**ENHANCEMENT OF HEAT AND MASS TRANSFER IN
MECHANICALLY-CONSTRAINED ULTRA-THIN FILMS
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SECTION 1.0 – INTRODUCTION AND BACKGROUND

Oregon State University (OSU) and the Pacific Northwest National Laboratory (PNNL) were funded by the U.S. Department of Energy to conduct research focused on resolving the key technical issues that limited the deployment of efficient and extremely compact microtechnology based heat actuated absorption heat pumps and gas absorbers. Success in demonstrating these technologies will reduce the main barriers to the deployment of a technology that can significantly reduce energy consumption in the building, automotive and industrial sectors while providing a technology that can improve our ability to sequester CO₂. The proposed research cost \$939,477. \$539,477 of the proposed amount funded research conducted at OSU while the balance (\$400,000) was used at PNNL. The project lasted 42 months and started in April 2001.

Recent developments at the Pacific Northwest National Laboratory and Oregon State University suggest that the performance of absorption and desorption systems can be significantly enhanced by the use of an ultra-thin film gas/liquid contactor. This device employs microtechnology-based structures to mechanically constrain the gas/liquid interface. This technology can be used to form very thin liquid films with a film thickness less than 100 microns while still allowing gas/liquid contact.

When the resistance to mass transfer in gas desorption and absorption is dominated by diffusion in the liquid phase the use of extremely thin films (<100 microns) for desorption and absorption can radically reduce the size of a gas desorber or absorber. The development of compact absorbers and desorbers enables the deployment of small heat-actuated absorption heat pumps for distributed space heating and cooling applications, heat-actuated automotive air conditioning, manportable cooling, gas absorption units for the chemical process industry and the development of high capacity CO₂ absorption devices for CO₂ collection and sequestration. The energy potential energy savings associated with these technologies is estimated to ultimately be 2.88 quads per year.

It has become clear that commercial application of these technologies depends on a deeper understanding of the thermal phenomena encountered in a mechanically constrained ultra-thin film device. Our lack of understanding is currently limiting both the performance of these devices and the potential for further size reductions. Barriers to successful commercial applications of the mechanically-constrained ultra-thin film contactors include poorly understood single and two phase flow phenomena in the thin film, the need for improved micromachined contactors and a poor understanding of the phenomena effecting the dimensional stability of the thin film.

The research included in this proposal is focused on research associated with resolving and removing these technical barriers to commercialization. The results of the research will significantly advance the prospects for the commercialization of the whole range to technologies that depend on improved gas/liquid contacting.

Gas/liquid contacting (absorption or desorption) is critical for absorption based heat-actuated heat pumps, many chemical industry processes and CO₂ collection. However, in most cases the size of the gas/liquid contactor is fundamentally limited by diffusion in the liquid film where the diffusivity in the gas phase can be three to five orders of magnitude greater than in the liquid phase. Falling films and droplets typically have characteristic dimensions on the order of 1 mm. If we were able to reduce the thickness of the liquid film in a gas/liquid contactor from 1 mm to 100 microns we would be able to increase mass transfer on the order of a factor of 100. When the resistances to mass transfer in gas desorption and absorption is dominated by diffusion in the liquid phase the use of extremely thin films can radically reduce the size of a

gas desorber or absorber. The development of compact absorbers and desorbers enables the deployment of small heat-actuated absorption heat pumps for distributed space heating and cooling applications, heat-actuated automotive air conditioning, manportable cooling absorption cooling units, and the development of high capacity CO₂ absorption devices for CO₂ collection and sequestration.

Recent developments at the Battelle, PNNL and OSU suggest that the performance of absorption and desorption systems can be significantly enhanced by the use of a micro technology based mechanically-constrained ultra-thin film gas/liquid contactor. This concept uses a membrane or micromachined contactor with many small diameter pores to prevent mixing between a gas and liquid while allowing the gas and liquid to be in contact. When the contactor is properly designed, surface tension prevents the liquid from entering the pores while the pores provide a path for gas to diffuse to the liquid surface. The contactor can then be used to form a film with a thickness less than 100 microns while allowing gas/liquid contact. When used with microchannel heat exchangers for heating (desorbers) or cooling (absorbers), extremely high rates of mass transfer can be attained. A schematic drawing of mechanical-constrained ultra-thin film contactor is shown in Figure 1.1.

Battelle has been funded by the Defense Advanced Research Projects Administration (DARPA) to develop a manportable cooling system using ultra-thin film gas/liquid contactors in a lithium bromide (LiBr) and water absorption heat pump. The proposed heat pump weighs less than 1 kg (Drost et. al. 1999). Results to date suggest that the device is technical feasible and can be inexpensive if advanced laminate fabrication techniques are used for mass production. While this work has been generally successful, it has become clear that successful commercial development will depend on a deeper understanding of the thermal phenomena encountered in a mechanically-constrained ultra-thin film device. Our lack of understanding of these phenomena is currently limiting both the performance of these devices and the potential for further size reductions. Barriers to successful commercial applications of mechanically-constrained ultra-thin film contactors include:

Single Phase Thin-Film Flow Issues

- The extent of flow maldistribution in the thin film needs to be determined, as does the impact of the design of the inlet and outlet headers on flow maldistribution.
- The impact of roughness, particularly roughness caused by the stiffening system on flow in the thin film needs to be understood. In some cases roughness may be used to add surface area for enhanced mass transfer.

Figure 1.1 Schematic Representation of a Mechanically Constrained Ultra Thin Film Gas Absorber

- Interactions between the flowing fluid and the stiffened membrane are not understood. We need to know the conditions that will cause the membrane to wrinkle, particularly when the contactor is at high temperature with the potential for differential thermal expansion.

Two-Phase Thin-Film Flow Issues

- During desorption, boiling in the thin film is not desirable because bubbles can agglomerate and ultimately block flow through the film. We need to understand limitations on the maximum heat flux that can be applied to the thin film without causing boiling.
- Some qualitative results suggest that using a slight positive pressure to force gas across the membranes, forming small bubbles, can significantly increase the mass transfer in the absorption mode. We need to understand the impact of bubble formation on mass transfer and fluid flow in the thin film to determine if this approach can be applied in a practical device.
- Impact of Non-Condensable Gases – Any non-condensable gases in the working solution will tend to come out of solution in the desorber. We need to understand the interaction of these bubbles with the bulk flow in the desorber thin film and identify any limits on the amount of off-gassing that will occur in the desorber

Membrane Issues

- Gas pressure drop across the membrane and the membrane stiffening system must be minimized

Stiffening System Issues

- Interactions between fluid dynamics in the film and the mechanical response of the stiffened contactor is poorly understood
- We need to understand how the operating temperature of the device affects the ability of the stiffening system to maintain the thin film

The research included in this proposal is focused on “bridge research” associated with resolving and removing the barriers identified above and on providing the research community with the ability to both optimize mechanically-constrained ultra-thin films and to extend this technology to other fluids and applications. If we are successful, we will significantly advance the prospects for the commercialization of an entire range of technologies that depend on improved gas/liquid contacting.

1.1 Advantages relative to Conventional Technology

Compared to a conventional absorption heat pump, one based on mechanically-constrained ultra-thin film absorption and desorption will have the following advantages.

- **Size** – The use of mechanically-constrained ultra-thin films can reduce the size of an absorption heat pump by perhaps a factor of 10. This makes the heat-actuated absorption heat pump a candidate for portable and distributed heating and cooling applications.
- **Efficiency** – The use of microchannel heat exchangers in the ultra-thin film desorber/absorber and recuperative heat exchanger of an absorption heat pump will allow significant improvements in cycle performance by reducing approach temperatures.
- **Cost** – While cost is beyond the scope of this study, laminate fabrication has the potential to enable high volume, low cost fabrication of small modular absorption heat pumps.
- **Modularity** – The availability of efficient and low cost small heat-actuated heat pumps will enable the use of multiple distributed heat pumps in place of one central heat pump, reducing cycling and ducting losses.
- **Orientation Independence.** - The use of a mechanically-constrained ultra-thin film will result in an absorption heat pump that is orientation independent. This is critical for portable applications such as manportable cooling and automotive cooling.

1.2 Cross-Cutting Nature of the Technology

Our research will contribute to removing the key barriers to the commercialization of extremely compact gas desorbers or absorbers. The development of compact absorbers and desorbers enables the deployment of a wide range of new devices. These include:

- **Distributed Heat-Actuated Heat Pump for Space Conditioning Applications** – The development of a compact and inexpensive heat-actuated heat pump will enable the use of multiple small heat pumps for distributed space conditioning, reducing the losses associated with ducting, zoning and cycling of a central heat pump. Often ducting and cycling losses can be as high as 25% to 50% of the output of a central heat pump. The use of multiple small heat pumps would eliminate ducting losses and significantly reduce losses associated with overheating or overcooling.
- **Heat-Actuated Heat Pump for Automotive Applications** – A compact heat-actuated air conditioner can be used in a conventional automobile with engine exhaust providing the source of heat for the air conditioner. This would improve fuel efficiency and decrease the impact of the air conditioner on engine performance. In other applications the air conditioner can be operated with thermal energy from a gasoline-fired version of a microchannel combustor developed by PNNL (and which received an R&D 100 award in 1999) decoupling the operation of the heat pump from the engine. This is critical for 1) air conditioning hybrid vehicles where the engine is frequently shut down, 2) allowing precooling of the vehicle before an occupant enters the car and 3) providing air conditioning for electric vehicles using a relatively clean fuel such as butane or natural gas. Through contacts with the automotive industry it is clear that market acceptance of hybrid or electric vehicles, particularly in hot climates such as California, will depend on the availability of air conditioning.

- Industrial Heat-Actuated Heat Pumps – Compact and inexpensive heat-actuated heat pumps can be used in many industrial applications to provide waste heat recovery, temperature amplification or process cooling without the use of electricity.
- Man portable cooling systems – The commercialization of a manportable cooling system will directly benefit DOE's missions associated with environmental clean-up (cooling of hazardous materials clothing) and national security (cooling of chemical and biological warfare clothing).
- Gas-Liquid Contactors for Chemical Process Industry – Numerous chemical processes include gas-liquid contacting. The development of a high performance gas-liquid contactor would have wide spread application in the chemical industry.
- CO₂ absorption – One barrier to CO₂ collection and sequestration is the high cost of CO₂ collection. PNNL has demonstrated that the mechanically constrained ultra thin film technology can be used to attain very high mass transfer rates in CO₂ absorption applications resulting in a significant reduction in size and cost

Our research will impact multiple sectors of the economy including the building sector (distributed heat pumps for space conditioning) transportation sector (heat-actuated heat pumps for automobiles and other transportation applications) and the industrial sector (high performance industrial heat pumps and compact gas-liquid contacting). In addition to energy conservation, the development of the mechanically constrained ultra thin film technology will improve the performance and cost of CO₂ absorption and sequestration and could be a key technology for in-situ resource processing for NASA.

1.3.Potential for Energy Efficiency Gains and Other Benefits

The development of compact absorbers and desorbers creates opportunities for many applications. The potential energy-related benefits of two of these applications, compact thermally activated heat pumps for space heating and cooling, and automotive cab cooling, are estimated below.

Building Space Heating and Cooling

Compact absorption heat pumps serving individual rooms have the potential to significantly reduce energy consumption compared to central HVAC systems coupled with ducted conditioned air distribution. Energy losses in ducting occur because of leaks and heat transfer through duct walls. These losses vary significantly depending on design, installation, and maintenance practices, but have been estimated to range from 20-40% of energy entering the ducting system. Smaller (collectively, as well as individually) heat pumps should also reduce cycling losses associated with the repeated heating and cooling of HVAC equipment. Finally, distributed heat pumps will allow better control of individual room temperatures, which should also reduce the required load.

Admittedly, there is uncertainty in the magnitude of savings possible from the above mechanisms. Ducting conditions vary widely. Losses from ducts within the conditioned space boundary provide an indirect heating and cooling benefit. Reduced cycling losses and zone control benefits are also highly variable and poorly documented. The following analysis assumes the combined benefit of avoiding duct losses, reducing cycling losses, and achieving better zone control result in a net 25% reduction in building space heating and cooling load. Additional savings result from differences in the efficiency of an absorption heat pump compared to the systems it would replace.

Compact absorption heat pumps would be applied most beneficially as an alternative to ducted systems, where the ducts are outside the conditioned space and where rooms have exterior walls that allow easy access to ambient air (for use as the heat source/sink). These conditions are most prevalent in residential buildings, but are also common in smaller commercial buildings. The following analysis focuses on the larger residential market.

According to the 1997 Residential Energy Consumption Survey (RECS), 56.6 million households were served by central (ducted) warm-air furnace systems. These systems consumed 3.31 Quads of energy (mostly natural gas and fuel oil) at a cost of \$24.53 billion. The efficiency of a typical central furnace is assumed to be about 80%, while the Coefficient of Performance (COP) of an absorption heat pump is estimated to be about 1.2. Thus, the 25% savings associated with ducting losses, etc., coupled with the increase in equipment efficiency would combine to cut energy use in half, resulting in energy savings of 1.66 Quads valued at \$12.26 billion per year.

Central (ducted) heat pumps provided heating for 9.7 million households according to the 1997 RECS. These electrically-driven devices consumed 0.13 Quads (measured at the site) at a cost of \$2.64 billion. According to figures presented in the 1997 Annual Energy Review, the combined conversion, transmission, and distribution efficiency for electricity was 30%. Thus, 0.13 Quads at the site is equivalent to 0.43 Quads at the source. Assuming a COP of 2.5 for an electrically-driven heat pump (compared to a COP of 1.2 for the absorption heat pump) and 25% savings for reduced ducting losses, etc., site energy use would increase from 0.13 Quads to 0.20 Quads. The absorption heat pump is not electrically-driven; so site and source energy are the same. Thus, the net source energy savings are 0.23 Quads per year. The cost of 0.20 Quads of fossil energy in the residential sector (based on RECS data for space heating) would be \$1.50 billion, resulting in net energy dollar savings of \$1.14 billion per year.

Central (ducted) air conditioning systems (via heat pumps or AC only systems) were used in 47.5 million households according to the 1997 RECS, consuming 0.34 Quads of electricity (measured at the site) at a cost of \$8.26 billion. This is equivalent to 1.13 Quads of source energy when energy electricity generation, transmission, and distribution losses are included. The absorption heat pump COP is only expected to be 0.65 in the cooling mode, compared to an assumed COP of 2.5 for the electrically-driven heat pump. Nevertheless, when coupled with 25% load savings for reduced ducting losses, etc., source energy consumption for the absorption heat pump is only 0.98 Quads, resulting in annual energy savings of 0.15 Quads. The 0.98 Quads of fossil energy is estimated to cost \$7.26 billion in the residential sector (based on RECS data for space heating), resulting in annual dollar savings of \$1.0 billion.

The combined annual savings for central (ducted) heating and cooling systems are 2.04 Quads (source energy) and \$14.4 billion. Site energy savings were estimated to be 0.47 Quads of electricity and 0.48 Quads of fossil energy. The latter is roughly 80% natural gas and 20% fuel oil.

Automotive Cab Cooling

Air conditioning of automobiles is currently accomplished with vapor compression devices that are driven by shaft power generated by the auto's engine. With an IC engine efficiency of about 20% and an automotive vapor compression COP of 0.8, overall efficiency is poor. Absorption coolers offer significant performance improvement by avoiding the inefficiencies of IC engine shaft power. Conventional absorption-based cooling systems are too bulky for the automotive application, however, so development of a compact absorption cooling system is required to take advantage of the efficiency improvement opportunity.

According to the Transportation Energy Data Book (Davis 1998), 130 million cars were driven 1.47 trillion miles or an average of 11,314 miles per car. The average speeds for the federal urban and highway driving cycles are 20 mph and 50 mph, respectively. Assuming that half of the annual mileage is accumulated at the urban rate and half at the highway rate, the total annual driving hours would be about 400. The number of air-conditioned driving hours would depend on climate and typical driving schedules. Lacking better data, air conditioning was assumed to be required half of the time.

A passenger car cooling system is commonly sized to provide up to 2 tons (24,000 Btu/hour) of cooling. The cooling unit operates at capacity when bringing a car down from a "hot soak" condition to a comfortable operating temperature. At steady-state the required cooling capacity is much lower. This analysis assumes the air conditioner operates at full capacity for 20% of the cooling hours, but only 20% of capacity for the rest of the cooling hours, for an average capacity factor of 0.36 or average capacity of 0.72

tons or 8640 Btu/hour. Thus, the annual average cooling load served by the air conditioning system is 1.728 MMBtu

With an IC engine efficiency of 0.20 and vapor compression COP of 0.8, the conventional automotive AC system consumes 10.8 MMBtu/year in the form of gasoline. The absorption cooler COP is estimated to be 0.5 in the automotive application. Its COP for the automotive application is less than for the space cooling application because the automotive condensing temperatures are generally higher. Although IC engine waste heat could provide part of the thermal input to the absorption cooler, the quantity available is not always adequate. This analysis assumes that all of the thermal input for the absorption cooler comes from combusting gasoline in a micro-channel combustor at an efficiency of 80% (i.e., 80% of the fuel's chemical energy is converted and transferred to the absorption cooler). Thus, the annual energy consumption for the absorption cooler is 4.32 MMBtu/year or a savings of 6.48 MMBtu/year. This is equivalent to 52 gallons of gasoline per year or a dollar savings of about \$78 per year.

If applied to the population of automobiles (130 million passenger cars), the total annual savings would be 0.84 Quads and \$10.1 billion.. These figures do not include the potential impact of 69 million light trucks (pickups, vans, and utility vehicles). Nor do these figures consider the potential impact of enabling air conditioning in future electric, fuel cell, or hybrid vehicles where the shaft power demand of a conventional vapor compression unit would be a significant burden.

SECTION 2.0 –SCOPE OF WORK

The project's scope of work consisted of 6 tasks. These tasks were selected to address the key issues associated with mechanically constrained ultra thin film absorption and desorption. The six tasks are described below. OSU was responsible for completing tasks 1, 3, 4 and 6 while PNNL directed tasks 2 and 5.

Task 1 Membrane Mass Flux Enhancement - There are qualitative absorption results that suggest that micromanufactured straight through pores can significantly reduce the pressure drop for gas diffusion across a contactor as compared to the complicated and tortuous flow paths encountered in commercially available membranes. This task compared the mass transfer performance of conventional membranes with contactors with engineered pores, to quantify the benefit from micromanufactured contactors. Task 1 was conducted by OSU and was completed in 12 months.

Task 2 Thin Film Absorption and Desorption Single-Phase Fluid Dynamics - This task involved the use of an existing Lithium Bromide-Water (LiBr) absorption/desorption test loops at PNNL to resolve the single phase flow issues.

Task 3 Experimental Investigations of Thin Film Absorption and Desorption Two-Phase Fluid Dynamics - This task involved the establishment of a flow visualization absorption/desorption test loop at OSU for the model problem. The thin film was visually observed while the device was operated as either an absorber or desorber. Task 3 was conducted by OSU and was completed in 42 months. The test loop was used to investigate the following phenomena: These goals were accomplished based on the following subtasks described below.

- **Subtask 3.1 Design, fabrication and testing of the desorption test loop** - This subtask involved the design, fabrication and start up of a test loop for evaluating absorption and desorption. The test fluids were selected to provide the best evaluation of the onset of boiling and how it affects the desorption process. Based on availability of extensive property data it is expected that either a LiBr-water or ammonia-water system near atmospheric pressure conditions will be used.
- **Subtask 3.2 Flow Evaluation During Desorption** - A series of experiments were carried out with the goal of evaluating the critical conditions for the on-set of boiling during desorption. These consisted of flow visualization to document size, occurrence and distribution of bubbles for a range of heat flux and flow rate conditions. Results consisted of the identification of the onset of bubble formation conditions versus flow rate for temperatures and pressures relative to the saturation conditions of the fluid. In addition, the desorption process was monitored during bubble formation to document the mass transfer rates in the presence of bubbles as a function of total liquid flow rate.
- **Subtask 3.3 Design, fabrication and testing of the absorption test loop for two phase flow studies** - The desorption flow loop was modified to accommodate the absorption two phase flow studies. The basic flow components of the loop were the same. The required cooling of the constrained thin film was achieved using a convective cooling channel on one side of the thin film contact surface. This channel was constructed with glass or quartz windows to allow visual data collection through the cooling channel into the test section. For laminar flow in the cooling channel a water mass flow rate of 0.03 kg/s at 8°C below the water ammonia mixture temperature will provide sufficient cooling with less than 1°C temperature rise of the coolant.

Task 4 Dimensional Stability of Thin Films - The enhanced heat and mass transfer afforded by ultra thin film gas/liquid contactors is a direct result of maintaining a thin film interface. These devices rely on mechanically stiffened structures backing up the membrane to create a thin liquid film with a thickness of less than 100 μm over a relatively large area (greater than 1 cm^2). The mechanical structure must also maintain its integrity with a high level of precision while the system internal pressure varies and the contactor undergoes thermal cycling to its operating temperature. This effort provided the primary means to

assess the mechanical performance of the structure. The other focus area was to model the effects of differential pressure and thermal cycling on the integrated structures in order to understand the important effects present in maintaining film dimensional integrity. This task included structural modeling of the stiffeners using experimental investigations a finite element simulation. Predicted deflections were compared with measured values for the purpose of both validating the modeling process and for predicting performance. This finite element modeling also allowed thermal stress and deflections to be determined due to thermal expansion mismatch of the various components of the design. Task 4 was conducted by OSU and was completed in 24 months.

Task 5 Lattice-Boltzmann Simulation - PNNL developed simulation models for single-phase and two-phase flow in model absorbers and desorbers and validate the resulting models with experimental results. Task 5 was conducted in conjunction with both experimental tasks (Tasks 2 and 3) and was completed in 42 months. PNNL has developed a simulation capability based on the lattice Boltzmann method for modeling the behavior of bubble formation, growth, deformation, breakup and agglomeration. The liquid-vapor or gas-liquid interface, which has an associated surface tension, is free to move through the lattice grid in response to flow and surface forces. In collaboration with researchers at OSU, PNNL developed engineering models to be used for contactor design based on lattice Boltzmann simulation results and experimental data. The model was validated with experimental results produced in tasks 2 and 3. The lattice Boltzmann simulation effort was divided into three subtasks: These are presented below.

- **Subtask 5.1 Discreet Two-phase Modeling** - PNNL developed and applied the lattice Boltzmann two-phase simulation capability to model onset of boiling, bubble augmentation of adsorption and the impact of non-condensable gases..
- **Subtask 5.2 Engineering Model Development** – In collaboration with researchers at OSU, engineering models were developed for use in contactor design projects. The engineering models were based on lattice Boltzmann simulation results and experimental data.
- **Subtask 5.3 Model Validation** - Experimental results were used to validate the lattice Boltzmann simulation method and engineering models. The computer program was validated using experimental results from Task 2 for single-phase applications and the results from Task 3 for two-phase phenomena.

Task 6 Administration - OSU administered the project. This task included administration, travel, and reporting activities.

Oregon State University provided technical management of the project and conducted tasks one, three and four. The PNNL scope of work included Task 2 (Thin Film Absorption and Desorption Single Phase Fluid Dynamics) and Task 5 (Simulation). All tasks are described in Section 4.0. Dr. Kevin Drost from OSU was the project principle investigator and provided technical direction for both the OSU and PNNL activities. Dr. Drost was the client contact for the project and was responsible for meeting the projects reporting requirements and deliverables. A task manager from the appropriate organization managed each task. Task managers at both PNNL and OSU reported to the principle investigator for technical direction.

Section 3.0 RESULTS

The results from the five technical tasks are summarized below. Section 3.1 discusses the results from task 1 while the results from tasks 2 through 5 are presented in sections 3.2, 3.3, 3.4 and 3.5.

3.1. Membrane Mass Flux Enhancement

Recent development of compact heat-actuated absorption cycle heat pumps at the Pacific Northwest National Laboratory and Oregon State University has found that the performance of gas/liquid absorption systems can be significantly enhanced by the use of thin film gas/liquid contactors. A contactor is a porous membrane that employs microtechnology-based structures to mechanically constrain the gas/liquid interface. This technology can be used to form very thin liquid films with a film thickness of less than 100 microns while still allowing gas/liquid contact (Davis, 1998; Drost, et al., 1999).

When the resistance to mass transfer in gas absorption into a liquid is dominated by diffusion in the liquid, the use of thin contactors (<100 microns) for gas absorption can radically reduce the size of gas/liquid absorbers. The development of compact absorbers enables the deployment of small heat-actuated absorption heat pumps for distributed space heating and cooling applications, heat-actuated automotive air conditioning, and manportable cooling (Champagne, et al., 2001). Gas/liquid contactors are also suitable for the development of high capacity CO₂ absorption devices for CO₂ collection and sequestration (Drost, et al., 1999; TeGrotenhuis, et al.).

One limiting factor for the development of heat-actuated absorption cycle heat pumps is the lack of driving pressure within the absorber. Therefore, pressure drop across the contactor membrane must be minimized in order to maximize mass transfer rates.

Previous findings have suggested that micromanufactured straight-through pores can significantly reduce the pressure drop for gas diffusion across a contactor as compared to the complicated and tortuous flow paths encountered in commercially available membranes. Our task has been to compare the mass transfer performance of conventional membranes with those having engineered pores, to quantify the benefit for heat pump contactors.

The main task has been divided into three subtasks. The first subtask involved generating a baseline of mass flux data for conventional membranes and analyzing this data to determine if correlations exist between membrane morphology and mass flux characteristics. The second subtask involved the use of a deep UV (266 nm) laser to micromachine straight-through pores in polyimide films and comparing the mass flux characteristics of this membrane with the baseline of data established in the first subtask. The third subtask involved the use of soft lithography (McDonald, et al., 2002) techniques to micromold a polydimethylsiloxane (PDMS) membrane and comparing its mass flux characteristics with the baseline.

Baseline Measurements

The first subtask involved defining a baseline for mass flux measurements across conventional membranes. To establish a baseline for mass flux data relative to conventional membranes, selection criteria were established to parse the enormous list of commercial membranes which were available for testing. The criteria used to choose membranes included that they be made from polymers with thicknesses between 50 and 150 μm and pore sizes from 1 to 10 μm . Polymers were chosen because the membrane was expected to be lightweight without the need for operating at high temperatures. In particular, hydrophobicity of the material was seen as a plus because it would improve the liquid breakthrough pressure of the membrane. The thicknesses and pore sizes were sized based upon estimated conditions necessary to eliminate liquid phase breakthrough. Tables 3.1.1 through 3.1.8 show a list of the membrane types selected for establishing the membrane mass flux baseline. Figures 3.1.1 through 3.1.8 provide a micrograph illustrating the morphology of each membrane type.

Table 3.1.1. Specifications for nylon membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						

Nylon	10	88.90	3.50	0.0026	square	N/A	1.14	Osmonics	R99SP320FX
Nylon	5	99.06	3.90	0.0243	25	0.49973303	1.14	Osmonics	R50SP02500
Nylon	1.2	106.68	4.20	0.0643	25	1.22788606	1.14	Osmonics	R12SP02500
Nylon	1	106.68	4.20	0.1014	47	0.54785969	1.14	Pall (Gelman)	66509
Nylon	1.2	101.60	4.00	0.0260	25	0.52132643	1.14	ADVANTEC MFS	N120A025A

Figure 3.1.1. Micrographs of a nylon membrane.

Table 3.1.2. Specifications for polyethersulfone membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						
Polyethersulfone - PES	5	106.68	4.20	0.0113	25	0.21579	1.37000	Osmonics	S50SP02500
Polyethersulfone - PES	1.2	114.30	4.50	0.0115	25	0.20497	1.37000	Osmonics	S12SP02500
Polyethersulfone - PES	0.8	129.54	5.10	0.0125	25	0.19658	1.37000	Osmonics	S08SP02500

Figure 3.1.2. Micrograph of a polyethersulfone membrane.

Table 3.1.3. Specifications for PVC membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						
Polyvinyl Chloride – PVC	5	55.88	2.20	0.0075	25	0.27342	1.40000	Pall (Gelman)	66466
Polyvinyl Chloride – PVC	5	152.4	6.00	0.0078	25	0.10427	1.40000	Millipore	PVC502500

Figure 3.1.3. Micrograph of a PVC membrane.

Table 3.1.4. Specifications for polypropylene membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						
Polypropylene	10	116.84	4.60	0.0234	25	0.40799	0.91000	Millipore	AN1H02500
Polypropylene	10	88.90	3.50	0.0947	47	0.61399	0.91000	Pall (Gelman)	61757
Polypropylene	5	101.60	4.00	0.0257	25	0.51531	0.91000	Millipore	AN5002500
Polypropylene	2.5	121.92	4.80	0.0412	25	0.68842	0.91000	Millipore	AN2502500
Polypropylene	1.2	116.84	4.60	0.0412	25	0.71835	0.91000	Millipore	AN1202500

Figure 3.1.4. Micrograph of a polypropylene membrane.

Table 3.1.5. Specifications for polyvinylidene fluoride membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						
Polyvinylidene Fluoride	5	109.22	4.30	0.0347	25	0.64723	1.78000	Millipore	SVLP02500

Figure 3.1.5. Micrograph of a polyvinylidene fluoride membrane.

Table 3.1.6. Specifications for PTFE membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Density (g/cm ³)	M. Density (g/cm ³)	Company	Part No
	Micron	Micron	Mil						
Polytetrafluoroethylene PTFE	10	132.08	5.20	0.0823	25	1.26938	2.19000	Osmonics	Z99WP02550
Polytetrafluoroethylene PTFE	10	93.98	3.70	0.0432	25	0.93644	2.19000	Millipore (Mitex)	LCWP02500
Polytetrafluoroethylene PTFE	5	162.56	6.40	0.0828	25	1.03764	2.19000	Osmonics	Z50WP02550
Polytetrafluoroethylene PTFE	5	157.48	6.20	0.0825	25	1.06723	2.19000	Millipore (Mitex)	LSWP02500
Polytetrafluoroethylene PTFE	5	134.62	5.30	0.1751	37	1.20972	2.19000	Pall (Gelman)	P4PH037
Polytetrafluoroethylene PTFE	3	127	5.00	0.0219	25	0.35129	2.19000	Millipore (Fluoropore)	FSLW02500

Figure 3.1.6. Micrograph of a PTFE membrane.

