



uOttawa

L'Université canadienne
Canada's university

Vacuum Desiccant Cooling for Personal Heat Stress Management

Yifan Yang

Thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
in partial fulfillment of the requirements
for the Doctorate in Philosophy degree in Chemical Engineering

Department of Chemical and Biological Engineering
Faculty of Engineering
University of Ottawa

© Yifan Yang, Ottawa, Canada, 2016

Résumé

L'objectif de ce projet de doctorat est de développer les membranes et les déshydratants nouveaux qui aideraient à développer un vêtement de refroidissement de déshydratant de vide de deuxième génération (VDC) qui est efficace, robuste, durable et qui respecte les porteurs. On l'a constaté que le matériel de support correctement choisi pourrait améliorer la force mécanique et le flux de vapeur pour le fluorure de polyvinylidène de feuille à plat (PVDF), dus à la structure de membrane et à l'intégrité améliorées de structure qui ont augmenté le transfert de masse de vapeur. De fermes déshydratants superbes ont été développés utilisant un polymère absorbant superbe (PAS), qui sont des granules de polyacrylate de sodium, comme matrices de centre serveur pour héberger le LiCl. En outre, un déshydratant nouveau basé sur le LiCl de chargement dedans aux membranes creuses hydrophobes de fibre et donc à la fibre déshydratante basée par membrane appelée (MDF), a été développé et démontré pour convenir au VDC. Le transfert de la chaleur et de la masse pour l'absorption de vapeur dans les MDF ont été analysés. Ces membranes et déshydratants, bien que développé pour l'application dans le VDC, peuvent également fonder des applications dans d'autres domaines tels que le traitement de l'eau, la climatisation, et la déshumidification de gaz naturel. En conclusion, basé sur les membranes et les déshydratants développés récemment, on propose trois plans d'étude des vêtements VDC de deuxième génération.

Abstract

The objective of this PhD project is to develop novel membranes and desiccants that would help develop a second generation vacuum desiccant cooling (VDC) garment that is efficient, robust, durable and wearer-friendly. It was found that properly chosen support material could improve both mechanical strength and vapor flux for flat sheet polyvinylidene fluoride (PVDF), due to improved membrane structure and structure integrity that enhanced vapour mass transfer. Super solid desiccants were developed using a super absorbent polymer (SAP), which are sodium polyacrylate granules, as the host matrices to harbour LiCl. Furthermore, a novel desiccant based on loading LiCl in to hydrophobic hollow fibre membranes and therefore called membrane based desiccant fiber (MDF), was developed and demonstrated to be suitable for VDC. Heat and mass transfer for vapor absorption in MDF were analyzed. These membranes and desiccants, although developed for application in VDC, may also found applications in other fields such as water treatment, air conditioning, and natural gas dehumidification. Finally, based on the newly developed membranes and desiccants, three conceptual designs of second generation VDC garments are proposed.

Acknowledgement

First of all, I would like to express my gratitude to both of my supervisors, Drs. Christopher Lan and Takeshi Matsuura, whose patience and kindness, as well as their invaluable academic experience to help and support me as I accomplished this thesis. They gave me ideas and strengths to conquer the hardness and confusedness during this PhD study period, and led me to this wonderful academic world.

I would like to express my deep and sincere gratitude to Dr. Dipak Rana for teaching me the membrane casting technique and supporting me with lots of detailed experimental works. My warm thanks are also due to his guidance on editing manuscripts.

I wish to express my warm thanks to Dr. Glen Kenny and his lab members: Brian Friesen, Martin Poirier for helping me with human trial tests and invaluable discussions associated with this study.

Laboratory assistance from Louis Tremblay, Franco Ziroldo and Gerard Nina and support from the Department of Chemical and Biological Engineering at the University of Ottawa is greatly appreciated.

I would also like to thank NSERC and CIHR for financial supports.

Last but not the least, thanks are due to my family and friends, including Licheng Peng, Zhiyu Wang, Gary Cui, Mohammadali Baghbanzadeh, Johnson Effoe Efome, Songyuan Zheng, Shan Guan and Zoulong Chen, who supported me tremendously in many different ways during the years.

Table of content

Résumé	II
Abstract	III
Acknowledgement	IV
Table of content.....	V
List of Figures.....	XII
List of Tables	XVI
List of Acronyms	XVII
Nomenclature	XIX
List of current and anticipated publications	XXII
Collaborator’s Contributions	XXIV
Chapter 1: Introduction.....	1
1.1 Project background and objectives.....	1
1.2 Thesis outline.....	4
1.3 Reference	5
Chapter 2: Recent development in microclimate cooling technologies	6
2.1 Types of microclimate cooling garment (MCGs)	7
2.1.1 Fluid cooling garments (FCGs).....	7
2.1.2 Phase change material garments (PCM)	8

2.1.3 Evaporative cooling garments (ECGs)	9
2.2 Heat dissipation mechanisms	11
2.2.1 Conduction.....	11
2.2.2 Convection	12
2.2.3 Radiation	12
2.3 Microclimate cooling garments design criteria	13
2.3.1 Cooling capacity	14
2.3.2 Operation duration	16
2.3.3 Portability and Mobility	16
2.3.4 Dryness of wearer skin.....	17
2.4 Conclusion.....	17
2.5 Reference	19
Chapter 3: Developments in evaporative cooling and enhanced evaporative cooling -A review	22
3.1 Abstract.....	23
3.2 Introduction	24
3.3 Evaporative cooling technologies.....	25
3.3.1 Air-mediated cooling	27
3.3.1.1 Air-mediated direct evaporative cooling	27
3.3.1.2 Air-mediated indirect evaporative cooling	29

3.3.2 Water mediated evaporative cooling.....	30
3.3.2.1 Water-mediated direct evaporative cooling.....	31
3.3.2.2 Water-mediated indirect evaporative cooling: Multi-layer membrane evaporative cooling for personal heat management.....	31
3.4 Enhanced evaporative cooling.....	34
3.4.1 Desiccant cooling.....	34
3.4.1.1 Liquid desiccant evaporative cooling system	35
3.4.1.2 Solid desiccant (desiccant wheels) cooling system	37
3.4.2 Membrane air drying enhanced cooling technology	38
3.4.3 Membrane assisted desiccant cooling	39
3.4.3.1 Membrane assisted liquid desiccant cooling	40
3.4.3.2 Membrane assisted vacuum desiccant cooling.....	41
3.4.3.3 Membranes for membrane-assisted desiccant cooling	43
3.5 Thermodynamic analysis - psychrometric chart.....	46
3.6 Conclusions	51
3.7 Reference	52

**Chapter 4: Criteria for the selection of support material to fabricate coated membranes
for life support device 58**

4.1 Abstract.....	59
4.2 Introduction	60

4.3 Experimental.....	62
4.3.1 Materials.....	62
4.3.2 Polymer characterization by average molecular weights measurement	63
4.3.3 Membrane preparation	63
4.3.4 Scanning electron microscopy (SEM) measurement	64
4.3.5 Porosity measurement	65
4.3.6 Contact angle measurement for calculation of surface energy	65
4.3.7 Liquid entry pressure of water (LEP _w) measurement	67
4.3.8 Permeation flux measurement by vacuum membrane distillation (VMD) setup	68
4.4 Results and discussion.....	69
4.5 Conclusion.....	76
4.6 Reference.....	79

Chapter 5: The heat and mass transfer of vacuum membrane distillation: effect of active layer morphology with and without support material 82

5.1 Abstract.....	83
5.2 Introduction	84
5.3 Mass transfer	85
5.4 Heat transfer	89
5.5 Experimental.....	91

5.6 Results and discussions	92
5.6.1 VMD experimental results	92
5.6.2 Solution of mass and heat transfer equations.....	93
5.6.3 Membrane characterization parameters	95
5.6.4 Calculation of TPC.....	99
5.7 Conclusion.....	100
5.8 Reference	101
Chapter 6: Development of solid super desiccants based on polymeric superabsorbent hydrogel composite	103
6.1 Abstract:	104
6.2 Introduction	105
6.3 Experimental.....	107
6.3.1 Materials.....	107
6.3.2 Preparation of superabsorbent hydrogel composite desiccant	108
6.3.3 Methods of characterization.....	109
6.3.3.1 Vapor absorption performance	109
6.3.3.2 Swelling measurements for different concentrations of LiCl solution	110
6.3.3.3 Surface morphology of the SHC desiccant.....	111
6.3.3.4 Surface area measurement	111

6.3.3.5 Lithium and sodium ion concentration measurement in SHC gel mixture leachates	111
6.4 Results and discussion	112
6.4.1 Effect of LiCl solution concentration on SAP swelling capacity	112
6.4.2 Effect of lithium chloride content on SHC vapor absorption performance	115
6.4.3 Effects of equilibrium duration on the ion exchange degree	117
6.4.4 Effects of the number of equilibrium steps on vapor absorption performance	118
6.4.5 Performance comparison with common solid desiccant.....	123
6.5 Conclusions	127
6.6 Reference.....	128

Chapter 7: Development of membrane-based desiccant fiber for vacuum desiccant cooling

7.1 Abstract.....	130
7.2 Introduction	131
7.3 Materials and methods.....	133
7.3.1 Materials.....	133
7.3.2 Preparation of membrane-based desiccant fiber (MDF).....	135
7.3.3 Vapor absorption test at ambient pressure for MDF	136
7.3.4 Preparation of MDF pad	139
7.3.5 Vacuum vapor absorption test for MDF pad	139

7.4 Results and discussion	141
7.4.1 Time-course profile of vapor absorption at ambient pressure	141
7.4.2 Suitability of MDF for application in a VDC	145
7.4.3 Mass and heat transfer analysis in vapor absorption process by MDF	150
7.4.3.1 Mass transfer.....	151
7.4.3.2 Heat transfer	154
7.4.3.3 Heat transfer coefficient at different LiCl loadings	156
7.4.3.4 Prediction at different ambient relative humidity at 25 °C for 22% ...	157
7.5 Conclusions	160
7.6 References	164
Chapter 8: Conclusions and recommendations for second generation vacuum desiccant cooling garment	168
8.1 Conclusions	168
8.2 Recommendations for 2nd generation vacuum desiccant cooling garment	172
8.2.1 Introduction of VDC garment design concept	173
8.2.2 Design proposals of second generation VDC garments.....	175

List of Figures

Figure 3-1 Schematic diagram of AMDEC	28
Figure 3-2 Schematic diagram of AMIEC.....	29
Figure 3-3 Schematic diagrams of three-layer laminate and the principle of water evaporation from the reservoir [56].....	33
Figure 3-4 The schematic system of desiccant enhanced IEC system.....	35
Figure 3-5 Schematic diagram for liquid desiccant aided vapor compression system	36
Figure 3-6 Schematic of desiccant dehumidification and cooling system (DDCS) [55].....	38
Figure 3-7 Schematic diagram of a membrane liquid desiccant air conditioning system [65].....	41
Figure 3-8 Schematic diagrams of A: the cross-section view of vacuum desiccant cooling pad. B: cross-sectional view of absorption core and cooling core. [66].....	42
Figure 3-9 Membrane heat pump prototype manufactured by Applied Membrane Technology, Inc. (AMT) [72]	46
Figure 3-10 Psychrometric diagram for direct evaporative cooling (left) and indirect evaporative cooling (right)	49
Figure 3-11 Psychrometric chart for membrane air drying direct evaporative cooling process (left) and for membrane assisted desiccant drying direct evaporative cooling process (right)	50
Figure 4-1 Top SEM images for 3396-support (A), E055100-85-support (B), 3329-support (C), 3229-support (D), and the line profiles.....	70
Figure 4-2 Contact angles for water, ethylene glycol (EG), and diiodomethane (DIM) on four non-woven fabric materials. (Contact angles for EG and DIM on non-woven fabric material C are both zero.)	71

