase. However, the Sc number is more sensitive to increases in viscosity than is the Pr number. An increase in the mass fraction, however, causes both the Pr and Sc numbers to increase.

The surface tension is shown in Fig. A.4 and shows an increase as mass fraction increases. The Ka number is directly proportional to surface tension; however, its effect is tempered by the density (Fig. A.5). Density is in the denominator of the Ka number, and an increase, with increasing mass fraction, will partially cancel the effect of surface tension. The surface tension of 62 wt% brine is about 25% larger than that of saturated liquid water, while the density increases from about 1 for water to about 1.78 for brine. The product of density and kinematic viscosity causes the Ka number to drop as the mass fraction increases.

In summary, the kinematic viscosity is the predominant transport property affecting the Pr, Sc and Ka numbers. Mass diffusivity strongly affects the Sc number. Thermal conductivity, density and surface tension have secondary effects on the Pr and Ka numbers.
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Fig. A.1. Mass diffusivity for different mass fractions and temperatures of LiBr brine.
Fig. A.2. Kinematic viscosity for different concentrations and temperatures of LiBr brine.
Fig. A.3. Thermal conductivity for different concentrations and temperatures of LiBr brine.
Fig. A.4. Surface tension for different concentrations and temperatures of LiBr brine.
Fig. A.5. Density for different concentrations and temperatures of LiBr brine.
Appendix B

NONINTRUSIVE TEMPERATURE MEASUREMENTS

In falling film absorbers a nonintrusive technique is needed to measure the interface temperature between the aqueous LiBr absorbent and the absorbate water vapor. Thermographic phosphors were successfully used to measure the temperature profile in the mini-absorber test stand. Testing was conducted at 60 wt% LiBr brine, 1.3 kPa pressure and 35°C coolant flowing at 3.8 L/m. Interface temperature measurements were made at several locations down the absorber tube. At the absorber inlet, the absorbent drives to equilibrium with the vapor pressure. The thermographic measurements yielded an inlet interface temperature within 2% of the brine’s entering equilibrium temperature.

B.1 Theory

The customized thermographic temperature measurement was originally developed jointly by a team of researchers at ORNL, Los Alamos National Laboratory (LANL) and EGG. This unique technique involves seeding the LiBr brine with thermographic phosphors in very low concentrations. Thermographic phosphors are rare earth ceramics that are chemically inert. They consist of phosphates which are doped by replacing a small amount of the ceramic with a different rare earth ion such as europium. The dopant atoms cause fluorescence in the phosphor. Exciting the thermographic phosphors causes them to emit a spectrum of unique emissions whose
intensity and fluorescence lifetime vary with temperature. With ultraviolet irradiation, these phosphors have an emission spectra consisting of many sharply defined visible spectral lines, some of which are a strong function of temperature (Allison and Cates 1989). The temperature dependence of the fluorescent spectrum is due to the atomic processes of absorption and emission of radiation by the phosphors. When excited by ultraviolet irradiation, the phosphor absorbs an activation energy and emits a photon of energy to return to its ground state; the return causes fluorescence.

The phosphor, lanthanum oxysulfide doped with europium (La$_2$O$_2$S:Eu), has spectral lines near 467 and 512 nm that have strong temperature dependence; Fig. B.1 shows a plot of these visible fluorescence spectra for testing at about room temperature. The lifetime of the fluorescent emission can be directly correlated with temperature; Fig. B.2 shows the decay time for the 512-nm spectral line. As seen in Fig. B.2, the temperature effect is very significant, and measurements using La$_2$O$_2$S:Eu have been determined within an uncertainty less than 0.5°C (Allison and Cates 1989).

**B.2 Calibration**

Tests were conducted to show whether the fluorescence from within aqueous LiBr would affect the decay-rate temperature dependence. Previously, in 1984, calibrations by ORNL scientists were done with La$_2$O$_2$S:Eu painted on a temperature-controlled surface. These data are included with calibration data for fluorescence detected from about 2.5 ppm of La$_2$O$_2$S:Eu suspended in a solution of 55 wt% LiBr brine. Results in
Fig. B.3 show both data sets to be well defined by a single regression curve. Therefore, the LiBr brine had little effect on the phosphorescence. The fluorescence lifetime vs temperature was correlated for all the calibration data and had a regression correlation $R^2$ of 0.998.

Lanthanum oxysulfide is used for temperature measurements ranging from 0 to 50°C, and its measurement accuracy is within $\pm 0.5^\circ$C (Allison and Cates 1989). The phosphor was thus selected because of its accuracy and its suitability for the application in aqueous LiBr falling-film absorbers having film temperatures ranging from 45 to 55°C.