Table 3.1.7. Specifications for MCE membranes included in the mass flux baseline.

Material	Pore size	Thickness		Weight (g)	Size (mm OD)	Company	Note	Part No
	Micron	Micron	Mil					
Mixed Cellulose Ester (MCE)	8	135	5.31	0.0579	47	Millipore	Hydrophilic	SCWP04700
Mixed Cellulose Ester (MCE)	5	160	6.30	0.0185	25	ADVANTEC MFS		A500A025A
Mixed Cellulose Ester (MCE)	5	135	5.31	0.0682	47	Millipore	Hydrophilic	SMWP04700
Mixed Cellulose Ester (MCE)	3	150	5.91	0.0799	47	Millipore	Hydrophilic	SSWP04700

Figure 3.1.7. Micrograph of a MCE membrane.

Table 3.1.8. Specifications for polyamide membranes included in the mass flux baseline.

Material	Pore size	Open Area	Thickness		Size (mm OD)	Company	Part No
	Micron		Micron	Mil			
Polyamide - PA	7	2%	78	3.07	TBD	SaatiTech	PA 7/2

Figure 3.1.8. Micrograph of a polyamide membrane.

- **Measuring membrane tortuosity**

Membrane technology is built on the knowledge of the performance of particular membranes under different external flow conditions. The better the membrane characteristics are understood and quantified, the better the chances are of success in new applications and systems (Plessis, 1992). For the contactor application in the heat pump, permeability (the mass transfer as a function of pressure difference across the membrane) is the dominant characteristic that needs to be quantified. Higher permeability shows the membrane has high mass transfer and low pressure difference. In previous studies, gas penetration tests have been utilized to quantify permeability (Iversen S.B., et al., 1997; Plessis, 1992; Shelekhin, et al., 1993).

The permeability L_p of a contactor membrane is defined by

$$L_p = \frac{\ddot{M}}{\Delta p} \quad (1)$$

where $\ddot{M}$ is the mass flux and Δp is the pressure difference across the membrane.

The mass flux can be expressed as a function of volume flow through the membrane J_v

$$\ddot{M} = \frac{J_v \cdot \rho}{A} = \frac{J_v \cdot \rho}{\frac{\pi}{4} \cdot d_m^2} \quad (2)$$

where A is the nominal area of the membrane exposed to the fluid, ρ is the density of the fluid and d_m is the diameter of the test fixture plenum.

Substituting equation (2) into equation (1), the permeability can be expressed as

$$L_p = \frac{\frac{J_v \cdot \rho}{\frac{\pi}{4} \cdot d_m^2}}{\Delta p} \quad (3)$$

$$\therefore L_p = f(J_v)$$

In the membrane literature, the volume flow through the membrane J_v follows the well-established Haigen-Poiseille relationship defined as

$$J_v = \frac{\Theta d_p^2}{32 \eta \psi} \left(\frac{\Delta p}{\Delta x} \right) \quad (4)$$

where Δp is the pressure difference, ψ is the mean tortuosity factor for all the pores, d_p is the equivalent or hydrodynamic pore diameter, Θ is the porosity (void volume per total volume), η is the absolute viscosity of the fluid (M/Lt*) and Δx is the membrane thickness (White, 1994). This equation has been found to apply to microporous membranes (W.S., et al., 1992; Marcel, 1990).

From Hagen-Poiseuille, $L_p = f(J_v) = f\left(\frac{1}{\psi}\right)$ for membranes which indicate that low tortuosity membranes are needed to maximize permeability. In the membrane literature, the tortuosity of a membrane is defined as the degree to which the pores in the membrane depart from uniform straight-through conditions. In particular, the tortuosity factor (ψ) for a membrane is a multiplier that takes into consideration the variation in the cross-sectional shape of pores in a membrane as well as the variation in angle between the pore axes and the mass flow direction (Salmas, et al., 2001; Saripalli, et al., 2002). To quantify the tortuosity of a membrane (commercial and engineered), the Hagen-Poiseuille equation is used (Marcel, 1990; Palacio, et al., 1999; W.S., et al., 1992).

From equation (4), the tortuosity factor ψ can also be solved as

$$\psi = \frac{\left(\frac{\Delta p}{\Delta x} \right)}{\left(\frac{32 \eta J_v}{\Theta d_p^2} \right)} \quad (5)$$

this suggests the slope of the plot of the numerator versus the denominator is an indicator of the tortuosity factor for the membrane. In order to quantify the tortuosity of a membrane, several quantities are needed. The absolute viscosity, η , is assumed to be constant. The variables $\dot{M}$ ($= \eta J_v$), ΔP and Θ are measured experimentally. The membrane d_p and Δx can be physically characterized.

One implication of equation (5) is the impact of open area or pore packing density (Θ). This parameter is easy to quantify for straight-through pores as it is a function of the pore cross-sectional area times the number of pores per unit membrane area (equation (6)). For fibrous or other tortuous path pores, it is more difficult to quantify. In this thesis, open area or pore packing density is quantified by the fractional density of the membrane. The fractional density of the membrane is equal to the measured density of the membrane divided by the density of the membrane material (equation (7)) (Nakao Shin-ichi, 1994).

The effect of the fractional density for straight-through pores is to impact the packing density as follows:

$$\Theta = \frac{n \cdot \frac{\pi}{4} \cdot d_p^2}{total\ surface\ area} \quad (6)$$

* M/Lt = 1 kg/(m·s) = 0.0209 slug/(ft·s)

where n is the number of pores in the exposed membrane area and d_p is the diameter of the pore.

The effect of the fractional density for fibrous or other tortuous path pores is to impact packing density as follows:

$$\Theta = 1 - \left[\frac{\left(\frac{w_m}{\pi \cdot r_m^2 \cdot \Delta x} \right)}{\rho} \right] \quad (7)$$

where r_m is the membrane radius (for a circular membrane), Δx is the membrane thickness, w_m is the weight of the membrane and ρ is the material density.

- **Microfabrication of low tortuosity membranes**

In the majority of the membrane literature, the morphologies of the membrane is fibrous or tortuous. Van Rijn (2004) has provided an exhaustive review of engineered membranes. Regarding polymer membranes, track-etched membranes (Kyu-Jin, et al., 1994) can be considered as straight-through pore membranes, but the thicknesses are too thin (less than 10 μm) to be used in heat pump applications. Laser micromachined polymer membranes have been produced but no comprehensive investigations have been reported comparing the mass transfer results of laser micromachined membranes with commercially available membranes on a standardized test loop.

In the laser micromachining literature, most of the research is concentrated on drilling larger pores (around 50 μm) in silicon wafer or other metals (Zhao, et al., 1999; Kikuchi, et al., 1997). For heat pump applications, polymer membranes have better characteristics over metal membranes since they are less reactive.

Previous results obtained by Dr. Whiteside's research group showed possibilities to fabricate the membrane with arrays of submicron pores using PDMS (Polydimethylsiloxane) (Duffy, et al., 1999; McDonald, et al., 2002). The challenge is to fabricate high aspect ratio membranes and verify the permeability (Jackman, et al, 1999).

Engineered Membrane Design and Fabrication

Two laser micromachined membranes were designed and fabricated. The first one was made at OSU with a nominally 75 μm thick Kapton (polyimide) membrane. The membrane was laser micromachined (266 nm) with an array of 64,516 straight-through holes (254 by 254 holes) with 100 μm center-to-center pore spacing both vertically and horizontally. The whole design spanned one inch by one inch. The second one was made by Electro Scientific Industries, Inc. (ESI) who has laser micromachining capabilities at their headquarters in Beaverton, Oregon. The membrane (nominally 20 μm thick polycarbonate) was laser micromachined (266 nm) with an array of 258,064 straight-through holes (508 by 508 holes) with 100 μm center-to-center pore spacing both vertically and horizontally. The array spanned two inch by two inch.

In addition, a micromolded membrane was intentionally designed to match the features of the laser micromachined membranes. The identical feature provides same packing density (open area) which helps when verifying the result during the normalization process.

- **Laser Micromachining Approach**

Material

To produce a straight-through membrane using laser micromachining, a deep UV laser was used to micromachine an array of pores. The laser used was a fourth-harmonic Nd:YAG laser outputting a TEM (1,0) beam beam at a wavelength of 266 nm. The beam shape was characterized by a Spiricon laser beam analyzer (LBA-400PC). In order to obtain better quality straight-through pores, both polycarbonate and

polyimide (Kapton) film were tested. Preliminary results showed that Kapton films have less thermal effect than polycarbonate films.

Method

Gaussian laser beams have two major characteristics. One characteristic is the effective beam radius, $w(z)$, defined by the waist of the beam at $1/e^2$ (13%) of the peak beam intensity. The other key characteristic is the radiated angle, $2\theta_a$. These beam properties are portrayed in Figure 3.1.9. The effective beam waist controls the pore size in the laser machining process. The radiated angle affects the beam waist with respect to the distance between the focusing lens and the workpiece material (the working distance).

Figure 3.1.9: Gaussian beam properties (Source: Laser Engineering, Keln J. Kuhn, 1998)

A critical parameter for consistently producing 5-15 micron holes across the surface of the membrane is the depth of field (Z_R) (Kuhn, 1998). The Gaussian beam expands rapidly beyond two times of the depth of field region. One half of the depth of field can be calculated as follows:

$$z_R = \frac{\lambda_0 f^2}{\pi n (\omega(f))^2} \quad (9)$$

where λ_0 is the wavelength of the laser, f is the focal length of the focusing lens and $\omega(f)$ is the laser beam waist before going through the focusing lens. The beam was focused down through a 0.5-inch focus lens to the material surface.

From equation (9), assuming a 266 nm laser, a 0.5-inch focal length lens and an incident beam diameter of 1 mm, one half of the depth of field is found to be 53 microns. Therefore, theoretically, the total depth of field under laboratory conditions is only 106 μm . Therefore, the depth of the material used in this study was significantly less than 100 μm . Also, in order to consistently machine the material, a repeatable procedure was developed to focus the laser beam onto the workpiece surface. In addition, efforts were made to reduce the flatness of the workpiece material to within 100 μm .

Focusing procedure

As the distance between the workpiece and objective lens extends beyond the focal plane, the laser beam waist expands (Figure 3.1.9). Therefore, a procedure was established to consistently focus the laser beam on the midplane of the material. The focusing procedure involved two major steps. The first step was to find the focus of the laser at the material surface. The second step involved bringing the focal point of the laser to the material midplane (half the height of the material).

The first step of this procedure was executed by machining a series of holes; each individual holes was machined at a different working distance from the objective lens. By examining the hole patterns through a microscope, the proper working distance of the laser could be determined. Figure 3.1.10 depicts

the hole patterns with 200 μm of height variance between holes. Based on the result from 200 μm height variance, the next step was to find the best hole patterns by 20 μm height variance (Figure 3.1.11).

Figure 3.1.10: Hole patterns with 200 μm height variance

Figure 3.1.11: Hole patterns with 20 μm height variance

After finding the focal point on the material surface, an adjustment was made to raise the stage half the height of the material to minimize the beam spread as it passed through the material.

Parallelism of workpiece

By using a similar technique as the focusing procedure, a hole pattern was made at each of the four corners and the center point of the workpiece to check the parallelism of the workpiece with respect to the focal plane. The parallelism of the workpiece was determined by inspecting the variation of the dimension of the holes of the hole patterns by a microscope. From formula (9), assuming the incoming laser beam was perpendicular to the workpiece and had uniform shape, the only element that can cause the shape variance is the difference of the working distance (Z_R) which relate to parallelism of the workpiece. Test results show the ability to hold a hole size variation of 4.98% across the workpiece which translates into a parallelism of the workpiece.

Beam profile

One other critical parameter to this work was the profile of the beam. The more Gaussian the beam shape, the more circular the hole. The spatial distribution of the beam was found to be TEM 1,0 with the use of a beam profiler (shown in Figure 3.1.12 and Figure 3.1.13). Much of the cause of the beam imperfections is due to the non-linear crystals used to double and quadruple the photon energy. The beam profile was found to change as a function of the amperage provided to the laser power supply. Figures 12 and 13 show the 3-D and 2-D view of the laser profile as measured by the beam profiler at 18 and 17 amps, respectively. It was found that the beam profile emulated a TEM 0,0 beam at around 17 amps. Because of this fluctuation in beam shape, the beam profile was verified both before and after machining to ensure repeatability. This beam profile was found suitable for drilling 5~15 micron holes in Kapton.

Figure 3.1.12: 3-D and 2-D view of laser profile at 18 amps

Figure 3.1.13: 3-D and 2-D view of laser profile at 17 amps.

- **Micromolded Approach**

Material

To produce a high aspect ratio micromolded membrane, a soft lithography technique was used to produce an elastomeric membrane. PDMS (Polydimethylsiloxane) was micromolded using patterned thick resist (SU8) to create an engineered membrane.

PDMS

PDMS is a synthetic polymer with elastic properties similar to that of rubber and is considered an elastomer. Its structural formula is as shown in Figure 3.1.14 where n can be on the order of thousands. Molecular weights of PDMS can reach 700,000 or higher.

Figure 3.1.14: Structural formula of PDMS.

The PDMS being used in this micromolding process is Dow Corning Sylgard 184. It is supplied as two constituents: the base oligomer (that contains vinyl-terminated dimethyl siloxane and a platinum catalyst) and the cross-linker (hydride – terminated dimethyl siloxane). The platinum-catalyzed addition reaction between the vinyl functional group ($\text{SiCH}=\text{CH}_2$) of the base oligomer and the hydride functional group (SiH) of the cross-linker results in the curing of a mixture of the two constituents. This reaction is known as hydrosilylation (hydrosilation). The normal mixing ratio of the base oligomer to cross-linker is 10:1, however, one can vary the mixing ratio to achieve a desired strength of the cured PDMS. Cured PDMS is stable and flexible from -50°C to $+200^\circ\text{C}$.

SU8

SU-8 2000 (formulated in cyclopentanone solvent) is a chemically-amplified, epoxy-based negative photoresist. Standard formulations are offered to cover a wide range of film thicknesses from 1 to $200\ \mu\text{m}$. SU-8 2000 resist has high functionality, high optical transparency and is photosensitive to near UV radiation. Images having exceptionally high aspect ratios and straight sidewalls are readily formed in thick films by contact-proximity or projection printing. Cured SU-8 2000 is highly resistant to solvents, acids and bases and has excellent thermal stability, making it well suited for applications in which cured structures are a permanent part of the device. Regarding the thickness of the membrane, the formulation that this thesis used was SU8 2050 which provides a thickness around $50\ \mu\text{m}$.

Substrate Selection

Glass slides and silicon wafers were evaluated for their suitability as SU8 substrates during spincoating. An adhesive promoter was also used to improve adhesion. Though glass substrates are cheaper, the experimental results in Figure 3.1.15 indicate that silicon wafers work better as SU8 substrates. The photomask used for the pattern in Figure 3.1.15 included an array of holes consisting of 5-micron diameter holes on a $100\ \mu\text{m}$ grid horizontally and vertically.

Glass substrate

Silicon wafer substrate

Figure 3.1.15: Comparison between glass and silicon substrate. (Adhesion promoter was used in both instances)

PEG sacrificial layer

To release the PDMS membranes from SU8 micromolds, PEG (Polyethylene Glycol) was used as a sacrificial layer. Methonal was used to dissolve the PEG powder with a ratio of 10:1 (10g of Methonal to 1g of PEG). The PEG solution was then spincoated on the silicon wafer with SU8 posts at 6000 rpm for 1 minute. The thickness of the PEG was approximately 2 to 5 μm . The reason for implementing this process was because the SU8 posts tend to break off from substrate during separation of the membrane from the micromold. A sacrificial layer added in between SU8 and PDMS can assist the membrane to release from the SU8 posts. To release the PDMS membrane, the whole substrate was submersed into DI water and ultrasonicated for 30 minutes. The PEG coating was dissolved and the PDMS membrane separated from the silicon wafer and SU8 posts.

Method

The PDMS membrane fabrication process can be divided into four major steps (Figure 3.1.16). The first step is to create SU8 posts on the substrate. The second step is to spincoat PDMS onto the substrate with SU8 posts in order to mold PDMS membranes with straight through pores. The third step is to spincoat a thin sacrificial layer of PEG. The fourth step is to separate the PDMS membrane from the SU8 mold and substrate. The permeability was evaluated from the test loop.

The silicon wafer was first immersed in etching solution (10% of HF and 90% of deionized water) to etch the silicon oxides before the spin coating process. To obtain maximum process reliability, the substrate needs to be clean and dry prior to applying the SU8 resist. The Si substrate is first rinsed with Acetone, Methanol and DI water to remove organic residuals. Then the Si substrate is etched for 10 minutes by using an etching solution (10% of HF and 90% of deionized water). After the etching process, the Si substrate was put into a hot plate oven for 15 minutes at 150°C to dehydrate the surface. Adhesion promoters (MicroChem's OmniCoat) was then spin coated on to the surface with 3000 rpm for 30 seconds. The substrate was then put into the oven for one minute at 100°C. Both the etching process and adding the adhesive promoter will help the structure to stay on the Si wafer surface.

The SU8 was then spincoated onto a Silicon wafer. From MicroChem's recommended coating conditions, 1 ml of SU8 per inch of substrate diameter should be used. For a 3-inch diameter Si wafer, 8 ml of SU8 was applied to the wafer. MicroChem also suggests using two steps to spin coat SU8. In the spread cycle, the coating machine was first ramped up to 500 rpm at 100 rpm/second acceleration and then the speed was held for 5-10 seconds to cover the entire surface. After the spread cycle was complete, the coating machine was ramped to final spin speed at an acceleration of 300 rpm/second and held for a total of 30 seconds.

After the resist is applied to the substrate, it must be soft baked to evaporate the solvent and densify the film. MicroChem recommends the bake time for 60- μm thickness to be 3 minutes of pre-bake at 65°C then 9 minutes of softbake at 95 °C. The photomask was then placed directly on the SU8, preceded by going through the i-line exposure tool for 15 minutes (Step A on Figure 3.1.16). The recommended dosage for 60- μm thickness is around 250 mJ/cm². The SU8 exposed from the UV was crosslinked. Following exposure, a post exposure bake (PEB) must be performed to selectively cross-link the exposed portions of the film. The substrate is pre-PEB for 1 minute at 65°C then PEB for 7 minutes at 95 °C in a hot plate oven.

Figure 3.1.16: Schematic of process steps for PDMS membrane fabrication

The substrate is then immersed in MicroChem's SU8 Developer for developing. The uncrosslinked SU8 was removed under developer (Step B on Figure 3.1.16). The substrate is fixed in the glass container and the container is placed on the magnetic stirrer. Stirring the developer helped to achieve high aspect ratio structure.

The SU8 posts were then spin coated with a sacrificial layer using polyethylene glycol (Step C on Figure 3.1.16). This prevents the PDMS (Polydimethyl siloxane) from having direct contact with the SU8 posts and readies the PDMS to perform the lift-off process (Step D on Figure 3.1.16). The lift-off process was performed by putting the substrate into the ultrasonicator with Deionized water and Iso-Propyl Alcohol. The PEG was dissolved in the solution to release the PDMS from the Si substrate and SU8 post structure.

EXPERIMENTAL APPROACH

- **Baseline Measurements**

Figure 3.1.17: A simple schematic of the membrane mass flux test loop.

To measure mass transfer performance, a pressure drop test loop capable of measuring the pressure drop across a membrane as a function of mass flux was developed. As shown in Figure 3.1.17 and Figure 3.1.18, the experimental setup for conducting the pressure drop testing across the conventional membranes involved flowing nitrogen from a tank through a needle valve (flow rate control) and into the lower plenum of a test fixture. Once in the test fixture, the nitrogen flowed across the membrane and into the upper plenum of the test fixture. The test fixture was necessary to ensure flow across a constant cross-section of each membrane. The diameter of the upper plenum was 2.0 inches while the lower plenum had a diameter of 0.4 inches. A stiffener was added to prevent the membranes from deflecting. The stiffener was 500 microns thick made from partially sintered stainless steel powder with a final pore size of 100 micron. A picture of the test fixture including gaskets and stiffener is shown in Figure 3.1.19. An OMEGA HHP-2000 digital manometer was used to measure pressure drop between the upper and lower plenums. A MKS Type M10MB (M10MB13CS3BV) mass flow meter was connected to the test loop at the output of the upper plenum. The test loop was designed to permit no more than 5% uncertainty in pressure drop (between 2 and 18 torr) and mass flux (between 200 and 1000 sccm).

Figure 3.1.18: Physical layout of the membrane mass flux test loop.

Figure 3.1.19: Physical layout of the membrane mass flux test fixture.

The protocol used to test each membrane involved securing the membrane within the test fixture using a SS stiffener (see Figure 3.1.19). The testing protocol involved opening the upper plenum cover and removing the SS stiffener along with the Viton gaskets. The test membrane was placed between the test gaskets and the stiffener/gasket/membrane assembly was reinstalled within the test fixture. The test was performed by first running the experiment up to the maximum recordable pressure drop or flow rate and then back down to zero. Between five and ten data points were collected in both directions.

In all, 27 commercial membranes had been obtained and 27 membranes were tested on the test loop. The repeatability error of the test loop results was found to be less than 7%.

- **Experimental approach for laser micromachining and micromolded membrane**

Two laser micromachined membranes (OSU and ESI) have been fabricated. A test sample of 0.5 inch by 0.5 inch were cut from the membrane and tested with the test loop. The micromolded membranes were fabricated and characterized. To manipulate the thin PDMS membrane, IPA was applied to swell the membrane and reduce friction from the substrate. Toluene can also be applied to the membrane to swell the membrane even more by 50% than its original size.

RESULTS AND DISCUSSION

- **Mass Flux Results for Commercial Membranes**

Baseline Results

Figure 3.1.20 shows results as a function of the average pressure drop and mass flux across for each membrane. These are raw data results and do not represent normalized data. Notice that the leftmost data plot shows the mass flux characteristics of the test fixture without a membrane.

Figure 3.1.20: Average pressure drop results as a function of mass flux across the baseline membranes.

Normalized Results for Non-Engineered Membranes

By normalizing the experiment data using Equation (5), the result is shown on Figure 3.1.21. From the results, it is apparent that certain membrane morphologies exhibit better mass flux properties than others. Two of the membranes which stand out are the PES membranes with 0.8 and 1.2 μm pore sizes. The performance of these two membranes indicates that there is something different about the morphology of these membranes that provide better mass flux characteristics (Quartarone, et al., 2002). While the performance of these membranes stands out from the rest, its performance is not as exceptional as the other membranes. The pressure drop across these membranes is about two times less than that of the nearest remaining membrane.

Figure 3.1.21: Normalized pressure drop results as a function of normalized mass flux across the baseline membranes.

Normalization was not performed for the MCE membranes because the material density data was not available. However, based on the morphology of the membranes, it is expected that it would also reside in the lower performing membranes particularly in light of their poor average performance in Figure 3.1.21.

To expand upon the observations above, an analysis of the effects of morphology and pore size on the performance of the membranes was performed. Reviewing section 1.1 above, the membrane morphologies can be classified into three broad categories: networked, fibrous, and tortuous. Networked membranes differ from fibrous and tortuous membranes in that the membrane is an interconnected web of material while fibrous membranes are not connected with one another. One difference in fibrous and tortuous morphologies is that fibrous and tortuous morphology may result in “dead ends” or flow terminations as the

fluid winds through the structure. Networked morphologies are incapable of terminating flow paths. Therefore, it is plausible that the tortuous structures could provide higher pressure drops than other structures.

Figure 3.1.22 shows the same normalized graph plotted for the three different morphologies investigated in the mass flux baseline. This supports the notion that in general, networked morphologies provide less pressure drop than fibrous and tortuous morphologies though need more understandings on PES morphologies.

Figure 3.1.22: Normalized pressure drop results for networked, fibrous, and tortuous structures

Figure 3.1.23 shows the same normalized plot from the perspective of pore size. As shown, only the smaller pore sizes such as PES tends to give better results. It is possible that the fluid dynamics are significantly different with membranes having smaller pore sizes so that even though the data has been normalized.

Figure 3.1.23: Normalized pressure drop results for different pore size structures

Normalized Results for Woven Membranes

One of the commercial membranes that was different from the rest was the Sattitech woven membrane. Figure 3.1.24 compares the 7 μm woven membrane with the other 5 to 10 μm commercial membranes. The Sattitech 7 μm pore membrane is a woven membrane with straight-through pores and clearly exhibits the best mass flux properties. The superior performance may be due to the fact that flow paths are not simply limited to the open area but that additional flow paths between woven fibers permit additional mass flow. In addition, it was quite difficult to estimate membrane thickness and porosity for this membrane. To test the actual performance of the membrane as a contactor, additional breakthrough tests should be performed. The 7 μm pore size is anticipated to be too large for breakthrough tests. At this time, the pore size for woven membranes cannot extend below 7 μm . It will be interesting to find out if there exists a limit on the smallest, repeatable pore size possible by woven membranes.

Figure 3.1.24: Comparison of woven membrane with commercial membranes with similar pore size.

- **Laser Micromachining Membrane Results**

Laser Micromachined Membranes

For the laser-micromachined membranes produced at OSU, the average pore size was found to be different on the front side than on the back side of the material due to the characteristic parabolic shape of the laser energy deposition. Pore size was sampled randomly at 30 different locations on the membrane by optical microscopy (200X). Figures 25 and 26 show the front and back sides, respectively, of the Kapton membrane (laser micromachined by OSU). By randomly sampling 30 different holes using optical microscopy, the average pore size was found to be $16.5 \pm 0.5 \mu\text{m}$ for the front side and 5.3 ± 0.8 for the back side.

Figure 3.1.25: Front side pore array with 100 μm spacing and average pore size of $16.5 \pm 0.5 \mu\text{m}$

Figure 3.1.26: Back side pore array with 100 μm spacing and average pore size of $5.3 \pm 0.8 \mu\text{m}$.

Figures 27 and 28 show the front and back side of the polycarbonate membranes made by ESI. By randomly sampling 30 different holes using optical microscopy, the average pore size was found to be $16.5 \pm 0.5 \mu\text{m}$ for the front side and 5.3 ± 0.8 for the back side.

Figure 3.1.27: Front side of the Polycarbonate pore with 200X

Figure 3.1.28: Back side of the Polycarbonate pore with 500X

Normalized Results for Laser Micromachined Membrane

The laser micromachined membranes were flow tested using the same test loop and procedure as before. Figure 3.1.29 shows the normalized results of the laser micromachined membranes with respect to the baseline of commercialized membranes shown in Figure 3.1.24. The mass flux results of the laser micromachined membrane shows a significant improvement over the commercial fibrous and tortuous membranes. This along with the performance of the woven membrane verifies that straight through pores have superior mass flux performance as compared to the bulk of the networked, fibrous and tortuous membranes. The one exception is the PES membranes which also show similar mass flux performance.

Figure 3.1.29: Normalized mass flux results for the laser micromachined membranes compared with Figure 3.1.16.

Several characteristics of the laser machined membranes were analyzed to infer relationships between the structure of the membranes and their performance. First, the laser ablation process is a thermal process. Therefore it is expected that in some of the pores, the surface roughness on the inside of the hole is greater than the surface roughness of either the tortuous or the fibrous membranes. In other words, pores that have rough surface roughness have more pressure drop than pores that have smooth surface roughness. Figure 3.1.30 provides some support indicating that the pore shape departed from being circular through the length of the pore. Figure 3.1.31 suggests that the backside exit of the pore particularly showed an observable level of roughness inside the pore.

Frontside of the pore (1500X)

Backside of the pore (1500X)

Figure 3.1.30: SEM Pictures of Frontside and Backside of the pore

Smooth Backside Pore (7000X)

Rough Backside pore (7000X)

Figure 3.1.31: SEM pictures showing evidence of surface roughness just inside the backside pore exit.

Another source of increased tortuosity might have been a variation in pore size. While the sampled consistency of pore size across the membrane was encouraging, not all 22,500 pores on the membrane were inspected. Prior tests have shown that if the membrane is not within its required parallelism, the out-of-focus can cause large variations in pore size including elimination of the pores altogether.

- **Permeability Versus Porosity, Thickness, and Pore Size**

To further differentiate the advantages of the engineered membranes, several additional contactor membrane requirements were considered. From the contactor requirement mentioned before, stiff contactors are preferred inside the heat pump. While membrane stiffness was not specifically measured in this study, general characteristics of the membrane were used to make inferences concerning membrane stiffness. Membranes with higher porosity tend to have less stiffness. Therefore, Figure 3.1.32 shows the permeability with respect of porosity. Desirable membranes would be in the bottom, left quadrant. In this

graph, the engineered membranes stand out from the rest. Further, the laser machined membranes are shown to be potentially much stiffer than the woven membranes due to more material.

Figure 3.1.32: Tortuosity versus porosity plot. Membranes found in the lower, left quadrant would tend to have higher permeability with lower stiffness.

The plot of membrane tortuosity and thickness is shown on Figure 3.1.33. The laser micromachined membrane by ESI has the thinnest thickness but by increasing 254% of the thickness (OSU membrane) the tortuosity is still low comparing with other membranes. In all, considering that solid sheets of material would be expected to be much stiffer than woven sheets, the circumstantial evidence suggests that the laser machined approach would provide much better stiffness at improved permeabilities. This also suggests that the desire is to move toward thinner membranes. Perhaps one approach that could balance stiffness requirements with mass flow requirements would be to add stiffening ribs to thin webs of membrane material that could be laser machined.

Figure 3.1.33: Tortuosity versus Thickness

Breakthrough of liquids into gases through contactor membranes has to do with pore size as well as the hydrophobicity of the membrane. Accordingly, Figure 3.1.34 shows that the woven membranes may have breakthrough problems since the size of the pores cannot currently be made below 7 μm . It is expected that the pore sizes of laser machined membranes can be further reduced.

Figure 3.1.34: Permeability versus Pore Size

In the end, these charts indicate that laser-machined membranes provide some opportunities for increasing the permeability of commercially available membranes, while also meeting the additional stiffness and breakthrough requirements of membranes. Additional testing is needed to verify this. One trend in the data is that as membrane thicknesses decrease, laser machined pore sizes decrease while permeability increases. This finding may have profound effects on future research directions.