Figure 4-3 Top SEM images for PVDF coated membranes and unsupported membrane. (A: PVDF-3396 coated; B: PVDF-E055100-85 coated C; PVDF-3329 coated; and D: PVDF-3229 coated membrane.).....	74
Figure 4-4 Vapor flux of A-coated, B-coated, and unsupported PVDF membrane.	75
Figure 5-1 Plot of $Km/1/T$ versus $1/T$	95
Figure 5-2 Membrane coating layer thickness comparison among fresh and after tests membranes by cross-sectional SEM imaging: (a) Unsupported fresh, (b) Unsupported after test, (c) A-supported fresh, (d) A-supported after test, (e) B-supported fresh, and (f) B-supported after test... ..	98
Figure 5-3 Feed temperature effect on temperature polarization coefficient.	99
Figure 6-1 The chemical structure of cross-linked sodium polyacrylate.....	108
Figure 6-2 Schematic diagram for vapor absorption test within water bath.....	110
Figure 6-3 SAP swelling capacities and LiCl retained amount with respect to the molarity of LiCl solution.	114
Figure 6-4 24 h absorption capacity versus molarity of LiCl solution for SHC preparation (1-h equilibrium duration).	116
Figure 6-5 24 h absorption capacity comparisons for 1-h and 4-h equilibrium durations.....	118
Figure 6-6 Vapor absorption performance with 2.5 M SHC prepared by different numbers of ion-exchange equilibrium.....	119
Figure 6-7 24 h vapor absorption capacity and ion exchange degree with respective to the numbers of equilibrium.....	120
Figure 6-8 SEM images for (A) 2.5 M 1-eq, (B) 2.5 M 3-eq SHC and (C) 2.5 M 5-eq SHC (magnification 60×).....	121

Figure 6-9 SEM-EDX elemental analysis results for (A) 2.5 M 1-eq, (B) 2.5 M 3-eq and (C) 2.5 M 5-eq.	122
Figure 7-1 Hollow fiber A: a-1, a-2 and a-3 are cross sectional, inside surface and outside surface morphology; hollow fiber B: b-1, b-2 and b-3 are cross sectional, inside surface and outside surface morphology.	135
Figure 7-2 Schematics of vapor absorption test device.	137
Figure 7-3 Weaved MDF pad by loom.	139
Figure 7-4 Vapor absorption of MDF with an ID of (a) 0.42 mm and (b) 0.70 mm when loaded with LiCl aqueous solution of different concentrations. (Absorption tests stopped at the point when sweat was detected at the MDF surface if the last data point was at 3.5 h or less).	142
Figure 7-5 (a) The time-course profiles of water evaporation of the cooling towel layer and (b) the temperatures of both the cooling tower and desiccant layers of a VMD lab setting at different vacuum degrees (i.e., atmospheric pressure and 25 inches of Hg).	148
Figure 7-6 Schematic illustration of a heat and mass transfer model in the hollow fiber membrane.	151
Figure 7-7 Average heat transfer coefficient changes with LiCl loading.	156
Figure 7-8 Solution temperature profile changes with LiCl loading.	157
Figure 7-9 Heat transfer coefficient change with time for 22 wt.% 0.7 mm MDF.	158
Figure 7-10 Heat transfer coefficient changes with solution temperature for 22 wt.% 0.7 mm MDF.	158
Figure 7-11 Absorption amount prediction for 22 wt.% loading 0.7 mm MDF at different ambient relative humidity.	159
Figure 8-1 Schematic diagram of the structure of a VDC pad	174

Figure 8-2 2 nd generation VDC garment proposal A	177
Figure 8-3 2 nd generation VDC garment proposal B	178
Figure 8-4 2 nd generation VDC garment proposal C	179

List of Tables

Table 2-1 Rate of metabolic heat generation of common activities [21].....	14
Table 2-2 Cooling capacities of commercial and prototype MCGs	15
Table 4-1 Van Oss, Chaudhury and Good Surface Tension Parameters of Liquids used in this Study	67
Table 4-2 Thickness, porosity, surface energy, and work of adhesion results for four support NWF materials.....	72
Table 4-3 Contact angle, LEPw, and VMD flux of the PVDF coated membranes.	75
Table 5-1 VMD experimental results.	93
Table 5-2 Constants used in heat and mass transfer analysis.	94
Table 5-3 Calculation of K_m and T_m for three membranes at different operating condition.....	95
Table 5-4 Membrane parameters used in the experimental validation.	96
Table 5-5 The calculated tortuosity and the membrane characteristic parameter from proposed model.....	99
Table 6-1 Comparisons of physical properties with common solid desiccants.	126
Table 7-1 Hollow fiber membrane specifications.....	134
Table 7-2 Summary of key parameters of MDF made of two different membranes with varied loading LiCl solution concentrations.	142

List of Acronyms

ACG	air cooling garment
CFC	halogenated chlorofluorocarbons
DEC	direct evaporative cooling
DIM	diiodomethane
DMAc	dimethylacetamide
DMF	dimethylformamide
ECG	evaporative cooling garment
EG	ethylene glycol
FCG	fluid cooling garment
HA	hygroscopic agent
HF	hollow fiber
HVAC	heating, ventilation, air-conditioning
IEC	indirect evaporative cooling
LCG	liquid cooling garment
LEP	liquid entry pressure
MCG	microclimate cooling garment
MDF	membrane based desiccant fiber
NBC	nuclear, biological and chemical protective clothes
NWF	non-woven fabric
PCM	phase change material
PVDF	polyvinylidene fluoride
PTFE	polytetrafluoroethylene

SAP	super absorbent polymer
SHC	superabsorbent hydrogel composite
TPC	temperature polarization coefficient
VCS	vapor compression system
VDC	vacuum desiccant cooling
VMD	vacuum membrane distillation
VME	vacuum membrane evaporation

Nomenclature

A_{log}	membrane area based on logarithmic mean of hollow fiber
membrane diameter (m^2)	
C_p	heat capacity of liquid water (J/kg K)
d_p	collision diameter of the transporting molecule (m)
G_r	Grashof number
ΔH_{evap}	heat of evaporation (43.99×10^6 J/kmol at 298.2 K) of water
h_f	heat transfer coefficient at the liquid boundary layer ($W/m^2 K$)
J_m	evaporation flux through the membrane ($kg/m^2 s$)
K	thermal conductivity of the fluid (W/m K)
k_B	Boltzmann constant(J/K)
K_m	membrane mass transfer coefficient ($kg/m^2 s Pa$)
Kn	Knudsen number
L_c	characteristic length (m)
M	molecular weight of water (18.02 kg/kmol)
P	average pressure within the membrane pore (Pa)
p_m, p_v	the partial water vapor pressure (Pa) at the membrane surface on the feed side and the permeate side
p_{sol}, p_∞	the partial water vapor pressure at the surface of LiCl solution and at ambient environment
P_r	Prandtl number
Q	the total heat flux (W/m^2)
Q_m	heat flux through the membrane (W/m^2)
Q_f	heat flux through the feed boundary layer (W/m^2)

Q_{eq}	hydrogel swelling capacity (g solution /g dry SAP)
R	universal gas constant ($8.314 \times 10^3 \text{ J/kmol K}$)
r	pore radius(m)
T	absolute temperature (K)
T_f, T_m layer	temperature (K) of the feed bulk and at membrane/feed boundary
T_{sol}, T_{∞} environment	temperature (K) of LiCl solution with MDF and at ambient
W_{HF}	weight of dry hollow fiber membrane weight (g)
W_0	weight of dry MDF (g)
W_t	weight of final MDF weight after absorption at time t (g)
N_u	Nusselt number

Greeks

λ	mean free path of the transported molecule
ε	membrane porosity
τ	pore tortuosity
δ	thickness(m)
μ	viscosity of water vapor (Pa s)
ρ, ρ_{sol}	density (kg/m ³) of liquid water and LiCl solution within MDF
β	volume thermal expansion of liquid water(1/K)
ω	LiCl solution concentration with MDF during absorption
γ	liquid surface tension
θ	liquid contact angle at membrane surface (°)

List of current and anticipated publications

Peer-reviewed articles

1. **Yang Y**, Rana D, Lan C.Q, Matsuura T. Development of membrane-based desiccant fiber for vacuum desiccant cooling, *ACS Applied Material & Interfaces* 8 (2016) 15778-15787. DOI: 10.1021/acsami.6b03006
2. **Yang Y**, Rana D, Matsuura T, Lan C.Q. The heat and mass transfer of vacuum membrane distillation: Effect of active layer morphology with and without support material, *Separation and Purification Technology* 164(2016) 56-62. DOI: 10.1016/j.seppur.2016.03.023
3. **Yang Y**, Rana D, Lan C.Q. Development of solid super desiccants based on a polymeric superabsorbent hydrogel composite. *RSC Advances* 73 (2015) 59583-59590. DOI:10.1039/C5RA04346H
4. Chen Z, Rana D, Matsuura T, **Yang Y**, Lan C.Q. Study on the structure and vacuum membrane distillation performance of PVDF composite membranes: I. Influence of blending, *Separation and Purification Technology* 133 (2014) 303-312. DOI: 10.1016/j.seppur.2014.07.015
5. **Yang Y**, Rana D, Matsuura T, Zheng S, Lan C.Q. Criteria for the selection of support material to fabricate coated membranes for life support device, *RSC Advances* 4(2014) 38711-38717. DOI:10.1039/C4RA04638B
6. **Yang Y**, Lan C.Q. Developments in evaporative cooling and enhanced evaporative cooling - A review, *Renewable and sustainable energy reviews* (under review)
7. **Yang Y**, Lan C.Q. Recent development in microclimate cooling technologies, *Applied Thermal Engineering*, (to be submitted)

Conference presentations

1. **Yang Y**, et al. “Membrane based Desiccant Fiber (MDF) development and modelling”, Pacifichem 2015, Hawaii, USA (Poster presentation, 2015. 12);
2. **Yang, Y**, et al. “Performance study of sodium polyacrlate based desiccant”, 98th Canadian Chemistry Conference and Exhibition, Ottawa, Canada, (Oral presentation, 2015. 06);
3. **Yang Y**, et al. “Heat and mass transfer analysis in vacuum membrane distillation”, Polymer Reaction Engineering IX, Cancun, Mexico (Poster presentation, 2015. 05);
4. **Yang, Y**, et al. “Development of solid super desiccants based on superabsorbent hydrogel composite”, Polymer Reaction Engineering IX, Cancun, Mexico (Poster presentation, 2015. 05);
5. **Yang, Y**, et al. “Effects of support materials on the structure and performance of hydrophobic micro-porous membranes”, 64th Canadian Chemical Engineering Conference, Niagara Fall, Canada, (Oral presentation, 2014. 10);

Collaborator's Contributions

Chapter 4 Criteria for the selection of support material to fabricate coated membranes for life support device

Songyuan Zheng, helped with some of the vacuum membrane distillation measurement.

Takeshi Matsuura and Christopher Lan provided theory discussion and revision of the manuscript.

Dipak Rana, provided with experimental guidance, revision, and submission of the manuscript.

Chapter 5 The heat and mass transfer of vacuum membrane distillation: effect of active layer morphology with and without support material

Takeshi Matsuura and Christopher Lan provided with the in-depth discussion on mathematical analysis, guidance, and revision of the manuscript.

Dipak Rana, helped with manuscript correction and submission.

Chapter 6 Development of solid super desiccants based on polymeric superabsorbent hydrogel composite

Christopher Lan, contributed in concept development, experimental guidance, revision of the manuscript.

Dipak Rana, helped with manuscript correction and submission.

Chapter 7 Development of membrane-based desiccant fiber for vacuum desiccant cooling

Zhiyu Wang, Gary Cui and Shan Guan helped with fabrication of MDF pad and some of the absorption measurements.

Christopher Lan contributed to concept development, guidance in reseach, and manuscript revision.

Takeshi Matsuura provided with the modelling analysis guidance and revision of the manuscript.

Dipak Rana, helped with manuscript correction.