The decay of the fluorescence occurs rapidly. The field of view of the collection optics system was made large enough to ensure that fluid motion did not affect the data. As example, at a solution flow rate of 1 kg/m, a fluorescing particle would move less than 0.1 mm in one lifetime, and would thus occur in the field of view of the collection optics.

**B.3 Proof of Concept**

At the onset of the study, testing was conducted to determine any problems with the thermographic phosphor technique. The experimental setup, used in proof-of-concept work, is illustrated in Fig. B.4. A Laser Science Incorporated VSL 337 nitrogen laser pulsed a 337-nm beam through a lens that focused the laser beam within a petri dish made of Pyrex (7740 borosilicate glass of 21/64-in. thickness). The petri dish
contained a solution of aqueous LiBr with $\text{La}_2\text{O}_2\text{S}:\text{Eu}$. A telescopic lens, located about 0.9 m from the petri dish, detected the phosphor emissions, and a photomultiplier tube converted photon emissions to an analog signal. An oscilloscope digitized the analog signal and measured the decay rate of the excited phosphor.

The attenuation of the $\text{N}_2$ laser beam was checked by directing the beam through different thicknesses of borosilicate glass. As compared to quartz glass, no attenuation could be observed through the borosilicate glass. The vertical column absorber, which is made of 7740 borosilicate glass, therefore would not block ultraviolet light emitted from the $\text{N}_2$ laser source.

Lanthanum oxysulfide is a rare earth ceramic and is fairly inert. No chemical reactions could be observed between either phosphor or aqueous LiBr solutions for temperatures ranging from 40 to 90°C.

Static pool testing was conducted with about 2.5 ppm (1 ppm = 1 mg/L) of phosphor suspended in 56 wt% LiBr brine. This concentration was adequate for visual observation of the spectral emissions. The laser beam was directed to traverse through the depth of aqueous LiBr solution, and a telescopic lens detected the phosphor’s emissions. The brine was heated, and an attempt was made to measure temperature along the path of the $\text{N}_2$ laser beam. As compared to a certified thermometer reading of 25°C, the thermographic phosphor technique using lanthanum oxysulfide yielded a temperature measure of 25.5°C.
The phosphors have a particle size of about 5 to 10 \( \mu \text{m} \) and in static pool tests remained in suspension for about 2 h. However, under falling film conditions, sedimentation of the larger particles was observed after 30 min. Agitation of the solution caused these particles to again suspend in solution. With no agitation, all the particles would settle in the boiler, and therefore the intensity of phosphorescence in the film would diminish. Further, the LiBr brine would itself fluoresce generating a blue flash for about 1 ms over a broadband of wavelengths, and if the intensity of the phosphor emission was too low, an accurate temperature measurement could not be made.

**B.4 Summary**

Particle buoyancy was not sufficient to prevent settling in the boiler of the mini-absorber. An intense fluorescence was produced in the film for a duration of about 50 ns. Yet despite these difficulties, a successful measure of the interface temperature was made on a single smooth-wall absorber tube of 0.01905 m OD and of 1.5 m length. From repeated measurements taken at the same location the data are judged to be about \( \pm 1.5^\circ \text{C} \) accurate.

The preliminary study showed that thermographic particles would be very useful for measuring the temperature profile of a thin falling film. Difficulties with the technique arose because of the dynamics of the falling film. The roll waves caused the falling film thickness to fluctuate over a period of about 0.2 s. However, Dukler (1976) and Brauner and Maron (1982) showed these roll waves induced secondary
flows within the wave that swept up fluid from the slower moving substrate and deposited a freshly churned film behind the wave. These hydrodynamics are a determining factor in assuming that the particles were dispersed more on the surface of the film than in its bulk. In the substrate, Chu and Dukler (1974) measured a substrate thickness of about 100 µm for a Re number of 1000. The thermographic particles are about 10 µm thick. Therefore about one-tenth of the substrate is composed of the phosphors, and the sweeping action of each successive roll wave is believed to have kept them near the surface.

The data measured near the absorber inlet yielded a temperature very close to the equilibrium temperature reached by the absorbent when it is first exposed to the ambient vapor. The correspondence is very promising and helps substantiate the accuracy of the interface measurements. A helium neon laser was split into two parallel beams and then focused to an intersection precisely at the object plane of the collection optics; this allowed precise positioning of the excitation region within the field of view of the collection system.