- **Discussion of Micromolded Membrane Results**

When a pressure was placed across the micromolded membrane in the test loop, no flow was found. Initially it was expected that this may have resulted from posts still embedded within the membrane. In many instances it was found that release of the PDMS from the SU8 posts was difficult even with PEG coatings. Maximum aspect ratios of membrane thickness to pore size were on the order of 3:1 due to the post release problem. (The thickness of the PDMS membrane was verified to be 15 μm with a post diameter of 5 μm .) Thicker membranes (higher aspect ratio) tended to result in the SU8 posts being

removed from the master mold and embedded within the membrane. To verify that the posts were not intact within 3:1 aspect ratio membranes, atomic force microscopy was used (Figure 3.1.35). According to the area scan of various pores, a post was not detected indicating that mold release was not an issue at 3:1 aspect ratio. Second, as shown in Figure 3.1.35, the pore seems to have collapsed.

To further investigate the shape of the pore, optical micrographs were taken before and after the application of IPA (Figures 36 through 38). The PDMS was known to swell in the presence of isopropyl alcohol (IPA). Figure 3.1.36 shows the pores before application of the IPA solution. After IPA application, the membrane starts to expand and eventually the sealed pore will be opened (Figures 37 and 38). In order to keep the holes from collapsing, it was found that the membrane was required to be immersed in IPA. Therefore readings of the pressure drop across the membrane were not forthcoming.

Figure 3.1.35: Front side of PDMS membrane pore

Figure 3.1.36: Sealed PDMS pores before application of IPA.

Using the AFM, the cross section of a collapsed pore was measured. The vertical height difference across two collapsed pores were 956.56 and 540.87 nm (Figures 39 and 40, respectively).

To eliminate the collapsing of the PDMS, further investigations could be performed to investigate the effect of the elastic modulus of the PDMS on the deformation of the pores by changing the ratio of the crosslinker from 1:10 to 1:5 or less. In other words, this process of reducing the base oligomer will stiffen the membrane since the membrane is more crosslinked. However, this could potentially make it more difficult to release the membrane from the mold posts. No further micromolding approaches were conducted.

Figure 3.1.39: AFM picture of a pore A

Figure 3.1.40: AFM picture of a pore B.

CONCLUSIONS

In this study, a mass flux data baseline was developed regarding the permeabilities of various commercial and microengineered liquid-gas contactor membranes for absorption cycle heat pump applications. Laser-machined membranes showed over 30 times the permeability of conventional membranes with same sized pores. Further, laser-machined membranes maintained the lowest porosities indicating that these membranes may ultimately be stiffer. A trend in the laser-machined membrane data suggests that thinner membranes would lead to both higher permeabilities with smaller pore sizes which is good for minimizing liquid-gas breakthrough. These findings have interesting implications for the future design of microengineered contractor membranes.

Some commercial membranes were also found to have excellent permeability as well. In particular, woven membranes were found to have the largest overall permeabilities found within the study. It is anticipated that the stiffness and breakthrough pressure of woven membranes would be a problem for future contactor applications. Also, PES membranes were found to have similar permeabilities with laser machined membranes. Of all the non-engineered membranes in this study, the PES membranes were found to perform best (by more than 10 times). Reasons include that the pores of the PES membranes most closely emulate those of straight-through pores. Issues with the PES membranes are that they are highly porous and may not be able to provide the stiffnesses required to maintain the dimensions of adjacent microchannels.

Permeability results for micromolded membranes were not obtained due to the collapsing of elastomeric pores. Recommendations had been made by changing the ratio of the crosslinker from 1:10 to 1:5 or less. This would stiffen the membrane and prevent collapsing of the PDMS pores.

Future studies are encouraged to take advantage of straight through pores by evolving a membrane structure that permits smaller laser-machined pores into a stiff, micromolded membrane structure with stiffening ribs and thin webs of membrane material in between. It is expected in these thin ($< 5\ \mu\text{m}$ thick) webs, laser micromachining could be optimized for one μm pore diameters. Future studies will need to take into consideration the breakthrough pressures of microengineered contactor membranes by considering the hydrophobicity and pore size of membrane materials.

References

- Champagne Peter R., Bergles Arthur E., "Development and Testing of a Novel Variable-Roughness Technique to Enhance, on Demand, Heat Transfer in a Single-Phase Heat Exchanger", vol. 8, pp. 341-352, 2001
- Davis, S.C., *Transportation Energy Data Book*, Oak Ridge National Laboratory, Oak Ridge, Tennessee
- Drost, M.K., "Mesoscopic Heat-Actuated Heat Pump Development", *Proceedings of the ASME Advanced Energy Systems*, AES-vol 39, pp. 9-19, 1999
- Duffy, D.C., Jackman, R.J., Vaeth, K.M., Jensen, K.F. and Whitesides, G.W. "Patterning Electroluminescent Materials with Feature Sizes as Small as $5\ \mu\text{m}$ Using Elastomeric Membranes as Masks for Dry Lift-off", *Adv. Materials*, vol. 11 (7), pp. 546-552, 1999
- Ho W. S. Winston, Kamallesh K. Sirkar, "Membrane Handbook", *Van Nostrand Reinhold*, 1992
- Iversen S. B., Bhatia V.K., Dam-Johansen K., Jonsson G., "Characterization of Microporous Membranes for Use in Membrane Contactors", *Journal of Membrane Science*, Vol. 130, pp. 205-217, 1997
- Jackman, R.J., Duffy, D.C., Chernavskaya, O and Whitesides, G.W., "Using Elastomeric Membranes as Dry Resists and for Dry Lift-Off", *Langmuir*, 15, pp. 2973-2984
- Kim Kyu-Jin, Paul V. Stevens, Anthony G. Fane, "Porosity Dependence of Pore Entry Shape in Track-Etched Membranes by Image Analysis", *Journal of Membrane Science*, vol. 93, pp. 79-90, 1994
- Kikuchi, Kaoru, Green, Peter W., Maeda, Ryutaro, "Micromachining of Silicon Wafer and Pyrex Glass with Excimer Laser", *Kikai Gijutsu Kenkyusho Shoho/Journal of Mechanical Engineering Laboratory*, v. 51, n. 2, Mar 1997

- Kuhn, Keln J., "Laser Engineering", Prentice-Hall, Inc, 1998
- TeGrotenhuis W.E., Cameron R.J., Viswanathan V.V., Wegeng R.S., "Solvent Extraction and Gas Absorption Using Microchannel Contactors", Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352 USA
- McDonald J. Copper, Whitesides George M., "Poly (dimethylsiloxane) as a Material for Fabricating Microfluidic Devices", *Accounts of Chemical Research*, vol. 35, no. 7, 2002
- Mulder Marcel, "Basic Principles of Membrane Technology", *Kluwer Academic Publishers*, 1990
- Nakao Shin-ichi, "Review: Determination of Pore Size Distribution 3. Filtration Membranes", *Journal of Membrane Science*, vol. 96, pp. 131-165, 1994
- Palacio L., Pradanos P., Calvo J.I., Hernandez A., "Porosity Measurements by a Gas Penetration Method and Other Techniques Applied to Membrane characterization", *Thin Solid Films*, vol. 348, pp. 22-29, 1999
- Plessis J.P., "Geometrical Models for Porous Membrane Morphologies", *Wat. Sci. Tech.*, vol. 25, no. 10, pp. 363-372, 1992
- Salmas Constantinos E., Androustopoulos George P., "A Novel Pore Structure Tortuosity Concept Based on Nitrogen Sorption Hysteresis Data", *Ind. Eng. Chem. Res.*, vol. 40, pp. 721-730, 2001
- Saripalli K. Prasad, Serne R. Jeffery, Meyer Philip D., McGrail B. Peter, "Prediction of Diffusion Coefficients in Porous Media Using Tortuosity Factors Based on Interfacial Areas", *Ground Water*, vol. 40, no. 4, pp. 346-352, Jul-Aug 2002
- Shelekhin A. B., Dixon A.G., Ma Y.H., "Adsorption, Diffusion and Permeation of Gases in Microporous Membranes. III.", *Journal of Membrane Science*, vol. 83, pp. 181-198, 1993
- White, Frank M., "Fluid Mechanics", McGraw-Hill Book Co., 1994
- Zhao J.X., Juettner, B., Menschig, A., "Micromachining with ultrashort laser pulses", *Proceedings of SPIE – The International Society for Optical Engineering*, vol. 3618, pp. 114-121, 1999
- Beuscher Uwe, Gooding Charles H., "The Permeation of Binary Gas Mixtures Through Support Structures of Composite Membranes", *Journal of Membrane Science*, vol. 150, pp. 57-73, 1998
- Bodzed Michal, Konieczny Krystyna, "The Influence of Molecular Mass of Poly (Vinyl Chloride) on the Structure and Transport Characteristics of Ultrafiltration Membranes", *Journal of Membrane Science*, vol. 61, pp. 131-156, 1991
- Childs William R., Nuzzo Ralph G., "Decal Transfer Microlithography: A New Soft-Lithographic Patterning Method", *Journal of American Chemical Society*, vol. 124, pp. 13583-13596, 2002
- Duchet J., Demoustier-Champagne S., "Study of Polystyrene Microstructures and Nanostructures Synthesised in Particle Track-Etched Membranes Used as Temples", *Polymer*, v. 41, pp. 1-8, 2000
- Kaneko Katsumi, "Determination of Pore Size and Pore Size Distribution 1. Adsorbents and Catalysts", *Journal of Membrane Science*, vol. 96, pp. 59-89, 1994
- Kokubo Ken-ichi, Sakai Kiyotaka, "Evaluation of Dialysis Membranes Using a Tortuous Pore Model", *AIChE Journal*, vol. 44, no. 12, pp. 2607-2619, Dec 1998
- Kreulen H., Smolders C.A., Versteeg G.F., Van Swaaij W.P.M., "Determination of Mass Transfer Rates in Wetted and Non-Wetted Microporous Membranes", *Chemical Engineering Science*, vol. 48, no. 11, pp. 2093-2102, 1993
- MacDonald Rosemary A., "Modelling Macromolecular Diffusion Through a Porous Medium", *Journal Membrane Science*, vol. 68, pp. 93-106, 1992
- Magistris A., Mustarelli P., Parazzoli F., Quartarone E., Piaggio P., Bottino A., "Structure, Porosity and Conductivity of PVdF Films for Polymer Electrolytes", *Journal of Power Sources*, vol. 97-98, pp. 657-660, 2001

- Maskell W.C., "Tortuosity Factor in Non-Homogeneous Membrane", *Ber. Bunsenges. Phys. Chem.*, no. 5, pp. 680-683, 1993
- Montassier N., Dupin L., Boulaud D., "Experimental Study on the Collection Efficiency of Membrane Filters", *Journal Aerosol Science*, vol. 27, suppl. 1, pp. S637-S638, 1996
- Sakai, K., "Determination of Pore Size and Pore Size Distribution 2. Dialysis Membranes", *Journal of Membrane Science*, vol. 96, pp. 91-130, 1994
- Quartarone E., Mustarelli P., Magistris A., "Transport Properties of Porous PVDF Membranes", *Journal of Phys. Chem. B*, vol. 106, pp. 10828-10833, 2002
- Tessendorf Stefan, Gani Rafiqul, Michelsen Michael L., "Modeling, Simulation and Optimization of Membrane-Based Gas Separation Systems", *Chemical Engineering Science*, vol. 54, pp. 943-955, 1999
- van Rijn, C.J.M., "Nano and Micro Engineered Membrane Technology," Elsevier, Amsterdam, 2004.
- White, Frank M., "Fluid Mechanics", McGraw-Hill Book Co., 1994
- Wolf Jeffery R., Strieder William, "Surface and Void Tortuosities for a Random Fiber Bed: Overlapping, Parallel Cylinders of Serveral Radii", *Journal of Membrane Science*, vol. 49, pp. 103-115, 1990
- Zeman Leos, "Characterization of Microfiltration Membranes by Image Analysis of Electron Micrographs. Part II. Functional and Morphological Parameters", *Journal of Membrane Science*, vol. 71

Section 3.2 Thin Film Absorption and Desorption of Single-Phase Fluids (Task 2)

Task 2 was focused on developing an improved understanding of single-phase flow in mechanically constrained thin films. The initial objectives of task 2.0 were to:

- Develop data for the lattice Boltzmann model validation.
- Understand the impact of roughness, including roughness caused by the contactor stiffening system and roughness added to enhance mass transfer, on flow in the thin film.
- Find the conditions that will cause the membrane to wrinkle, particularly when the contactor is at high temperature with the potential for differential thermal expansion.

This task involved the use of an existing Lithium Bromide-Water (LiBr) absorption/desorption test loop at PNNL. Absorption and desorption experiments in single microchannel gas-liquid contactor devices were conducted to support simulation development and to validate results. Model gas-liquid systems was used, and the properties of the absorbent liquid stream were varied to cover a range of key simulation parameters. Difficulties in attaining a repeatable mass balance limited the scope of the investigations.

During the second year, we conducted six desorption tests, analyzed the data, dismantled the test article and cleaned it, cleaned the test loop and prepared the test loop for static time. The test variables were inlet pressure, inlet temperature (subcooling), heater power and refrigerant throttle valve position.

The test sequence involved ramping up solution flow rate and heater power to design conditions. For the two test periods on July 2, 2002, heater power was held constant at 49W and on July 3 the heater settings were 58W and 74W. The tests were held steady for periods of 16 to 21 minutes. The desorption tests conducted in March 2002 maintained the heater power between 70 and 100W for periods of 7 to 20 minutes.

3.2.1 Mass Balance Results

In spite of extensive efforts to match flowmeter response, the difference between solution inlet and outlet mass flow rates again proved not to be a good measure of vapor generation rate. Small errors in inlet or outlet flow rate translate to very large percent errors in the difference compared to vapor generation rate. The difference after taking moving averages of the solution mass flow rates, shows that we are not able to infer vapor rates from solution differential rates even when they are averaged over several minutes. Direct, albeit sporadic, estimates of vapor flow were obtained by recording the weight of the vapor tank every few minutes. The vapor flow rate, so measured, is reasonably uniform ranging between 0.40 and 0.70 g/m for 56 of the 77 minutes of scale readings and averaging about 1.0 g/m for the other 21 minutes.

Another way to infer vapor flow rate from measurable variables is to use the change in concentration:

$$\dot{m}_{\text{Vapor}} \sim \Delta X \cdot (\dot{m}_{\text{Inlet}})$$

The method did not work well for either this or the previous test. This outcome is most likely the result of small bias errors in one or both of the density measurements. A relatively small bias in either the inlet or outlet density measuring instrument will result in a large inferred vapor rate error.

An independent check on the density instrumentation was made by measuring mass of known volumes of solution samples taken from the supply and receiver tanks. Tank sample densities and temperatures have been converted to concentrations and the water loss inferred (based on 4466 g entering the desorber between 15:13 and 17:45 on 2002.07.03) using the same procedure applied to micro-motion density data. The results are summarized below.

During the warmup period the two micromotion sensors should have indicated the same concentration but the indicated outlet concentration was ~1% lower than the indicated inlet concentration. This explains the difficulty of inferring desorbed mass from the Micro-motion density data when the actual concentration difference is on the order of only 2%. The most direct way to measure desorbed vapor mass is by the scale. The result is consistent with vapor rate based on one-time tank density. Scale accuracy is nominally 0.1 g

but there are additional sources of error to consider including LiBr carryover and shifting of the apparatus attached to the weigh tank. It appears, nevertheless, that the scale readings provided a very good measure of vapor generation.

3.2.2 Energy Balance

Energy streams crossing the test article control volume include the solution inlet and outlet enthalpy rates, the vapor enthalpy (energy out), jacket losses (energy out), and the electric heaters (energy in). Power input to the block heater, PblkHtr, is measured directly. The formulas for other components of the energy balance are summarized below:

$$\begin{aligned} m \cdot h_{\text{SolnIn}} &= m_{\text{DotSolnIn}} \cdot \text{solnEnthalpy}(x_{\text{SolnIn}}, T_{\text{SolnIn}}) \cdot K_u \\ m \cdot h_{\text{SolnOut}} &= m_{\text{DotSolnOut}} \cdot \text{solnEnthalpy}(x_{\text{SolnOut}}, T_{\text{SolnOut}}) \cdot K_u \\ m \cdot h_{\text{VaporOut}} &= m_{\text{DotVapor}} \cdot h_{\text{gSteam}}(\text{vapDens}, T_{\text{vapor}}, B, C) \cdot K_u \\ \text{vapDens} &= \text{rhoSteam}(P_{\text{vapor}}, T_{\text{vapor}}, B, C) \\ B &= \text{virial2}(T_{\text{vapor}}); C = \text{virial3}(T_{\text{vapor}}) \\ \text{JacketLoss} &= U A_{\text{wrtBlkHtr}} \cdot (T_{\text{htr}} - T_{\text{room}}) \text{ or } U A_{\text{wrtTopPlate}} \cdot (T_{\text{topPlate}} - T_{\text{room}}) \\ P_{\text{topPlateHtr}} &= V_{\text{topPlateHeater}}^2 / R_{\text{topPlateHeater}} \\ K_u &= 1/60 \text{ [min/s]} \end{aligned}$$

The energy balance input error is given by the sum of energy components with positive sign indicating energy flow into the test article:

$$\text{PinError} = P_{\text{blkHtr}} + P_{\text{topPlateHtr}} + h_{\text{SolnIn}} - h_{\text{SolnOut}} - h_{\text{VaporOut}} - \text{jacketLoss}$$

The energy balance components and resulting energy balance input error are plotted in Figure 3.2.1 Heat balance errors for the four quasi-steady periods range from 12.8 to 28.3W representing 18 to 38% of heater power or 31 to 144% of vapor enthalpy rate.

Figure 3.2.1 Energy balance components and energy balance error as a net energy input for 2002.07.03.

3.2.3 Test Results

Vapor rates of 0.44 to 0.98 grams per minute were obtained at 49 to 75 watts heater power with 13 to 50 torr pressure differential across the contactor. The solution entered at 75 to 88 deg. C with subcooling of 7 to 13.4 deg. C and exited at 82 to 94 deg. C with vapor leaving the contactor at 78 to 96 deg. C. Solution inlet mass flow rate was 28 to 31 grams per minute. Five of the tests produced data with low errors on the mass and energy balance so they will be used for computer code validation.

The last test produced almost twice as much vapor generation as the previous tests just by opening the throttle valve between the test article vapor plenum and the refrigerant vapor receiving tank. The implication is that the desorption rate was being constrained by the pressure drop across the valve to the receiving tank. Tests have and will be conducted for the U.S. Army that will also be used for the validation of the computer model. Average test conditions for each of the six test periods are shown in Figures 3.2.2 through 3.2.7

Figure 3.2.2 Average Test Conditions for 2002.07.03 17:25 – 17:45.

Average Test Conditions for 2002.07.03 16:51 – 17:09

Note: Pin and Pout are now measured from the respective header spaces.

* Bulk concentration for receiver tank taken for solution entering from 15:13 to 17:45.

Figure 3.2.3. Average Test Conditions for 2002.07.03 16:51 – 17:09.

Average Test Conditions for 2002.07.03 16:13 – 16:28

Note: Pin and Pout are now measured from the respective header spaces.

* Bulk concentration for receiver tank taken for solution entering from 15:13 to 17:45.

Figure 3.2. 4. Average Test Conditions for 2002.07.03 16:13 – 16:28.

Average Test Conditions for 2002.07.03 15:42 – 16:02

Note: Pin and Pout are now measured from the respective header spaces.

* Bulk concentration for receiver tank taken for solution entering from 15:13 to 17:45.

Figure 3.2.5. Average Test Conditions for 2002.07.03 15:42 – 16:02.

Average Test Conditions for 2002.07.02 16:44 – 17:10

Note: Pin and Pout are now measured from the respective header spaces.

* Bulk concentration for receiver tank taken for solution entering from 15:40 to 17:10.

Figure 3.2.6. Average Test Conditions for 2002.07.02 16:44 – 17:10.

Average Test Conditions for 2002.07.02 16:06 – 16:31

Note: Pin and Pout are now measured from the respective header spaces.

* Bulk concentration for receiver tank taken for solution entering from 15:40 to 17:10.

Figure 3.2.7. Average Test Conditions for 2002.07.02 16:06 – 16:31.

3.3.4 Comparison with Simulation

The experimental results presented above were used to validate the lattice-Boltzmann computational fluid dynamics computer code described in section 3.5. The results of the comparison are presented in Section 3.5.

3.2.5 Observations

The end-of-test receiver tank solution density measurement was key to corroborating the weigh-scale data. A few additional measurements would provide a much higher level of confidence: all three tank weights should be taken at start and end of testing or use scales with data output ports that can be written to disk. In addition to solution tank temperatures and densities, it would also be useful to quantify lithium bromide carryover by measuring refrigerant receiver tank density and temperature.

It appears that solution mass flow and density measurements cannot be made with sufficient accuracy to infer refrigerant generation rates using the existing apparatus. Solution and refrigerant tank masses, densities and concentrations at start and end will still be needed for corroboration. Inserting a by-pass loop around the test article so that the two mass flow and density meters can be calibrated to one another at the beginning and end of each test. Use of solution mass flow difference to infer vapor separation rate faces the additional problem of variable mass holdup in the test article.

The test article was removed from the test stand and opened up for cleaning and observation. There were no holes in the contactor though it had quite a bit of rust on it. It was good to see that the test article could be used for multiple tests without having to remove and change the contactor in between tests. The contactor had been washed in-situ with deionized water in between tests in March and July

SECTION 3.3 Experimental Investigations of Thin Film Absorption and Desorption Two-Phase Fluid Dynamics (Task 3)

Task 3 has been divided into several subtasks. The first subtask was undertaken during the first year of the project and consists of the design, fabrication and initial testing of the test loop components to be used for the global measurements as well as the flow visualization of both the absorption and desorption within the thin constrained film. The design of the testing facility flow loop was extensive because of several revisions necessary to obtain reliable and accurate data. The iterations used to arrive at the final flow loop and instrumentation has been documented in the quarterly and annual reports previously submitted and are not repeated in this final report. The design of the system is based on meeting the requirement of developing a unique capability for flow visualization in an absorption/desorption test loop for the study of the model problem. The system was designed to allow a thin, constrained, film of a binary fluid to be visually studied for bubble formation and bubble dynamics. Tests were designed to be carried out over a range of relevant operating conditions. The flow visualization is coupled with precise measurements of the operating conditions to allow accurate assessment of the global energy and mass balances associated with process. As discussed in the Year One annual report the design process was preceded by the development of a detailed flow loop operational analysis model. Both the absorption and desorption process were studied. This predictive model allows input of a wide range of operating parameters and fluid properties. Much of the design was driven by a design stage uncertainty analysis that allowed selection of appropriate instrumentation for flow rate, pressure and temperature data collection, with specific regard to sensitivity of the various data to the overall desorption/adsorption energy balance calculations. It should be noted that several iterations were required before arriving at the final test section used in the results reported in this final report. These have been documented in the previous annual reports and are not repeated here.

BACKGROUND

The desorption process of a binary fluid consists of extracting at least one component by adding heat at the required temperature and pressure so as to drive off the more volatile component as a vapor. The result is a change of mass fraction of the binary fluid as it flows through the system in a continuous flow process. Much work has been done in the study of film desorption, where a thin film flows along a wall with a free surface from which desorption occurs. The film thickness offers a diffusive resistance which limits the rate of desorption. Interesting phenomena that contribute to this effect include the vapor-liquid equilibrium condition as well as the interfacial mass transfer process, Wadekar and Hills [1]. The conditions of the film surface have been shown to have a strong effect on the transport rates through the film. Persson and Holmberg [2] investigated the result of film instabilities on the transport of heat and mass in a lithium bromide aqueous solution. By the addition of surfactants Persson and Holmberg were able to show changes in the film flow regime. Damping of the surface waves with increased surfactants, as well as delaying the onset of turbulence in the film, decreased the transport properties of the films. Obviously, increasing the transport rate of the volatile vapor, per flow rate of binary fluid, would be advantageous to the overall efficiency of absorption refrigeration systems.

The most obvious means of reducing the film resistance would be to decrease the film thickness, all other parameters remaining the same, Drost, et al. [3]. However, in falling film desorbers the film thickness is not easily controlled. Consequently, an alternative approach would be to use an ultra-thin constrained film which allows vapor transport through one or both sides of the film. The discussion that follows is based on the use of an aqueous lithium bromide mixture, where water is desorbed by adding heat. In such a system, if a channel can be designed to a very high aspect ratio, with one or both sides of the wide channel walls made from a hydrophobic porous membrane, then an extremely small film thickness is possible. Vapor removal is achieved by applying a pressure difference across the membrane. The hydrophobic property would allow a reasonably high pressure difference to exist across the membrane without allowing liquid transport through the membrane. In addition to the pressure difference required to remove the vapor, the vapor desorption rate is also determined by the evaporation rate at the liquid surface formed at the membrane. Such a system is not necessarily new. For instance, vacuum membrane distillation relies on a similar configuration where a pressure differential across a porous membrane in the distiller drives the vapor content of the high temperature mixture out of the feed plenum. A review of membrane distillation is given by Lawson and Lloyd [4]. The transport rate, and thereby the distillation

efficiency, is influenced by the mass fraction and temperature gradients across the channel, Kurokawa, et al. [5], Tomaszewska [6], Bandini and Sarti [7], and Sudoh et al. [8]. The membrane flux characteristics are typically modeled based on a form of Darcy's law with a linear relationship between the mass flux and the partial pressure gradient across the membrane, which is defined by the membrane permeability, Martinez-Diez and Vazquez-Gonzalez [9]. However, more complex models may be needed depending on the pore characteristics and thermodynamic conditions. For instance, Knudsen limited diffusion occurs when the mean free path of the vapor molecules becomes large relative to the pore size. Also, in the microscale system described in this paper, questions arise as to the effects of high flow rates near the membrane surface and how this flow condition affects the vapor-liquid surface equilibrium.

In this study a new approach to increasing desorption effectiveness is evaluated for potential use in small scale applications. The goal is to reduce the size and weight of an absorption refrigeration cycle by taking advantage of the high transport rates associated with using microscale energy transfer devices. By using an ultra-thin film, in which one wall of the channel is defined by a hydrophobic membrane, reduced mass transfer resistance can be realized. In addition, by controlling the flow rates and heat flux levels the temperature and concentration gradients will be controlled, to some extent.

In contrast to membrane distillation, the ultra-thin film membrane desorption process utilizes heat addition through the membrane surface. The configuration used in this study is a high aspect ratio channel, with heating of the binary mixture occurring at the membrane surface. This results in a favorable temperature gradient at the membrane surface; the higher temperature near the membrane supports enhanced desorption in the vicinity of the membrane. This is in contrast to membrane distillation that typically must overcome an adverse temperature gradient at the membrane. The objectives of the present work are to: (i) show the feasibility of desorption of a lithium bromide mixture in a high aspect ratio microchannel with one wall defined by a hydrophobic porous membrane, (ii) identify the influences of the heat input, inlet mass flow rate, and pressure difference across the membrane, on the desorption rate.

EXPERIMENTAL TEST FACILITIES

The desorber test section for the desorption process study is presented in exploded view in Fig. 3.3.1. Defining the channel is a 381 μm thick silicone gasket layer. Four circular openings in the gasket allow for the use of 350 μm shims to ensure the even compression of the gasket which defines the channel thickness. The upper wall of the channel is defined by a 0.95 cm (3/8 inch) polycarbonate top plate. The porous membrane defines the lower wall of the channel; a PTFE (Teflon[®]) membrane with 0.45 μm pore size on a polypropylene backing structure. This PTFE membrane is naturally hydrophobic preventing liquid transport, while the pores allow vapor transport through the membrane. The water break-through pressure is reported by the manufacturer to be approximately 16 psi. A breakthrough pressure facility was constructed and static tests were run on all membranes prior to inserting them in the test section.

Figure 3.3.1 Exploded view of the test section.

Due to the pressure difference between the channel and the vapor plenum, the membrane is supported by a porous aluminum stiffener. The porous aluminum has a nominal pore size of 15 μm and an upper temperature limit of 230 $^{\circ}\text{C}$. Because of the significant pore size difference between the membrane and the porous aluminum, the latter has virtually no contribution to the overall pressure loss of the vapor out of the test section. Within the porous aluminum stiffener, a 0.305 mm (0.012 inch) nickel chromium heating wire is embedded with epoxy in a spiral pattern to provide an even distribution of heat flux on the lower wall of the channel. The main body and back plate were machined from polysulfone. To minimize heat loss to the environment, the entire structure was insulated.

Initially heating was designed to be supplied through the transparent wall used for visualization. To accomplish this a transparent heater was needed. Figure 3.3.2 shows the vapor deposited ITO heater onto a glass substrate. There are two vapor deposited copper leads on either side of the heater to which external connection are made. The heater resistance was measured and found to be uniform across a random number of sampling points, thereby providing uniform heat flux to the channel. This was not used in the reported results since it was determined that heating from the porous membrane side of the test section would eliminate adverse thermal gradient effects. However it may be advantageous in future studies of extremely thin channels where these gradients may be reduced.

Figure 3.3.2. Vapor deposited ITO heater on a glass substrate with copper strips on either side acting as bus bars.

A representative schematic of the flow loop is shown in Fig. 3.3.3 with photographs given in Fig. 3.3.4. The flow was driven by a pressure difference between the supply tank and the collection tank. This difference in pressure was maintained constant through the use of vacuum regulators on each tank. Due to the decrease in mass of the supply tank over time the pressure in the tank decreases. To maintain a constant pressure in the supply tank a vacuum regulator was connected to the tank and opened to atmosphere. A vacuum pump initially decreases the pressure in the supply tank to the desired setting. The pressure in both the vapor and LiBr collection tanks increases over time due to the influx of mass into each tank. Both tanks were maintained at constant pressures through the use of vacuum regulators connected to a low pressure source. A surge tank in connection with a vacuum switch and a vacuum pump was used to maintain the lower pressure source.

Figure 3.3.3. Schematic of the flow loop.