Chapter 1: Introduction

1.1 Project background and objectives

Various occupations expose workers to excessive heat stress, which may result in lowered performance due to physical fatigue, heat-related diseases, and in extreme cases, death. Heat stressed individuals are more prone to accidents due to lowered mental alertness, reduced manual dexterity, and physical discomfort. This can lead to irritability, anger, and other emotional states [1-3]. These impairments can have dangerous consequences. For example, there were 1816 heat-related injuries reported among active American soldiers in 2002 [2] . From 1992 to 2006, there were 68 fatalities reported among U.S. farm workers resulting from exposure to environmental heat, which represents an average annual heat-related death rate of 0.39 per 100,000 crop workers, compared to the U.S. civilian average heat-related death rate of 0.02 per 100,000 workers [4]. Some common occupations, i.e. doctors and chemical specialists, are also exposed to extreme heat stress in certain cases. Daily mail has published reports on Nov 24th, 2014, mentioning doctors who treat the deadly infectious virus: Ebola, had to wear specially designed protective suits involving two pairs of gloves, thick boots and a domed helmet, etc., in 30 °C heat. The protective suit can stop virus-carrying fluids like blood and vomit getting through, but only allowing doctors to work 45-minute shift. Similar cases also apply to chemical specialists. Xinhua news reported a serious explosion on August 15th, 2015, in Tianjin, North China, at a dangerous chemical storage warehouse. The government sent over 50 chemical specialists onsite to obtain ground water and air samples to examine pollutants and to plan out the post treatment procedure. Those specialists had to wear nuclear, biological and chemical

(NBC) protective clothes which again allow them to work 45 minutes shift before being exposed to heat exhaustion.

When the human body is overheated, it first starts to develop a tingling sensation in the skin, as well as headache and nausea. Then more serious diseases such as heat exhaustion may develop, in an extreme case, heat stroke when the core body temperature exceeds 40 °C and the person stops sweating. This symptom if not treated properly, can cause death. The human body has its own self-thermoregulation system. For example, by dilating of the vessels near the skin surface, pumping more blood to skin to allow more surface area for heat exchanges can lower the body temperature. Sweating is another important method for the body to cool itself by evaporation. However, the human body has its own limitation, and can lose its function when under extreme heat stress, therefore auxiliary equipment is needed for certain occupations.

To help manage heat stress in working environments, and more importantly, to ensure the safety of the personnel who has to work under heat stress, a variety of different microclimate cooling technologies have been developed in the last few decades. These include fluid cooled garments (FCGs), phase change material (PCM) garments, evaporative cooled garments (ECGs), etc. FCGs achieve cooling by circulating refrigerated coolants or ambient air through tubing close to the skin of wearers for heat management. In general, they have a high cooling efficiency, but are not man-portable due to the requirement of refrigeration units and continuous power supply. PCM cooling vests, which employ phase change materials (e.g., ice) to absorb heat, have better portability compared to the FCGs. However, their cooling capacity and functional duration are limited by the relatively small heat of fusion of PCM. ECGs, which utilize the large latent heat of water evaporation for purpose of cooling, are becoming more attractive. However,

conventional ECGs have small cooling capacities due to the limited fluxes of natural evaporation. It is important to develop novel strategies to overcome the limitations on conventional microclimate cooling technologies, for enabling the design of portable personal cooling garments that are efficient for applications in different working environments.

We have proven the concept of vacuum desiccant cooling (VDC) and applied it to develop the 1st generation VDC garment [5, 6] during my Master's thesis project. Encouraging data from the 1st generation prototype has shown the potential of VDC garment to be a cutting-edge portable personal cooling garment, with great cooling capacity and no continuous power requirement. However, it has a few disadvantages that hinder its commercial application. First, the commercial PTFE (Teflon) membrane used in the 1st generation prototype was fragile and non-sticky. Consequently, it was very difficult to fabricate VDC pads, which often failed due to water leakage. Second, the desiccant used in the 1st generation VDC pads was lithium chloride powder, which has high water affinity, but becomes corrosive after absorbing water vapor to become an aqueous solution. This raised safety concerns to both the wearer and the equipment they carry or operate. Due to the above mentioned two major flaws, the 1st generation VDC was not reusable and causes cost concerns due to the limits derived from the fragile membrane, the corrosive desiccant and the outer bag design. It is therefore important to find proper solutions to make the VDC garment more robust, more efficient, and safer. This PhD project aims to solve these main issues, and eventually to design a 2nd generation VDC garment with enhanced reliability, cooling capacity, work duration and cost-effectiveness, thus paves the way to its commercialization.

1.2 Thesis outline

Chapter 2 and chapter 3 of this thesis introduce the recent microclimate cooling technologies and the membrane aided desiccant cooling technologies to identify knowledge gaps and to clarify the research direction.

Chapter 4 focuses on the development and optimization of hydrophobic supported membrane with satisfactory liquid entry pressure of water (LEP_w), enhanced mechanical strength, and large vapor flux, based on the hypothesis that applying a layer of proper supporting material, the supported membrane can exhibit good mechanical strength, enhanced flux, large LEP_w as well as better processability. Chapter 5 further examines the heat and mass transfer process of the previously developed supported membrane, and identifies the effect of backing material on the membrane structures.

Chapter 6 and chapter 7 targets the desiccant challenges. Chapter 6 reports the development of a super absorbent polymer (SAP) based super solid desiccant by impregnating hygroscopic agent (HA) in the proper host matrix (e.g., hydrogel) to create a novel desiccant that can maintain the hygroscopic nature of HA while being safe and easy to process. Chapter 7 reports the development of membrane based desiccant fiber (MDF), and the related heat and mass transfer modelling work. MDF desiccant performances at different relative humidity environment were predicted.

Finally, chapter 8 presents a summary of conclusions of this study, three proposals for the design of 2nd generation VDC garments using the newly developed membrane and desiccants, and suggested future works.

1.3 Reference

- [1] The Eastman Kodak Company. Kodak's Ergonomic Design for People at Work (2nd Edition):588-617.
- [2] Goldfrank LR, Flomenbaum NE. Goldfrank's Toxicologic Emergencies. McGraw-Hill, Medical Publishing Division; 2006, p. 255-265.
- [3] Harris RL. Patty's Industrial Hygiene (5th Edition) Volumes 1-4. John Wiley & Sons; 2000, p. 925-985& 1247-1289.
- [4] Luginbuhl RC, Jackson LL, Castillo D, Loring KA. Heat-Related Deaths Among Crop Workers, Morbidity and Mortality Weekly Report (MMWR). 2008;649-653.
- [5] Yang Y, Stapleton J, Diagne BT, Kenny GP, Lan CQ. Man-portable personal cooling garment based on vacuum desiccant cooling. Appl Therm Eng 2012;47:18-24.
- [6] Yang Y. Personal-portable Cooling Garment Based on Adsorption Vacuum Membrane Evaporative Cooling. Master's thesis. University of Ottawa, ON. 2011.

Chapter 2: Recent development in microclimate cooling technologies

Microclimate cooling garment has been established in many scenarios as an efficient means of heat management for personnel who are exposed to heat stress during work. Compared to space cooling, which targets on supplying lower temperature air or increasing air flow within a controlled space, microclimate cooling is focused on regulating human body surface temperature. Microclimate cooling garments are designed for those who need to work with special personal protective equipment (i.e. bomb disposal suits, military demining suits, firefighter suits, astronaut space suit, etc.) as well as those who work in an open environment where cooling a large space is very costly, impractical, or even impossible. Such cases include hot open environments and large workplaces such as deserts, steel mills, foundries, mines, and metallurgy plants. In these situations, microclimate cooling is the preferred method of temperature regulation. Proper microclimate cooling systems are expected to reduce the personnel's core temperature, skin temperature, heart rate as well as sweat rate in order to increase working duration, maintain physical performance and decrease in hydration needs, etc.

Traditionally, an efficient cooling method should address both skin temperature and core body temperature to provide effective heat mitigation [1,2]. However, recent research has revealed other important parameters that help monitor the microclimate environment, for example, the humidity change [3], and the rate of heat storage [4] during tests.

The first systems delivering personal cooling (PC) to individuals were designed in the late 1950's and early 1960's for pilots who were operating in aircrafts and exposed to hot

conditions [1, 5] . Since then, many different devices have been engineered to cover a wide range of professions where individuals are exposed to hot environments. The microclimate cooling garments (MCGs) are categorized into three main types such as fluid cooling garments (FCGs), phase change materials (PCMs) and evaporative cooling garments (ECGs).

2.1 Types of microclimate cooling garment (MCGs)

2.1.1 Fluid cooling garments (FCGs)

FCGs are systems that circulate cold coolant (i.e. water) or air (compressed or ambient air) through a tube-lined shirt or garment. The water or air is recycled by the regeneration unit. Both liquid-cooled (LCGs) and air-cooled garments (ACGs) applications are limited by their power requirement and system size. These types of cooling garments are advantageous for the personnel working in vehicles simply because it is easy to attach the refrigeration unit or the compressed air system. A continuous power supply is essential to FCGs, and the system involves the parts like pumps, blowers, refrigeration system, etc., and also requires a large footprint. As advances in battery and motor technology develop, the range, efficiency and mobility of LCGs can consequently improve but to a limited extent. Most developments in the field of ACGs relate to the development of efficient air channelization within the microclimate to increase residence time and maximize surface area exposure. One of the major disadvantages for this type of cooling garment is that, this type of garment limits the body's natural respiration and therefore causes discomfort for the wearer. Non-evaporated sweat is a waste of cooling potential and should be utilized to improve the cooling effect [6]. Other than the above mentioned ACGs, ventilation garments are another type of fluid cooling garment. They contain built-in fans to

blow ambient air on skin surface to facilitate sweat evaporation. Their cooling performance could be limited by the hot air from ambient.

Researchers have already designed a hybrid garment, which has a vaporizing function with oozing cold water from the knitted tubes to cool the body without raising humidity in the garment [3]. Recent advances in miniaturizing vapor-compression technology have also made vapor-compression air-cooled garments a viable personal cooling method [7].

2.1.2 Phase change material garments (PCM)

PCM systems employ phase changing material to store energy with a narrow temperature variation when changing from solid to liquid state or vice versa. It has been continually improved with advances in material science to expand their cooling capacity, particularly with salt hydrates and paraffins [8]. Researchers have attempted to counter some of the limitations of salt hydrates by using chemical, physical and mechanical means such as stability improvement during the phase change (such as the use of thickening agents and dispersions of high conductivity particles against phase segregation and loss of conduction upon the re-solidification of salts mixed with these agents) [9-11]. Similarly, to enhance paraffins' conductive properties, researchers have explored various heat transport improvements, including better structure of the paraffin casing unit (metal matrix structures) and addition of high conducting materials in the paraffin wax (e.g. metallic fillers) [8]. However, the issues associated with PCM garments are generally the limited operation time, since it requires regeneration as soon as all the PCM has changed phase and reached the upper limit of heat storage. Researchers have also compared PCM garment with ventilation jacket which is equipped with two small fans embedded at the left and right belly of

the jacket. When having the participants exercising at the same ambient environment, the ventilation jacket has a slightly better performance in terms of torso skin temperature, better microclimate humidity and body thermal sensation and body thermal comfort [6]. This research also indicates that ventilation is important in the cooling garment designs. It is reported that under ideal conditions, the evaporation of 500 ml of sweat eliminates approximately 1200 kJ, which can dissipate the metabolic heat of 333 W during 1 h of work. This potential is wasted by applying the insulation capabilities of protective clothing [12].

2.1.3 Evaporative cooling garments (ECGs)

Finally, ECGs are a group of cooling garments that take advantage of the large latent heat of water evaporation for cooling. ECGs can have a fairly long working duration with a relatively small amount of water. The disadvantage of conventional ECG is that it is not functional when it is worn under protective garments and its effectiveness is greatly reduced if the ambient humidity is high. Faulkner et al [4] have studied the effect of incorporating the conductive cooling into the traditional evaporative cooling garment. A novel design of a frozen cooling garment based on evaporative cooling was used in their study and different precooling conditions for the garment were tested. The results have shown that the combination of evaporative and cold conductive cooling had the greatest benefit to the performance, indicating evaporative cooling can be enhanced by the precooling technology. Moreover, the enhancement of sweat evaporation by optimising the ECGs technical conditions is considered as the most effective “physiological” way for heat dissipation, which has become the current research trend [12].