The decay time of the fluorescence occurs rapidly. Therefore, for falling film testing the field of view of the collection optics system was made large enough to ensure that fluid motion had minimal effect on the data. For example, at a solution flow rate of 1 kg/m, a fluorescing particle would move less than 0.1 mm in one lifetime and would thus occur in the field of view of the collection optics. Hence, some fluctuations in measurements were observed because of the fluctuations in the film thickness. However, the film is principally covered by the thin substrate (Fig. 2.1), and the interface measures are judged to be an average over the field of view on the interface.
B.5 References


Fig. B.1. The emission spectrum of lanthanum oxysulfide doped with europium (La₂O₂S:Eu) (Allison et al. 1989).
Fig. B.2. The lifetime of the fluorescence for the 514-nm spectral line of lanthanum oxysulfide doped with europium (La$_2$O$_2$S:Eu) (Allison et al. 1989).
Fig. B.3. Calibrations were conducted using lanthanum oxysulfide (La$_2$O$_2$S:Eu) suspended in two different mediums. The visible emission spectrum are for 514 nm.
Fig. B.4. The bench-test setup for studying the feasibility of using the thermographic phosphor technique for fluid temperature measurements.
Appendix C

EXPERIMENTAL HEAT AND MASS TRANSFER DATA

The salient features of the 304L stainless steel absorber tube are given in the
Table C.1 along with a descriptive of the tabulated data. The mini-absorber test stand
is described in Fig. C.1, which also gives the locations of the measurements
corresponding to the descriptions in Table C.1. Data for testing at 62 wt% and 35°C
are listed in Tables C.2, C.3 and C.4. Section 3.6 describes the algorithm used to
calculate the equilibrium state point of the absorbent at the exit of the dispenser,
when first exposed to the test tube.
Table C.1. Salient data and measurement descriptions

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**Mini-Absorber Data**

| P_v         | Pressure of absorbate vapor                      | kPa        |

**Strong Solution data**

| \(\dot{m}_{f,\text{in}}\) | Mass flow rate of the falling film               | kg/s       |
| T_f,\text{in}            | Brine temperature entering absorber              | °C        |
| 100 \(\cdot \) X_{f,\text{in}} | Brine concentration entering the absorber      | % LiBr    |
| \(\dot{m}_{f,eq}\)         | Mass flow rate leaving the dispenser            | kg/s       |
| T_f,\text{eq}            | Equilibrium temperature leaving the dispenser    | °C        |
| 100 \(\cdot \) X_{eq}     | Equilibrium concentration leaving the dispenser | % LiBr    |

**Weak Solution data**

| T_f,\text{ex}         | Brine temperature leaving absorber              | °C        |
| 100 \(\cdot \) X_{f,\text{ex}} | Brine concentration leaving absorber      | % LiBr    |

**Coolant Data**

| \(\dot{m}_{c}\)          | Mass flow rate of the coolant                   | kg/s       |
| T_{c,ex}                | Exit coolant temperature                        | °C        |
| T_{c,ex}                | Inlet coolant temperature                        | °C        |

**Reduced Data**

| q                       | Heat transfer rate                               | J/s       |
| \(\dot{m}_{V}\)         | Mass absorbed                                    | kg/s      |
| \(\Delta T_f\)          | Subcooling at outlet of the absorber             | °C        |
| Nu                      | Overall Nusselt number                           |           |
| Sh                      | Overall Sherwood number                          |           |
Fig. C.1. Flow circuit describing measurement locations in Table C.1.
Table C.2. Testing at 62 wt%, 35°C coolant and vapor pressure of 1.17 kPa

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Table C.3. Testing at 62 wt%, 35°C coolant and vapor pressures of 1.3 and 1.5 kPa

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Table C.4. Testing at 62 wt%, 35°C coolant and vapor pressure of 1.5 kPa

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Appendix D

UNCERTAINTY ANALYSIS OF THE LOAD AND MASS ABSORBED

The intrinsic variability of instruments will always cause measurements to have error. The exact value and the exact error associated with a measurement are unknown. Different instruments, of the same or different types, or different setups can and most likely will yield different values from a total population of an individual measurement. Because the true value of a measurement is not known, it is more correct to infer an experimental uncertainty than an experimental error. The calculation of uncertainty was presented by Kline and McClintock (1953) and is composed of two parts, a random error and a systematic error. Random error occurs because of the scattering of data about the average of the measurement population. Random error is well described by the standard deviation about the statistical average; it is termed the “precision of measurement.” Systematic error is characterized as a shift from the true average and will cause repeated readings to be biased by roughly the same amount. Systematic errors are minimized by calibrating the instruments to a given standard. Once calibrated, instrumentation can be assumed to be free of bias, and the uncertainty analysis includes only the precision of recorded measurements. However, instruments can and do shift in calibration over time. Hence, the uncertainty analysis for the present study includes the effects of both random and systematic errors for calculating the maximum uncertainty.
Preliminary analysis used for design of the test stand showed the concentration and the coolant temperature gradients across the absorber as the two major sources of unacceptable error. Hence, the coolant flow rate was limited to the transitional turbulent regime, and a probe was inserted through the bore of the test tube to promote turbulence in the annular gap. Static tests with fluids of different densities and flow tests using distilled water were conducted to improve and validate the accuracy and temperature trending of the in situ densitometers. As result, the heat balance between the coolant side and the film side agreed within about 10%.