Each tank's pressure, the desorber inlet pressure, and vapor plenum's pressure, were measured with vacuum transducers connected to the data acquisition system. The pressure transducers were calibrated versus a standard digital manometer from 32.4 kPa to 101 kPa (0 to -10 psig). The differential pressure between the inlet and exit plenums of the test fixture was measured with a pressure transducer calibrated against a micro-manometer up to 6.89 kPa (0 to 1 psig). Pressure signals were recorded at a sampling rate of 100 samples per second.

The flow rate of the mixture through the system was maintained by controlling the pressure difference between supply and collection tanks, and setting the upstream and downstream needle valves. Coriolis mass flow meters were used to measure the flow rate and density of the mixture, and were calibrated versus a catch and weigh method throughout the desired operational range of 0 to 8 g/min.

(a)

(b)

Figure 3.3.4. (a). Photograph of the test loop supply tanks and computer data acquisition system. (b) Photograph of the test loop showing the exposed test section on the lower left.

The corresponding frequency signal for the mass flow rate was 0 to 12 kHz. The frequency of the signal was measured through digital counters in the data acquisitions system with a gate time of 0.2 seconds, corresponding to a sample rate of 5 samples per second. Both the density and temperature outputs were measured at each mass flow meter and recorded in the data acquisition system through milliamp outputs at a sample rate of 100 samples per second.

To set the inlet temperature, a constant temperature bath upstream of the desorber was used. The bath was controlled by a PID controller and maintained within 0.2 °C. Inlet, exit, and vapor temperatures were measured with T-type thermocouples, connected to a data logger. Temperature values were read by the data acquisition system at the beginning of each recorded interval.

A heat exchanger downstream of the desorber cooled the exiting mixture down to room temperature, i.e. the same temperature as the upstream mass flow meter. This temperature control helped decrease the uncertainty in density measurements.

The measurements were recorded by the data acquisition system at 20 second intervals, in both voltage and calibrated value files. At each interval the mean and standard deviation of each of the individual measurements over a 3 second time period were recorded. This corresponds to 300 samples for each of the pressure and density measurements, as well as the mass flow meter temperature measurements. For the mass flow rate a total of 15 samples were averaged and recorded. At the same time period the data acquisition system read the temperature values from the data logger. The instantaneous signals of the inlet pressure, differential pressure, densities, and mass flow rates were also recorded separately for further study of the time dependent results.

Imaging System for Flow Visualization

The flow visualization system is designed to observe and record the two phase flow phenomena inside the constrained film. In order to do this one side of the channel is made transparent using a quartz plate. This plate was machined to fit into the test section. The rectangular quartz, approximately 6 mm thick has a 3 mm recessed ledge around the periphery which has a gasket to seal the window. A high speed camera (run at 1000 fps) was used to record the boiling process, and a slow speed camera (run at 30 fps) was used to monitor boiling in the non-boiling set of tests.

Energy Balance model and Data Analysis

Identifying the inlet, exit, and vapor streams as shown in Fig. 3.3.5, the mass balance for the control volume defining the desorber is given by:

$$\dot{m}_i = \dot{m}_e + \dot{m}_v \quad (1)$$

where $\dot{m}$ represents the mass flow rates of the respective inlet, exit, and vapor streams, denoted by the i, e, and v subscripts, respectively. The mass fraction, X, of the mixture is defined as:

$$X = \frac{m_{\text{LiBr}}}{m_{\text{H}_2\text{O}} + m_{\text{LiBr}}} \quad (2)$$

Figure 3.3.5 Schematic of the test section mass and heat flow

Species balances for the water and lithium bromide in the mixture stream are, respectively:

$$(1 - X_i)\dot{m}_i = \dot{m}_v + (1 - X_e)\dot{m}_e \quad (3)$$

$$X_i\dot{m}_i = X_e\dot{m}_e \quad (4)$$

An energy balance for the control volume of the desorber can be written as follows:

$$q = \dot{m}_v h_v + \dot{m}_e h_e - \dot{m}_i h_i \quad (5)$$

with q representing the heat input to the desorber and h the enthalpy of the respective streams.

Based upon the collected measurements given previously, the mass fraction change of the mixture can be determined along with the mass flow rate of vapor, and heat input to the desorber. The mass fraction calculation is based on the correlation from Fried and Segal [10], using the measured temperatures and densities at the upstream and downstream mass flow meters. Even though a binary mixture requires three independent properties (density, temperature, and pressure) to determine its mass fraction, the pressure has a negligible effect on mass fraction in the range tested (43 to 101 kPa).

Equations (1), (3), and (4) can be rearranged to yield the mass flow rates of the exit and vapor streams, based on the measured inlet mass flow rate and the mass fraction ratio X_i/X_e

$$\dot{m}_e = \frac{X_i}{X_e} \dot{m}_i \quad (6)$$

$$\dot{m}_v = \left(1 - \frac{X_i}{X_e}\right) \dot{m}_i \quad (7)$$

where only water vapor is assumed to pass through the porous membrane.

Substituting the exit and vapor mass flow rates, using Eqs. (6) and (7), into the global energy balance, Eq. (5), yields:

$$q = \left[\left(1 - \frac{X_i}{X_e}\right) h_v + \left(\frac{X_i}{X_e}\right) h_e - h_i \right] \dot{m}_i \quad (8)$$

which determines the heat input to the desorber based on the inlet mass flow rate, and mass fractions at the inlet and exit. The enthalpies of the mixture stream at the inlet and exit were determined from the mass

fraction and temperature at the respective locations. Mean saturation conditions of the mixture in the channel were used to determine the enthalpy of the vapor. The heat flux, q'' , to the desorber and the mass flux of vapor, G_v , are both defined by dividing q and $\dot{m}_v$, respectively, by the surface area of the membrane in the channel.

The uncertainties for the measurements were calculated for all of the operating conditions. These uncertainties include both the instrument's bias and precision errors. The Kline-McClintock method was used to find the propagation of the measurement uncertainties into the calculated values. Typical results for the uncertainties of the calculated mass fraction, vapor mass flow rate, and heat input are 0.27%, 7.6%, and 6.9%, respectively.

RESULTS

Two primary sets of experiments were run in the test facility to determine the operating characteristics of the ultra-thin membrane vapor extraction during desorption. The first set, labeled "Non-boiling Desorption", were based on runs where no observed bubble formation occurred within the channel. In these tests the inlet concentration was held constant and was run with heating levels below that required for observed boiling within the test section. In this set one pressure differential across the membrane was used. The second set of experiments, labeled "Boiling Desorption", were those tests where the input heat flux resulted in both no boiling as well as observed boiling in the test section channel. When bubbles did occur, however, runs were limited to those where no bubbles were observed to leave through the exit port of the channel used to extract the LiBr-water mixture. That is, all vapor produced in the test section extracted the test section through the membrane. In this second set results are obtained for two different film thicknesses and for two pressure differences across the membrane.

Results: Non-boiling Desorption

All of the results presented below are for an average inlet mass fraction of 42.3 ± 0.1 percent, an average pressure difference across the membrane of $1.97 \pm .04$ psi, and an average inlet pressure of 6.97 ± 0.02 psia. At the given operating conditions the inlet saturation temperature was 94.4 ± 0.3 °C which resulted in an inlet subcooling of 12.6 ± 1.6 °C. Four mass flow rates between 4 and 7 g/min were run with seven heat flux levels at each mass flow rate. The inlet mass flow rates were held to within 0.1 g/min of the desired flow rate for each heat flux. The channel height was measured to be 320 ± 60 μm over the 4 cm by 3 cm channel area. For each inlet mass flow rate the heat flux was increased to the first evidence of boiling was observed in the defined 4 cm by 3 cm channel area.

Figure 3.3.6. Mass flux of vapor versus calculated heat flux into the thin film

Figure 3.3.7. Ratio of vapor mass flow rate to inlet mass flow rate versus calculated heat flux into the thin film

The mass flux of vapor versus the calculated heat flux is shown in Fig 3.3.6. Evident from these results is that there is a linear dependence of mass flux of vapor to heat flux into the constrained thin film which is independent of the inlet mass flow rate. Thus, for the cases studied up to the point of boiling, the desorber did not reach a diffusion limit condition. If the desorber became diffusion limited it would be observed that the slope of mass flux of vapor would decay with increasing heat flux. The ratio of vapor mass flow rate to inlet versus the calculated heat flux into the thin film is shown in Fig 3.3.7. The trend at a given heat flux was an increase in vapor flow rate ratio with a decrease in inlet mass flow rate. That is, more vapor is removed by the desorber per inlet mass flow rate as the flow rate decreases. In comparing the ratios for inlet flow rates of 4 g/min and 7 g/min at a heat input of 0.62 W/cm² there was a 59% increase in the ratio of mass flow of vapor to inlet mass flow rate. Therefore in an application where there is a limit to the available supplied heat flux then the inlet mass flow rate should be kept relatively low.

Figure 3.3.8. Mass flux of vapor versus wall superheat

Figure 3.3.9. Ratio of mass vapor flow rate to inlet mass flow rate versus wall superheat

Figures 3.3.8 and 3.3.9 show the mass flow rate of vapor and the ratio of mass flow of vapor to inlet mass flow rate versus the amount of wall superheat, respectively. The wall superheat is the temperature difference between the mean wall temperature and the inlet saturation temperature based on inlet pressure and concentration. The mean wall temperature was determined from wall temperature measurements located at the inlet of the channel area, center of the channel and exit of the channel area along the centerline of the channel. For each inlet mass flow rate there is a linear relationship between the wall superheat and mass flux of vapor produced. With the exception of the 6 g/min case, the slope of the linear trend decreases with a reduction in mass flow rate. For a given superheat temperature more vapor is removed at a higher mass flow rate. In contrast to the results from Fig 3.3.7, the results from Fig 3.3.8 suggest that if there is a temperature limitation for the desorber, higher relative inlet mass flow rates should be used. By scaling the mass flow rate of vapor by the inlet mass flow rate, collapses all the cases onto a single linear trend, as shown in Fig 3.3.9. This suggests that the change in slope of the trends in Fig 3.3.8 is directly proportional to the change in inlet mass flow rate.

Figure 3.3.10. Mass flux of vapor versus the fraction of latent heat flux to total heat flux

Figure 3.3.11 Fraction of mass flow rate of vapor to inlet flow rate versus the fraction of latent heat flux to total heat flux.

Figure 3.3.10 and Figure 3.3.11 show the mass flux of vapor and the ratio of vapor mass flow rate of to inlet mass flow rate versus the ratio of the latent heat flux to the total heat flux into the desorber, respectively. The total heat flux was calculated with the measured inlet and exit temperatures, whereas the latent heat flux was calculated from the saturation inlet and exit temperatures. As the ratio of latent heating to total heating increases the mass flux of vapor increased, as expected. Due to the inlet subcooling, there is a large amount of sensible heating from these results. If the inlet subcooling was reduced it is expected that less energy would be required. For a vapor mass flux of 0.1 g/min/cm^2 40 percent less heat input would be required. Thus if a system is limited to the available heat flux, and has minimal inlet subcooling, higher inlet mass flow rates may be used than a system with greater inlet subcooling. By scaling the mass flow rate of vapor by the inlet flow rate, all of the curves collapse onto a single curve as shown in Fig 3.3.11.

Table 3.3.1. Boiling heat flux for inlet mass flow rates

$\dot{m}_i \text{ [g/min]}$	4.0 ± 0.1	5.0 ± 0.1	6.0 ± 0.1	7.0 ± 0.1
$q''_{\text{boil}} \text{ [W/cm}^2\text{]}$	0.62 ± 0.06	0.76 ± 0.06	0.70 ± 0.07	0.9 ± 0.09

Table 3.3.1 lists the heat flux when boiling was first observed for each mass flow rate. As expected, the heat flux required for boiling increases with increasing mass flow rate, with the exception of the 6 g/min case where there is a slight decrease of heat flux at the onset of boiling. The reason for this is not known at this time and these results will be retested.

Result: Boiling Desorption

Data are presented for the desorption behavior under varying conditions of the inlet concentration, pressure difference across the membrane, and channel height. Results are depicted in two ways: the first shows the trends between the ratio of vapor mass flow rate to inlet mass flow rate versus the wall superheat temperature, and the second set shows the effectiveness ratio, q''/Φ , versus the vapor mass flow to inlet mass flow rate ratio. Within these two comparisons the results are further divided up to show the effect of the three parameters varied: inlet concentration, pressure differential, and channel height.

The wall superheat temperature is defined as the temperature difference between the average wall temperature and the inlet saturation temperature. Other parameters are calculated such as the vapor mass

flow rate, $\dot{m}_v$, and the heat input, q'' . While the inlet mass flow rate, $\dot{m}_i$, and energy input flux, Φ , are measured.

In the figure legend, the data sets are identified by the nominal inlet concentrations, pressure difference across the membrane, and channel height. Three different inlet concentrations, two pressure differentials, and two channel heights were tested. These data sets are summarized in the Table 3.3.2.

Figure 3.3.12 gives a representation of three stages of boiling observed within the microchannel for a single test case, although all test cases behaved similarly. Boiling in the early stages consisted of sporadic nucleation occurring every 3 to 5 seconds. The bubbles were observed to nucleate within the channel and grow in size quite rapidly. They tended to travel vertically (caused by buoyancy forces) and slightly downstream within the channel until they were drawn off through the membrane. At the higher heat flux settings nucleation occurred more frequently and a larger void fraction in the channel occurred. It was observed that the bubbles nucleated and grew faster as ΔP was decreased. Both cases were not heated beyond the point where the void fraction in the channel was approximately 60 to 70%.

Table 3.3.2. Boiling data test cases indicating inlet concentration, membrane pressure difference, and channel height.

Test Case	Inlet LiBr Concentration [%]	Pressure Differential [kPa]	Channel Height [μm]
#1	30	6.21	150
#2	30	12.4	150
#3	40	6.21	150
#4	40	12.4	150
#5	50	6.21	150
#6	50	12.4	150
#7	30	6.21	750
#8	30	12.4	750
#9	40	6.24	750
#10	40	12.4	750
#11	50	6.21	750
#12	50	12.4	750

At this point the bubbles were beginning to approach the exit of the channel. Therefore all cases reported were such that vapor formed in the channel was ultimately extracted through the membrane, and did not flow out the exit with the mixture. The nucleation and growth of the bubbles were influenced by the temperature of the porous stiffener and pressure difference across the membrane. While not presented in here, pure water were run through the desorber and the results for nucleation within the channel are quite different. Comparing boiling of the lithium bromide mixture to pure water, much higher wall superheats are required to nucleate in the channel, which can be explained by the diffusion resistance imposed by the lithium bromide. Due to the high superheat for the LiBr mixture, the bubble formation shows a much more rapid bubble growth than in the case of pure water. Once the water vapor is released from the mixture, it expands rapidly as it becomes superheated. At higher values of ΔP , the increase in transport through the membrane decreases the growth rate of the bubbles in the channel. For a specified heat flux the vapor formed at the interface tended to nucleate only if it was not drawn off fast enough. Thus the higher ΔP allowed more vapor to be drawn directly off at the interface instead of nucleating into the channel.

Presented in Figs 3.3.13, 3.3.14, and 3.3.15 is the comparison between the ratio of vapor mass flow rate per inlet mass flow rate versus the wall superheat temperature. The fixed conditions in each figure are the inlet concentration and channel height, of 150 microns. Thus the effect of the pressure differential across the membrane on the vapor mass flow rate is shown. In all three figures there is a linear trend to the data, in that as the wall superheat temperature increases, the fraction of vapor desorbed also increases linearly. As anticipated increasing the pressure difference across the membrane increases the amount of vapor that is desorbed, therefore these cases are not limited by the vaporization rate within the channel.

Figure 3.3.12 Photographs taken within the microchannel during (a) the onset of nucleate boiling (0.24 W/cm^2), (b) higher heat input (0.30 W/cm^2), and (c) the highest heat input (0.54 W/cm^2), for a membrane pressure difference of $8.96 \text{ kPa } \Delta P$, a flow rate of 3 g/min .

Fig 3.3.13. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 30% inlet concentration and a channel height of 150 microns

Fig 3.3.14. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 40% inlet concentration and a channel height of 150 microns

Fig 3.3.15. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 50% inlet concentration and a channel height of 150 microns

In Figs 3.3.16, 3.3.17, and 3.3.18 the effect of the pressure differential on the amount of vapor desorbed is shown, but for a fixed channel height of 750 microns. Similar to the trends shown for the 150 micron channel, a higher fraction of vapor per inlet mass flow rate is generated for the same wall superheat temperature as the pressure differential is increased. Another point is that the maximum wall superheat temperature varies between the different inlet concentrations and the channel height. Higher wall superheat

temperatures can be achieved (or are allowed) as the inlet concentration decreases and as the channel height increases. Consequently the maximum vapor mass flow rate ratio per inlet mass flow rate also increases as the inlet concentration decreases.

Fig 3.3.16. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 30% inlet concentration and a channel height of 750 microns

Fig 3.3.17. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 40% inlet concentration and a channel height of 750 microns

Fig 3.3.18. Comparison of vapor mass flow rate ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 50% inlet concentration and a channel height of 750 microns

Fig 3.3.19. Comparison of vapor mass flow rate ratio between 30%, 40%, and 50% inlet concentrations, with a channel height of 150 microns and pressure difference of 6.21 kPa

In Figs. 3.3.19, 3.3.20, 3.3.21, and 3.3.22, the effect of changing the inlet concentration with fixed channel heights and pressure differential is shown. A linear trend is seen between the vapor mass flow rate ratio and the wall superheat temperature. In slight contrast, however, to the previous figures showing the effect of the pressure differential, there is less vapor flow rate difference between the different inlet concentrations for a fixed pressure differential and channel height.

Fig 3.3.20. Vapor mass flow rate ratio with inlet concentrations of 30%, 40%, and 50%, channel height of 150 microns and a pressure difference of 12.4 kPa

Fig 3.3.21. Vapor mass flow rate ratio with inlet concentrations of 30%, 40%, and 50%, channel height of 750 microns and a pressure difference of 6.21 kPa

Fig 3.3.22. Vapor mass flow rate ratio with inlet concentration of 30%, 40%, and 50%, channel height of 750 microns and a pressure difference of 12.4 kPa

Fig 3.3.23. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 40% and pressure difference of 6.21 kPa

Similar to the trends seen in plots comparing different pressure differentials, Figs 3.3.23, 3.3.24, and 3.3.25 show the influence of the channel height on the vapor mass flow rate ratio for a given wall superheat temperature. In these three plots the pressure differential is held fixed at 6.21 kPa. As the channel height decreases, the vapor mass flow rate per inlet mass flow rate increases for a fixed wall superheat temperature.

Fig 3.3.24. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 30% and pressure difference of 6.21 kPa

Fig 3.3.25. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 50% and pressure difference of 6.21 kPa

As in the previous figures for a fixed pressure differential of 6.21 kPa, Figs 3.3.26, 3.3.27, and 3.3.28, for a fixed pressure difference of 12.4 kPa, show that decreasing the channel height increases the vapor mass flow rate for a fixed wall superheat temperature. This trend hold true for all three of the inlet concentrations. Other points to note are that the highest vapor mass flow rate ratio and the highest wall superheat temperatures occur in the 30% concentration cases.

Fig 3.3.26. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 30% and pressure difference of 12.4 kPa

Fig 3.3.27. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 40% and pressure difference of 12.4 kPa

Plotted in Figs 3.3.29, 3.3.30, and 3.3.31 is the effectiveness ratio, q'' / Φ , versus the vapor mass flow rate ratio. The effectiveness ratio is representative of the “losses” in the system by comparing the Thermodynamic heat input requirement for a certain amount of desorption, compared to the actual amount of energy put into the system. In contrast to the trends shown for the comparison of the vapor mass flow rate ratio and the wall superheat temperatures, there is little separation between the two pressure differentials when comparing the effectiveness ratio.

Fig 3.3.28. Comparison of vapor mass flow rate ratio between 150 and 750 micron channels for an inlet concentration of 50% and pressure difference of 12.4 kPa

Fig 3.3.29. Comparison of effectiveness ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 30% inlet concentration and a channel height of 150 microns

Fig 3.3.30. Comparison of effectiveness ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 40% inlet concentration and a channel height of 150 microns.

Fig 3.3.31. Comparison of effectiveness ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 50% inlet concentration and a channel height of 150 microns

Continuing the investigation into the effectiveness ratio dependency on the pressure difference across the membrane, shows that the trends for 750 micron channel are similar to the 150 micron channel cases, these results are given in Figs. 3.3.32 through 3.3.34. There is little difference in the effectiveness ratio as the pressure difference varies while the inlet concentration and channel height are fixed. Two trends shown in the previous figures are that the effectiveness ratio is dependent upon the inlet concentration and that there appears to be two different slopes to the data sets. Initially a line through the first few points has a higher slope than the remaining points. This can be related to the transition to boiling in the microchannel

which was typically found to occurred after the third or fourth data point from the minimal heat input, for these sets of results.

Fig 3.3.32. Comparison of effectiveness ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 30% inlet concentration and a channel height of 750 microns

Fig 3.3.33. Comparison of effectiveness ratio between 6.21 kPa and 12.4 kPa pressure differential cases with a 40% inlet concentration and a channel height of 750 microns

Fig 3.3.34. Effectiveness ratio with a pressure differential of 6.21 kPa and 12.4 kPa with a 50% inlet concentration and a channel height of 750 microns

The dependency of the effectiveness ratio on the inlet concentration is shown in Figs. 3.3.35, 3.3.36, 3.3.37, and 3.3.38. For these cases the pressure differential and channel height are fixed. All four plots show an increasing effectiveness ratio as the inlet concentration decreases for a fixed vapor mass flow rate ratio. Also, the variation of the slopes through points within each data set, as noted previously, can also be seen. Some of the reasoning for the higher effectiveness as the inlet concentration decreases is the lower concentration gradients within the channel. As the concentration gradients increase, the mass transport of water is inhibited and thus requires more energy to desorb water.

Fig 3.3.35. Effectiveness ratio with inlet concentrations of 30%, 40%, and 50%, channel height of 150 microns and a pressure difference of 6.21 kPa

Fig 3.3.36. Effectiveness ratio with inlet concentrations of 30%, 40%, and 50%, channel height of 150 microns and a pressure difference of 12.4 kPa

Fig 3.37. Comparison of effectiveness ratio between 30%, 40%, and 50% inlet concentrations, with a channel height of 750 microns and a pressure difference of 6.21 kPa

Fig 3.38. Comparison of effectiveness ratio between 30%, 40%, and 50% inlet concentrations, with a channel height of 750 microns and a pressure difference of 12.4 kPa

Figures 3.3.39, 3.3.40, and 3.3.41 show the effect of the channel height on the effectiveness ratio, while holding the inlet concentration and pressure differential fixed. The most separation between the cases is shown in the 30% inlet concentration case. Both the other cases show little separation in the effectiveness ratio for different channel heights. But the trend seen in the 30% case is that the 150 micron channel has a higher effectiveness ratio than the 750 micron case.

Fig 3.3.39. Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 30% and pressure difference of 6.21 kPa

Fig 3.3.40. Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 40% and pressure difference of 6.21 kPa

Fig 3.3.41. Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 50% and pressure difference of 6.21 kPa

The trends in Figs. 3.3.42, 3.3.43, and 3.3.44 show that there is little effect of the channel height on the effectiveness ratio for a fixed inlet concentration and pressure differential across the membrane. As the inlet concentration increases, the effectiveness ratio decreases and the maximum vapor mass flow rate

achieved also decreases. These results, showing little separation between the different channel heights, agree with the 40% and 50% cases for the pressure differential of 6.21 kPa in Figs. 3.3.40 and 3.3.41, but not the 30% case in Fig. 3.3.39.

Fig 3.3.42 Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 30% and pressure difference of 12.4 kPa

Fig 3.3.43 Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 40% and pressure difference of 12.4 kPa

Fig 3.3.44 Comparison of effectiveness ratio between 150 and 750 micron channels for inlet concentration of 50% and pressure difference of 12.4 kPa.

CONCLUSIONS OF DESORPTION STUDIES

Desorption within a film using membrane separation has been demonstrated using an aqueous lithium bromide mixture. The desorption rate, for a given inlet mass fraction and flow rate, is shown to have a linear relationship with heat flux. The mixture exit mass fraction increases with decreasing inlet mass flow rate for a given heat flux. Bubble formation within the film was observed for the high heat input cases, but was found not to influence the overall performance based on the relationship of vapor flux produced to heat input. However, there is evidence of bubble formation adversely affecting the transfer of heat to the mixture within the channel. Increased wall superheat temperature increases the mass of vapor desorbed linearly. Increasing the pressure differential across the membrane can increase the vapor desorption provided the conditions are not vaporization limited. Decreasing the film thickness for a given superheat temperature and total heat input is shown to have a significant positive effect of increasing the vapor desorption rate. Fundamental issues concerning the diffusion rates within the film, the effect of cross-film thermal gradients, and the impact of bubble formation are needed to optimize the design of future microscale membrane desorption.

SECTION 3.4: INVESTIGATION OF THE DIMENSIONAL STABILITY

Several aspects of the ultra-thin film contactor remain poorly understood, an important one of which is the phenomena affecting the dimensional stability of the liquid film. Early studies have shown that contactor performance is highly dependent on film thickness: for a specified width and mass transfer rate, the required contactor length decreases theoretically as the inverse square of the film thickness [1,2]. The potential for size reduction of absorption and desorption systems employing such ultra-thin film gas/liquid contactors is therefore highly dependent on the ability to reduce the liquid film thickness. However, maintaining a uniform film thickness becomes increasingly difficult as the film thickness is reduced. The focus of this work is on gaining an improved understanding of the viability of using a porous contactor surface to form an ultra-thin film of uniform thickness, and to maintain the integrity of the film thickness during operation of the contactor. This section of the report is condensed from a much longer document that is the primary reference for the data and results presented here (see reference [3]).

Use of a Porous Membrane as the Contactor Surface

The primary goal behind the design of a contactor test section was to use a porous membrane as the permeable surface separating the vapor and liquid phases. A schematic of this setup is shown in Fig. 3.4.1 for both the absorber (Fig. 3.4.1-a) and desorber (Fig. 3.4.1-b) configurations. The test section uses a thin, flexible membrane with a highly-characterizable pore size to mechanically form and constrain a liquid film with a thickness on the order of 100 μm . The membrane requires a stiffening system in order to provide support over a contactor area of several square centimeters. As such, a second goal was to investigate the viability of supporting the membrane using a stiffener plate.

Fig. 3.4.1 Experimental setup for an ultra-thin film contactor utilizing a porous membrane as the contactor surface. (a) Absorber and (b) desorber configurations (solid arrows represent mass flow/transfer; dashed arrows represent heat transfer)

Specific Task Objectives

In order to investigate current capabilities to form an ultra-thin liquid film using a porous membrane as the contactor surface, and to maintain uniform thickness under operating conditions, the following two tasks were identified.

Finite Element Modeling of Stiffener Deflection

The first task was to construct finite element models of the stiffener plate used to support the porous membrane over the contactor area. Specifically, the finite element models were used to investigate the effects of loading the stiffener plate under the maximum pressure differential and operating temperature to be encountered in the desorber setup. The goal was to verify the accuracy of the model results against

actual film thickness measurements. This would allow the modeling technique developed to be used to predict the performance of design changes to the stiffener plate.

Experimental Verification of Film Thickness

The second task was to experimentally measure the film thickness during steady-state operation of the contactor in the desorber configuration. The test section investigated was designed with the goal of limiting the variations in the film thickness to 10 percent of the nominal value. This task therefore required the development and validation testing of a film thickness measurement system capable of characterizing variations in the film thickness on the order of $10\text{ }\mu\text{m}$. Specifically, this involved characterizing both the spatial uniformity of the film thickness at a given pressure differential and steady-state operating temperature, as well as the overall variation in film thickness due to changes in the pressure differential and operating temperature.

Measurement Technique Selected: Laser Triangulation

Laser triangulation sensors measure the distance to a target surface by projecting a beam of laser light (typically visible laser light) onto the surface. Reflected light from the surface is viewed at an angle by a detector consisting of either a pixel linear array or a position-sensing detector (PSD). The distance between the target surface and a reference plane can then be calculated based on the location of the reflected light on the detector.

Operating Principle behind Laser Triangulation Sensors:

The operating principle behind laser triangulation sensors has been widely documented in commercial and other literature. A schematic of a typical laser triangulation sensor is shown in Fig. 3.4.2. A solid-state laser diode generates a beam of visible laser light that is focused by a lens, creating a spot at the standoff distance. The optical design controls the spot diameter, which in turn represents the spatial lateral resolution of the sensor. This lateral resolution is larger at the extremes of the measurement range than at the standoff distance due to the

Fig. 3.4.2 Schematic diagram of a laser triangulation sensor.

beam waist formed by the focusing lens. The imaging lens collects light reflected diffusely off the target surface and images it onto a linear array detector. As shown in Fig. 3.4.2, the location of the spot on the detector depends on the location of the target surface within the measurement range. Each element of the array generates a voltage corresponding to the amount of light incident upon it. The precise location of the spot on the detector is then determined by calculating the weighted centroid of the array data, which gives

the center of the spot to a fraction of a pixel. This in turn can be used to very accurately calculate the location of the target surface.

Application to the Current Liquid Film Thickness Measurement Task

In order to measure the liquid film thickness, the two surfaces constraining the liquid film needed to be imaged: the front of the membrane and the back of the quartz viewing window. However, laser triangulation is not well-suited for measuring the distance to a transparent surface such as the back of the quartz window. Instead, an idea was conceived to coat small, selected regions on the back of the quartz window with a very thin opaque film, forming a grid of film thickness measurement points. As shown in Fig. 3.4.3, this would allow the sensor to image both the near side of the film (when the laser was incident upon the opaque film) and the far side (when the laser was incident upon the membrane). The difference between adjacent measurements to these two surfaces, once corrected for the effects of refraction, would provide a direct measurement of the local film thickness. Commercial vapor-deposition processes allow alloys such as nickel-chromium (NiCr) to be deposited on quartz with film thicknesses on the order of 100 nm. Such a thin coating would be required in order to avoid affecting the flow of liquid through the test section.