Another interesting development for the improvement of the ECG performance is the multi-layer evaporative cooled garments. It is the integration of hygroscopic materials, either desiccant or super-absorbent materials such as cellulose, cross-linked polyethylene oxide, polyacrylates or carboxy-methyl-cellulose, to either absorb vapor produced from perspiration/evaporation or to absorb a liquid coolant included within an internal reservoir. Many researchers have worked with desiccant-aided evaporation systems and proved that adding desiccant can substantially increase the water evaporation rate and therefore cooling capacity [13, 14]. In the space cooling applications, desiccant or absorption cooling is a well-known air conditioning technique, using the hygroscopic agent to absorb vapor and subsequently decrease the temperature to produce cooled air. At the microclimate cooling scale, studies have shown an enhanced performance of ECG when desiccants were employed. In one study, 200 W of heat removal was reported for an operation period of four hours by an absorbent evaporative system [15], which was more efficient than that from a 3-layer evaporative fabric garment [16] with the cooling rates of less than the 100 W. As a most recent development, our team has shown that a cooling capacity of up to 373.1 W/m^2 could be achieved by novel vacuum desiccant cooling (VDC) garment [17]. This method combines the existing desiccant-aided cooling and vacuum cooling to further improve the overall performance.

The VDC garment requires the use of membrane technologies to separate the water in the cooling core from the desiccant in the absorption core. The desired polymeric membranes need to be water-proof (hydrophobic), but water-vapor-permeable to let water vapor pass, while condensed water is retained. Such hydrophobic membrane can be made out of PTFE, PVDF, polyurethane or polyester [18]. This type of breathable membranes may also find applications in pervaporation and membrane distillation. Mass transfer across the membrane in the vacuum

membrane evaporation (VME) is very similar to that of vacuum membrane distillation except that pure water is used in VME. It requires a hydrophobic membrane that has a LEP_w of 1 bar or higher to provide the barrier to separate the liquid water and water vapor when evaporative cooling is taking place [16, 19, 20]. VDC, after initialization with a vacuum pump, relies on vapor absorption or adsorption by the desiccant to maintain the driving force for water evaporation. Therefore, the desiccants should absorb vapor fast enough and the vapor pressure on the surface of desiccant should be low so that water evaporation could continuously take place at a high rate and at low temperatures.

2.2 Heat dissipation mechanisms

To better understand the principles of various types of microclimate cooling garments, mechanisms of heat dissipation are studied and summarized in the following section, including conduction, convection, radiation, and evaporation.

2.2.1 Conduction

Conduction is the heat transfer method that occurs along a thermal gradient between materials that contact with each other at different temperature. From microclimate cooling point of view, a worker's warm body will transfer heat to a contacted cooler object. Parameters affect the efficiency of heat transfer through conduction including the temperature difference between the skin of the wearer and the cooling medium, the thermal conductivity of the materials that separate the cooling medium from the skin, and the effective contacting area through which heat

is transferred from the skin to the cooling medium. Conduction is the primary means of heat transfer in FCGs and PCM garments.

2.2.2 Convection

Convection is the primary heat removal mechanisms for ventilation garments. Parameters that could be manipulated for more efficient cooling include air flowrate, air temperature and distribution of air current. Heat transfer by convection is minimal, if any, in most of LCGs and PCM garments.

2.2.3 Radiation

Radiation is an important heat transfer mechanism. The heat loss by radiation is more noticeable on a cold day or during the period after sunset. It is usually considered as negligible comparing with other heat loss mechanisms in terms of microclimate cooling garment design.

However, radiation is usually one of major means of heat transfer that contributes to the heat stress on the workers. Examples of radiation include sunshine, hot furnaces, and high temperature reactors. Simple engineering controls, such as shields, are commonly used to reduce radiant heat when applicable. The reflective surface of the shield should be kept clean to maintain its effectiveness. However, surfaces that exceed 35°C (95°F) are sources of infrared radiation that can add to the worker's heat load. Flat black surfaces absorb heat more than smooth, polished ones.

Sweat evaporation is the primary way of cooling the body in warm environment naturally. Sweating cools body through sweat evaporation, latent heat is removed from the sweat that remains on the skin resulting cooler skin surface. Latent heat of water evaporation is large making it a particularly effective evaporative cooling agent. At room temperature (20°C), the latent heat of water evaporation is 2454 kJ/kg. However, the rate of sweat evaporation is greatly affected by the ambient relative humidity. For example, under the atmospheric conditions of 35 °C and 100% relative humidity, sweat does not evaporate at all.

Evaporation is the primary cooling mechanism of ECGs. ECGs generally utilize water evaporation from a wet medium or surface to cool the contacting body skin, or facilitate the sweat evaporation. In areas of high humidity, the evaporative cooling becomes less effective. When dry bulb temperature is higher than 35 °C (95 °F), the hot air passing over the skin can actually make the worker hotter. However, if the dry bulb temperature is more than 35°C but the air is dry, evaporative cooling becomes the only means of cooling for ventilation garments.

2.3 Microclimate cooling garments design criteria

According to Standards ISO 7730 - 2005 and ASHRAE 55-2004, thermal comfort is defined as being “that condition of mind which expresses satisfaction with the thermal environment”. Two conditions must be fulfilled to maintain thermal comfort. One is that the actual combination of skin temperature and the body’s core temperature provides sensation of thermal neutrality. The other is the fulfilment of the body’s energy balance: the heat produced by metabolism should be equal to the amount of heat loss from the body.

The detailed design parameters for microclimate cooling garments are discussed in the following sections.

2.3.1 Cooling capacity

Typical metabolic rates of common activities have been summarized and reported by International Organization for Standardization (Table 2-1). In the table, “met” is defined as metabolic unit, which is equal to 58.2 W/m^2 . The rate of metabolic heat generation as reported in Table 2-1 could provide as a reference for efficiency judgment of MCGs since, as mentioned earlier, a MCG should have a cooling capacity that is sufficient to remove all or most of the metabolic heat to avoid or minimize buildup of metabolic heat in body.

Table 2–1 Rate of metabolic heat generation of common activities [21]

Activity	Metabolic rate	
	W/m^2	met
Reclining	46	0,8
Seated, relaxed	58	1,0
Sedentary activity (office, dwelling, school, laboratory)	70	1,2
Standing, light activity (shopping, laboratory, light industry)	93	1,6
Standing, medium activity (shop assistant, domestic work, machine work)	116	2,0
Walking on level ground:		
2 km/h	110	1,9
3 km/h	140	2,4
4 km/h	165	2,8
5 km/h	200	3,4

As an illustrative example, the metabolic heat is estimated to be approximately 236 W for a 70 kg man in active exercise mode (taking consideration that body surface area is roughly 1.8 m²) [22]. Reference from Table 2-1 indicates that the status of “active exercise” used in the reference is roughly equivalent to walking at around 3 km/h. For a more demanding workload such as walking at a speed of 5.0 km/h, the metabolic heat generation is 200 W/m² according to Table 2-1, corresponding to a total metabolic generation rate of approximately 360 W for an average person with a bodyweight of 70 kg and a body surface area of 1.8 m². Table 2-2 summarized the cooling capacities of some commercial or prototype MCGs.

As listed in Table 2-2, VDC is one of the systems that have a relatively large cooling capacity. It is advantageous in comparison with other two systems of comparable cooling capacities, LCG (70-600 W) and ACG (312 W), since no continuous power supply is required and the system is, as a result, light and portable.

Table 2-2 Cooling capacities of commercial and prototype MCGs

	Cooling capacity (watts)	System weight (pounds)	Working duration
LCG [23]	70-600	~11	Batteries (autonomous function capacity: 3-6 h, recharging time: 2-14 h)
ACG [24]	312 (30% relative humidity)	~10	Dependent on AC power supply, and compressed air supply
PCM [24]	139	~10	21 min
ECG [25]	69.4	2.4~6.13	2.45
VDC* [26]	373	7.5	1-2 h

*1st generation of VDC garment developed by our group

2.3.2 Operation duration

The requirement on operation duration varies remarkably depending on the wearers' occupations. For instance, cooling garments designed for military personnel such as mounted drivers and infantry soldiers and civilian outdoor workers would ideally be able to work continuously for 12 h or even longer. On the other hand, cooling garments that could provide efficient heat relief for up to two hours or even 30 minutes would be able to provide meaningful protection for emergency workers such as firefighters and demining personnel. Nonetheless, designing an enhanced working duration MCGs without sacrificing the cooling capacity is always a desirable improvement in R&D of MCGs.

For powered cooling devices such as FCGs, the work duration would rely primarily on the availability of power. Whereas for unpowered cooling devices such as PCMs and ECGs, the working duration would be dependent primarily on the latent heat of phase change of PCMs or coolant in ECGs.

2.3.3 Portability and Mobility

The portability and mobility of MCGs mainly depend on the systems total weight and ability of being AC power independent. Personal cooling devices should not only serve as a cooling-aid device but also be needed to allow the user to perform their duty as normal, which demands the garment to have certain extent of flexibility and minimize restriction on wearer's mobility. PCMs and ECGs are mostly light-weight and thus portable, with periodic replacing of

PCM pad or wet absorbent for ECG, good mobility is achieved. To reduce the power dependency of the MCG is an important aspect of designing novel VDC garment.

2.3.4 Dryness of wearer skin

Dryness of the wearer's skin is another important issue in designing MCGs. Both ACGs and LCGs are designed to be an insulated garment, thus prohibit body's natural sweating process. Researchers have demonstrated that incorporating sweat evaporation by adding ventilation components can enhance the MCGs cooling effect. This is essential in some occupations such as medical doctors, who are often required to maintain dryness (e.g., when operating a surgery) [27, 28]. This flaw is also applied to PCMs, which could not help create a dry microclimate for the wearer comparing to the previous two types of MCGs. Furthermore, there is a risk of LCGs to fail, causing spill of water onto wearer's skin. For the 1st generation VDC garment design, dryness is also a concern since the garment does not have the ability to facilitate sweat evaporation, and human trial testers reported that the sweat accumulation between skin and VDC garment would reduce the comfort for the wearer after 40 minutes during the testing period. Therefore, maintaining the body's microclimate relative humidity is another trend for designing more efficient MCGs.

2.4 Conclusion

To conclude the above mentioned design parameters, improved cooling performance, cooling duration, mobility and portability with less power required are the primary goals. These

requirements have all been successfully achieved by the 1st generation of VDC garment, however, with certain flaws which limit its reusability and robustness. Also, maintaining the wearer's skin dryness is the MCGs designing trend which needs to be considered and improved in the following 2nd generation VDC garment design.

2.5 Reference

- [1] Nunneley S. Water cooled garments: A review. *Space Life Sci* 1970;2:335-360.
- [2] Lim C, Leong, Byrne C, Lee J, KW. Human Thermoregulation and Measurement of Body Temperature in Exercise and Clinical Settings. 2008, p. 347-353.
- [3] Tanaka K, Nakamura K, Katafuchi T. Self-perspiration garment for extravehicular activity improves skin cooling effects without raising humidity. *Acta Astronaut* 2014;104:260-265.
- [4] Faulkner SH, Hupperets M, Hodder SG, Havenith G. Conductive and evaporative precooling lowers mean skin temperature and improves time trial performance in the heat. *Scand J Med Sci Sports* 2015;25:183-189.
- [5] Chauhan DT. Review of literature on cooling garments. *Ergonomics Australia Journal*. 1999;13:1-5.
- [6] Zhao M, Gao C, Li J, Wang F. Effects of two cooling garments on post-exercise thermal comfort of female subjects in the heat. *Fibers Polym* 2015;16:1403-1409.
- [7] Ernst TC, Garimella S. Wearable engine-driven vapor-compression cooling system for elevated ambients. *ASME International Mechanical Engineering Congress and Exposition, Proceedings* 2008;15:79-92.
- [8] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Therm Eng* 2003;23:251-283.
- [9] Erkan G. Enhancing The Thermal Properties of Textiles with Phase Change Materials. *Research Journal of Textile and Apparel* 2004;8:57-65.
- [10] Tan FL, Fok SC. Cooling of helmet with phase change material. *Appl Therm Eng* 2006;26:2067-2072.