The collected data were analyzed to determine the experimental uncertainty in the load and the mass absorbed. The mass absorbed was based on a direct measure of the density of the aqueous LiBr at the inlet and the exit of the mini-absorber. Given the density and the temperature of the solution, the concentration was calculated from an empirical correlation, and the mass absorbed was derived from a continuity balance. We also back-calculated the mass absorbed from the load measured on the coolant side. Our goal then was to use uncertainty analysis to document the validity and accuracy of the data as well as to justify the approach used for data reduction and correlation.

**D.1 Formulation of Uncertainty Due to Random Error**

In a given test, the instruments were scanned every 10 s for 300 s. The 30 scans were used to develop an average and standard deviation for each measurement. In fact, for each test the running average, running standard deviation and instantaneous values
were recorded to separate electronic data files. These statistical data were then used
to determine the uncertainty due to the precision of all instruments. The
instantaneous scans were used to reduce an instantaneous load and mass absorbed
from which averages and standard deviations were calculated for each reduced
parameter.

The 30 scans collected during a test represent a relatively small sample from all the
possible values for each measurement. We therefore do not know the true arithmetic
mean or the true standard deviation. Gosset, as reported by Benedict (1977),
recognized this deficiency and devised a method called Student $t$ to better estimate the
standard deviation for small sample experiments. His $t$ statistic inflates the
confidence interval to reduce the effect of underestimating the standard deviation.
For 30 samples, the $t$ statistic for a 95% confidence interval would be 2.042.

The propagation of uncertainty into the load and mass absorbed was calculated from
a first-order analysis based on the following formulation:

$$
U_{r_{\text{random}}} = \left\{ \frac{\partial R}{\partial x_1} C_{I_1}^2 + \frac{\partial R}{\partial x_2} C_{I_2}^2 + \cdots + \frac{\partial R}{\partial x_n} C_{I_n}^2 \right\}^{1/2}, \quad (D.1)
$$

where

- $U_{r_{\text{random}}}$ = the uncertainty due to propagation of individual errors,
- $x_i$ = the independent variables of flow, temperature, concentration,
  and pressure,
- $\sigma_i$ = the standard deviation about the scatter for $x_i$,
- $R$ = the dependent variables of load and mass absorbed,
D.2 Formulation of Uncertainty Due to Systematic Error

The systematic error requires estimates for the confidence intervals of Eq. D.1. Here the confidence interval is not a pure guess, rather, it is derived mainly from historical calibration data and/or from in situ comparisons with another standard. Propagation of systematic error is calculated using a formulation similar to Eq. D.1

\[ \frac{CI_i}{
\sqrt{\frac{\sigma_i}{n}}\right] = t_{n} \cdot U_{\text{systmt}} \]  

\[ U_{\text{systmt}} = \left\{ \left( \frac{\partial R}{\partial X_1} U_1 \right)^2 + \left( \frac{\partial R}{\partial X_2} U_2 \right)^2 + \cdots + \left( \frac{\partial R}{\partial X_n} U_n \right)^2 \right\}^{1/2} \]  

where \( U_{\text{systmt}} \) = the best estimate of the uncertainty in the independent variables of flow, temperature, concentration and pressure.

D.3 Overall Uncertainty Interval

A conservative approach was used for the formation of the overall uncertainty. We calculated a maximum possible error, and assumed there would be no canceling of errors (i.e., all errors were in the same direction). The maximum uncertainty was therefore simply calculated as

\[ U_{\text{max}} = \left( \frac{U_{\text{random}} + U_{\text{systmt}}}{2}\right) \]  

Assuming a normal distribution of the data, the Student \( t \) statistic was selected for a 95.5% confidence. The probability of all the data falling within the uncertainty

259
interval is approximated by the Gauss-Laplace normal distribution. It implies that 95.5% of data will fall within a tolerance of 2·\(U_{\text{max}}\). Hence, the error bars reported in the present study have the following connotation:

\[
\overline{X} \pm U_{\text{max}} (95.5\%)
\]

(D.4)

### D.4 Uncertainty in the Load

The load reported in the present study was measured on the coolant side using the following first-law energy balance:

\[
q = C_l \{C_p\rho V\} e\left[ T_{c_{\text{in}}} - T_{c_{\text{in}}} \right].
\]

(D.5)

The dependent variable \(q\) is easily seen as a function of the independent variables of specific heat, density, volumetric flow rate and temperature. Mathematically, we can express the independent variable's dependence as \(R = R(x_1, x_2, ..., x_n)\). To determine the propagation of error due to each independent variable, we invoke the definition for the derivative of a function. A variation \(\partial x_i\) in \(x_i\) would cause \(R\) to vary according to

\[
\partial R = \frac{\partial R}{\partial x_i} \partial x_i.
\]