Fig. 3.4.3 Film thickness measurement technique utilizing a laser triangulation sensor and vapor-deposited NiCr

A laser triangulation sensor produced by Acuity Research, Inc. was purchased in order to verify whether or not the technique was feasible for the given measurement task. The particular model purchased was the high-resolution, 5 mW version of the AR600-0125, which uses a 670 nm red diode laser and has a resolution of 0.32 μm and a linearity of $\pm 0.95 \mu\text{m}$ [4]. Initial testing quickly revealed that using the sensor to image the NiCr coating, which had a mirror-like finish on the smooth quartz surface, resulted in unreliable data. As discussed in the literature, the primary limitation on the accuracy of laser triangulation sensors arises due to their reliance on the diffuse component of light reflected from the target surface. Highly specular surfaces (e.g., mirrors or polished metals) can be difficult to measure if too little diffusely-reflected light reaches the detector. In order to minimize this problem, a technique was developed that involved particle-blasting selected regions of the quartz window before deposition of the NiCr. Implementing the proposed liquid film thickness measurement technique also involved a method to correct

for refraction that occurred at the air-quartz and quartz-liquid interfaces. This will be described in a later subsection.

THEORETICAL ANALYSIS

Early in the design of the ultra-thin film contactor test section, analytical modeling techniques were used to assess the effects of the stiffener plate size, test section construction, and operating conditions on the mechanical deformation of the stiffener plate. The analytical deflection equations used in these analyses are described below. In a separate analysis, a theoretical approach for correcting the readings from the laser triangulation sensor for refraction is described, and the resulting relationships are presented.

Analytical Beam and Plate Deflection Equations

A primary design goal of the test section construction was to limit the stiffener plate deflection to a specified amount during operation of the device at a specified maximum pressure differential. To accomplish this, various plate materials and dimensions (length, width, and thickness) were considered. In addition, several potential configurations of the stiffener plate in the test section were investigated. These primarily involved variations in the number of supported edges (either all four edges or the two long edges only) and variations in the method used to secure the plate at its supported edges. To investigate these size, material, and configuration possibilities, the stiffener plate was modeled analytically as both a beam (two supported edges) and a plate (four supported edges) loaded in bending under a uniformly distributed load equal to the maximum pressure differential to be encountered under operating conditions.

The maximum elastic deflection, $w_{\max}$, at the center of a beam with simple supports at both ends and subject to a uniformly distributed load, q (units of force per unit length), is given by [5,6]

$$w_{\max} = \frac{5qL^4}{384EI} \quad (1)$$

where L is the length of the span, E is the elastic modulus of the beam material and is constant, and I is the second moment of area about the neutral bending axis and is constant. For a beam with a rectangular cross section, I is given by

$$I = \frac{bh^3}{12} \quad (2)$$

where b is the breadth of the beam and is constant, and h is the height of the beam cross section and is constant. On the other hand, if both simple supports are replaced by clamped supports, the maximum elastic deflection is given by [5]

$$w_{\max} = \frac{qL^4}{384EI} \quad (3)$$

Similarly, the maximum “small” elastic deflection, $w_{\max}$, at the center of a “thin” rectangular plate subject to a uniformly distributed load, p (units of force per unit area), is given by [7]

$$w_{\max} = C_{S,F} \cdot (1 - \nu^2) \cdot \frac{pL_2^4}{Eh^3} \quad (4)$$

where E is the elastic modulus of the plate material and is constant, ν is Poisson’s ratio of the plate material and is constant, h is the thickness of the plate material and is constant, L_1 and L_2 are the length and width of the plate, respectively (with L_2 being the shorter of the two), and $C_{S,F}$ is a constant whose value depends on both the ratio L_2/L_1 and on the types of supports at the plate edges. In the derivation of these equations, $w_{\max}$ is assumed to be much less than the plate thickness h , and the strains and midplane

slopes are assumed to be much less than unity (the “small” deflection assumption). In addition, h is assumed to be at least one order of magnitude less than the spans L_1 and L_2 (the “thin” plate assumption). For a plate with four simply-supported edges, C is denoted by the subscript S and is given by [7]

$$C_S = \frac{0.16}{1 + 2.4(L_2/L_1)^3} \quad (5)$$

On the other hand, for a plate with four clamped edges, C is denoted by the subscript F and is given by

$$C_F = \frac{0.032}{1 + (L_2/L_1)^4} \quad (6)$$

In order to facilitate direct comparison of the deflection results obtained for a stiffener plate with a fixed size but supported along either all four edges or the two long edges only, it is instructive to rearrange the beam equations to depend on the same load and length parameters as the plate equations. This can be accomplished by replacing the parameter q (force per unit length) in Eqs. (1) and (3) with the parameter p (force per unit area) multiplied by the appropriate beam dimension. To model the scenario in which the stiffener plate is supported on the two long edges (as opposed to the two short edges), the appropriate dimension is the width, b (as opposed to the length, L).

$$q = pb \quad (7)$$

When combined with Eqs. (2) and (7), Eqs. (1) and (3) become, respectively,

$$w_{\max} = \frac{5}{32} \cdot \frac{pL^4}{Eh^3} \quad (8)$$

and

$$w_{\max} = \frac{1}{32} \cdot \frac{pL^4}{Eh^3} \quad (9)$$

In addition, the parameter L in Eqs. (8) and (9) must be replaced by the appropriate plate span dimension. Again, since the intent is to model the scenario in which the stiffener plate is supported on the two long edges, the shorter of the two dimensions, L_2 , is the appropriate choice for this substitution. The deflection equations for a simply-supported beam and a clamped beam then become, respectively,

$$w_{\max} = \frac{5}{32} \cdot \frac{pL_2^4}{Eh^3} \quad (10)$$

and

$$w_{\max} = \frac{1}{32} \cdot \frac{pL_2^4}{Eh^3} \quad (11)$$

It is also important to note that the plate equations are only valid if both the “small” deflection and “thin” plate requirements are met. The deflections involved in the present analysis easily satisfy the small deflection requirement. However, the thin plate requirement is only approximately met, and will demonstrate more error for the thicker stiffener plates examined.

Correcting for Refraction Effects – Theoretical Method

The laser triangulation sensor operates by focusing a beam of visible laser light onto the surface to be measured, with the beam oriented orthogonally to the surface. The line scan camera inside the device then views at an angle the portion of the laser light that is scattered diffusely by this surface. In the present measurement task, the sensor must view the laser spot through various mediums with varying optical properties: air, the transparent quartz window of the test section, and, for the measurements to the

membrane, the liquid in the ultra-thin film. Since the camera views the laser spot at an angle, the effects of refraction must be taken into consideration. The following describes one approach based on a theoretical model of the ray optics involved.

Relating the Apparent and Actual Local Film Thicknesses

The apparent local film thickness, ΔZ_{app} , is calculated by taking the difference between adjacent distance measurements to the membrane surface and the NiCr film on the quartz viewing window (Z_m and Z_n , respectively).

$$\Delta Z_{app} = Z_m - Z_n \quad (12)$$

Deriving an explicit function that describes the dependence of the actual film thickness, ΔZ_{act} , on ΔZ_{app} is not feasible; however, it is possible to calculate ΔZ_{act} from ΔZ_{app} by solving the system of equations describing the ray optics involved.

The law of refraction from optics, more commonly known as Snell's Law, is required to describe how a beam of light is "bent" when it passes from one medium into another,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (13)$$

where n_1 and n_2 are the indices of refraction of mediums 1 and 2, respectively, and θ_1 and θ_2 are the respective angles formed between the incident beam in mediums 1 and 2 and the normal of the plane containing the medium boundary. Figure 3.4.4 schematically shows the parameters involved in this theoretical correction for the effects of refraction. It also illustrates the effect that refraction has on the measured film thickness, causing the laser triangulation sensor to "see" an apparent film thickness less than the actual film thickness.

The following mediums are involved in the refraction correction problem: 1.) air, 2.) fused quartz (used for the viewing window); and 3.) the liquid that comprises the ultra-thin film (either aqueous LiBr solution or, in the tests conducted in the present study, water).

Fig. 3.4.4 Parameters involved in theoretical correction for refraction

The refractive indices of these three mediums are denoted as n_A , n_Q , and n_L , respectively, and are published in the previous literature. The thickness of the quartz window is denoted as t_Q and can be measured directly with the test section unassembled.

The angles of incidence formed by the light received from the membrane surface are denoted as θ_{mA} , θ_{mQ} , and θ_{mL} , respectively, in the three mediums. On the other hand, the light received from the NiCr surface on the quartz viewing window only passes through the air and the quartz; these angles of incidence are denoted as θ_{nA} and θ_{nQ} , respectively, in these two mediums. The lateral distances traversed by the light received from the membrane surface in each of the three mediums are denoted as x_{mA} , x_{mQ} , and x_{mL} , respectively. The lateral distances traversed by the light received from the NiCr surface are denoted as x_{nA} and x_{nQ} , respectively, in the air and the quartz. By inspection of Fig. 3.4.4,

$$L_H = x_{mA} + x_{mQ} + x_{mL} \quad (14)$$

$$L_H = x_{nA} + x_{nQ} \quad (15)$$

where L_H is a fixed parameter that represents the horizontal distance between the laser beam (as it emerges from the laser diode) and the center of the imaging lens. This parameter can be estimated by visual inspection of the laser triangulation sensor.

Using the definition of the sine, the following equations can be written describing the angles of incidence in the three mediums:

$$\sin \theta_{mA} = \frac{x_{mA}}{\sqrt{x_{mA}^2 + t_A^2}} \quad \sin \theta_{nA} = \frac{x_{nA}}{\sqrt{x_{nA}^2 + t_A^2}} \quad (16), (17)$$

$$\sin \theta_{mQ} = \frac{x_{mQ}}{\sqrt{x_{mQ}^2 + t_Q^2}} \quad \sin \theta_{nQ} = \frac{x_{nQ}}{\sqrt{x_{nQ}^2 + t_Q^2}} \quad (18), (19)$$

$$\sin \theta_{mL} = \frac{x_{mL}}{\sqrt{x_{mL}^2 + \Delta Z_{act}^2}} \quad (20)$$

Additionally, applying Snell's Law at each of the medium interfaces yields the following equations:

$$\frac{n_Q}{n_A} = \frac{\sin \theta_{mA}}{\sin \theta_{mQ}} \quad \frac{n_Q}{n_A} = \frac{\sin \theta_{nA}}{\sin \theta_{nQ}} \quad (21), (22)$$

$$\frac{n_L}{n_Q} = \frac{\sin \theta_{mQ}}{\sin \theta_{mL}} \quad (23)$$

The standoff distance, D_S , is the distance between the laser triangulation sensor package and the first refraction boundary – in this case, the outer surface of the quartz viewing window. An appropriate estimate for this parameter can be formulated by measuring the standoff distance typically required to locate the liquid film within the sensor's measurement range. The imaging lens offset constant, C_1 , is defined as the distance between the sensor window and the center of the imaging lens. The total air gap, t_A , is then given by

$$t_A = D_S + C_1 \quad (24)$$

The imaging lens offset constant, C_1 , can be determined experimentally, as described in the following section.

The differences between the apparent and actual distances measured to the membrane and NiCr surfaces are denoted as δ_m and δ_n , respectively. The vertical length parameter, L_V , is defined as

$$L_V = t_A + t_Q \quad (25)$$

Additionally, by observation of Fig. 3.4.4, the following relations are true by similar triangles:

$$\frac{t_A}{x_{nA}} = \frac{L_V - \delta_n}{L_H} \quad (26)$$

$$\frac{t_A}{x_{mA}} = \frac{L_V + \Delta Z_{act} - \delta_m}{L_H} \quad (27)$$

Finally, by defining the distance x_1 as shown in Fig. 3.4.4, the following equations may also be written:

$$\tan \theta_{mA} = \frac{x_1}{\Delta Z_{app}} \quad (28)$$

$$\frac{t_A}{x_{mA}} = \frac{L_V - \delta_n}{L_H - x_1} \quad (29)$$

Equations (14) through (29) present a system of 16 equations with 16 unknowns, which are summarized for reference in Table 3.4.1. The system relies on the eight input parameters summarized in Table 3.4.2. Using this system of equations, a corresponding value for ΔZ_{act} can be calculated based on an input value for ΔZ_{app} . If the system of equations is solved over a range of values for ΔZ_{app} , a calibration curve can effectively be generated by plotting ΔZ_{act} against ΔZ_{app} and fitting a curve to the data.

Table 3.4.1 Sixteen unknowns in the system of equations describing the theoretical correction for refraction

ΔZ_{act}	θ_{mA}	θ_{mQ}	θ_{mL}	θ_{nA}	θ_{nQ}	x_{mA}	x_{mQ}
x_{mL}	x_{nA}	x_{nQ}	t_A	δ_m	δ_n	L_V	x_1

Table 3.4.2 Eight input parameters in the system of equations describing the theoretical correction for refraction

ΔZ_{app}	n_A	n_Q	n_L	t_Q	L_H	D_S	C_1
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In fact, as will be discussed later, the resulting calibration curve has a constant slope – i.e., the theoretical calibration “curve” in this case is better described as a theoretical calibration “coefficient,” C_T , as given by the ratio

$$C_T \equiv \frac{\Delta Z_{act}}{\Delta Z_{app}} \quad (30)$$

which is essentially constant for all values of ΔZ_{app} . The approach used to quantify the uncertainty associated with the results of this analysis is fully described in reference [3]. The results for C_T are discussed in the Results and Discussion section.

Determining the Imaging Lens Offset Constant

The imaging lens offset constant, C_1 , can be determined experimentally utilizing a piece of transparent material with a known thickness and index of refraction. In this case, the fused quartz viewing window from the test section was used. The method involves taking the difference, δ^* , between two distance readings of the same surface with the laser triangulation sensor fixed in place: one reading of the surface alone, and a second reading through the quartz window as it rests on the surface. The experiment and the parameters involved are depicted in Fig. 3.4.5.

The parameters n_A , n_Q , t_Q , and L_H retain their definitions as described in the previous section. The lateral distances traversed by the light in the air and quartz layers are denoted by x_A^* and x_Q^* , respectively. The angles of incidence in the two mediums are denoted by θ_A^* and θ_Q^* . By observation and by application of Snell’s Law, the following set of five equations can be developed:

$$L_H = x_A^* + x_Q^* \quad (31)$$

$$\sin \theta_A^* = \frac{x_A^*}{\sqrt{(x_A^*)^2 + (t_A^*)^2}} \quad (32)$$

$$\sin \theta_Q^* = \frac{x_Q^*}{\sqrt{(x_Q^*)^2 + t_Q^2}} \quad (33)$$

$$\frac{n_Q}{n_A} = \frac{\sin \theta_A^*}{\sin \theta_Q^*} \quad (34)$$

$$\tan \theta_A^* = \frac{x_Q^*}{t_Q - \delta^*} \quad (35)$$

This system of five equations can be solved for x_A^* , x_Q^* , θ_A^* , θ_Q^* , and t_A^* , where t_A^* is the total air gap between the quartz window and the imaging lens.

Fig. 3.4.5 Parameters involved in experimental determination of imaging lens offset constant

The standoff distance measured with the quartz in place is denoted as D_S^* . If D_S^* is measured at the same time the measurement of δ^* is taken, and with t_A^* calculated using Eqs. (31) through (35), C_1 is given by

$$C_1 = t_A^* - D_S^* \quad (36)$$

The parameter C_1 is fixed by the sensor design, and as such can be used in the calculations described in the previous section.

Theoretical Calibration Uncertainty Analysis

Since the system of equations used to solve for ΔZ_{act} involves a large number of variables, it is not feasible to use the general approach (involving partial derivatives) for propagation of uncertainty. A numerical technique known as sequential perturbation can be used to estimate the uncertainty propagation in situations where a result has been obtained by solving a system of equations with a large number of variables. Details of this uncertainty analysis can be found in [3].

DESIGN EVALUATION OF THE STIFFENER PLATE

A design evaluation of the stiffener plate was performed in order to predict the mechanical deformation under the operating conditions of the contactor test section in a desorber configuration. Analytical beam and plate models of the stiffener plate were used to estimate the performance of various porous materials considered for the stiffener plate. A set of finite element models were then developed in order to numerically model the stiffener plate deflection.

Evaluation of Material Selection Using Analytical Deflection Models

The anticipated worst-case operating conditions of the contactor test section in the desorber configuration include a uniform device temperature of 80 °C (176 °F) and a pressure differential across the membrane and stiffener plate of 69 kPa (10 psi). The goal behind the design of the stiffener plate was to have the largest possible contact area (at least several square centimeters) while still demonstrating the following characteristics:

- a maximum deflection $w_{\max}$ at the center of the plate of not more than 10 μm (10 percent of the nominal 100 μm film thickness);
- a thickness h of not more than about 10 mm, in order to minimize the resistance offered by the porous stiffener plate to gas diffusion; and
- a mean pore diameter on the order of 10 μm (in order to minimize local deflection of the membrane into the pores of the stiffener plate).

Evaluation of Porous Polymers

Initially, commercially-available porous polymers such as polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE) were evaluated. The benefits of using a porous polymer material for the stiffener plate include their wide availability and their resistance to the corrosive effects of aqueous LiBr.

Material properties (namely, the elastic moduli) of these porous polymers are not immediately available in the product literature, much less as functions of temperature. However, for the purposes of this design evaluation, the elastic moduli can be estimated by multiplying the nominal values by two factors – one, f_P , to account for the effect of the porosity, and another, f_T , to account for the elevated operating temperature.

$$E_{POLY}^C = E_{POLY} \cdot f_P \cdot f_T \quad (37)$$

As an example, the evaluation conducted for porous PTFE is summarized below.

A review of commercial product literature revealed that porous PTFE sheets with suitable thicknesses and mean pore diameters are available with typical void volumes in the range of 30 to 60 percent [8-13]. Additionally, a review of the previous literature regarding the relationship between void volume and elastic modulus was conducted. The previous literature indicated that for several constituent material models, a void volume between 35 and 50 percent typically corresponds to a reduction in the elastic modulus of about 55 to 85 percent of the nominal value, with an average of around 70 percent [14-19]. A factor of $f_P = 0.3$ can therefore be used to roughly account for the effect of porosity on the nominal elastic modulus of PTFE.

Similarly, the previous literature was consulted in order to determine an estimate for the effect of the elevated operating temperature on the elastic modulus. Most non-reinforced polymers (excluding ketones) for which material property information was available demonstrate a reduction in elastic modulus of about 50 to 70 percent of the nominal value when the specimen temperature is increased from room temperature (23 °C) to 80 °C [20]. A factor of $f_T = 0.4$ can therefore be used to roughly account for the effect of the elevated working temperature on the nominal elastic modulus of PTFE.

The nominal elastic modulus for PTFE is 550 MPa (80,000 psi) [20]. Using Eq. (37), the result for the corrected elastic modulus of porous PTFE at an operating temperature of 80 °C is given by

$$E_{PTFE}^C = (550 \text{ MPa}) \cdot (0.3) \cdot (0.4) = 66 \text{ MPa}$$

The corrected value is roughly one-tenth of the nominal value, which represents a substantial reduction in the stiffness of the material due to the porosity and elevated operating temperature.

Figure 3.4.6 shows the results obtained for the maximum deflection by modeling the stiffener as a clamped plate (i.e., clamped supports along all four edges) using Eqs. (4) and (6). An elastic modulus of $E_{PTFE}^C = 66$ MPa and a Poisson's ratio of $\nu = 0.3$ are assumed as the material properties for porous PTFE at an operating temperature of 80 °C. The results for w_{max} are plotted as a function of the stiffener width L_2 for several values of h , as calculated for a stiffener length L_1 of 4 cm.

Fig. 3.4.6 Porous PTFE model: maximum deflection for various thicknesses.
(Calculated as a function of stiffener width)

This model indicates that achieving the design goals of $w_{max} \leq 10$ μ m and $h \leq 10$ mm for a contactor length of 4 cm is possible only if the contactor is fairly short (around 2.5 cm) in the width direction.

Figure 3.4.7 is similar to Figure 3.4.6, but shows the maximum deflection results obtained for a stiffener thickness of 10 mm by modeling the stiffener with a variety of end conditions using Eqs. (4), (5), (6), (10), and (11). An elastic modulus of $E_{PTFE}^C = 66$ MPa and a Poisson's ratio of $\nu = 0.3$ are assumed as the material properties for porous PTFE at an operating temperature of 80 °C. The results for w_{max} are plotted as a function of the stiffener width L_2 for several end conditions, as calculated for a stiffener length L_1 of 4 cm. The plot is intended to demonstrate

Fig. 3.4.7 Porous PTFE model: maximum deflection for various end conditions. (Calculated as a function of stiffener width)

the dependence of $w_{\max}$ on the stiffener width, number of supported edges, and type of edge supports, given the stiffener thickness, differential operating pressure, estimated material properties, and an arbitrary but suitable selection for the stiffener length. This model indicates that a stiffener with simply-supported edges (whether the two long edges only or all four edges) demonstrates a deflection that is several times the desired deflection of $w_{\max} \leq 10 \mu\text{m}$ over the entire range of stiffener widths considered. In other words, the model indicates that achieving the design goals of $w_{\max} \leq 10 \mu\text{m}$ and $h \leq 10 \text{ mm}$ for a contactor length of 4 cm is possible only if a strong clamping effect is achieved on at least the two long edges of the stiffener.

Evaluation of Porous Aluminum Composite

The next material evaluated for use in the stiffener plate was a porous aluminum produced by the Swiss company Portec Ltd. The material, known by the trade name Metapor, is a composite made from aluminum granules and epoxy resin [21]. It is gas-permeable and can be machined without losing this characteristic. The specific version of the product evaluated was BF 100 AL, some published specifications for which are summarized in Table 3.4.3 [22]. The material has a low coefficient of thermal expansion, is rated to an operating temperature of over 100 °C, and has a suitable mean pore diameter.

As with the porous polymers, published values for the elastic modulus as a function of temperature are not immediately available. However, unlike the polymers, the published elastic modulus value already includes effects of porosity. The corrected value can therefore be estimated by multiplying the nominal value by a single correction factor, f_T , to account for the elevated operating temperature.

$$E_{AL}^C = E_{AL} \cdot f_T \quad (38)$$

Table 3.4.3 Selected properties of Metapor BF 100 AL

Property	Value
Density	1.8 g/cm ³
Elastic Modulus	9000 N/mm ²

Coefficient of Thermal Expansion	$30.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Dimensional Stability	108 $^{\circ}\text{C}$
Mean Pore Diameter	15 μm
Total Porosity	15 %

A suitable estimate for f_T can be formulated by investigating the reduction in the elastic modulus of pure aluminum that occurs when the temperature is raised from room temperature to 80 $^{\circ}\text{C}$. A review of the previous literature revealed that the elastic modulus of pure aluminum is fairly insensitive to temperature over the range 23 to 80 $^{\circ}\text{C}$, demonstrating a drop of only about 2 percent. The corrected elastic modulus of the porous aluminum composite is therefore

$$E_{AL}^C = (9.0 \text{ GPa}) \cdot (0.98) = 8.8 \text{ GPa}$$

This is only a rough approximation of the effect of the elevated operating temperature on the elastic modulus, in that it neglects the presence of epoxy resin in the composite (which constitutes 10 to 35 percent of the material). Compared to the corrected elastic modulus value of 66 MPa for the PTFE, this result (a full two orders of magnitude larger) clearly suggests that the porous aluminum material retains a much higher degree of stiffness under the worst-case operating conditions than the PTFE or any of the other polymer materials evaluated.

A set of models much like those constructed for the polymer materials was constructed for the aluminum composite. Figure 3.4.8 shows the results obtained for the maximum deflection by modeling the stiffener as a clamped plate (i.e., clamped supports along all four edges) using Eqs. (4) and (6). An elastic modulus of $E_{AL}^C = 8.8 \text{ GPa}$ and a Poisson's ratio of $\nu = 0.3$ are assumed as the material properties for the porous aluminum composite at an operating temperature of 80 $^{\circ}\text{C}$. The results for $w_{\max}$ are plotted as a function of the stiffener width L_2 for several values of h , as calculated for a stiffener length L_1 of 4 cm. The plot is intended to demonstrate the dependence of $w_{\max}$ on the stiffener width and thickness, given the number of supported edges, type of edge supports, differential operating pressure, estimated material properties, and an arbitrary but suitable selection for the stiffener length. This model indicates that the design goals of $w_{\max} \leq 10 \mu\text{m}$ and $h \leq 10 \text{ mm}$ for a contactor length of 4 cm would be achieved over the entire range of stiffener widths considered. In fact, for a 4.0 cm by 3.0 cm stiffener plate, the model suggests that the thickness could be reduced to less than 3 mm ($\sim 1/8$ in) while still achieving the desired deflection of $w_{\max} \leq 10 \mu\text{m}$.

Fig. 3.4.8 Porous aluminum model: maximum deflection for various thicknesses. (Calculated as function of stiffener width)

Figure 3.4.9 is similar to Figure 3.4.8, but shows the maximum deflection results obtained for a stiffener thickness of 6 mm ($\sim 1/4$ in) by modeling the stiffener with a variety of end conditions using Eqs. (4), (5), (6), (10), and (11). An elastic modulus of $E_{AL}^C = 8.8 \text{ GPa}$ and a Poisson's ratio of $\nu = 0.3$ are assumed as the material properties for the porous aluminum composite at an operating temperature of 80°C . The results for $w_{\max}$ are plotted as a function of the stiffener width L_2 for several end conditions, as calculated for a stiffener length L_1 of 4 cm. The plot is intended to demonstrate the dependence of $w_{\max}$ on the stiffener width, number of supported edges, and type of edge supports, given the stiffener thickness, differential operating pressure, estimated material properties, and an arbitrary but suitable selection for the stiffener length. This model indicates that a porous aluminum stiffener achieves the desired deflection of $w_{\max} \leq 10 \mu\text{m}$ over the entire range of stiffener widths considered.

Fig. 3.4.9 Porous aluminum model: maximum deflection for various end conditions. (Calculated as a function of stiffener width)

These design evaluations suggest that the porous aluminum composite is much more suitable than any of the polymers for the stiffener plate material. It possesses stiffness characteristics that are by far superior to the commercially-available porous polymers, thus greatly reducing the degree to which it deflects under the worst-case operating conditions.

Evaluation of Stiffener Plate Deflection Using Finite Element Models

The stiffener plate was made from the porous aluminum composite and was further evaluated using ANSYS finite element models. These models enabled a more precise evaluation of the stiffener plate geometry and loading conditions. The final design selected for the stiffener plate used a nominal contactor area of 4 cm by 3 cm and a thickness of approximately 6 mm (1/4 in). The stiffener plate also had a “lip” extending around all four edges. The lip was clamped between the adjacent layers of the contactor test section, such that a clamping effect was achieved around the entire perimeter of the stiffener plate. A dimensioned sketch of the stiffener plate is included for reference in Fig. 3.4.10. In addition to the temperature and pressure loads investigated in the analytical deflection models, the finite element models also investigated the potential effects of thermal expansion mismatch between the stiffener plate and the other components of the test section. Two models were primarily investigated: (1) a simple model utilizing shell elements, and (2) a more complicated 3-D model using tetrahedral elements.

Fig. 3.4.10 Approximate dimensions of stiffener plate.
(Dimensions shown in millimeters)

Fig. 3.4.11 Basic loading configuration for finite element models

Finite Element Model Using Shell Elements

The first finite element model used four-node elastic shell elements, with the stiffener plate modeled as two areas: one for the 4 cm by 3 cm contactor area, and a second area for the lip. Thicknesses

of 6.2 mm and 2.8 mm were assigned to the contactor and lip areas, respectively. A displacement constraint in the direction normal to the stiffener plate was applied to the lip area. The model was then further constrained using various combinations of lateral displacement constraints, which were applied to the lines bounding the two areas. The intent was to simulate the effects of constrained thermal expansion of the stiffener plate due to thermal expansion mismatch between the stiffener plate and the clamping structure. Depending on the exact construction of the test section, such a mismatch could cause certain surfaces of the lip geometry to be more tightly clamped than others. For each of the constraint configurations investigated, a pressure of 69 kPa was applied to the 4 cm by 3 cm contactor area, and a temperature of 80 °C was applied to the entire model.

Table 3.4.4 Material properties and loading conditions for finite element models

Property / Condition	Value
Elastic modulus	8.8×10^9 Pa
Poisson's ratio	0.3
Coefficient of thermal expansion	$30 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$
Reference temperature	23 °C
Operating temperature	80 °C
Pressure differential	69×10^3 Pa
Mesh size	0.0015 m

Table 3.4.5 Summary of results for the shell finite element model

Clamping Configuration	Schematic	Net Deflection Variation Over Contactor Area
Free lateral elongation (basic loading configuration)		0.9 μm
Lip clamped laterally		0.9 μm
Contactor area clamped laterally		0.9 μm
Fully clamped		0.9 μm

The basic loading configuration shown in Fig. 3.4.11 was first investigated, followed by the various configurations of lateral displacement constraints. The net deflection variation over the contactor area – i.e., the maximum height difference between the edges and the center of the stiffener plate – was taken to be the best measure of the expected non-uniformity in the film thickness caused by deflection of the stiffener plate. The results obtained for the net deflection variation over the contactor area for each of the various clamping configurations investigated are summarized in Table 3.4.5. As an example, the graphical results obtained for the basic loading configuration are shown in Fig. 3.4.12. This result is

essentially identical to that predicted by the analytical solution for a clamped plate of thickness 6 mm. This indicates that the shell modeling technique is not able to capture the effects of constrained thermal expansion of the stiffener.

Fig. 3.4.12 Shell model stiffener deflection: free lateral elongation

Finite Element Model Using Tetrahedral Elements

The second finite element model utilized 10-node tetrahedral elements. This model fully captured the 3-D geometry of the stiffener plate shown in Fig. 3.4.10. A displacement constraint in the direction normal to the stiffener plate was applied to the top of the lip area. As with the shell model, the tetrahedral model was then further constrained using various combinations of lateral displacement constraints, which were applied to the sides of the lip, the sides of the contactor area, and the bottom of the lip. For each of the constraint configurations investigated, a pressure of 69 kPa was applied to the 4 cm by 3 cm contactor surface, and a temperature of 80 °C was applied to the entire model.

The basic loading configuration shown in Fig. 3.4.11 was first investigated, followed by the various configurations of lateral displacement constraints. As with the shell element model, the net deflection variation over the contactor area was taken to be the best measure of the expected non-uniformity in the film thickness caused by deflection of the stiffener plate. The results obtained for the net deflection variation over the contactor area for each of the various clamping configurations investigated are summarized in Table 3.4.6.