- [11] Ernst TC, Garimella S. Wearable Engine-Driven Vapor-Compression Cooling System for Elevated Ambients. *Journal of Thermal Science and Engineering Applications* 2009;1:025001-025001.
- [12] Glitz KJ, Seibel U, Rohde U, Gorges W, Witzki A, Piekarski C, et al. Reducing heat stress under thermal insulation in protective clothing: microclimate cooling by a 'physiological' method. *Ergonomics* 2015;58:1461-1469.
- [13] Dai YJ, Wang RZ, Zhang HF, Yu JD. Use of liquid desiccant cooling to improve the performance of vapor compression air conditioning. *Appl Therm Eng* 2001;21:1185-1202.
- [14] Zadpoor AA, Nikooyan AA. Development of an Improved Desiccant-Based Evaporative Cooling System for Gas Turbines. *Journal of Engineering for Gas Turbines and Power* 2009;131:034506-034506.
- [15] Rothmaier M, Weder M, Meyer-Heim A, Kesselring J. Design and performance of personal cooling garments based on three-layer laminates. *Med Biol Eng Comput* 2008;46:825-832.
- [16] Lee D, Hwang Y. Subminiature Cool Pad Applying Sorption Cooling Effect. *HVAC&R Research* 2006;12:797-806.
- [17] Yang Y, Stapleton J, Diagne BT, Kenny GP, Lan CQ. Man-portable personal cooling garment based on vacuum desiccant cooling. *Appl Therm Eng* 2012;47:18-24.
- [18] Rother M, Barmettler J, Reichmuth A, Araujo JV, Rytka C, Glaied O, et al. Self-Sealing and Puncture Resistant Breathable Membranes for Water-Evaporation Applications. *Adv Mater* 2015;27:6620-6624.
- [19] Johnson DW, Yavuzturk C, Pruis J. Analysis of heat and mass transfer phenomena in hollow fiber membranes used for evaporative cooling. *J Membr Sci* 2003;227:159-171.
- [20] Decker LO. Consider the cold facts about steam-jet vacuum cooling. *Chemical Engineering Progress* 1993;89:74-77.

- [21] International Organization for Standardization (ISO). Ergonomics of the thermal environment-analytical determination and interpretation of thermal comfort using calculation of the PMV and PPD indices and local thermal comfort criteria (Standard No. ISO 7730:2205). Geneva, Switzerland: ISO 2005.
- [22] Guyton AC. Textbook of Medical Physiology. Am J Med Sci 1967;253:772-832.
- [23] Flouris AD, Cheung SS. Design and Control Optimization of Microclimate Liquid Cooling Systems Underneath Protective Clothing. Ann Biomed Eng 2006;34:359-372.
- [24] Kari Babski-Reeves GT. Performance evaluations of micro-climate cooling products 2003.
- [25] Brad Laprise, Walter Teal, Leah Zuckerman, Jason Cardinal. Evaluation of commercial off-the-shelf and government off-the-shelf microclimate cooling system 2005;Natick/TR-05/019.
- [26] Yang Y, Stapleton J, Diagne BT, Kenny GP, Lan CQ. Man-portable personal cooling garment based on vacuum desiccant cooling. Appl Therm Eng 2012;47:18-24.
- [27] Crockford GW, Hellon RF. Design and evaluation of a ventilated garment for use in temperatures up to 200 degrees C. British journal of industrial medicine 1964;21:187-196.
- [28] Nunneley SA. Design and Evaluation of Clothing for Protection from Heat Stress: An Overview. School of aerospace Medicine Brooks AFB TX. 1986:1-12.

Chapter 3: Developments in evaporative cooling and enhanced evaporative cooling -A review

Yifan Yang, Christopher Q. Lan

Department of Chemical and Biological Engineering

University of Ottawa

161 Louis Pasteur Private, Ottawa, ON, K1N 6N5, Canada

3.1 Abstract

Evaporative cooling is one of the widely employed cooling methods with advantages mainly on energy-saving and utilization of low grade energy. It has found more and more applications in areas such as HVAC, industrial process cooling, and personal microclimate cooling, as stand-alone cooling processes or in combination with conventional cooling technologies such as the vapour compression cycles. According to different criteria, evaporative cooling could be classified into different categories such as air-mediated vs water-mediated evaporative cooling and direct vs indirect evaporative cooling. When necessary, evaporative cooling could be enhanced by desiccant vapour sorption, membrane separation, and the combination of desiccant and membrane technologies. This paper strives to provide a comprehensive review on the recent developments and applications of different evaporative cooling technologies. A novel system for classifying different evaporative cooling technologies has also been proposed.

Key words: evaporative cooling; desiccant cooling; dehumidification; membrane cooling; enhanced evaporative cooling

3.2 Introduction

Temperature control is essential in industrial processes and human health and evaporative cooling have been widely used in processing the cooling water of industrial processes using cooling towers [1, 2], in space cooling as part of a heat, ventilation, and air conditioning (HVAC) system [3, 4], and in microclimate cooling, which focuses on regulating the temperature of the microclimate surrounding equipment or personnel [5].

As an illustrative example, evaporative cooling systems have been used as stand along cooling units [3, 6] or in combination with conventional vapor compression systems (VCSs) [7] for HVAC of buildings. It has been demonstrated that the use of evaporative cooling in HVAC is not only environment-friendly since it does not involve the use of refrigerants such as chlorofluorocarbons (CFCs), which causes the concern of ozone layer depletion, but also lead to significant energy savings [8]. As a matter of fact, buildings worldwide account for a surprisingly high 40% of the global energy consumption and the resulting carbon footprint significantly exceeds those of all transportation combined [9]. Air-conditioning (AC) systems contribute to 50% of building energy consumption, therefore more energy efficient AC systems are required to improve the indoor air quality and reduce energy consumption.

Microclimate cooling is another important application for evaporative cooling technologies, which has been studied intensively for astronaut life support system [10] and beyond. While microclimate cooling could be achieved by different approached including chilled liquid circulating garments [11, 12] and phase change material cooling garments (e.g., ice cooling garments) [13, 14], evaporative cooling enjoys many advantages including larger cooling

capacity, more portability [6] and is regarded as among the most promising microclimate cooling technologies [15, 16].

This review strives to provide a comprehensive account on recent developments in evaporative cooling technologies, with a focus on enhanced evaporative cooling assisted by desiccants, membranes, or the combination of desiccants and membranes.

3.3 Evaporative cooling technologies

Evaporative cooling is based on the fact that water must absorb heat in order to change from liquid state to vapor state, converting sensible heat to enthalpy of vapour, resulting the reduction of system temperature. The benefits of evaporative cooling include substantial energy and cost saving, no CFCs usage, reduced CO₂ other power plant emissions, improving indoor air quality, life-cycle cost effectiveness, and greater regional energy independence. [17, 18]

All evaporative cooling process involves at least a water volume (or stream) and an air volume (or stream), which serves as either the cooling medium or the complimentary medium. The cooling medium is the fluid (water or air) that is first chilled as a result of water evaporation and then used to cool the object of interest and a complimentary medium is the fluid (water or air) that is required for water evaporation to take place but is not used to cool the object of interest directly. According to the choice of cooling medium, evaporative cooling could be classified as air-mediate and water mediated cooling. Air-mediated cooling is a process where air serves as the cooling medium and water the complimentary medium. In such a process, air is first cooled as a result of the evaporation of water and the chilled air is consequently used as the medium to deliver the cooling effects to the object of interest. In air-mediated cooling, water is often

supplied at a quantity that is substantially smaller than the moisture carrying capacity of the air so that the resulted air as the cooling medium is not saturated with moisture. A typical application of air-mediated cooling is provide chilled and humidified air in HVAC system or in air-mediated personal cooling. On the other hand, water-mediated cooling refers to a process where water is chilled as a result of the evaporation of a portion of the water body, and then the chilled water is then used as the medium to deliver the cooling effects. Water is always supplied in a quantity that is more than the moisture carrying capacity of the air, which is the complimentary medium in this scenario. Typical water mediated evaporative cooling is the cooling towers, where hot water is atomized into a steam of fine water droplets or to the surfaces of solids fillings in a tower and a stream of dry air is blown upward to facilitate water evaporation.

According to whether the cooling medium is in direct contact with the complimentary medium, evaporative cooling could be classified into two categories, direct and indirect evaporative cooling. In direct evaporative cooling, the cooling medium is a product of the water evaporation takes place in it, no matter it is air-mediate or water mediated cooling. For instance, in cooling tower, air is the complimentary medium and water is the cooling medium. Water evaporation takes place inside the cooling tower as water droplets get in touch with the air flow to cause the chilling down of the remain water, which is used as the cooling medium. On the other hand, in indirect evaporative cooling, water evaporation takes place in compartment that is physically separated from the air stream that is used as the cooling medium in the case of air-mediated cooling or as complimentary medium in the case of water-mediated cooling.

Furthermore, evaporative cooling could be classified in to ambient evaporative cooling or enhanced evaporative cooling, where the former employs ambient air as either the cooling medium or the complimentary medium and the latter refers to a process where ambient air is processed first to reduce its moisture content before being used.

3.3.1 Air-mediated cooling

As aforementioned, air-mediated cooling refers to an evaporative cooling process where an air stream or volume is used as the cooling medium and a water volume or stream as the complimentary medium. In such a process, air is chilled as a result of water evaporation and then used to deliver the cooling effect directly. Air-mediated cooling could be further divided into air-mediated direct evaporative cooling and air-mediated indirect evaporative cooling.

3.3.1.1 Air-mediated direct evaporative cooling

Air-mediated direct evaporative cooling (AMDEC) is a process in which the air used as cooling medium is put in direct contacts with water as shown in Figure 3-1. It is the oldest and simplest type of evaporative cooling configuration. AMDECs are also known as swamp coolers. These are most commonly found in homes and small business areas that are located in dry and hot climates. Generally speaking, in AMDEC systems, ambient or dried air passes through the water-soaked pad/ or stream of water droplet, the water evaporates and cools the air by as low as 20 °F (6.7 °C), when simultaneously humidifies the air. As a result, the relative humidity of the chilled air can increase to 60% or as high as 80% in humid conditions, which is not suitable for direct supply to buildings [18].

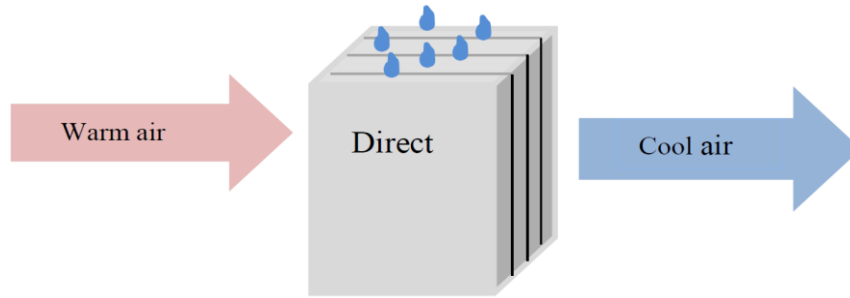


Figure 3-1 Schematic diagram of AMDEC

The air which has a high relative humidity can cause rusting problems, and the water-borne bacteria contained in the air can also cause safety issues for people. Therefore AMDECs are only appropriate in dry and hot climates. Usually an ambient relative humidity below 30% is recommended [6].

AMDEC also has other disadvantages. For example, water from a water reservoir is pumped to the porous interface (e.g., a metal mesh) where water and air is put in contact for continuous evaporation. Minerals and bacteria contained in water could be deposited on such an interface, which requires regular and frequent maintenance. The system also requires a lot of pipes for pumping and water recycle, and any leakage at valves and sensors can lead to the waste of water source. These problems limit the application of direct evaporative coolers in large areas.

The current research directions for AMDECs are focused on the pads material (the porous water absorbents). Pad materials include metal pads [19, 20], cellulose pad [21, 22], organic pad [23], inorganic pad [24], PVC pad, porous ceramic pad [25], etc. [18]. Thermodynamic properties, corrosion, fire resistance, and filtering performances of different types of pads were summarized [26].

3.3.1.2 Air-mediated indirect evaporative cooling

Air-mediated indirect evaporative cooling (AMIEC) was first proposed by Dr. Willi Elfert in 1903 [18, 27]. A schematic diagram of AMIEC is shown in Figure 3-2. It contains two air streams; a primary air stream that serves as the cooling medium and the secondary air stream is cooled by water evaporation and in turn cools the primary airstream. In such an arrangement, the water evaporation in the secondary air stream could take place before entering the heat exchanger or on the surfaces of the heat exchanger. In this arrangement, the cooling medium, which is the primary air stream, is never in contact with the water stream or the secondary air stream, both serve as the complimentary streams. As a result, addition of moisture to the primary air stream is avoided and a stream of low temperature and low humidity cooling medium is produced.