(D.6)

Eq. D.6 is referred to as the sensitivity factor and is used in Eqs. D.1 and D.2 to estimate the effect of each respective independent variable on the error in the dependent variable, \(R\). The fractional effect is convenient for quick review of the contribution made by each independent parameter. Normalizing Eq. D.6 by \(R\) yields the fractional contributions as
The term \( \hat{\pi}_i \) represents, for the random error, the standard deviation; for the systematic error, it represents the uncertainty interval. For example, Eq. D.1 for the random error in the load takes the form

\[
\frac{\partial R_i}{R} = \frac{1}{R} \frac{\partial R}{\partial \hat{\pi}_i} = \frac{R_i}{R} \frac{\partial R}{\partial \hat{\pi}_i}. \quad (D.7)
\]

The systematic error follows as

\[
UI_{\text{random}} = \frac{t_{90} \sqrt{30}}{\sqrt{\sum \left( \frac{\sigma_{C_\rho}}{C_\rho} \right)^2 + \left( \frac{\sigma_C}{C} \right)^2 + \left( \frac{\sigma_V}{V} \right)^2 + \left( \frac{\sigma_{T_{ex}}}{T_{ex} - T_{in}} \right)^2 + \left( \frac{\sigma_{T_{in}}}{T_{ex} - T_{in}} \right)^2}}. \quad (D.8)
\]

The systematic error follows as

\[
UI_{\text{systmt}} = \left\{ \frac{(UI_{C_\rho})^2}{C_\rho} + \left( \frac{UI_C}{C} \right)^2 + \left( \frac{UI_V}{V} \right)^2 + \left( \frac{UI_{T_{ex}}}{T_{ex} - T_{in}} \right)^2 + \left( \frac{UI_{T_{in}}}{T_{ex} - T_{in}} \right)^2 \right\}^{1/2}. \quad (D.9)
\]

The load for the test conditions outlined in Chapter 4 was 937 W. Substituting the results of Eqs. D.8 and D.9 into Eq. D.3 yields a maximum uncertainty of ±7.1% for that particular test. As might be expected, the inlet and exit coolant temperatures comprised about 96.7% of the total 7.1% uncertainty in the load. The uncertainty algorithms were coded into a FORTRAN-77 data reduction program and run for all the test data. Results showed the average maximum uncertainty for all testing was about ±12.1% of the load measured on the coolant side. The range of uncertainties is plotted as a function of the coolant temperature gradient in Fig. D.1. The largest uncertainty was 20% for testing at 62 wt% and 46°C coolant, where the coolant temperature gain was only 1.5°C. An increase in load corresponds to an increase in temperature gain. Testing at 35°C coolant yielded the largest load, and as seen in Fig. D.1, incurred the least error.
D.5. Uncertainty in the Mass Absorbed

The direct measure of the mass absorbed was based on the density measurements of aqueous LiBr at the inlet and the exit of the mini-absorber. Given the density and the temperature of the solution, the concentration is calculated from an empirical correlation, and the mass absorbed is derived from continuity balances for the solute and for the total flow. These continuity balances are combined to form the following relation

\[ \dot{m}_v = (\dot{m}X)_\text{in} \left\{ \frac{1}{X_{\text{ex}}} - \frac{1}{X_{\text{eq}}} \right\} . \quad (\text{D.10}) \]

The sensitivity factors for Eq. D.10 are complicated by the dependence of \( \dot{m}_v \) on \( X \), which in turn is dependent on both temperature and density. To determine the second-order effect, we used the chain rule for a derivative and developed the following dependence:

\[ \frac{\partial \dot{m}_v}{\partial \rho} = \frac{\partial \dot{m}_v}{\partial X} \frac{\partial X}{\partial \rho} \text{, and } \frac{\partial \dot{m}_v}{\partial T} = \frac{\partial \dot{m}_v}{\partial X} \frac{\partial X}{\partial T} . \quad (\text{D.11}) \]

An empirical relationship was used to define the functional dependence of the wt% LiBr on both temperature and density:

\[ (A + B \cdot T)X^2 + (C + D \cdot T)X + (E + F \cdot T - \rho) = 0 . \quad (\text{D.12}) \]

Evaluating the derivatives in Eq. D.11 yields the following for the density dependence:
Combining these derivatives according to Eq. D.11 results in the sensitivity factor for density:

\[
\left( \frac{\partial m_v}{\partial X_{in}} \right) = \frac{1}{X_{in} \cdot \left( (C + D \cdot T)^2 - 4(A + B \cdot T)(E + F \cdot T - \rho) \right)^{1/2}}.
\] (D.14)