Table 3.4.6 Summary of results for the tetrahedral finite element model

Clamping Configuration	Schematic	Net Deflection Variation Over Contactor Area
Free lateral elongation (basic loading configuration)		1.3 μm

Lip clamped laterally		44 μm (deflection into channel)
Contactor area clamped laterally		17 μm
Fully clamped		2.3 μm (deflection into channel)
Free lateral elongation with lip thickness clamped		1.3 μm
Lip clamped laterally with lip thickness clamped		52 μm (deflection into channel)
Contactor area clamped laterally with lip thickness clamped		16 μm
Fully clamped with lip thickness clamped		5.8 μm (deflection into channel)

Unlike the shell models, the tetrahedral models demonstrated a wide variation in the results for the net deflection variation over the contactor area. The net deflection variation was at a minimum (1.3 μm) for the two cases when no lateral constraints were applied. This suggests that constrained thermal expansion of the stiffener plate is indeed an undesirable condition, as it causes the stiffener plate to deflect and deform more than it would otherwise. Interestingly, in each of the four cases where lateral constraints were applied around the lip, the direction of the stiffener plate deflection was opposite the direction of the applied pressure (i.e., toward the membrane). This suggests that if the lateral clamping around the lip of the stiffener were strong enough, the effects of thermal expansion would overcome those of the 69 kPa pressure on the stiffener plate, and the stiffener would effectively collapse in on the liquid film. This negative deflection was most severe in the two cases where lateral constraints were applied around the lip but not around the contactor area (44 μm and 52 μm).

Fig. 3.4.13 Tetrahedral model stiffener deflection: free lateral elongation

However, it should be noted that these finite element models are all simulating a worst-case scenario in which the other major components of the test section (which comprise the clamping structure for the stiffener plate) have a thermal expansion coefficient of essentially zero. In reality, the thermal expansion coefficient of the porous aluminum composite is relatively low compared to that of Delrin, from which the other major components of the device were made. As such, the rest of the test section has not only a higher coefficient of thermal expansion, but also a lower modulus of elasticity. When the device heats up to the operating temperature of 80 °C, it is unlikely that the rest of the device will impart much of a lateral clamping effect around the edges of the stiffener plate. The models that most likely provide an accurate estimation of the stiffener plate deflection are the shell and tetrahedral models loaded under the basic loading configuration (no lateral clamping). These models predict net deflection variations of 0.9 and 1.3 μm , respectively, over the contactor area, both of which are well in line with the deflection of 0.8 μm predicted by the analytical clamped plate model.

EXPERIMENTAL METHOD

A primary goal of this investigation was to experimentally measure the thickness of the liquid film during steady-state operation of the test section in the desorber configuration. This required the development and validation testing of a film thickness measurement system capable of characterizing variations in the film thickness on the order of $10\text{ }\mu\text{m}$.

Fig. 3.4.14 Film thickness measurement setup

Film Thickness Measurement Setup

A laser triangulation sensor produced by Acuity Research, Inc. was used to measure the thickness of the flowing ultra-thin film. The particular model used was the high-resolution version of the AR600-0125. A schematic of the film thickness measurement setup is shown in Fig. 3.4.14. The laser triangulation sensor was mounted on a pair of motorized stages produced by Sigma Koki Co., Ltd. of Japan (sold in the U.S. by the affiliate OptoSigma Corporation). The stages were oriented in the lateral X - and Y -directions (parallel to the liquid film) and were controlled using a Mark-202, a two-axis controller also produced by Sigma Koki. The controller was in turn connected through a serial port to a PC running LabVIEW 6.1. This enabled accurate positioning of the laser spot to within a few microns over the entire 4 cm by 3 cm liquid film. The motorized stages, which provided movement in the lateral directions, were mounted to a manual stage oriented in the Z -direction (normal to the liquid film).

In order to verify the liquid film thickness, the laser triangulation sensor was used to measure the distances to the two surfaces constraining the liquid film – the back side of the quartz viewing window and the front side of the porous PTFE membrane. Measuring to the membrane surface was accomplished by directing the laser beam through the transparent quartz viewing window and liquid film directly onto the membrane. Measuring to the back side of the quartz window was accomplished by directing the laser beam onto small NiCr-coated regions on the backside of the quartz viewing window.

Technique for NiCr Vapor Deposition on Quartz Window

Using the laser triangulation sensor to measure the distance to the back of the transparent quartz viewing window required the development of a technique to coat the quartz with a thin layer of opaque material. The coating was required to meet the following criteria:

- it had to be opaque (or semi-opaque) when wetted;
- it had to exhibit primarily a diffuse (as opposed to specular) reflectance pattern when viewed through the front side of the quartz window, in order to scatter the laser light;
- it had to preserve the flatness of the quartz surface, in order to both maintain the dimensions of the channel and not interfere with the flowing liquid film;

- it had to be durable enough to withstand prolonged exposure to flowing, aqueous LiBr solution at a temperature of 80 °C; and
- it had to be applied only on select, well-defined regions of the quartz window, so that sufficient optical access to the membrane surface was maintained.

By trial and error, a technique was developed that utilized a two-step method in which selected regions of the quartz window were first particle-blasted and then coated with a layer of vapor-deposited NiCr.

For the particle-blasting procedure, the quartz window was masked with a photochemical-etched stencil made from copper shim stock with a thickness of 127 μm (0.005 in). The stencil defined a shadow mask of the regions to be covered with the coating process. A technical drawing of the stencil used can be found in [3]. The stencil was attached using stainless steel fasteners to an aluminum frame that was designed to fit snugly around the 4 cm by 3 cm region of the quartz window. This allowed for accurate, repeatable positioning of the entire stencil assembly on the quartz window. Once positioned, the weight of the frame held the copper stencil firmly in place against the quartz window. In addition, the stencil assembly was fastened to the quartz window using clear tape, so that the entire unit could be handled during particle-blasting. The masked quartz window was then particle-blasted using a miniature air-abrasive blast system and 600 grit (16 μm average particle diameter) silicon carbide abrasive.

After particle-blasting, the quartz window was thoroughly scrubbed with a solution of Liqui-Nox and de-ionized water. The quartz window was then rinsed with de-ionized water and wiped clean with methyl alcohol. The old stencil, which was damaged by the particle-blasting process, was removed from the aluminum frame. The frame and fasteners were scrubbed with the solution of Liqui-Nox and water to remove the residual silicon carbide particles. A new, identical stencil was then attached to the aluminum frame, and the entire stencil assembly was repositioned on the quartz window. The stencil assembly was held to the quartz window using clear tape, but care was taken to keep a distance of at least several millimeters between the tape and the quartz surfaces not covered by the stencil. This was due to the fact that during the NiCr vapor deposition process, some tapes tended to outgas, causing the metal to adhere poorly to the quartz surface.

The NiCr vapor deposition process was performed using a Veeco thermal evaporator. A variety of process parameters were tested until a combination was found that resulted in a suitable coating of metal on the particle-blasted quartz surface. The finalized process parameters included the following:

1. 80/20 blend NiCr used as stock (evaporation temperature of 1285 °C);
2. a deposition thickness of 1000 Angstroms;
3. a current of around 300 A, generating a deposition rate of 5000 Angstroms/s;
4. a vacuum level of 1.3×10^{-4} Pa (1×10^{-6} Torr).

The quality of the metal coating achieved seemed to be most sensitive to the deposition rate and vacuum level parameters. Other process parameters that did not produce desirable results included the following: higher rates of deposition (12,000 and 15,000 Angstroms/s); low vacuum (4.7×10^{-4} Pa [3.5×10^{-6} Torr]); and thicker coatings (2000 Angstroms).

Film Thickness Data Collection Procedure

This section provides details about the procedure used to collect film thickness data during operation of the desorber flow setup. Initial steps included locating the ultra-thin film within the laser triangulation sensor's measurement range and aligning the laser spot with the pattern of NiCr-coated regions on the quartz viewing window.

Locating the Film in the Laser Triangulation Sensor's Range

The first task that had to be accomplished was locating the ultra-thin liquid film in the range of the laser triangulation sensor. This was accomplished simply by adjusting the manual *Z*-axis stage (see Fig. 3.4.14) until it was apparent that the data being collected from sensor was in fact coming from the two surfaces of interest (the membrane and the NiCr-coated regions on the back of the quartz viewing window). The sensor was designed to have a nominal range of 0.125 inches, located at a distance of 0.500 to 0.625 inches away from the sensor package. However, the effects of viewing the membrane and NiCr-coated regions through the 1/4-inch-thick quartz window significantly changed the location and size of the sensor's usable range. Refraction caused the sensor's range to be located more than 0.500-0.625 inches away from the sensor package, which was beneficial as it provided much-needed additional clearance between the sensor and the front cover of the test section. On the other hand, the sensor's usable range was reduced from the nominal 0.125 inches due to the presence of the front surface of the quartz window. When

the sensor was moved in too close to the test section, the front surface of the quartz would (either by secondary reflection or some other means) confuse the sensor, causing it to output erroneous data and effectively cutting off the near end of its range.

Zeroing the Laser Spot on the Pattern of NiCr-Coated Regions

The program that was used to collect film thickness data is the LabVIEW VI Acquire_Thickness_Data.vi, which is described in detail in [3]. The VI requires the coordinates of the centers of the NiCr-coated regions to be entered in spreadsheet form. Since the masks used to make the pattern of NiCr-coated regions were manufactured using a precision photochemical-etching process, the distances between NiCr-coated regions were simply given by the drawings used for manufacture. However, before these distances were of any use, the location of the laser spot relative to the pattern of NiCr-coated regions had to be determined. This was accomplished by manually centering the laser spot on the lower-left NiCr-coated region and zeroing the stage controller at that location (manual operation of the stage controller involved the use of a joystick to modify a series of operating parameters that were described in detail in the user's manual). This established the X and Y coordinates of the center of the first NiCr-coated region as (0, 0).

Achieving Steady-State Operation of the Desorber Flow Setup

With the laser spot zeroed on the first NiCr-coated region, the desorber flow setup was allowed to run for a sufficient length of time to achieve steady-state operation. The flow setup was determined to be operating at steady-state when the following conditions were met:

- no large bubbles were trapped in the channel;
- the three temperatures that were being monitored ($T_{liq.in}$, $T_{plate.in}$, and $T_{plate.out}$) were within about 10°C of each other and were remaining relatively constant;
- the level of the vacuum drawn in the vapor plenum (as indicated by the gauge on the pump itself) was remaining relatively constant; and
- consecutive readings from the mass flow meter were remaining relatively constant.

Film Thickness Data Reduction and Uncertainty Analysis

As described previously by Eq. (12), the apparent local film thickness value, ΔZ_{app} , for each pair of measurement groups is given by the difference between the Z -values for each group

$$\Delta Z_{app} = Z_m - Z_n \quad (39)$$

(The subscripts m and n denote the membrane and NiCr surfaces, respectively.) The standard deviations can be combined by calculating the square root of the sum of their squares.

$$\sigma_{\Delta Z_{app}} = \sqrt{(\sigma_{Z_m})^2 + (\sigma_{Z_n})^2} \quad (40)$$

Next, the average value for ΔZ_{app} can be calculated for the set of n pairs of measurement groups.

$$\overline{\Delta Z_{app}} = \frac{1}{n} \sum_{i=1}^n (\Delta Z_{app})_i \quad (41)$$

The actual local film thickness, ΔZ_{act} , for the set is then given by

$$\Delta Z_{act} = C_{T,E} \cdot \overline{\Delta Z_{app}} \quad (42)$$

where $C_{T,E}$ is the calibration coefficient (either derived theoretically, C_T , or measured empirically, C_E) used to correct for the effects of refraction. Finally, the horizontal and vertical coordinates for the set can be calculated by taking the average X and Y values, respectively, for the entire set.

$$\bar{X}, \bar{Y} = \frac{1}{n} \sum_{i=1}^n (X, Y)_i \quad (43)$$

The uncertainty associated with ΔZ_{act} can be estimated using a modified form of multiple-measurement uncertainty analysis described by Figliola et al. [23]. In this method, the uncertainty is composed of bias and precision error components, just as in a standard uncertainty analysis of a measured quantity. Namely,

$$u_{\bar{R}} = \sqrt{B^2 + (t_{n,95\%} \cdot P)^2} \quad (44)$$

where R is the measured quantity of interest, B is the bias error in the individual measurements of R , and the product $t_{n,95\%} \cdot P$ is the precision error at a 95% confidence interval if n measurements of R are taken. In a typical uncertainty analysis, where R is a quantity that is measured directly n times, P is simply equal to σ_R . However, if R is not measured directly, but is calculated from averaged values (which themselves have associated standard deviations) of other, directly-measured quantities, then P has two components. The first component, P_1 , incorporates the effect of the data scatter in the n calculated values of R . The second component, P_2 , incorporates the effect of the data scatter within the measured quantities from which R is calculated. These components are given by

$$P_1 = \frac{\sigma_R}{\sqrt{n}} \quad (45)$$

$$P_2 = \frac{\sqrt{\frac{1}{n} \sum_{i=1}^n (\sigma_{Ri}^2)}}{\sqrt{n \cdot N}} \quad (46)$$

where σ_R is the standard deviation of the n calculated values of R , $\sqrt{\frac{1}{n} \sum_{i=1}^n (\sigma_{Ri}^2)}$ is the RMS value of the n standard deviations associated with the n individual σ_{Ri} values, and $\sqrt{n \cdot N}$ is the total number of degrees of freedom for the system. These components can be combined to give P as

$$P = \sqrt{P_1^2 + P_2^2} \quad (47)$$

This method of estimating u_R typically results in values that are substantially lower than if P were taken to be σ_R (that is, if the set of R values were treated simply as a quantity that had been measured directly n times, with a standard deviation of σ_R).

Equations (45) through (47) can be applied to calculate the value of P for $\overline{\Delta Z}_{app}$. In order to calculate $u_{\overline{\Delta Z}_{app}}$ using Eq. (44), an estimate of the bias error is required. Since one film thickness measurement requires a minimum of two readings from the laser triangulation sensor, the bias error

associated with $\overline{\Delta Z}_{app}$ is given by combining the bias errors from two laser readings as the square root of the sum of the squares. This gives

$$B_{\overline{\Delta Z}_{app}} = \sqrt{2 \cdot B_{laser}^2} \quad (48)$$

With a value for $u_{\overline{\Delta Z}_{app}}$ known, $u_{\Delta Z_{act}}$ can be calculated using the equation

$$\left(\frac{u_{\Delta Z_{act}}}{\overline{\Delta Z}_{act}} \right)^2 = \left(\frac{u_{C_{T,E}}}{C_{T,E}} \right)^2 + \left(\frac{u_{\overline{\Delta Z}_{app}}}{\overline{\Delta Z}_{app}} \right)^2 \quad (49)$$

The uncertainties associated with $\overline{X}$ and $\overline{Y}$ can be calculated simply by applying Eq. (44) directly to the entire set of values used to calculate each (since $\overline{X}$ and $\overline{Y}$ are calculated by directly averaging all the X and Y values for each set, and the individual values from which the averages are calculated are essentially taken to have standard deviations of zero). The bias error in the stage coordinates returned by the controller can be ignored, since its effect on the resulting uncertainty value is insignificant compared to the effect of the spatial scatter in the pool of values used. In other words,

$$u_{\overline{X}, \overline{Y}} = t_{n, 95\%} \cdot \sigma_{X, Y} \quad (50)$$

Reduction of the film thickness data was accomplished using the LabVIEW VI Analyze_Thickness_Data.vi, which is described in detail in [3].

As a final step, an overall characterization of the film thickness, $\overline{\Delta Z}$, can be made for each set of flow conditions investigated by calculating the spatially-averaged value of all local film thickness values, given by

$$\overline{\Delta Z} = \frac{1}{k} \sum_{i=1}^k (\Delta Z_{act})_i \quad (51)$$

where k is the total number of local film thickness measurements. The uncertainty associated with this value, $u_{\overline{\Delta Z}}$, can be calculated by applying the modified multiple-measurement uncertainty analysis technique, using the individual $u_{\Delta Z_{act}}$ values in place of the required $\sigma_{\Delta Z_{act}}$ values. This yields a conservative estimate for $u_{\overline{\Delta Z}}$, since the $u_{\Delta Z_{act}}$ values are roughly twice as large as the related $\sigma_{\Delta Z_{act}}$ values.

Temperature, pressure differential, and mass flow rate data was recorded in order to provide some level of information about the flow conditions for each data set collected. The test section temperature, T_{ave} , is calculated as the average of the six temperatures (high and low values for $T_{liq.in}$, $T_{plate.in}$, and $T_{plate.out}$) recorded for each set.

$$T_{ave} = \frac{1}{6} \sum_{i=1}^6 T_i \quad (52)$$

The effective pressure differential for each data set is given by the difference between the average values of P_{inlet} and P_{vapor} .

$$\Delta P = \bar{P}_{inlet} - \bar{P}_{vapor} \quad (53)$$

Finally, the mass flow rate through the test section is simply given by the average of the mass flow rate values recorded for each data set.

$$\dot{m} = \bar{\dot{m}}_i \quad (54)$$

The calibration equations used to convert the readings from the pressure transducers from units of volts to pressure are given in reference [3]. The calibration equation used to convert the readings from the bubble flow meter from units of frequency to mass flow rate is also given in reference [3]. Uncertainty analyses were not performed on these quantities, as inspection of the raw data reveals that data scatter was minimal, and because they are used as reference values only.

Correcting for Refraction Effects – Empirical Method

The laser triangulation sensor operates by focusing a beam of visible laser light onto the surface to be measured, with the beam oriented orthogonally to the surface. The line scan camera inside the device then views at an angle the portion of the laser light that is scattered diffusely by this surface. In the present measurement task, the sensor must view the laser spot through various media with varying optical properties: air, the transparent quartz window of the test section, and, for the measurements to the membrane, the liquid in the ultra-thin film. Since the camera views the laser spot at an angle, the effects of refraction must be taken into consideration. In addition to the theoretical approach outlined earlier, a second approach for compensating for refraction based purely on an empirical method was developed. The results will not be presented here, but details can be found in [3].

RESULTS AND DISCUSSION

This chapter describes the results of the data collection and reduction. Results of the theoretical and empirical calibration techniques are presented and compared for accuracy. Graphical results are shown for several example film thickness data sets, and discussions of trends in the data are included.

Theoretical and Empirical Calibration Methods

The following sections summarize the results obtained for the theoretical and empirical calibration coefficients, C_T and C_E , which were described earlier. An overall discussion of the two calibration techniques is also provided.

Theoretical Calibration Coefficient Results

Developing the theoretical calibration curve began with the experiment described previously for determining C_1 , which in turn required measurements of t_Q , D_S^* , and δ^* . The raw data, reduction, and uncertainty analyses for t_Q , D_S^* , and δ^* are summarized in Appendices I, J, and K, respectively in reference [3]. The results of these measurements were

$$\begin{aligned}t_Q &= 6.287 \pm 0.022 \text{ mm} \\D_S^* &= 16.104 \pm 0.204 \text{ mm} \\\delta^* &= 2.756 \pm 0.035 \text{ mm}\end{aligned}$$

Determining C_1 also required calculation of t_A^* , which was performed using the Mathcad worksheet shown in Appendix L (in reference [3]) to solve the system of five equations given by Eqs. (31) through (35). The uncertainty associated with this value, $u_{t_A^*}$, was calculated using the sequential perturbation method. The results of this analysis are summarized in Appendix M (in reference [3]). In addition to t_Q and δ^* , the parameters n_A , n_Q , and L_H were required in order to perform the calculations for t_A^* and $u_{t_A^*}$. The values used for these parameters were

$$\begin{aligned}n_A &= 1.00 \pm 0. \\n_Q &= 1.46 \pm 0. \\L_H &= 25 \pm 2 \text{ mm}\end{aligned}$$

The length L_H could only be approximated, due to the fact that the imaging lens was only partially visible through the laser triangulation sensor window; as such, a relatively large uncertainty was assigned to this value. Finally, the results obtained for C_1 using Eq. (36) were

$$C_1 = 6.456 \pm 2.344 \text{ mm}$$

With C_1 known, the value of ΔZ_{act} could be calculated given a value for ΔZ_{app} . This was performed using the Mathcad worksheet shown in Appendix N to solve the system of 16 equations given by Eqs. (14) through (29). In addition to t_Q , n_A , n_Q , L_H , and C_1 , the parameters D_S and n_L were required in order to perform the calculation for ΔZ_{act} . The values used for these parameters were

$$\begin{aligned}D_S &= 16.1 \pm 0.5 \text{ mm} \\n_L &= 1.33 \pm 0.01\end{aligned}$$

The standoff distance D_S was estimated based on the clearance typically required between the laser triangulation sensor and the test section in order to locate the ultra-thin film within the sensor's measurement range. The calculation of ΔZ_{act} was performed for several values of ΔZ_{app} over the range 0 to 200 μm . The results for ΔZ_{act} were plotted against ΔZ_{app} to generate the calibration curve shown in Fig. 3.4.15. A linear regression revealed that the relationship between ΔZ_{act} and ΔZ_{app} is in fact linear. The uncertainty associated with this value, u_{CT} , was calculated using the sequential perturbation method. The results of this analysis are summarized in [3], giving C_T as

$$C_T = 1.501 \pm 0.043$$

Fig. 3.4.15 Calibration curve generated using theoretical model

Empirical Calibration Coefficient Results

A single value for C_E was calculated by simply ignoring the various conditions under which it was measured and taking the average of all 50 values computed in the 10 x 5 matrix. The uncertainty associated with this value was calculated by applying the modified multiple-measurement uncertainty analysis technique, and using the 50 u_{CE} values in place of the required σ_{CE} values. (This was considered a conservative estimate for the overall uncertainty associated with C_E , since the u_{CE} values are roughly twice as large as the related σ_{CE} values would be.) The details of these calculations are summarized in [3]. The final result for C_E was

$$C_E = 1.499 \pm 0.019$$

This result is compared in the following section to that obtained using the theoretical approach.

Comparison of Calibration Methods

Clearly, the agreement between the results for C_T and C_E is remarkable, lending confidence to the accuracy of the two values. The fact that these two separate calibration techniques produced such similar results indicates that the refraction occurring when the laser triangulation sensor is used to measure the film thickness through the quartz viewing window is well characterized. The fact that no noticeable dependence of C_E on $\overline{\Delta Z}_q$ was found to exist is not surprising, given how little the value of C_T changed over the entire range of ΔZ_{app} values investigated.

Temperature, Pressure Differential, and Mass Flow Rate Results

Temperature, pressure differential, and mass flow rate data were recorded as described in Section 5.3. The test section temperature, T_{ave} , was calculated for each data set using Eq. (52). Averages were calculated for each data set for the readings from the two pressure transducers and the bubble flow meter, and were converted to units of pressure and mass flow rate, respectively, using the following calibration equations:

$$\begin{aligned} P_{inlet} [psig] &= -2.9608 [V] + 1.5432 \\ P_{vapor} [psig] &= -2.9463 [V] + 1.6305 \\ \dot{m} [g/min] &= \frac{5}{10000} [s^{-1}] \cdot 0.999567645 - 0.000121646 \end{aligned}$$

The effective pressure differential, ΔP , and the average mass flow rate through the test section, $\dot{m}$, were then calculated for each data set using Eqs. (53) and (54), respectively. The raw data for each set of flow conditions investigated is tabulated in Appendix Q (in reference [3]). The results of the data reduction are summarized in Table 3.4.7, with ΔP values shown in units of both kPa and psi. Uncertainty analyses were not performed on these quantities, as they are used primarily for reference purposes, and inspection of the raw data reveals that data scatter was minimal.

Table 3.4.7 Summary of steady-state flow conditions investigated

Data Set No.	T_{ave} [°C]	ΔP [kPa]	ΔP [psi]	$\dot{m}$ [g/min]
1	23.3	43.4	6.30	0.02
2	23.5	43.3	6.29	4.65
3	23.4	43.3	6.29	0.02
4	24.0	43.7	6.34	4.53
5	68.3	43.8	6.35	5.16
6	70.9	39.4	5.71	5.46
7	72.8	29.8	4.33	4.99
8	73.7	15.9	2.31	4.11
9	70.2	71.5	10.4	4.43
10	51.1	43.4	6.30	4.64

Selected Film Thickness Results

Film thickness data was collected in the order shown for each of the 11 combinations of flow conditions listed in Table 3.4.7. The data was collected using *Acquire_Thickness_Data.vi*, as described in detail in Section 5.3 and Appendix D of reference [3]. The raw film thickness data was then reduced using *Analyze_Thickness_Data.vi*, as described in Section 5.4 and Appendix E of reference [3]. The 11 sets of reduced film thickness data are tabulated for reference in Appendix R of reference [3]. Each data set consists of 56 data points – one for the leading edge and one for the trailing edge of each of the 28 NiCr-coated regions on the quartz viewing window. In addition, a spatially-averaged value for the film thickness, $\overline{\Delta Z}$, was calculated for each of the 11 data sets using Eq. (51). The uniformity of each film thickness was characterized by calculating $u_{\overline{\Delta Z}}$ using the modified multiple-measurement uncertainty analysis technique described previously. The results for $\overline{\Delta Z}$ and $u_{\overline{\Delta Z}}$ are summarized in Appendix R (reference [3]) along with the tabulated reduced data for each of the 11 data sets.

A series of plots was generated for each of the 11 data sets using OriginLab plotting software. The plots were generated by converting each data set to matrix form using the Origin Lab option “Random XYZ Gridding.” The parameters used for this procedure are summarized for reference in Table 3.4.8. This generated a matrix of film thickness values representing a surface fit for the data, with spacing between the matrix data points of roughly 2.0 mm in the X -direction and roughly 2.2 mm in the Y -direction. The following sections present the graphical results for several example data sets representing a variety of flow conditions of interest..

Table 3.4.8 OriginLab parameters used for converting film thickness data to matrix form

Parameter	Value Used
Gridding Method	Correlation
No. Columns	21
No. Rows	11
Search Radius	2
Smoothness	0.3

Room Temperature with No Flow

Data set no. 1 was collected at room temperature with zero flow through the test section. The pressure differential was roughly 43 kPa (6.3 psi), which was regarded as a typical setting required for operation of the device as a desorber. These conditions essentially represented a nominal check of the construction of the test section, before extensive testing had occurred. A 3-D surface plot of the film thickness data is shown in Fig. 3.4.16 and a contour plot is shown in Fig. 3.4.17. The plots suggest that the nominal film thickness was somewhat larger than the expected value of 120 μm (based on the channel construction described previously). This observation is evident in the result for the average film thickness, which was

$$\overline{\Delta Z} = 153.8 \pm 4.2 \mu\text{m}$$

Fig. 3.4.16 Data set no. 1: 3-D surface plot of film thickness

The plots also reveal that the film was initially quite uniform in thickness – more so, in fact, than for any of the data sets collected subsequently.

Figure 3.4.18 shows three profiles of the 3-D surface fit, each of which is aligned with one of the three rows of NiCr-coated regions on the quartz viewing window. The graphs show error bars representing the uncertainties associated with

Fig. 3.4.17 Data set no. 1: contour plot of film thickness

the $\bar{X}$ and ΔZ_{act} values, allowing the surface fit generated by OriginLab and the actual film thickness data to be directly compared. (No profile plots are shown that allow for the uncertainties associated with the $\bar{Y}$ values to be considered in this comparison. However, it suffices to note that for all data sets, the $u_{\bar{Y}}$ values were roughly half as large as the corresponding $u_{\bar{X}}$ values.) The profile plots reveal that for this data set, the quality of the surface fit obtained was very high, as the surface is fairly smooth and lies within the uncertainty ranges of all 56 data points.

Fig. 3.4.18 Data set no. 1: comparison of surface fit to experimental data

Room Temperature

Data set no. 2 was collected at room temperature with a mass flow rate through the test section of roughly 4.7 g/min (where mass flow rates within the range of 4.0 to 5.5 g/min were regarded as a level typically required for operation of the device as a desorber). The pressure differential was near the nominal

setting of 43 kPa (6.3 psi). These flow conditions essentially represented a check of the test section operation before ramping up to the required temperature of around 70 °C. A 3-D surface plot of the film thickness data is shown in Fig. 3.4.19 and a contour plot is shown in Fig. 3.4.20. The plots suggest that when flow was applied, the downstream end of the membrane tended to collapse toward the quartz window. This result was initially considered a malfunction of the film thickness measurement system, not of the ultra-thin film. Subsequent testing, however, suggested otherwise. Data set no. 3 was collected under conditions similar to that of data set no. 1, and the thickness and uniformity of the film seemed to rebound. Data set no. 4 was then collected under conditions similar to that of data set no. 2, and the downstream end of the membrane again collapsed. (Plots of data set nos. 3 and 4 are included in Appendices S.1 and S.2, respectively of reference [3].)

Figure 3.4.21 shows three graphs comparing profiles plots of the 3-D surface fit to the actual film thickness data. The profile plots reveal that for this data set, the quality of the surface fit obtained was moderate. The surface is smooth but lies outside the uncertainty ranges of four of the data points.

Fig. 3.4.19 Data set no. 2: 3-D surface plot of film thickness

Operating Temperature

Data set no. 5 was collected at an elevated operating temperature of roughly 68 °C (where temperatures within the range of 65 to 75 °C were regarded as a level typically required for operation of the device as a desorber). The pressure differential was near the nominal setting of 43 kPa (6.3 psi) and the mass flow rate was within the nominal range of 4.0 to 5.5 g/min. These flow conditions essentially represented a first check of the test section running at operating temperature. A 3-D surface plot of the film thickness data is

shown in Fig. 3.4.22 and a contour plot is shown in Fig. 3.4.23. The plots suggest that when the test section was ramped up to

Fig. 3.4.20 Data set no. 2: contour plot of film thickness

Fig. 3.4.21 Data set no. 2: comparison of surface fit to experimental data

Fig. 3.4.22 Data set no. 5: 3-D surface plot of film thickness

operating temperature, the downstream end of the film thickened severely. This observation is consistent with the result for the average film thickness, which was

$$\overline{\Delta Z} = 172.2 \pm 5.9\text{ }\mu\text{m}$$

It is unclear whether this thickening of the downstream end of the film was due to a flaw in the test section construction or other phenomena; in any case, it was observed in nearly every subsequent data set collected (see, for example, the results for data set nos. 9 and 11 in Sections 6.3.5 and 6.3.6, respectively in reference [3]).