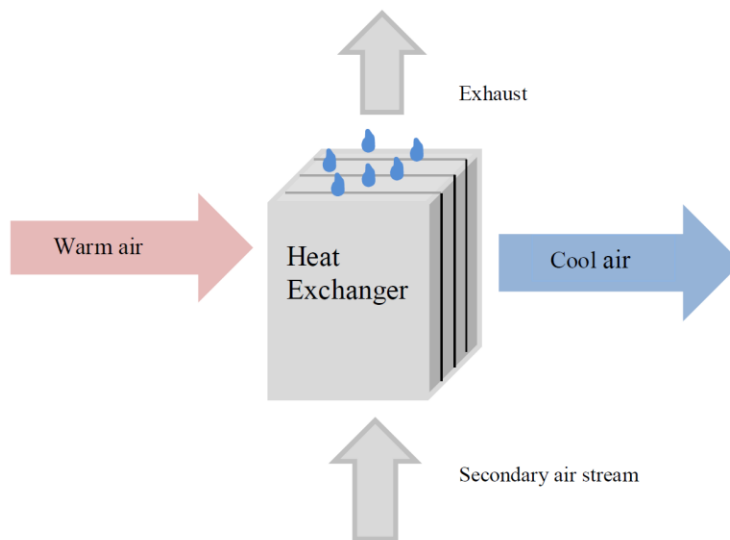


Figure 3-2 Schematic diagram of AMIEC

Based on the principle, many configurations of AMIEC have been developed. For instance, a large variety of different AMIEC heat and mass exchanger have been developed, including flat-plate-stack, tube, heat pipe and potentially wave-form, etc. [26]. Materials used for making the exchanger elements are all of topics of intensive studies and materials investigated range from aluminum plate/tube to ceramic plate/tube [28]. The design of the geometric design of the heat exchanger is a topic of profound interests and the cross flow AMIEC, which is shown in Figure 3-2, is considered the favourite choice [29, 30]. A more complicate multi-stage AMIEC called Maisotsenko-Cycle (M-Cycle) was developed, which is a 20-stage process that could provide more energy efficient cooling. The cumulative result is a lower primary/product air temperature than is not possible with conventional evaporative cooling technologies [31, 32]. AMIECs are also used in combination with other cooling technologies to create hybrid systems such as two-stage IEC/DEC evaporative cooler [33], IEC/vapor compression system [34, 35] and IEC/desiccant system.

3.3.2 Water mediated evaporative cooling

In water-mediate evaporative cooling, water is the cooling medium and air serves as the complimentary medium. In this scenario, water is over supply and the evaporation of water as a result of in contact with dry air causes the remaining water body to cool down and the chilled water is used for cooling. Similar to air-mediated evaporative cooling, water mediated evaporative cooling could be divided into two groups, direct and indirect water-mediated evaporative cooling.

3.3.2.1 Water-mediated direct evaporative cooling

A typical example of water mediated direct evaporative cooling technology is the cooling tower, which is widely used in HVAC for buildings and in cooling of recycled industrial process cooling waters. In a cooling tower, hot water is atomized from the top to produce a stream of fine water droplets, which provides large surfaces for water evaporation. Counter-currently, ambient air is blown upward from the bottom of the tower as the sweeping gas for water evaporation. Since water is over supplied in this process, a portion of the water would evaporate to take away the latent heat. As a result, the remaining water is cooled to produce a chilled water stream as the feed to a refrigeration system for further cooling or directly recycled to the building or industrial facilities as the cooling water.

In a water-mediated direct cooling process, water is directly put in contact with the complimentary medium, i.e., the up-blown air stream. Contamination of air borne dusts and bacteria to the recycling water and deposition of mineral due to over evaporation of the recycling water are some of the disadvantages of the this approach, among other limitations such the bulkiness and noisy nature of a cooling tower [36].

3.3.2.2 Water-mediated indirect evaporative cooling: Multi-layer membrane evaporative cooling for personal heat management

As indicated literally by the name, in a water-mediated indirect evaporative cooling process, the cooling medium, i.e., water, is not directly in contact with the complimentary medium, i.e., air. Multi-layer membrane evaporative cooling garment [37], which is designed for personal cooling, is good example of such a process.

As shown in Figure 3-3, a multi-layer layer cooling garment as developed by Rothmaier et al.[37] is based on a three layer composite assembled from two hydrophobic membranes which are water-proof but vapor permeable with a hydrophilic fabric sandwiched in between. Water absorbed by the fabric can evaporate by absorbing the body heat. This design allows the garment to be flexible, lightweight, and the laminate's high adaptiveness makes it possible to produce cooling garments even for difficult anatomic topologies.

The membranes used in this particular design were dense membranes made of polyetherester, a co-polymer of hydrophobic ester and hydrophilic ether. These dense membranes allow water vapor to diffuse through the bulk polymer, driven by the difference between the saturation vapour pressure at the skin temperature and the partial vapour of air in the ambient. In such a setting, water is the cooling medium while the ambient air is the complimentary medium.

Advantage for this type of dense membrane is that it can be washed in a standard laundry process, without getting blocked by residues like dirt particles, salts from washing powder and sweat, etc. In terms of mechanical strength concern similar like micro porous membrane, the dense membrane used in this design were very thin (10-15 μm), therefore an air permeable mesh was applied on top to protect the membrane. This development has given a great insight for membrane material in practical applications.

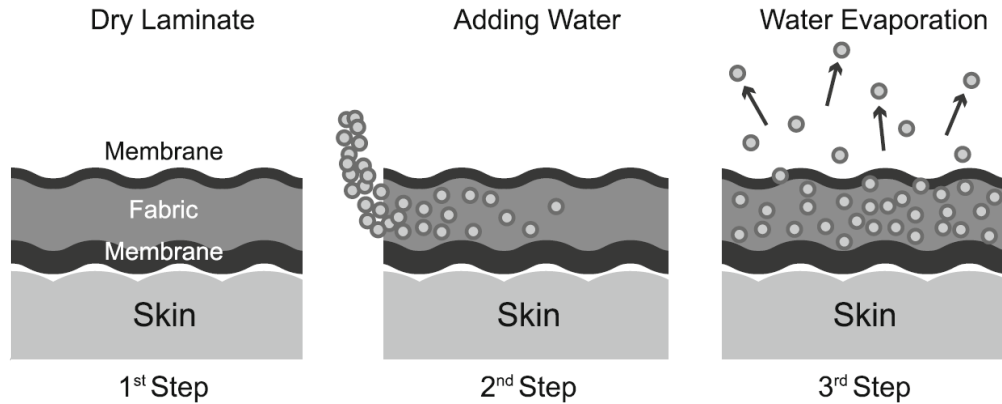


Figure 3-3 Schematic diagrams of three-layer laminate and the principle of water evaporation from the reservoir [56]

There are certain limitations for this design to be applied underneath the personal protective clothes (PPC). First of all, the cooling capacity was limited by the amount of water contained by the hydrophilic fabric, adding water to the laminate when necessary can certainly increase the cooling performance. Secondly, the water evaporation was restricted due to high level of humidity within microclimate covered underneath the impermeable material of PPC, additional desiccant need to be added within the garment to maintain driving force for water evaporation. By doing so, the problem of dissipating the adsorption heat from desiccant pad effectively will be one of the design challenges.

Similar concept of using semi-permeable membranes, i.e., waterproof but breathable membranes [10] for dissipation of body heat had also been applied in the textile industry for weather protective clothing. These clothes allow body-generated moisture to pass the membrane while preventing wind and rain from penetrating the fabric thus keeping the body dry [38].

3.4 Enhanced evaporative cooling

When ambient air is used directly to an evaporative cooling process, the capacity of it to hold moisture depends on its temperature and moisture content and the cooling efficiency is very low under humid conditions. To increase the cooling efficiency of an evaporative cooling system, the air, not matter it is used as the cooling medium or as the complimentary medium, could be pre-dried (i.e., dehumidified) to enhance the cooling efficiency. Such an evaporative cooling process involving the pre-drying of air is called enhanced evaporative cooling. Enhanced evaporative cooling are mainly applied where low dew point is required, such as in supermarkets, museums, indoor pools, etc., where high humidity can damage assets or where high air quality is necessary, e.g., hospitals, laboratories, and pharmaceutical production facilities [39, 40]. While desiccant sorption is the most common technology used for air dehumidification, membranes may also be used alone or in combination with desiccants to pre-dry air, and therefore enhance the cooling efficiency of evaporative cooling processes.

3.4.1 Desiccant cooling

Desiccant cooling, alias desiccant-enhanced evaporative cooling, is a fast growing evaporative cooling technology for sustainable HVAC in buildings and in other applications [3, 35]. Desiccants are either natural or synthesised materials which are capable of absorbing water or water vapor due to the partial vapor pressure difference between desiccant surface and surrounding air. Desiccants can be categorized into two main groups, liquid desiccant and solid desiccant. Both liquid and solid desiccants have been employed for air dehumidification.

3.4.1.1 Liquid desiccant evaporative cooling system

Liquid desiccant are mostly absorbents. Liquid desiccant dehumidifiers (absorbers), uses mostly hygroscopic aqueous solutions, such as tri-ethylene glycol (TEG), $\text{CaCl}_2\text{-H}_2\text{O}$, $\text{LiBr-H}_2\text{O}$, $\text{LiCl-H}_2\text{O}$, etc. Liquid desiccant has been applied into different existing cooling systems, since liquid desiccants can undergo more efficient dehumidification at low regeneration temperatures, 50-70 °C [41, 42]. Other advantages include smaller pressure drop and easy transportation to the source of regeneration unit [43, 44]. One of the examples is called desiccant enhanced evaporative (DEVAP) air conditioning [45]. As shown in Figure 3-4, lithium chloride solution (LiCl) is used in DEVAP system, it is reported to have 40% and 85% energy savings and 80% peak energy demand reduction compared to the most efficient vapor compression air conditioners [46]. However, it has a lot of design concerns associated with the actual application and is still open to study for specific application conditions.

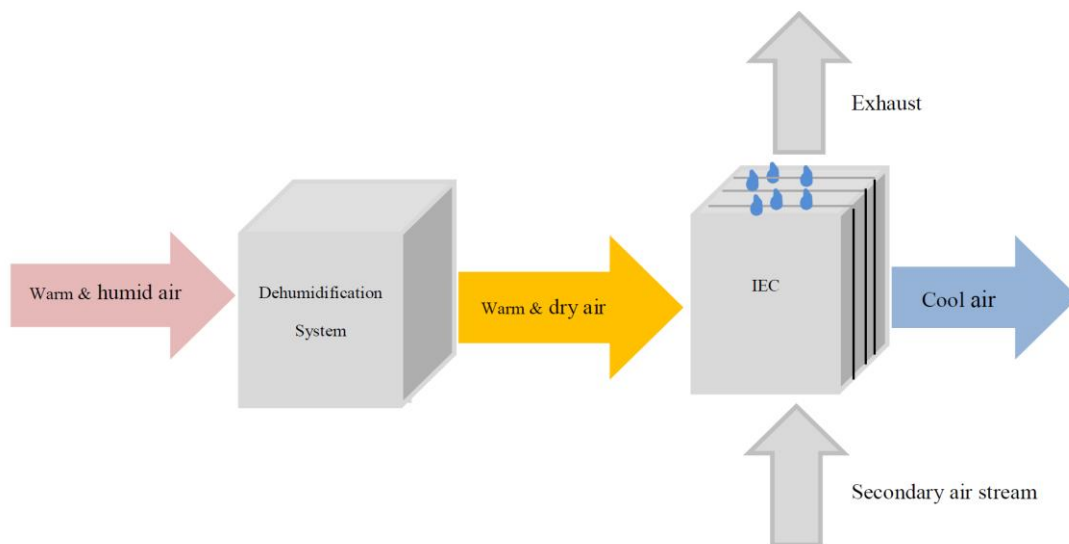


Figure 3-4 The schematic system of desiccant enhanced IEC system

The common problem associated with the liquid desiccant system is the high equipment maintenance cost, the air leakage between the dry and wet streams, and the use of large intake air stream to absorb the heat released during dehumidification [6].