The formulation for the temperature sensitivity factor is derived in similar fashion, and is described by the following relationship:

\[
\left( \frac{\partial m_v}{\partial T_{pin}} \right) = \frac{1}{X_{in} \cdot \left( (C + D \cdot T)^2 - 4(A + B \cdot T)(E + F \cdot T - \rho) \right)^{1/2}} \cdot \frac{B(C + D \cdot T) - D(A + B \cdot T)}{2(A + B \cdot T)^2}.
\] (D.15)

The mass absorbed for thermographic phosphor testing was about \(2.64 \cdot 10^{-4}\) kg/s. Substituting the sensitivity factors of the form shown in Eqs. D.14 and D.15 into Eqs. D.8 and D.9 yields a maximum uncertainty of about ±40% for direct measure of the absorbate mass. The Coriolis densitometers are about ±0.005 g/cc accurate. If the
densitometer were an order of magnitude more accurate (i.e., ±0.0005 g/cc vs the calibrated ±0.005 g/cc), the uncertainty would improve to ±23%. The concentration gradient across the mini-absorber was therefore the major contributor to the uncertainty in the mass absorbed. Results showed the average maximum uncertainty for all testing was a huge ±60% of the mass absorbed. The range of uncertainties is plotted as a function of the concentration gradient in Fig. D.2(a). The largest uncertainty equaled the magnitude of the mass absorbed for testing at 62 wt% and 46°C coolant. The concentration gradient, ΔX, had to exceed 0.5 wt% LiBr for the maximum uncertainty to drop below 50%. The largest gradient was observed for testing at 46°C coolant and 64 wt% LiBr and also for 35°C coolant and 60 wt% LiBr. Uncertainties for these tests were about 40% as seen in Fig. D.2(a).

The uncertainty is too large, especially if data is to be correlated. We therefore back-calculated the mass absorbed from the load measured on the coolant side. Our goal here is to use uncertainty analysis to justify a data-reduction approach for the mass absorbed based on coolant-side temperature measurements rather than on a film-side concentration gradient. The mass absorbed can be back-calculated from the load by the following energy balance:

$$m_v = \frac{(mX)_n}{X_{eq}} \left\{ \frac{i_{eq} - i_{fg}}{i_{ex} - i_{fg}} - 1 \right\} - \frac{q}{i_{ex} - i_{fg}}.$$  \hspace{1cm} (D.16)

Here, the mass absorbed is dependent on the solution mass flow rate, entering density, temperature and enthalpy of the brine, the latent heat and the load. For example, the sensitivity factor for the load’s effect on the absorbate becomes
The uncertainty in the load was taken from the calculated maximum value from Eq. D.3 (i.e., summation of Eqs. D.8 and D.9) and the standard deviation for the load was calculated from the 30 instantaneous scans recorded per test. Using this conservative approach, the load contributed to 94% of the total uncertainty. However, the maximum uncertainty was only 11.6% of the back-calculated mass absorbed. The improved uncertainty is due simply to the fact that it is easier to measure temperature with a thermometer than it is to measure density with the densitometer. The average error in the maximum uncertainty for all test data was about ±25% of the back-calculated value, which is tolerable. Results can be seen in Fig. D.2(b), and are consistent with uncertainties plotted in Fig. D.1. The uncertainty analysis therefore helps justify using the back-calculation as the primary measure of the absorbate mass.

As a final point, the densitometers were very sensitive to the RTD temperature signal. We had modified the vendor’s setup to better measure the bulk temperature of the metered fluid. The meters tracked the density of distilled water very well (Fig. 3.7); however, tests conducted at 64 wt% LiBr showed significant error between the two calculation approaches used for the mass absorbed. Fig. D.3 shows the error between the density measurement approach and the back-calculation approach. Data at 60 and 62 wt% are within ±15% agreement; however, the 64 wt% data are overpredicted by the density measurement approach. At issue is the temperature
measurement used by the densitometer. Testing at 64 wt% LiBr brine required hotter brine temperatures to protect against crystallization. Again, Fig. 3.7 shows an increasing trend to overpredict the mass absorbed as the metered temperature increases. Hence, we decided to use the densitometer measurements only as references to check the back-calculation of the mass absorbed.

Perusal of Fig. D.2(a) and D.2(b) is very helpful for identifying data with the least error on both the coolant and film side of the absorber. For example, testing at 62 wt% and 1.5 kPa had a low uncertainty for densitometer based mass and a low uncertainty for the coolant-side load. The data are therefore valid points and are very useful for comparing against correlations or data in the open literature.

D.6 References


Fig. D.1. The maximum uncertainty in the load, measured on the coolant side, drops as the temperature gain of the coolant increases.
(a) Average Ulmax is about \( \pm 60\% \) for densitometry-based reduction of \( m_v \).