Fig. 3.4.23 Data set no. 5: contour plot of film thickness

Figure 3.4.24 shows three graphs comparing profile plots of the 3-D surface fit to the actual film thickness data. The profile plots reveal that for this data set, the quality of the surface fit obtained was moderate. The surface is fairly smooth but lies outside the uncertainty ranges of two of the data points.

Fig. 3.4.24 Data set no. 5: comparison of surface fit to experimental data

Operating Temperature with Reduced Pressure Differential

Data set no. 8 was collected at an elevated operating temperature of roughly 74 °C and a reduced pressure differential of roughly 16 kPa (2.3 psi). The mass flow rate was within the nominal range of 4.0 to 5.5 g/min. These flow conditions essentially represented a check of the effect of a sharp decrease in the

pressure differential across the membrane. A 3-D surface plot of the film thickness data is shown in Fig. 3.4.25 and a contour plot is shown in Fig. 3.4.26. The plots reveal a marked non-uniformity in the film thickness. These results suggest that when the pressure differential was too low, the effects of the interaction between the membrane and the flowing liquid film tended to dominate, and the film became unstable.

Figure 3.4.27 shows three graphs comparing profile plots of the 3-D surface fit to the actual film thickness data. The profile plots reveal that for this data set, the quality of the surface fit obtained was poor, as the surface lies outside the uncertainty ranges of nine of the data points. This result is not entirely unexpected, however, considering the variation of the film thickness data.

Operating Temperature with Elevated Pressure Differential

Data set no. 9 was collected at an elevated operating temperature of roughly 70 °C and an elevated pressure differential of roughly 72 kPa (10 psi). The mass flow rate was within the nominal range of 4.0 to 5.5 g/min. These flow conditions essentially represented a check of the effect of a sharp increase in the pressure

Fig. 3.4.25 Data set no. 8: 3-D surface plot of film thickness

differential across the membrane. A 3-D surface plot of the film thickness data is shown in Fig. 3.4.28 and a contour plot is shown in Fig. 3.4.29. The plots suggest that when the pressure differential was increased, the entire film tended to thicken. This observation is consistent with the result for the average film thickness, which was $\overline{\Delta Z} = 189.6 \pm 7.6\text{ }\mu\text{m}$.

Fig. 3.4.26 Data set no. 8: contour plot of film thickness

This thickening may have been at least partly attributable to the fact that at increased pressure differentials, the PTFE membrane could visibly be seen to deflect into the mesh structure of the polypropylene backing over the entire contactor area. (At lower pressure differentials, this deflection was observed over some of the contactor area, but not over its entirety.) Notably, these results exhibit the same thickening of the downstream end of the film observed in data set no. 5.

Fig. 3.4.27 Data set no. 8: comparison of surface fit to experimental data

Fig. 3.4.28 Data set no. 9: 3-D surface plot of film thickness

Figure 3.4.30 shows three graphs comparing profile plots of the 3-D surface fit to the actual film thickness data. The profile plots reveal that for this data set, the quality of the surface fit obtained was high, as the surface is fairly smooth and lies outside the uncertainty range of only one data point.

Fig. 3.4.29 Data set no. 9: contour plot of film thickness

Room Temperature after Extended High-Temperature Run

Data set no. 11 was collected at about 33 °C (near room temperature) and at the nominal pressure differential of 43 kPa (6.3 psi). The mass flow rate was within the nominal range of 4.0 to 5.5 g/min. These flow conditions essentially represented a check of the effect of returning the test section to “cold flow” conditions after an extended run at elevated temperatures. A 3-D surface plot of the film thickness data is shown in Fig. 3.4.31 and a contour plot is shown in Fig. 3.4.32.

Fig. 3.4.30 Data set no. 9: comparison of surface fit to experimental data

Fig. 3.4.31 Data set no. 11: 3-D surface plot of film thickness

The plots suggest that when the temperature was decreased, the entire film tended to decrease in thickness from the levels observed at higher temperatures (see, for example, the results for data set no. 9 in the previous section). This observation is consistent with the result for the average film thickness, which was

$$\overline{\Delta Z} = 168.7 \pm 5.4\text{ }\mu\text{m}$$

Fig. 3.4.32 Data set no. 11: contour plot of film thickness

Interestingly, the downstream end of the membrane did not appear to collapse as had occurred in previous cold flow tests (see, for example, the results for data set no. 2). Furthermore, the film thickness did not return entirely to the nominal thickness of roughly $154\text{ }\mu\text{m}$ observed in data set no. 1. This appeared to be due at least in part to the membrane receiving somewhat of a “permanent press” during the extended run at elevated temperature and pressure. These results once again exhibit a thickening of the downstream end of the film, as was observed in data set nos. 5 and 9.

Figure 3.4.33 shows three graphs comparing profile plots of the 3-D surface fit to the actual film thickness data. The profile plots reveal that for this data set, the quality of the surface fit obtained was high. The profile plots reveal that for this data set, the quality of the surface fit obtained was high, as the surface is very smooth and lies outside the uncertainty range of only one data point.

Fig. 3.4.33 Data set no. 11: comparison of surface fit to experimental data

References for Section 3.4:

1. Drost, K., 1999, "Mesoscopic Heat-Actuated Heat Pump Development," *Proc. ASME Advanced Energy Systems Division – 1999*, ASME, New York, AES-Vol. 39, pp. 9-14.
2. Drost, M. K., Friedrich, M., Martin, C., Martin, J., and Cameron, R., 1999, "Recent Developments in Microtechnology-Based Chemical Heat Pumps," *Microreaction Technology: Industrial Prospects – IMRET 3: Proc. Third International Conf. on Microreaction Technology*, W. Ehrfeld, ed., Springer-Verlag, Berlin, pp. 394-401.
3. Peterson, Jerrod, 2004, "Investigation of the Dimensional Stability of an Ultra-Thin Film Gas/Liquid Contactor," Oregon State University, M.S. Thesis.
4. Acuity Research, Inc., 2003, "AccuRange600 Laser Displacement Sensors With Measurement Capabilities from Inches to Feet," Homepage, Accessed 5/21/04, <http://www.acuityresearch.com/pdf/ar600-data-sheet.pdf>.
5. Shigley, J. E., and Mischke, C. R., 1989, *Mechanical Engineering Design*, 5th ed., McGraw-Hill, Inc., San Francisco, pp. 738, 742.
6. Gere, J. M., and Timoshenko, S. P., *Mechanics of Materials*, 4th ed., PWS Publishing Company, San Francisco, pp. 607-608.
7. Boresi, A. P., and Schmidt, R. J., 2003, *Advanced Mechanics of Materials*, 6th ed., John Wiley & Sons, Inc., New York, pp. 482-484.
8. GenPore, Inc., 2002, "Advantages of Porous Plastic Materials," Homepage, Accessed 7/16/03, <http://www.genpore.com/mat.htm>.
9. M. A. Industries, Inc., "Material Capabilities," Homepage, Accessed 7/16/03, <http://www.maind.com/capa.htm>.
10. MicroPore Plastics, Inc., 2003, "Materials," Homepage, Accessed 7/16/03, <http://www.micropore.thomasregister.com/olc/74048661/material.htm>.
11. Porex Porous Products Group, 2002, "Mupor™ Microporous and Porous PTFE," Homepage, Accessed 7/17/03, <http://www.porex.com/english/products/muporproducts.asp>.
12. Rhopore, Inc., 2003, "Tech Data," Homepage, Accessed 7/16/03, <http://www.rhopore.com/techdata.htm>.
13. Scientific Commodities Incorporated, "Porous Sheets," Homepage, Accessed 7/16/03, http://www.scicominc.com/porous_sheets.htm.
14. Meille, S., and Garboczi, E. J., 2001, "Linear Elastic Properties of 2-D and 3-D Models of Porous Materials Made From Elongated Objects," *Model. Simul. Mater. Sci. Eng.*, **9** (5), pp. 371-390.
15. Levin, V. A., Lokhin, V. V., and Zingerman, K. M., 2000, "Effective Elastic Properties of Porous Materials With Randomly Dispersed Pores: Finite Deformation," *J. Appl. Mech.*, **67** (4), pp. 667-670.
16. Herakovich, C. T., and Baxter, S. C., 1999, "Influence of Pore Geometry On the Effective Response Of Porous Media," *J. Mater. Sci.*, **34** (7), pp. 1595-1609.
17. Mukhopadhyay, A. K., and Phani, K. K., 1998, "Young's Modulus – Porosity Relations: An Analysis Based On a Minimum Contact Area Model," *J. Mater. Sci.*, **33** (1), pp. 69-72.

18. O'Rourke, J. P., Ingber, M. S., and Weiser, M. W., 1997, "The Effective Elastic Constants of Solids Containing Spherical Exclusions," *J. Compos. Mater.*, **31** (9), pp. 910-934.
19. Kupkova, M., 1993, "Porosity Dependence of Material Elastic Moduli," *J. Mater. Sci.*, **28**, pp. 5265-5268.
20. Harper, C. A., ed., 1996, *Handbook of Plastics, Elastomers, and Composites*, 3rd ed., McGraw-Hill, Inc., San Francisco, App. C.
21. Portec Ltd., 2003, "Metapor – Micro-porous, Air-permeable Aluminium," Homepage, Accessed 6/30/03, <http://www.portec.ch/>.
22. Hopkins, S. W., "Porous Aluminum Mold Materials: 'The New Thermoform Tooling Advantage,'" Accessed 6/30/03, http://www.imsteel.com/productpdf/porous_aluminum_molds2_020702.pdf.
23. Figliola, R. S. and Beasley, D. E., 2000, *Theory and Design for Mechanical Measurements*, 3rd ed., John Wiley & Sons, Inc., New York, pp. 161-163, 181-183.

SECTION 3.5 LATTICE BOLTZMANN SIMULATION (TASK 5)

The overall performance of microchannel devices depend on the microscopic heat- and mass-transport behavior at the membrane and within the channel. To optimize the performance of these devices, we need to have a clear understanding of this transport behavior. The purpose of this task was to provide simulation and modeling support for both the single-phase and multi-phase experimental efforts.

The primary simulation tool was the lattice Boltzmann (LB) computer program developed by staff at PNNL. There are several advantages for using the lattice Boltzmann method for these analyses. One is that the LB method is inherently parallelizable and capable of simulating very detailed systems. Another is that phase interfacial forces may be incorporated into the equations, allowing the modeling of discrete bubbles and droplets within a microchannel.

Section 3.5.1 describes the basic lattice Boltzmann equations and solution method. Section 3.5.2 describes the simulation of single-phase lithium bromide solution microchannel desorption. Section 3.5.3 discusses the simulation of boiling in microchannels. Conclusions are presented in Section 3.5.4.

Section 3.5.1 Lattice Boltzmann Simulation Method

Conventional computational fluid dynamics (CFD) methods begin by discretizing the relevant transport partial differential equations, such as the Navier-Stokes equation, and solving directly for the transported quantities. However, certain assumptions are used in the development of these equations, such as an isotropic pressure tensor. The lattice Boltzmann methods begins with the microscopic kinetics equations and applies the appropriate closures to obtain a more general form of the transport equations [1,2].

The single particle distribution function $f(\mathbf{x}, \mathbf{v}, t)$ is the probability of finding particles at position $\mathbf{x}$ with velocity $\mathbf{v}$ at time t . The Boltzmann equation describes the evolution of the distribution function

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = -\frac{f - f^{eq}}{\tau} \quad (3.5.1)$$

where τ is the relaxation time and the equilibrium Maxwell distribution is

$$f^{eq} = N\rho(x) \exp\left[-\frac{(\mathbf{v} - \mathbf{u})^2}{2RT}\right] \quad (3.5.2)$$

where N is a normalization factor, ρ is the density and $\mathbf{u}$ is the average velocity.

To solve this equation on a computer, the spatial domain is discretized into a finite number of lattice sites, where each lattice site has values for density, pressure, flow, etc. The single-particle distribution function, which describes the probability of a particle traveling along a particular direction and speed, is discretized to form a finite set of displacement vectors connecting each lattice site to adjacent sites. The displacement vectors for two- and three-dimensional systems are shown in Figure 3.5.1.

Figure 3.5.1 Lattice displacement vectors for two- and three-dimensional systems

The lattice Boltzmann equation describes the evolution of the discretized particle distribution function, $f_i(\mathbf{x}, t)$, along direction i as a function of time. The new time distribution function is given by the equation

$$f_i(x + \Delta t e_i, t + \Delta t) - f_i(x, t) = -\frac{1}{\tau} [f_i(x, t) - f_i^{eq}(x, t)] \quad (3.5.3)$$

where τ is a linear relaxation parameter and f_i^{eq} is the local equilibrium distribution. The direction vectors for two dimensions are

$$e_i = \begin{cases} 0, & i = 0 \\ \{\cos[(i-1)\pi/2], \sin[(i-1)\pi/2]\}c, & i = 1-4 \\ \sqrt{2}\{\cos[(i-5)\pi/2 + \pi/4], \sin[(i-5)\pi/2 + \pi/4]\}c, & i = 5-8 \end{cases} \quad (3.5.4)$$

The local equilibrium is expressed in the form of a quadratic expansion of the Maxwellian distribution

$$f_i^{eq} = w_i \rho \left[1 + \frac{3e_i \cdot u}{c^2} + \frac{9(e_i \cdot u)^2}{2c^4} - \frac{3u^2}{2c^2} \right] \quad (3.5.5)$$

where c is the reference lattice speed, $c = \Delta x / \Delta t$. The weight coefficients, w_i for a three-dimensional system are

$$w_i = \begin{cases} \frac{1}{3} & i = 0 \\ \frac{1}{18} & i = 1-6 \\ \frac{1}{36} & i = 7-18 \end{cases}$$

The linear relaxation parameter, τ , is related to the kinematic viscosity by the expression

$$\nu = (\tau - 0.5)\Delta t c / 3 \quad (3.5.6)$$

Solution methods consist of a streaming stage and a collision stage for each time step. During the streaming stage, each lattice site transmits distribution information with adjacent neighbor sites. The incoming information is then relaxed toward an equilibrium distribution, which is determined by local conditions. The new time pressure and velocity values are determined using the expressions

$$p = \frac{c}{3} \sum_i f_i \quad (3.5.7)$$

$$\rho u = \sum_i f_i e_i \quad (3.5.8)$$

This procedure is repeated for the specified number of time steps until a steady-state solution is obtained. The result is a second-order solution to the Navier-Stokes and continuity equations

$$\rho \frac{\partial u}{\partial t} + \rho u \cdot \nabla u = -\nabla p + \rho \nu \nabla^2 u \quad (3.5.9)$$

$$\nabla \cdot (\rho u) = 0 \quad (3.5.10)$$

Section 3.5.2 Single-phase Microchannel Desorber Simulations

The effectiveness of microchannel desorber/adsorber devices may be limited by the rate of mass transfer through the channel. Work done under Task 2 and Task 4 (described in Sections 3.2 and 3.4) determined the vapor mass rate as a function of power, concentration, temperature and water vapor pressure. Lattice Boltzmann models were developed to evaluate the experimental data and to provide insight into the mass and energy transport behavior in these microchannels. Section 3.5.2.1 describes the new transport model used in the lattice Boltzmann simulations. Section 3.5.2.2 presents the validation of the model using the PNNL desorber data. Section 3.5.2.3 describes the evaluation of the OSU desorber data.

Section 3.5.2.1 Lattice Boltzmann Scalar Transport Model

The simulation of microchannel desorbers involves scalar transport of energy and chemical species. The existing lattice Boltzmann scalar transport models have significant limitations. The most popular one involves a separate distribution function, similar to that used for flow, for each scalar field [3]. The relaxation time is used to control the conductivity or diffusivity. Major limitations include the memory storage required, the interface between the fluid and solid regions for energy and time step limitations.

A new scalar transport model has been developed to solve the advection-diffusion equation

$$\frac{\partial \phi}{\partial t} = \nabla \cdot u \phi - \nabla \cdot D \nabla \psi + R_{\phi} \quad (3.5.11)$$

where ϕ is the scalar quantity, D is the diffusion coefficient, ψ is the diffusion potential and R is the source term. The first term on the right hand side, advection transport, is calculated using an advection transport distribution function, f_{adv} , which describes the net transfer of mass from a lattice site to every connected site. The change in scalar value due to advection is given by the expression

$$\phi(r, t + \Delta t) = \phi(r, t) - \frac{1}{\rho} \sum_i f_{adv,i} \phi^* \quad (3.5.12)$$

where ϕ^* is the upwind value. The same advection transport distribution is used for all scalar fields. The explicit scalar transport equation combines terms to form

$$\phi(r, t + \Delta t) = \phi(r, t) - \frac{1}{\rho} \sum_i f_{adv,i} \phi^* - \Delta t \sum_i D_i [\psi(r, t) - \psi(r + \Delta t e_i, t)] + R \Delta t \quad (3.5.13)$$

where D is the diffusivity coefficient, ψ is the diffusion potential (such as temperature for energy) and R is the volumetric generation rate. The primary advantages of this approach are that it requires only one additional distribution function, significantly reducing the memory requirement, and it simplifies the coupling with the solid region energy equation. The primary disadvantage is that the explicit formulation is subject to time step limitations.

The scalar transport equation may be expressed in an implicit form by dividing the convection term into incoming and outgoing sums

$$\begin{aligned} C_0 &= \frac{1}{\rho} \sum_i f_{adv,i} \phi^* & f_{adv,i} < 0 \\ C_1 &= \frac{1}{\rho} \sum_i f_{adv,i} & f_{adv,i} > 0 \end{aligned} \quad (3.5.14)$$

In addition, the diffusion potential may be linearized with respect to the new time scalar value

$$\psi = \psi_0 + \psi_1 \phi \begin{cases} \Psi_0 = \Delta t \sum_i D_i [\psi_0(r, t + \Delta t) - \psi(r + \Delta t e_i, t + \Delta t)] \\ \Psi_1 = \Delta t \sum_i D_i \psi_1(r, t + \Delta t) \end{cases} \quad (3.5.15)$$

Combining these terms, we get the expression

$$\phi(r, t + \Delta t) = \frac{\phi(r, t) - C_0 - \Psi_0 + R\Delta t}{1 + C_1 + \Psi_1} \quad (3.5.16)$$

This expression may be generalized to obtain a Crank-Nicholson scheme for greater temporal accuracy. A journal article is being submitted on this development [4].

Section 3.5.2.2 Validation with PNNL Desorber Data

The application of the lattice Boltzmann method to the analysis of microchannel desorbers/absorbers was validated using data taken from the desorber system described in Section 3.2 by PNNL. The membrane desorber consists of a metal test article containing a narrow cavity, which is divided into a vapor and fluid channel region using a porous hydrophobic membrane. The fluid slit channel is approximately 100 microns high, 15.24 cm. wide and 5.5 cm. long. The lithium bromide solution is maintained at a slightly positive pressure to prevent vapor from entering the fluid region, but sufficiently low to avoid “breakthrough” of the fluid through the membrane into the vapor space. Additional information on this test section may be found in Section 3.2.

A lithium bromide solution with a specified temperature and composition flows through a header into the entrance of the channel. As the solution flows through the channel, water vapor evaporates from the solution through the membrane into the vapor space, which is maintained at a constant vapor pressure. The temperature is maintained by applying heat to the metal surface beneath the fluid channel using resistance elements. The excess vapor is collected in a condensing tank and measured over a period of time.

A series of desorber tests were performed under Task 2 on 3/8/02 (Cases 1-2) and 7/2-3/02 (Cases 3-8). The operating conditions for each case are listed in Table 1. The inlet temperature ranged from 56.9 to 88.4 C, the vapor pressure varied from 65.7 to 141.7 Torr and the heat generation ranged from 49.3 to 88.0 watts.

Simulation Model

The lattice Boltzmann simulation model is divided into fluid, metal, membrane and vapor regions. The fluid region is represented by a grid of lattice sites that provide flow, temperature and concentration profiles. The flow rate is controlled by specifying pressure boundary conditions at the channel inlet and exit.

The original desorber simulation model had a constant heat flux boundary condition applied to the bottom of the fluid channel. The metal plate between the resistance heaters and the fluid channel has the effect of transferring heat laterally to the colder region near the flow inlet. Therefore, the metal region is represented by a grid of lattice sites used to solve the energy equation. A constant heat flux boundary condition is applied to a specified region on the bottom of the plate. Based on thermocouple readings and a simple heat transfer analysis, it was assumed that approximately 10% of the heat generated in the resistance heaters was lost to ambient.

The membrane model is based on a series of assumptions. One is that the solution at the liquid-vapor interface is in thermodynamic equilibrium with the water vapor. Therefore, the surface concentration is determined by the vapor pressure and local temperature. The vapor pressure is adjusted to account for pressure loss due to vapor flow through the membrane. During operation, water is constantly evaporating at a rate to maintain the equilibrium concentration. Another assumption is that the liquid-vapor interface is located at the outer surface of the membrane and the solution does not penetrate into the porous structure. The formation of a stagnant fluid layer within the membrane would severely degrade the mass transport of the device. The vapor region was assumed to be at constant pressure.

Results and Discussion

Lattice Boltzmann simulations were performed for the tests performed on 3/8/02 (Cases 1-2) and 7/2-3/02 (Cases 3-8). The calculated desorption rates results for the desorber test article are compared to experimental data in Table 3.5.1.

Table 3.5.1. Comparison of Lattice Boltzmann Simulation Results with Desorber Data

Case	Tin (K)	Conc. (wt%)	Qin (W)	Flow (g/min)	Pvap (Torr)	Rate-data (g/min)	Rate-sim (g/min)	Diff (%)
1	56.9	52.4	73.6	30.0	75.0	0.5	0.537	+7.4
2	56.9	52.4	88.0	34.9	82.4	0.7	0.606	-13.4
3	72.0	53.4	49.5	27.7	65.7	0.442	0.438	-0.8
4	77.5	53.5	49.3	30.8	69.3	0.444	0.488	+9.8
5	87.8	53.7	58.4	31.0	111.4	0.500	0.563	+12.6
6	87.6	53.7	58.3	29.0	141.7	0.525	0.486	-7.4
7	87.9	53.7	74.6	28.0	127.8	0.442 (0.712)	0.758	-23.6 (+5.2)
8	88.4	53.7	74.3	31.2	129.1	0.981 (0.712)	0.749	+71.5 (+6.5)

The predicted desorption rates match the experimental values to within 15%, except for cases 7 and 8. The description of the tests indicated that a valve between the vapor space and the condensation tank was restricting vapor flow during case 7. The valve was opened before case 8 and the desorption rate increased dramatically (more than doubled). One possible explanation of this is that some of the condensed vapor for case 7 was being trapped in the vapor lines. When the valve was opened, the trapped condensation may have been pushed out of the line into the tank, indicating a much higher desorption rate. Since the operating conditions for the two cases are very similar, we make the assumption that the actual desorption rate is the average of the measured values for the two cases (shown in parentheses). The simulation results for these two cases are within 7% of the averaged value.

Figures 3.5.2 and 3.5.3 show the temperature and water concentration profiles at the top and bottom channel surfaces, along with the flow average values. All three temperature profiles jump quickly at the channel entrance to near their final values. This is due to the efficient lateral heat transfer through the metal plate. Note also that the separation between profiles is narrow, due to the relatively high thermal conductivity through the solution.

Figure 3.5.2 Temperature profiles for Case 8 as a function of location.

Figure 3.5.3 Water concentration profiles for Case 8 as a function of location

The top surface lithium bromide solution is assumed to be in equilibrium with the water vapor space. Therefore, the composition is determined by the vapor pressure and local temperature. For this reason, the top surface profile jumps quickly to near its final value near the entrance of the channel. The mass diffusion rate is significantly less than the thermal diffusion, resulting in a slower change in the flow average and bottom surface concentrations.

A major limitation to increasing the desorption rate by increasing the heat generation is the possibility of boiling in the microchannel. If boiling occurs, the flow may be blocked by the formation of bubbles spanning the channel. If the design of the channel and membrane does not induce the rapid transport of the bubble vapor through the membrane, the performance of the desorber will be degraded.

The risk of boiling occurs when the saturation pressure at any given point significantly exceeds the solution pressure. The flowing solution is kept a slightly higher pressure relative to the vapor space to prevent vapor breakthrough. The liquid is constrained by the membrane and forms menisci with radii of curvature corresponding to the pressure differential and surface tension. The solution pressure is highest at the

channel inlet and decreases linearly to the exit. The inlet pressure cannot exceed the liquid breakthrough point.

At the top surface, the saturation pressure is, by definition, the vapor pressure. The margin of safety is the difference between the vapor and solution pressures. The margin decreases as we move away from the interface. The greatest risk for boiling occurs at the bottom surface, where the temperature is highest and the water concentration is greatest (corresponding to the highest saturation pressure).

Figure 3.5.4 shows a comparison of the top and bottom surface temperature profiles and the local saturation temperature profile (based on the solution composition and pressure) for two different exit pressures. The first exit pressure corresponds to the measured value for case 8. Note that for the lower exit pressure, the calculated bottom temperature profile exceeds the saturation temperature by a degree of superheat. When the exit pressure is increased, it creates a margin of safety of a few degrees.

Figure 3.5.4. Comparison of top and bottom surface temperature profiles for Case 8.

The risk of boiling may be reduced in a number of ways, including:

- Increase the exit pressure – The limitation to this approach is the breakthrough pressure of the membrane. If the membrane can be designed to increase the breakthrough value, it will allow a higher exit pressure.

- Microchannel mixing – The concept is to design the microchannel to induce mixing in the vertical direction. This approach will have two positive effects. It will increase the rate of desorption for given operating conditions, and it will reduce the difference between the top and bottom surface conditions.
- Gas side heating – If the heat could be applied to the top surface, through the gas space, the vapor generation would preferentially occur at the liquid-vapor interface. The problem is the high thermal resistance will result in low heat transfer efficiency. More discussion on this may be found in Section 3.5.2.3.
- Vapor bubble management – The formation of water vapor is good if it can be effectively separated from the liquid phase. If the vapor bubbles can be captured and united with the vapor phase, then boiling is not a limitation.

Section 3.5.2.3 Analysis of OSU Desorber Data

A series of membrane desorber tests were performed by Oregon State University which are described in Section 3.4. The membrane desorber consists of a metal test article containing a narrow cavity, which is divided into a vapor and fluid channel region using a porous hydrophobic membrane. The fluid slit channel has a width ranging from 100 microns to 750 microns, is 3 cm. wide and 6 cm. long. The lithium bromide solution is maintained at a slightly positive pressure to prevent vapor from entering the fluid region, but sufficiently low to avoid “breakthrough” of the fluid through the membrane into the vapor space.

A lithium bromide solution with a specified temperature and composition flows through a header into the entrance of the channel. As the solution flows through the channel, water vapor evaporates from the solution through the membrane into the vapor space, which is maintained at a constant vapor pressure. The temperature is maintained by applying heat to the membrane using resistance elements.

The lattice Boltzmann simulation model is divided into fluid, membrane and vapor regions. A grid of lattice sites that provide flow, temperature and concentration profiles, represented the fluid region. Specifying pressure boundary conditions at the channel inlet and exit controlled the flow rate.

The membrane model is based on a series of assumptions. One is that the solution at the liquid-vapor interface is in thermodynamic equilibrium with the water vapor. Therefore, the surface concentration is determined by the vapor pressure and local temperature. The vapor pressure is adjusted to account for pressure loss due to vapor flow through the membrane. During operation, water is constantly evaporating at a rate to maintain the equilibrium concentration.

Another assumption is that the liquid-vapor interface is located at the outer surface of the membrane and the solution does not penetrate into the porous structure. The formation of a stagnant fluid layer within the membrane would severely degrade the mass transport of the device. The vapor region was assumed to be at constant pressure.

A series of desorber tests with a channel widths of 100 and 750 microns were conducted and the results are presented in Section 3.4. Over a hundred lattice Boltzmann simulations were performed using the operating conditions specified in the test matrix. Some selected results are presented in Figures 3.5.5 through 3.5.9 and Tables 3.5.2 through 3.5.7.

The lithium bromide mass fraction profiles for the 100 μm and 750 μm channel are presented in Figures 3.5.5 and 3.5.6. The x-axis dimensions have been contracted for easier viewing. Note that the concentration boundary layer spans the 100 μm channel but only partially penetrates the 750 μm channel. As the concentration boundary layer grows, the resistance to the diffusion of water to the membrane surface increases. The local concentration at the membrane increases as a function of distance from the inlet. Since the water vapor at the surface is nearly constant, the temperature must also increase along the surface.

The total vapor generation rate was calculated for each test condition. Figure 3.5.7 shows a typical comparison with measured and predicted vapor generation rates for a 100 μm channel (40 wt%, ~ 21 kPa) for different input power levels. The predicted values are in the range of the measured values, but the predicted rates flatten as the power goes up while the measure values appear to accelerate. The predicted values suggest that there is significant mass diffusion limiting.

The effect of inlet concentration on vapor generation rate is shown in Figures 3.5.8 and 3.5.9 for the two different channels. The 100 μm channel shows a significant decrease in vapor rate with increasing inlet concentration. The 750 μm channel shows less of an effect, although still noticeable.

A comparison of measured and calculated vapor generation rates are presented in Tables 3.5.2 through 3.5.7. The rates are also expressed in terms of percent of the power input. The energy applied to the desorber is divided between latent heat of evaporation for vapor generation, sensible heat of the remaining solution and heat losses from the device.

The measured and calculated vapor generation rates increases as the vapor generation decreases and as the inlet concentration decreases. However, the trends with respect to power input do not agree. In general, the fraction of power used for vaporization tend to increase with power while the values from the lattice Boltzmann simulation tend to decrease with power. The decrease of the simulated values are a result of the increased diffusion resistance through the concentration boundary layer. One possible explanation for the discrepancy is a disproportionately high heat loss at lower power, based on solution temperature.