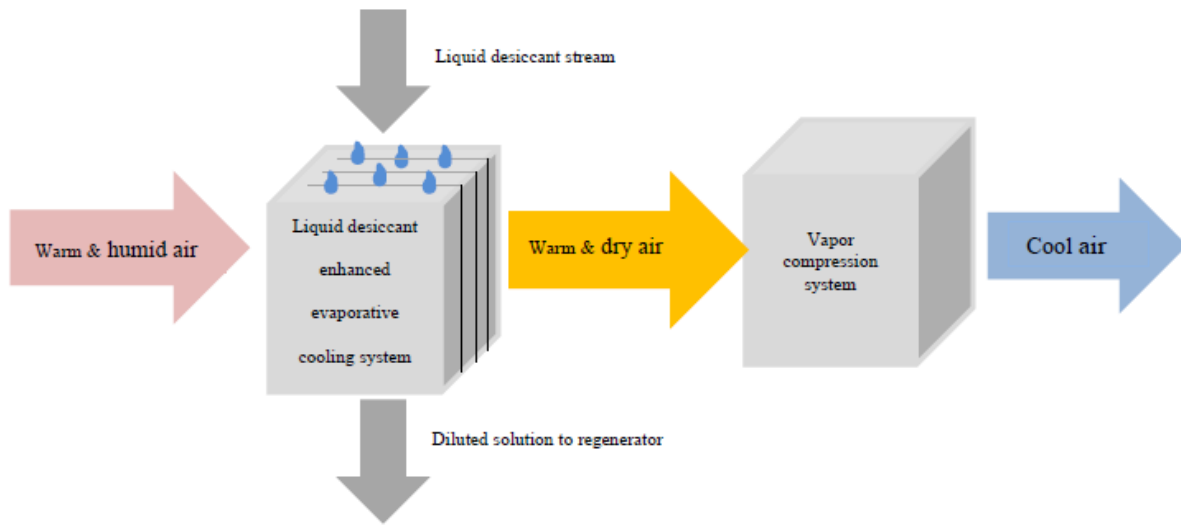


Figure 3-5 Schematic diagram for liquid desiccant aided vapor compression system

Figure 3-5 shows a combined system of evaporative coolers and mechanical vapor compression, which has a higher energy consumption rate than the stand-alone evaporative cooling system [35]. However, the energy consumption is lower than that of the conventional vapor compression system. One of the drawbacks is the corrosive nature of lithium chloride/lithium bromide solution which makes the regeneration unit more complicated. Also, the desiccant solution concentration tends to have a gradient along the collector plate/pipe, which

reduces the vapor pressure difference between the solution and the air, making the regeneration difficult [35].

3.4.1.2 Solid desiccant (desiccant wheels) cooling system

Solid desiccants are compact, having less chance of corrosion and cross-contamination. The most popular solid desiccant is silica gel which is a naturally occurring mineral made of silicon dioxide ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$). It has a large surface area of $650 \text{ m}^2/\text{g}$ with the pore size ranging from 2-3 nm (type A) to about 0.7 nm (type B) and the heat of adsorption that nearly equals to 2800 kJ/kg [47].

One of the typical applications is desiccant wheel (also known as rotary dehumidifier), which consists of a slowly rotating wheel impregnated or coated with the solid desiccant into a light weight honeycomb or corrugated matrix. This desiccant wheel is usually divided into two sections. One part of the wheel treats the incoming air stream while the rest of it is being regenerated. Another arrangement used the packing of solid desiccants to form adsorbent beds that are exposed to the incoming air stream. However, the bed induces a high pressure drop which requires an excessive fan power [48, 49].

Common solid desiccants are adsorbents, such as zeolite, silica gel, activated alumina, molecular sieves, etc. Those types of adsorbents normally require at least $80\text{-}100^\circ\text{C}$ regeneration temperature to achieve sufficient dryness for the next cycle of dehumidification [48, 50, 51]. Desiccant wheel has received growing interest because it is compact and fairly corrosive-free [52]. Many studies use silica-gel desiccant wheel coupled with a heat exchanger and evaporative cooler [53, 54].

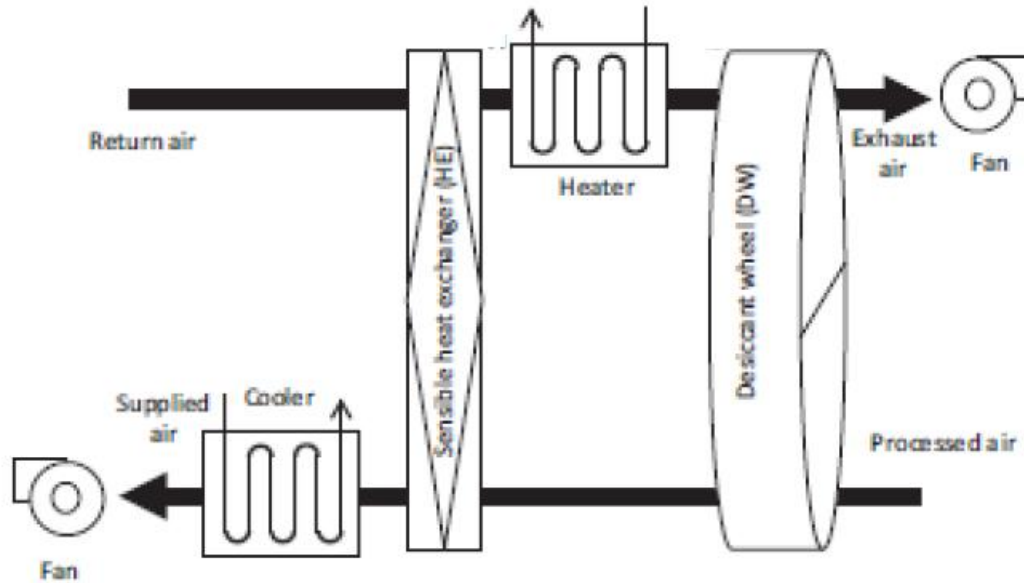


Figure 3-6 Schematic of desiccant dehumidification and cooling system (DDCS) [55]

One of the limitations of solid desiccants is the short active lifetime of the desiccant material due to the inability to release all of the bound water molecules. Many studies have been targeting on developing more effective desiccant material [52]. Among isotherms of common solid desiccant, i.e., silica gel, active alumina, molecular sieve, etc, static saturation adsorption capacity is all less than 45% [52, 56]. Composite solid desiccants, i.e. silica gel incorporated with lithium chloride, or silica gel incorporated with calcium chloride, etc. [57-59] have larger vapor absorbency and high diffusion rate constant, and thus exhibit better dehumidification and desiccant cooling performance.

3.4.2 Membrane air drying enhanced cooling technology

Membrane air drying is an emerging technology for air dehumidification, where the membrane acts as a selective barrier to separate moisture from air. For membrane enhanced cooling process, the water vapor is usually the permeate, and thus the membranes need to be permeable to water vapor and selective to water vapor over other species [60]. During this drying process, water vapor molecules are selectively adsorbed by membrane over through the membrane over other gas molecule, mainly N_2 and O_2 , and could therefore reduce the moisture content of the processed air. Membrane drying is an isothermal process and does not generate heat during the permeation of water vapour in the air through the membrane [6]. Customized membrane which has water-selective feature was studied and tested by Xing's group [61] and others [62, 63]. The dry air produced in such a fashion could be used in place of ambient air for both water mediated and air-mediated evaporative cooling and for direct or indirect evaporative cooling. It could also be used as a dehumidifier in combination with conventional vapor compression refrigerators to enhance the cooling energy efficiency [63].

3.4.3 Membrane assisted desiccant cooling

Desiccant cooling, whether involves liquid desiccants or solid desiccant has the risk of cross-contamination of air stream by the desiccant and the deactivation or contamination of the desiccant by the dusts in the air stream. To avoid such difficulties, membrane assisted desiccant cooling has proven to be an advantageous approach.

3.4.3.1 Membrane assisted liquid desiccant cooling

Membrane separation technology is also studied for liquid desiccant regeneration process. The primary advantage of membrane assisted liquid desiccant cooling is to prevent cross-contamination by desiccant droplet to the air stream. It also has additional improvements such as a modular and smaller scale setup. Membrane separation technology is also studied for liquid desiccant regeneration process, the primary advantage of membrane assisted liquid desiccant cooling is to prevent cross-contamination by desiccant droplet to the air stream. It also has additional improvements such as a modular and smaller scale setup, better drying efficiency [64], etc. The detailed thermodynamic process is therefore analyzed.

Researchers have developed prototypes for HVAC devices using porous membranes with pore sizes ranging from 0.03 to 1 μm . Abdel-Salam et al. [65] reported a membrane liquid desiccant air conditioning system. In the system, the dehumidifier and regenerator act as the liquid-to-air membrane energy exchangers [4] in counter-current mode as shown in Figure 3-7. The proposed membrane is made of flat-sheet PTFE membrane. Simulation has shown that it is capable of achieving recommended supply air conditions for productive, comfortable and healthy environments. It is also recommended to set the desiccant solution inlet temperatures to the dehumidifier and regenerator at 15-20 °C and 45-55 °C.

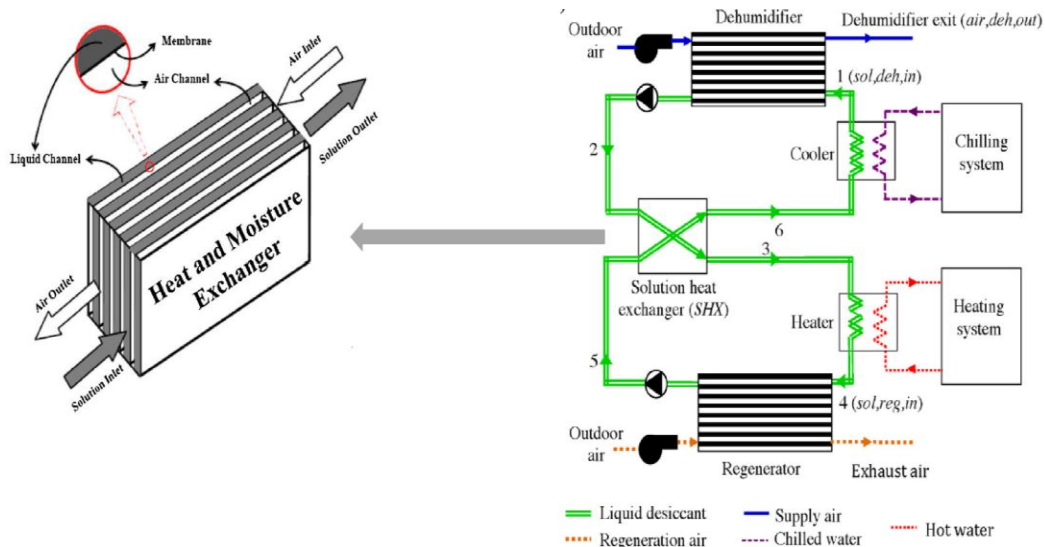


Figure 3-7 Schematic diagram of a membrane liquid desiccant air conditioning system [65]

A hollow fiber membrane dehumidification module has been developed by Zhao et al. [5] of the National University of Singapore to be operated under a vacuum of 0.78 bar at the lumen side. Polyacrylonitrile (PAN)/PDMS composite hollow fiber membrane was fabricated and used in their study.