(b) Average Ulmax is about \( \pm 25\% \) for \( m_v \), back-calculated from the load.

**Fig. D.2.** The mass absorbed is better represented by coolant-side temperature measurements than by the film-side concentration measurements.
Fig. D.3. The error in the mass absorbed based on density measurements as compared to the value back-calculated from the load.
Appendix E

CORRELATION OF THE COOLANT-SIDE Nu NUMBER USING WILSON’S METHOD

The data-reduction technique used to map the temperature and concentration profile required an accurate coolant-side heat transfer correlation. The absorber tube had a 0.00635-m OD probe inserted through its bore. The probe measured the coolant profile and also enhanced turbulence in the flow. Some RTD leads were also run through the bore of the test tube. We therefore needed to either correlate or validate an existing correlation for calculating the coolant-side heat transfer coefficient.

A method was needed to separate the measured overall thermal resistance into its individual components. Wilson (1915) devised a useful technique for determining the individual resistance from the overall resistance. He was interested in determining the effects of water temperature and velocity on the overall coefficient for steam condensers. Wilson developed a technique whereby for constant property conditions, the convective coefficient is a predominant function of water velocity and its mean temperature (an effect due to viscosity), as well as tube diameter. He discovered that the overall thermal resistance to heat flow could be correlated by a straight-line dependence on \( \frac{1}{h_{cl}} \) as shown in Fig. E.1. Wilson expressed \( h_{cl} \) as a function of both velocity and temperature as follows:

\[
h_{cl} = a u^{0.8}(1.0 + 0.011T_{el}), \quad (E.1)
\]

where \( a = \) coefficient to be determined from Wilson’s method.
He substituted the expression in Eq. E.1 into the well-known relationship for the overall thermal resistance in a condenser tube. The overall heat transfer coefficient was expressed as follows:

\[
\frac{1}{(HA)_o} = \frac{1}{(hA)_o} + \frac{\ln\left(\frac{D_o}{D_i}\right)}{(2\pi k_p) L} + \frac{1}{au^{0.8}(1.0 + 0.011T_{cl}) A_i}.
\]  \hspace{1cm} (E.2)

where \(h_o\) = outside (shell-side) heat transfer coefficient.

Wilson showed that as the water velocity is extrapolated to infinity (i.e., \(u^{0.8} = 0\)), the straight-line correlation intercepts the y-axis at point b (Fig. E.1). The total resistance then (i.e., the b intercept in Fig. E.1) is due to the wall and the shell-side resistance. The tube thermal conductance is known, and therefore the outside fluid coefficient, \(h_o\), can be calculated. Wilson further reasoned that a parallel line drawn through the origin would give the resistance on the coolant side. Hence, the slope of the lines, illustrated in Fig. E.1, represents the term \(1/a_i\). Knowing the value of a from the slope of the curves in Fig. E.1, we can calculate the water-side convective coefficient. Thus, Wilson showed that Eq. E.2 is suitable for linear regression having the following simple form:

\[y = b + mx,\]

where

\[y = \frac{1}{(HA)_o},\]

\[b = \frac{1}{(hA)_o} + \frac{\ln\left(\frac{D_o}{D_i}\right)}{(2\pi k_p) L},\]
\[ \frac{1}{u^{0.8} (1 + 0.01 T_{cl})} \]

\[ m = \frac{1}{aA_i} \]

Given the tube-side heat transfer coefficient from a simple linear regression of Wilson-type data, one can formulate a correlation or validate the use of literature correlations such as Dittus Boelter for predicting the tube-side heat transfer coefficient. Once validated, this, in turn, supported the predictive algorithm and also enabled a back-calculation of the local tube wall temperatures along the running length of the mini-absorber.

**E.1. Methodology**

The mini-absorber test stand was charged with distilled water, and steam condensing tests were conducted according to Wilson's method. The technique tacitly assumes that the outside resistance remains constant as the coolant velocity and hence the inside resistance changes. We maintained a fixed outside resistance by controlling the heat flow to the coolant. When the coolant flow was increased, the coolant temperature was also increased a corresponding amount to maintain a constant heat flow. This in turn, for a constant steam pressure, fixed the ΔT from the condensing steam to the coolant and kept the outside resistance constant.

The mini-absorber test stand had been leak-checked, and no noncondensables were detected in the absorber (see Fig. E.3). Three series of tests were conducted at steam
pressures of about 4.7, 6 and 7 kPa. The steam was generated in the boiler from the charge of distilled water, and no impurities (organic contamination) were observed on the test tube during testing. Any impurities could cause the condensation process to change from filmwise to dropwise condensation. Best results are seen with filmwise condensation where the test tube is fully wetted.