Certain observations can be made based on these results:

- The water vapor is in equilibrium with the LiBr solution at the liquid-vapor interface. The composition and temperature of the solution must fall on the vapor pressure line in the phase diagram. For example, as water is desorbed, the solution moved to a higher concentration of LiBr. Part of the heat must then go to heating the solution to maintain equilibrium with the vapor space. Therefore, the heat applied to the channel will be divided between desorption and sensible heating of the solution (and heat loss from the system).
- The ratio of latent heat to sensible heat depends on the channel operating conditions, especially the vapor pressure. Holding the other operating conditions constant, a higher vapor pressure results in a larger fraction of the heat going to sensible heat of the solution. A lower vapor pressure results in a larger amount of water desorption. An accurate measurement of the solution exit temperature and vapor generation is critical for determining this ratio.

Figure 3.5.5. LiBr mass fraction profile for 100 μm channel (3.11 g/min, 27.9 kPa, 20.87 W)

Figure 3.5.6. LiBr mass fraction profile for 750 μm channel (3.27 g/min, 26.6 kPa, 20.0 W)

Figure 3.5.7. Predicted vs. measure vapor generation rates for 100 μm channel (40 wt%, ~21 kPa)

Figure 3.5.8. Vapor generation rate vs. LiBr concentration for 100 μm channel.

Figure 3.5.9. Vapor generation rate vs. LiBr concentration for 750 μm channel.

**Table 3.5.2 Comparison of measured and calculated vapor generation rate for
100 μ m channel (31.6 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
9.11	3.3309	73.0995	27.14	0.1219	51.8	0.1674	71.1
11.24	3.4317	73.1294	27.85	0.1654	56.9	0.1934	66.7
14.10	3.4397	75.0543	28.21	0.2381	65.3	0.2381	65.3
17.01	3.3092	76.3458	28.42	0.2956	67.2	0.2765	62.9
18.91	3.3541	76.4775	27.49	0.3516	71.9	0.3064	62.6
23.10	3.3567	77.7847	27.62	0.4426	74.1	0.3527	59.0
7.07	3.2243	71.3942	21.14	0.0748	40.9	0.1603	87.7
9.93	3.1775	72.9030	21.09	0.1394	54.3	0.2170	84.5
12.55	3.3164	74.8672	21.39	0.1834	56.5	0.2616	80.6
15.03	3.3410	75.1242	20.68	0.2404	61.9	0.3051	78.5
18.32	3.1902	76.0979	21.47	0.3344	70.6	0.3461	73.1
21.72	3.3040	76.9889	21.75	0.3876	69.0	0.3860	68.7
26.21	3.1159	79.3313	21.88	0.5145	75.9	0.4338	64.0

**Table 3.5.3 Comparison of measured and calculated vapor generation rate for
100 μ m channel (40 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
8.78	3.2856	76.0853	28.92	0.0801	35.3	0.1091	48.1
10.22	3.2298	75.8343	28.20	0.1017	38.5	0.1241	47.0
12.16	3.3525	76.8544	28.10	0.1328	42.2	0.1482	47.1
14.01	3.2568	77.6027	28.01	0.1514	41.8	0.1716	47.4
16.17	3.2696	78.7864	27.63	0.1923	46.0	0.1975	47.2
18.59	3.1453	80.3027	27.74	0.2262	47.1	0.2219	46.2
20.87	3.1092	81.8708	27.90	0.2632	48.8	0.2430	45.0
24.36	3.2747	83.0959	27.62	0.3378	53.6	0.2716	43.1
12.99	3.3226	75.4590	22.02	0.1606	47.4	0.1937	57.2
14.66	3.2945	78.1006	21.94	0.1783	46.6	0.2193	57.3
17.14	3.2248	77.9340	21.84	0.1964	43.9	0.2449	54.8
20.42	3.3080	79.6473	21.96	0.2794	35.7	0.2778	52.1
22.70	3.1775	81.6055	22.21	0.2951	49.8	0.2994	50.6
25.01	3.3666	82.7656	22.38	0.3637	55.7	0.3191	48.9
27.39	3.1868	83.0111	22.39	0.4031	56.4	0.3337	46.7
30.65	3.1358	84.9649	22.57	0.4834	60.5	0.3586	44.8

**Table 3.5.4 Comparison of measured and calculated vapor generation rate for
100 μ m channel (50.2 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
9.18	3.2351	86.0763	27.21	0.0351	14.5	0.05376	22.3
10.22	3.3042	86.0694	27.41	0.0422	15.7	0.06059	22.6
11.93	3.2790	86.6321	27.40	0.0640	20.4	0.07290	23.3
13.86	3.2756	87.4491	27.40	0.0981	26.9	0.08726	24.0
15.48	3.2897	88.1871	27.47	0.1200	29.5	0.09790	24.1
18.04	3.2766	89.9930	27.51	0.1525	32.2	0.11497	24.2
21.11	3.2539	92.1101	27.54	0.1921	34.6	0.12258	22.1
9.18	3.2661	85.7493	21.26	0.0130	5.4	0.0854	35.4
12.01	3.3297	87.0339	21.74	0.0458	14.5	0.1090	34.5
14.78	3.1690	87.9022	23.06	0.1185	30.5	0.1185	30.5
16.92	3.2496	87.9607	21.44	0.1034	23.3	0.1460	32.8
19.49	3.2865	88.4432	21.53	0.1320	25.8	0.1606	31.4
21.99	3.2615	92.6761	21.46	0.1781	30.8	0.1794	31.0
24.97	3.2074	91.2073	21.43	0.2174	33.1	0.1904	29.0

**Table 3.5.5 Comparison of measured and calculated vapor generation rate for
750 μ m channel (31.65 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
7.94	3.2854	72.6578	27.23	0.0511	24.5	0.1194	57.2
10.44	3.3897	73.3161	27.00	0.1038	37.8	0.1542	56.2
12.72	3.3316	75.3594	27.09	0.1555	46.5	0.1868	55.9
15.75	3.3129	76.4328	27.25	0.1405	33.9	0.2202	53.2
18.33	3.2945	77.8956	27.31	0.2545	52.8	0.2508	52.1
22.15	3.3517	80.4551	27.29	0.3550	61.0	0.2906	49.9
25.42	3.3735	77.8914	27.25	0.3911	58.5	0.3146	47.1
7.63	3.3053	70.7412	20.71	0.0665	33.2	0.1262	62.9
10.88	3.3663	72.9312	20.73	0.0931	32.6	0.1728	60.4
13.78	3.2196	75.1345	20.72	0.2048	56.6	0.2126	58.7
16.56	3.2390	76.4156	20.77	0.2676	61.5	0.2434	55.9
19.90	3.2726	79.6696	20.74	0.3467	66.3	0.2825	54.0
23.76	3.2884	79.4798	20.93	0.4291	68.7	0.3151	50.5
27.61	3.2671	81.961	20.99	0.4912	67.7	0.3493	48.1

**Table 3.5.6 Comparison of measured and calculated vapor generation rate for
750 μm channel (40 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
9.52	3.3418	79.0669	26.70	0.0734	29.3	0.1235	49.4
11.47	3.2603	78.7020	26.65	0.1025	34.0	0.1449	48.1
13.86	3/2584	80.3645	26.60	0.1589	43.6	0.1735	47.6
16.83	3.1808	82.9327	26.55	0.2014	45.5	0.2069	46.8
20.00	3.2704	84.5714	26.63	0.2568	48.9	0.2392	45.5
22.79	3/1507	85.3216	26.75	0.3292	55.0	0.2650	44.2
26.79	3.5133	85.5112	26.67	0.4193	59.6	0.2969	42.2
11.47	3.3241	79.6988	21.22	0.1337	44.4	0.1593	52.8
16.38	3.4009	83.3460	20.09	0.1903	44.2	0.2175	50.5
20.39	3.2548	86.6564	20.68	0.2489	46.4	0.2571	48.0
23.43	3.3260	88.4228	21.33	0.2931	47.6	0.2809	45.6
26.90	3.3005	88.4630	21.38	0.4308	60.9	0.3075	43.5
30.38	3.2983	90.1750	21.41	0.4028	50.4	0.3385	42.4

**Table 3.5.7 Comparison of measured and calculated vapor generation rate for
750 μm channel (50.2 wt% LiBr)**

Power Input (W)	Inlet Flow Rate (g/min)	Inlet T (C)	Vapor Pressure (kPa)	Measured Vapor Flow (g/min)	Fraction of Power In (%)	Calculated Vapor Flow (g/min)	Fraction of Power In (%)
10.95	3.2660	86.4539	27.04	0.0258	8.9	0.1067	36.7
12.80	3.2349	87.3864	27.07	0.0508	14.9	0.1262	37.1
15.05	3.3934	90.7675	27.05	0.0922	23.0	0.1529	38.2
17.30	3.4356	93.6949	27.07	0.1286	28.0	0.1786	38.8
19.21	3.3033	96.3132	27.10	0.1447	28.3	0.1994	39.0
21.22	3.3440	96.1881	27.16	0.1947	34.5	0.2153	38.2
23.54	3.3120	95.4131	27.18	0.2072	33.1	0.2326	37.2
10.44	3.3483	86.8813	22.42	0.0363	13.1	0.1117	40.2
12.17	3.3692	87.9642	22.34	0.0593	18.3	0.1319	40.8
14.53	3.3451	88.9045	22.43	0.0813	21.0	0.1555	40.3
16.56	3.3747	96.3338	22.37	0.1199	27.2	0.1854	42.1
19.31	3.4019	100.2719	22.41	0.1521	29.6	0.2141	41.7
23.65	3.4379	92.8289	22.50	0.2271	36.1	0.2375	37.8
25.99	3.3677	97.9506	22.51	0.2457	35.6	0.2618	37.9

Section 3.5.3 Simulation of Boiling in Microchannels

Two-phase flow in microchannels differs from that in macroscopic systems because bubbles may be large relative to the size of a microchannel. Bubbles constrained in microchannels will have high curvatures, and surface tension forces will control bubble stability and growth rate. In macroscopic systems, the bubbles are typically small compared to the dimension of the system, so that the two-phase mixture may be treated as continuum fields with averaged properties. However, in two-phase flow microchannels under certain conditions (i.e., low flow and/or high heat flux) the bubbles are so large relative to the size of the channel that the continuum approximation breaks down and discrete simulation of individual bubbles becomes necessary. This will be accomplished using the lattice-Boltzmann method.

Unlike the Navier-Stokes equations, the Boltzmann equation does not assume that the pressure is isotropic. This makes it possible to simulate multiphase systems in a straightforward way, without the introduction of complicated front tracking routines. Swift et al. [6] have demonstrated this approach by specifying terms based on a Cahn-Hilliard type free energy functional for the equilibrium distribution functions. Researchers at PNNL have recently developed a thermal model [7], based on internal energy, which is capable of simulating phase change behavior such as evaporation and condensation. This approach has been demonstrated by simulating evaporation from a liquid film, the evaporation of a liquid drop, condensation in a slit pore and bubble growth and detachment from a heated surface. Section 3.5.3.1 describes the lattice Boltzmann multiphase model. Section 3.5.3.2 describes an adaptive mesh refinement scheme to reduce computational time and memory requirements. Section 3.5.3.3 describes the models used to examine three-dimensional bubble nucleation and growth

Section 3.5.3.1 Lattice Boltzmann Thermal Two-phase Model

Unlike the Navier-Stokes equations, the Boltzmann equation does not assume that the pressure is isotropic. This makes it possible to simulate multiphase systems in a straightforward way, without the introduction of complicated front tracking routines.

The lattice Boltzmann method has several advantages over alternative approaches for discrete modeling of multiphase systems. Alternative simulation methods include the volume of fluid method (VOF) approach and the front tracking method. In both cases, the liquid-vapor or liquid-gas interface is treated as a discontinuous boundary between two distinct fluids. Although it is difficult to compare different simulation techniques, there are a number of advantages that the lattice-Boltzmann method has over these other simulation techniques:

- Lattice Boltzmann has the ability to incorporate surface tension and wettability terms directly into the equations of motion.
- Unlike the front tracking method, there is no problem with singularities associated with bubble or droplet pinch off. In addition the lattice Boltzmann method is easily extended to three dimensions, which is not true for front tracking methods.
- The lattice Boltzmann method developed by PNNL allows mass transfer due to evaporation or condensation. Absorption of gas into the fluid is also included.
- The lattice Boltzmann is inherently parallelizable, allowing the detailed simulation of large and complex systems.

The multiphase lattice Boltzmann model developed by Swift et al. [6] is based on the Cahn-Hilliard free energy functional with a gradient-squared approximation to define the fluid phase interface

$$\Psi = \int dr \left(\psi(T, \rho) + \frac{\kappa}{2} (\nabla \rho)^2 \right) \quad (3.5.17)$$

where ψ is the bulk free-energy density and the second term gives the free-energy contribution from density gradients in an inhomogeneous system. The parameter κ controls the surface tension of the interface. The pressure tensor is given by the expression

$$P_{\alpha\beta}(r) = p(r)\delta_{\alpha\beta} + \kappa \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} \quad (3.5.18)$$

with

$$p(r) = p_o - \kappa \rho \nabla^2 \rho - \frac{\kappa}{2} |\nabla \rho|^2 \quad (3.5.19)$$

and p_o is the equation of state of the fluid.

We incorporate the pressure tensor into the lattice Boltzmann method by modifying the equilibrium distribution function to include an additional term

$$f_i^{eq} = w_i (A + B u_\alpha e_{i\alpha} + C u^2 + D u_\alpha u_\beta e_{i\alpha} e_{i\beta} + G_{\alpha\beta} e_{i\alpha} e_{i\beta}) \quad (3.5.20)$$

where G is defined as

$$G_{\alpha\beta} = \frac{\kappa}{2c^4} \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} \quad \alpha \neq \beta \quad (3.5.21)$$

$$G_{\alpha\beta} = \frac{\kappa}{2c^4} \left\{ \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\beta} - \frac{1}{D} \frac{\partial \rho}{\partial x_\alpha} \frac{\partial \rho}{\partial x_\alpha} \right\} \quad \alpha = \beta \quad (3.5.22)$$

the repeated indices implies summation and D is the dimension of the system.

The fluid energy is treated as a passive scalar and is modeled using the method described in the previous section. The energy is specified as a function of both density and temperature. As energy is added to the system, the pressure near the interface increases, inducing the movement of mass through the interface, resulting in a conversion of energy due to latent heat.

This approach has been demonstrated by simulating evaporation from a liquid film, the evaporation of a liquid drop, condensation in a slit pore and bubble growth and detachment from a heated surface (see Figure 3.5.10).

Figure 3.5.10. Lattice-Boltzmann simulation results of bubble growth and detachment from a heated surface.

Section 3.5.3.2 Adaptive Mesh Refinement

The simulation of multi-phase systems requires a level of grid resolution sufficiently fine to capture the density profile through the liquid-vapor interface. However, the rest of the flow system does not require nearly that fine a grid. In addition, as the locations of the interfaces change, the grids must be able to refine/derefine with relatively little effort and impact on the simulation.

The approach taken to address this challenge is to divide the computational domain into a hierarchical system of data blocks containing a fixed number (for example, a $10 \times 10 \times 10$ array) of lattice sites. Information is passed from the surface planes of each block to the corresponding planes on the adjacent blocks as boundary conditions. The use of multiple data blocks rather than one large array reduces the total storage requirements for a simulation because only those arrays containing permanent information (velocities, temperature, etc.) must be stored for all blocks. All arrays containing temporary information (which includes quantities, such as transport properties, which are functions of temperature, etc.) are calculated and stored only for the current block as they are used.

In regions where grid refinement is desired, the lattice spacing is reduced by a factor of two and the block is subdivided into a number of smaller blocks (four for two dimensions, eight for three dimensions). The larger block is designated the parent block and a smaller one is a child. Another level of refinement is achieved when a child block is subdivided and becomes the parent for another set of children. This procedure is repeated until the desired level of refinement is achieved. Information that is passed from the surface of a higher resolution block to a lower, or vice versa, is obtained by interpolation/extrapolation of values near the boundary. The grid structure is constrained so those adjacent blocks differ by only one level of refinement (factor of two).

Block refinement may be triggered by a number of factors. For multi-phase flow simulations, the maximum absolute values for the density derivative or the density Laplacian may be used to identify the location of the interface and flag those blocks requiring the minimum level of refinement. For irregular or moving solid surfaces, the presence of solid surface sites may be used to trigger grid refinement. Detailed flow structures, such as vortex eddies, may use local shear or velocity gradients to trigger refinement.

The original lattice Boltzmann method is explicit in time and subject to a variety of time step limitations. The Courant limit specifies that the time step cannot exceed the lattice spacing divided by the maximum absolute velocity in the system, in other words, the flow cannot travel more than one lattice spacing per time step. Diffusion time limits also exist for the energy and chemical species transport equations. These time step limitations are discussed in more detail in Section 3.5.2.1. In all cases, a reduction in lattice grid size results in a corresponding reduction in the maximum time step size.

The time step for each block in the adaptive mesh refinement scheme depends on the level of refinement. As the lattice spacing is divided by a factor of two, the time step is also divided by a factor of two, maintaining the same Courant ratio. Therefore, a refined block experiences two time steps for each coarse block time step. This adds a level of complexity to the boundary conditions passed between blocks of different refinement. For example, the boundary information to be passed from fine blocks to a coarse block must be collected from multiple fine blocks and summed over two time steps.

The use of this refinement scheme is demonstrated on a simple two-dimensional multi-phase system, where droplets of various sizes are suspended in vapor. The fluid density profile is shown in Figure 3.5.11. The darker regions indicate a higher level of refinement. The original grid consists of a 8x8 block array, where each block contains 20x20 lattice sites. Blocks which contain the liquid-vapor phase interface are refined by one level. The final grid consists of 38,800 lattice sites, as compared to 102,400 for the same level of refinement for the whole system, almost a factor of three. The CPU time reduction is roughly a factor of four, including the time step differences. The reduction is expected to be more dramatic as we move to three-dimensional systems, smaller block sizes and greater levels of refinement.

Figure 3.5.11. Fluid density profile for an adaptive mesh refinement of a simple two-dimensional, multi-phase system.

The result of the work so far is the development of a static adaptive mesh refinement capability. As the simulation progresses, the phase interfaces (or moving boundaries, etc.) move from one block to the next, requiring the refinement/derefinement of additional blocks.

Section 3.5.3.3 Three-dimensional Bubble Nucleation and Growth

As the heat flux to the desorber membrane is increased, the vapor generation rate begins to exceed the rate of extraction through the membrane and bubbles form in the liquid side of the desorber membrane. The formation of these bubbles may interfere with the solution flow and performance of the desorber. A three-dimensional lattice Boltzmann simulation model was developed to simulate microchannel boiling. The purpose of this model is to understand the boiling behavior as a function of flow rate and heat flux. The results will help define the range of operating conditions for thermal microchannel devices, such as the desorber.

Simulation Model

The simulation model consists of a liquid region, a vapor region, and a membrane. The top of the fluid region is bounded by a membrane consisting of a solid mesh with open regions bridged by the liquid-vapor interface. The backing is represented by a Darcy resistance to vapor flow. The vapor region is bounded on top by a specified pressure boundary. The liquid region is bounded on the bottom by a slip boundary. Liquid flow in the lateral direction is induced using upstream and downstream pressure boundaries in the fluid region.

As heat is applied to the membrane, the energy is conducted into the fluid and contributes to the latent heat of phase change. The vapor flows through the membrane and the vapor region to the pressure boundary. If a pore in the membrane is not connected, it can act as a nucleation site to form an independent bubble. Figure 3.5.12 shows a simulation of a bubble growing on a region membrane that is partially blocked.

As the bubble grows it may overlap an open pore that allows the vapor to escape. Two pressure differences contribute to this vapor flow: 1) the positive pressure difference between the liquid channel and the vapor space, and 2) the pressure difference across the bubble interface due to surface tension. As the bubble grows and the radius of curvature increases, the second contribution decreases. There is a critical bubble size (which is a function of heat flux and liquid-vapor pressure difference) beyond which the bubble will continue to grow. If there is a nucleation region large enough to allow the bubble to grow to critical size, then channel two-phase behavior will occur.

Another important question is that is bubble evolution and detachment. Two sets of flow boundary conditions are possible. One is to model the entire liquid channel by using inlet and exit pressure boundaries and a no-slip boundary on the bottom surface. The other is to specify a slip boundary on the bottom and model just the liquid near the membrane surface (for smaller bubbles). The rate of flow and heat flux may be varied to determine the bubble behavior.

Figure 3.5.12. Density isosurface of a bubble growing on membrane mesh. The four membrane pores under the bubble are closed to vapor flow.

As the heat flux to the desorber membrane is increased, the vapor generation rate begins to exceed the rate of extraction through the membrane and bubbles form in the liquid side of the desorber membrane. The formation of these bubbles may interfere with the solution flow and performance of the desorber. A three-dimensional lattice Boltzmann simulation model was developed to simulate microchannel boiling. A series of simulations were performed under different operating conditions. The results suggested an analytical model that could represent the essential features of the system. The purpose of this analytical model is to understand the boiling behavior as a function of flow rate and heat flux. The results will help define the range of operating conditions for thermal microchannel devices, such as the desorber.

The top of the microchannel fluid region is bounded by a membrane consisting of a porous mesh bridged by the liquid-vapor interface. The backing is represented by a Darcy permeability, K , and thickness, L , which are used to calculate the resistance to vapor flow. As a heat flux, q'' , is applied to the membrane, the energy is conducted to the fluid interface and contributes to the latent heat of phase change.

The rate of growth of a vapor bubble (expressed in terms of grams of water vapor) is the rate of vapor generation minus the rate of vapor flow through the membrane. A clean membrane with no flaws will have a pore radius of r_p . The rate of bubble growth is given by the expression

$$Rate = \frac{q'' \pi r_p^2}{h_{fg}} - \left(\frac{2\sigma}{r} + \Delta P_{mem} \right) \frac{K}{L} \pi r_p^2 \rho_v \quad (3.5.23)$$

where r is the radius of curvature, σ is the surface tension, ΔP is the pressure difference across the membrane and ρ_v is the vapor density.

The radius of curvature begins at infinity for a zero heat flux and decreases as the flux increases. The bubble growth rate essentially remains zero until the radius of curvature exceeds the pore radius. For typical membrane pore sizes, this would require an unrealistically large heat flux compared to those typically used for practical applications. Yet microchannel desorbers experience bubble growth for relatively low heat fluxes. This implies that there must be some sort of flaw or blockage in the membrane to achieve a reasonable radius of curvature.

The pores of a membrane may be blocked for a variety of reasons, including manufacturing flaws, trapping of solid particles, fouling due to corrosion or oxidation products, etc. Assume a circular blocked region with radius r_0 . The rate of bubble growth then becomes

$$Rate = \frac{q'' \pi r^2}{h_{fg}} \quad r \leq r_0 \quad (3.5.24)$$

$$Rate = \frac{q'' \pi r^2}{h_{fg}} - \left(\frac{2\sigma}{r} + \Delta P_{mem} \right) \frac{K}{L} \pi (r^2 - r_0^2) \rho_v \quad r > r_0 \quad (3.5.25)$$

where r is the bubble radius.

The membrane flow only occurs when the bubble radius exceeds the blocked region radius. As the bubble radius increases, there may be a point where the rate becomes zero. In this case, the bubble is limited to a specific maximum radius. The point of the analysis is to determine, given a blockage radius and heat flux, whether the bubbles will be limited to a particular size or continue growing without limit. This would lead to the boiling behavior observed for higher heat fluxes.

3.5.4 Conclusions

- The lattice Boltzmann simulation method is a useful tool for both understanding and predicting the behavior of microchannel membrane desorbers.
- A new passive scalar transport model based on the lattice Boltzmann flow solution has been developed by PNNL. This model is used for solving the energy and chemical species equations for the membrane desorber.
- The LB microchannel desorber model was validated using data obtained from the desorber tests described in Section 3.2. The predicted desorption rates match the experimental values to within 15% in practically all cases.
- Data from the OSU microchannel desorber device was compared to results from LB simulations. The measured and calculated vapor generation rates increase as the vapor generation decreases and as the inlet concentration decreases. However, the fraction of power used for vaporization tend to increase with power while the values from the lattice Boltzmann simulation tend to decrease with power. One possible explanation for the discrepancy is a disproportionately high heat loss at lower power, based on solution temperature.
- The LiBr solution at the liquid-vapor interface is in thermodynamic equilibrium with the water vapor. Therefore, the surface concentration is determined by the vapor pressure and local

temperature. The fraction of input power that is used for vapor generation is limited by the development of a concentration boundary layer extending in from the membrane surface.

- The LB simulation method is capable of simulating thermal two-phase behavior, such as boiling in microchannels. An adaptive mesh refinement capability was added to extend the range of systems that can be modeled.
- A combination of LB simulation and analytical modeling was used to establish the relationship between the size of nucleation sites and heat rate to the initiation of boiling.

References used in Section 3.5:

1. Succi, S., 2001, *The Lattice Boltzmann Equation for Fluid Dynamics and Beyond*, Oxford University Press, Oxford.
2. Chen, S. and Doolen, G.D., 1998, "Lattice Boltzmann for Fluid Flows," *Ann. Rev. of Fluid Mech.*, **30**, pp. 329-364.
3. Palmer, B. and Rector, D.R., 2000, "Lattice Boltzmann algorithm for simulating thermal flow in compressible fluids," *J. Comp.Phys.*, **161**, pp. 1-20.
4. Rector, D.R. and Stewart, M.L., 2004, "A Passive Scalar Transport Model Based on the Lattice Boltzmann Flow Solution," to be submitted to *J. Comp. Phys.*
5. American Society of Heating, Refrigerating and Air-Conditioning Engineers, 1985, "ASHRAE Handbook: Fundamentals," Atlanta.
6. Swift, M.R., Orlandini, E., Osborn, W.R. and Yeomans, J.M., 1996, "Lattice Boltzmann simulations of liquid-gas and binary fluid," *Phys. Rev. E*, **54**, pp. 5041-5052.
7. Palmer, B. and Rector, D.R., 2000, "Lattice-Boltzmann algorithm for simulating thermal two-phase flow," *Phys. Rev. E*, **61**, pp. 5295-5306.

SECTION 4.0 –CONCLUSIONS

The results the research documented in this report have significantly improved our understanding of the thermal and fluid dynamics processes associated with ultra-thin film desorption and absorption. Key findings from the project include

4.1 Impact

As reported in Section 1.0, the successful development of a microtechnology-based absorption heat pump will impact a number of cooling applications for military, space and commercial applications. The wide spread deployment of a microtechnology-based absorption heat pump could result in a national energy saving of in excess of 2 quads of energy.

4.2 Phenomenological Observations

The results of the various phenomenological investigations have improved our understanding of mechanically constrained thin film desorption. Specific observations include:

- The use of engineered pores in membranes can radically reduce the resistance to mass transfer in the membrane, perhaps by a factor of 100. While we don't have a good method for fabricating membranes with engineered pores on the order of 1 micron in diameter, clearly the development of a membrane with engineering pores would have a significant impact on a wide range of chemical, biological and medical processes.
- Desorption at mass fluxes of interest for heat pump applications will result in boiling within the thin film. Bubble formation within the film was observed for the high heat input cases, but was found not to influence the overall performance based on the relationship of vapor flux produced to heat input. However, there is evidence of bubble formation adversely affecting the transfer of heat to the mixture within the channel.
- The desorption rate, for a given inlet mass fraction and flow rate, is shown to have a linear relationship with heat flux and increasing the pressure differential across the membrane can increase the vapor desorption provided the conditions are not vaporization limited.
- Decreasing the film thickness for a given superheat temperature and total heat input is shown to have a significant positive effect of increasing the vapor desorption rate.
- Given the importance of film thickness on desorption rate the implications of task 4 are significant. First, we were able to develop a film thickness measurement technique that could be used to measure film thickness at operating temperature and pressure. The results demonstrated that operating at elevated temperature and pressure could result in significant film thickening and variation in film thickness across the membrane area. Clearly additional research and technology development needs to be focused on the issues associated with maintaining a uniform film thickness.

4.3 Design Tool Development

The lattice-Boltzmann computer code proved to be a flexible and effective simulation tool for two-phase flow in microscale films. The code was successfully validated with desorption data produced by both PNNL and OSU. Key conclusions from Task 5 include:

- The lattice Boltzmann simulation method is a useful tool for both understanding and predicting the behavior of microchannel membrane desorbers.

- The LB microchannel desorber model was validated using data obtained from the desorber tests described in Section 3.2. The predicted desorption rates match the experimental values to within 15% in practically all cases.
- Data from the OSU microchannel desorber device was compared to results from LB simulations. The measured and calculated vapor generation rates increase as the vapor generation decreases and as the inlet concentration decreases. However, the fraction of power used for vaporization tend to increase with power while the values from the lattice Boltzmann simulation tend to decrease with power. One possible explanation for the discrepancy is a disproportionately high heat loss at lower power, based on solution temperature.
- The LiBr solution at the liquid-vapor interface is in thermodynamic equilibrium with the water vapor. Therefore, the surface concentration is determined by the vapor pressure and local temperature. The fraction of input power that is used for vapor generation is limited by the development of a concentration boundary layer extending in from the membrane surface.
- The LB simulation method is capable of simulating thermal two-phase behavior, such as boiling in microchannels. An adaptive mesh refinement capability was added to extend the range of systems that can be modeled.
- A combination of LB simulation and analytical modeling was used to establish the relationship between the size of nucleation sites and heat rate to the initiation of boiling

We plan to use the code for any future engineering design studies on thin film desorbers and absorbers.

4.4 Future Research

While we have made significant progress in understanding the performance of ultra thin film desorbers there are still outstanding research issue that need to be resolved.

- We need to understand the fundamental issues associated with the extremely low resistance to mass transfer in engineered membranes and we need to develop fabrication techniques that will allow the mass production of engineered membranes with pore sizes on the order of .1 to 1 micron.
- Additional research on fundamental issues concerning the diffusion rates within the film, the effect of cross-film thermal gradients, and the impact of bubble formation are needed to optimize the design of future microscale membrane desorption.
- Given the importance of film thickness on the performance of the desorber we need additional research on methods for controlling film thickness when the membranes are at operating temperature and pressure.

While we made significant progress in understanding the performance of ultra thin film desorbers we need to gain a similar understanding of ultra thin film absorption.