The latent heat from the condensing steam was measured on the coolant side. A log-mean-temperature difference was calculated from the condensing steam and coolant temperatures and was used to reduce the overall heat transfer coefficient by the following equation:

\[
\frac{1}{(HA)_o} = \frac{\left( \frac{T_{sat} - T_{cl_x}}{T_{sat} - T_{cl_m}} \right) - \left( \frac{T_{sat} - T_{cl_m}}{T_{sat} - T_{cl_m}} \right)}{\ln \left( \frac{T_{sat} - T_{cl_x}}{T_{sat} - T_{cl_m}} \right)} \]  
(E.3)

Wilson plots were then developed by plotting the reciprocal of the overall heat transfer coefficient as a function of Wilson's coolant heat transfer correlation (Eq. E.1).

**E.2. Laboratory Results**

The a coefficient of Eq. E.2 was calculated by correlating the reciprocal of the overall heat transfer coefficient against the reciprocal of the convective coefficient (Fig. E.2). The slopes of the individual curves in Fig. E.2 were determined by least-square fits to the data from which the a constant was calculated. Each test series had a correlation
coefficient squared of 0.95 or better in predicting the variations of the overall thermal resistance. Results of the linear regressions are shown in Fig. E.2.

In another approach, all the data were correlated using the formulation from the Dittus Boelter correlation. We did this to directly compare the Wilson correlation against the more generic Dittus Boelter correlation. The Nu number \( \left[ \frac{h_c D_{hy}}{k} \right] \) for the Wilson data is plotted in Fig. E.3 as a function of the product \( (Re^{0.8}) \times (Pr^{0.4}) \). Results show the Wilson correlation about 25% high of Dittus Boelter in predicting the tube-side heat transfer coefficient.

The results demonstrate that the water-side convective coefficient is not accurately predicted using the Dittus Boelter correlation with Pr number raised to the 0.4 power. Sleicher and Rouse (1975) reported that the Dittus Boelter correlation is inaccurate over certain ranges of the Re and Pr numbers. It is 10–25% high for gases, and as much as 40% low for water at high Re numbers. Mini-absorber testing was conducted at coolant flows in the transitional turbulent regime. Generally, established correlations are very uncertain in this region because of entrance effects and because of the instability of the phenomena itself. Donne and Bowditch (1963) experimentally observed that the transition between turbulent and laminar flow followed two distinct paths: an upper one, which is a prolongation of the turbulent regime in the transition regime; and a lower one, which is the prolongation of the laminar regime. The laminar transition path is less stable than the turbulent transition path. As previously stated, the test tube had RTD lead wires and a coolant temperature probe within its bore. The entrance effects and the uncertainty of the
flow phenomena led us to use the Wilson correlation over that of the Dittus Boelter, which incidentally was formulated for fully developed turbulent flow. Hence, the coolant-side heat transfer coefficient was calculated from the correlation listed in Fig. E.3 for heat and mass transfer testing conducted in the present study.

E.3. References


Fig. E.1. Wilson plot.
Fig. E.2. The results of stream condensation tests conducted at condensing pressures of 4.7, 6 and 7 kPa vapor pressure.
Fig. E.3. Dittus Boelter underpredicts the coolant-side correlation derived from Wilson’s method. The coolant Re number is about 5500.

\[ \text{Nu} = 0.02846 \text{Re}^{0.8} \text{Pr}^{0.4} \]

\[ R^2 = 0.978 \]
VITA
VITA

William A. Miller was born in Dayton, Ohio, on March 18, 1952. He attended St. Paul's parochial school through the eighth grade and then entered the public school system in Tullahoma, Tennessee, where he earned his high school education in June 1970. He enrolled in the University of Tennessee's College of Agriculture and for a year was a member of the university's golf team. He received a Bachelor of Science degree in agronomy in 1974 and in mechanical engineering in 1978. In the College of Engineering, he was an active co-op student working several semesters, first at John Deere Plow & Planter Works, Moline, Illinois, and later at Milliken's Magnolia Finishing Plant, Blacksburg, South Carolina. The heat transfer projects at Milliken challenged him and confirmed his desire to continue graduate education. He worked at ORNL while on assistantship at UTK and earned the Master of Science degree in mechanical engineering. He has served as a research engineer at ORNL, and has designed and directed the setup of numerous refrigeration systems, including a continuously variable-speed heat pump test stand, a compressor calorimeter test stand, psychrometric chambers, airflow loops, and an aqueous LiBr mini-absorber test stand.

In 1990, the opportunity to pursue the doctorate degree arose through a nonfederally funded contract awarded ORNL by GRI. He received his doctorate in May 1998. He is presently working at ORNL in the Thermally Activated Heat Pump Program and is studying coupled heat and mass transfer in absorption chillers for commercial and residential use.