3.4.3.2 Membrane assisted vacuum desiccant cooling

A portable personal cooling garment based on vacuum desiccant cooling (VDC) was developed in our lab [66] and shown in Figure 3-8A. It is composed of four main components, i.e., a cooling core, a spacer, an absorption core and an outer bag. The cooling core was a hybrid bag containing pre-determined amount of water made of soft impermeable plastic water bag with one side replaced with semi-permeable Teflon membrane. A piece of soft cotton cloth (Towel III)

was used to cover membrane for protection. A piece of perforated aluminum foil was used on top of Towel III to minimize the radiation heat transfer from the hot absorption core to the cold cooling core. The spacer made of honeycomb served to separate cooling core from absorption core. The absorption core was composed of two layers of cotton towel glued together with lithium chloride powder being sandwiched in the middle of them. An outer bag was made of a plastic bag connected to vacuum pump for initialization. This VDC garment required 5 minute initialization period to allow system reach desired vacuum pressure, and then garment was sealed and disconnected with vacuum pump. It was designed to operate power-off to ensure the portability.

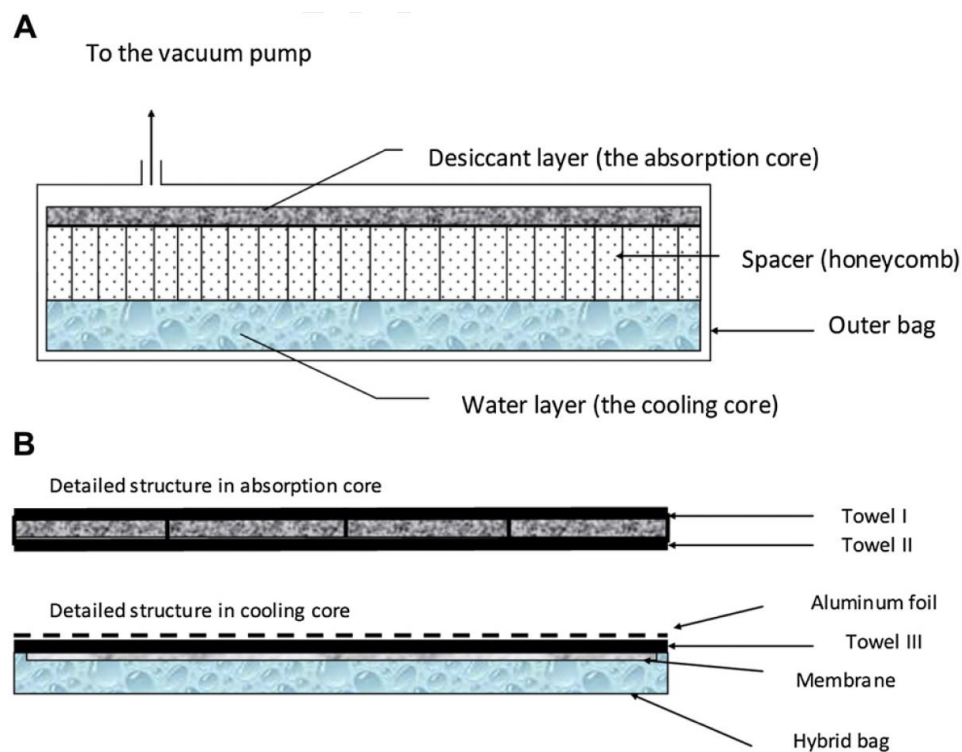


Figure 3-8 Schematic diagrams of A: the cross-section view of vacuum desiccant cooling pad. B: cross-sectional view of absorption core and cooling core. [66]

The vacuum desiccant cooling utilized the evaporation of water for cooling and employs desiccants to remove the moisture in a closed space to maintain the driving force for water evaporation. A key component in this design is the vacuum gap, which separates the cold water layer from the hot desiccant layer. It not only facilitates the diffusion of vapor molecules from the water layer surface to the desiccant layer surface to increase the cooling capacity but also minimizes the heat transfer from the desiccant layer to the water layer. It should be pointed out that, in application, the water layer would be facing the skin of wearer while the hot desiccant layer the ambience. Since the vacuum gap minimize the heat transfer from the latter to the former, heat would dissipate mainly, if not solely, from the desiccant layer to the ambience and will have little impact on the cooling performance. Being further away from the water layer than the desiccant layer, the ambience temperature would have little impact on the overall cooling performance except its influence on the heat dissipation and temperature of the desiccant layer.

3.4.3.3 Membranes for membrane-assisted desiccant cooling

Needless to say, membranes are a key component of membrane-assisted desiccant cooling and a large variety of different membranes are available thanks to the fast development in membrane technology. Some key membrane properties are summarized below for applications in membrane-assisted desiccant cooling, i.e., membrane assisted desiccant cooling and membrane-assisted vacuum desiccant cooling.

1) Liquid entry pressure (LEP)

The major function of the membrane in a membrane-assisted desiccant cooling system, no matter it is a continue liquid desiccant system for HVAC or a membrane-assisted VDC for

personal cooling, is two-fold: 1) holding the desiccant in place to avoid cross contamination, and 2) provide large surface for vapor absorption. For such an application, liquid entry pressure of water (LEP_w), which is defined as the pressure difference across membrane required for the liquid water to enter the membrane pores, is an important parameter. In fact, it must be large enough to prevent the desiccant solution from leaking under the intended operational conditions.

LEP depends primarily on the maximum pore size and the hydrophobicity of the membrane, Laplace (Cantor) equation can be used to calculate LEP [67]. For vacuum induced evaporative cooling, e.g., VDC, the membrane LEP needs to be at least 1 bar.

$$LEP = \frac{-2\gamma \cos \theta}{r_{max}} \quad (3.1)$$

Where γ is the liquid surface tension, θ is the liquid contact angle at membrane surface, and r_{max} is the largest pore size (radius).

2) Flux

Since the vapor molecules from the water layer must diffuse across the membrane before being absorbed by the desiccant on the other side, the flux of vapor transportation across a particular membrane under given conditions is another key parameter in determine the suitability of the membrane for application in membrane-assisted desiccant cooling. The membrane permeation flux can be calculated by equation 3.2. It is one of the most important parameters for membrane, since it directly related to the cooling performance.

$$J = K * (P_w^{sat} - P_d^{sat}) \quad (3.2)$$

Where J , in unit of $\frac{kg}{m^2h}$ is the evaporation flux; K , in unit of $\frac{kg}{m^2hPa}$, is the mass transfer coefficient; P_W^{sat} and P_D^{sat} , in unit of Pa, is the saturation vapor pressure of water at the water layer temperature and the saturation vapor pressure at the desiccant surface, respective. The vapor pressure difference represents the driving force for vapor transfer through membrane.

3) Membrane durability

Polymeric membranes are usually fragile, and if not used properly, can be damaged. Researchers have been conducting studies to improve the physical properties of the membrane by incorporating additives to the membrane casting dope, casting the membrane on a support material, etc. Rother et al. [38] reported development of the self-sealing and puncture resistant breathable membrane for water evaporation applications. In one of our previous studies, a supported membrane with much mechanical strength was developed for application at the temperature typical for membrane-assisted desiccant cooling [68], which was further improved by employing polymers of different molecular weights [69], and by adding nanoparticle to create a favorable structure [70].

4) Membrane configurations

There are typically two forms of membrane configurations: flat-sheet membranes and hollow fiber membranes. Flat-sheet membranes are sheets which are usually have a thickness in an order of 100 μm [60]. Both flat-sheet and hollow fibre membranes have found application in membrane-assisted desiccant cooling. For instant, Woods et al. [71] reported a membrane absorption heat pump module (shown in Figure 3-9), which contains two rows of hollow fibers

with stagnant air in between to reduce conductive heat transfer. This system is designed to work at atmospheric pressure. One of the benefits of this membrane heat pump is that the air gap can prevent heat transfer from the hot desiccant solution side to the cooled water side, and thus potentially reduce cost, and requires less complex equipment. On another development, the VDC shown in Figure 3-8 employs plat-sheet membranes on the water bag.

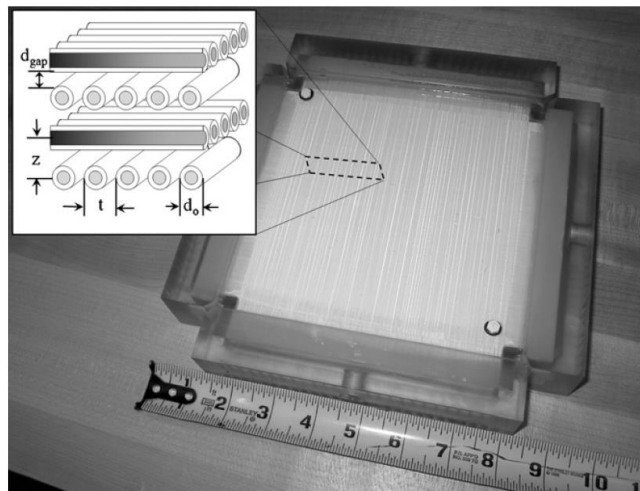


Figure 3-9 Membrane heat pump prototype manufactured by Applied Membrane Technology, Inc. (AMT) [72]

3.5 Thermodynamic analysis - psychrometric chart

The psychrometric chart is a graphical representation that describes the relationships between the air temperature and relative humidity at constant pressure. Specifically, psychrometric processes include physical and thermodynamic properties, including dry bulb temperature (DBT), wet bulb temperature (WBT), relative humidity, enthalpy, moisture content and air density (usually shown as humid volume with unit of m^3/kg dry air on chart). The wet-bulb temperature (WBT) is defined as the temperature a volume of air would have if cooled

adiabatically to saturation by evaporation of water into it, all latent heat being supplied by the volume of air. In contrast, the dry-bulb temperature (DBT) is the temperature of air measured by a thermometer freely exposed to the air but shielded from radiation and moisture. DBT is the temperature that is usually thought of as air temperature.

As shown in Figure 3-10, the DBT is represented as vertical line in the chart, air temperature increases from left to right; WBT is indicated at diagonals, and similarly like DBT, diagonal lines also represent enthalpy at saturation lines with unit of kJ/kg dry air, both of them increase from left to right; moisture content with unit of kg/kg dry air is represented as horizontal lines on the chart; another important property indicated on psychrometric chart is relative humidity lines. Lines are curves, 100% curve on the left side, shown as the left bound line on Figure 3-10. These curves usually shown in intervals of 10, and decrease moving downward (not presented in Figure 3-10 for ease graph reading), till the 0% line completely overlap with the bottom bound (DBT bound) of the figure. The ASHRAE-style psychrometric chart was pioneered by Willis Carrier in 1904, and it is often used as a graphical equation of state [73] in thermodynamic analysis for cooling process.

The principles of previously described evaporative cooling processes can be expressed in psychrometric chart. The direct evaporative cooling is a constant enthalpy process, also known as adiabatic process, where water evaporation takes place within the volume of air that is the object of cooling. The process of direct evaporative cooling is presented by the psychrometric chart on the left side of Figure 3-10. The black arrow points to the cooling process direction, which is on an isenthalpic line. At the end of the cooling process, The WBT is constant (shown as WB_1 in

Figure 3-10), while the DBT drops from DB_1 to DB_2 . The direct cooling process can be expressed by the following energy balance equation:

$$(m_{WBT} - m_0) * H_{evap} = (T_0 - T_{WBT}) * C_{p,air} \quad (3.3)$$

where m_{WBT} is the moisture content of the air at saturation (WBT) and m_0 the initial moisture content of air (unit $kg_{H_2O}/kg_{dry\ air}$); H_{evap} is the latent heat of water evaporation at particular temperature and pressure, T_0 is the initial air temperature (K), T_{WBT} is the saturated air temperature (K), and $C_{p,air}$ is specific heat of air (J/kg·K).

For an indirect evaporative cooling process, water evaporation takes place in an air volume (or stream) that is different from the air volume that is to be cooled. As a result, both the DBT and WBT of the cooled air are reduced while the moisture content of it is not affected. In the process, heat is removed from the cooled air, resulting in enthalpy decrease of it. As shown in the psychrometric chart on the right side of Figure 3-10, the indirect evaporative cooling process follows the horizontal black line with arrow head. As pointed out earlier, the moisture content of the cooled air is maintained constant while the dry bulb temperature decreases from DB_1 to DB_2 . Furthermore, the dew-point temperature (DPT) is highlighted at the intersection point of the extended DBT line and the WBT curve, is much lower than DB_2 . DPT is the temperature at which water vapor starts to condense out the air, at which air becomes completely saturated. A DPT that is much smaller than the DBT shows that the air relative humidity is low, which could be advantageous in certain applications.

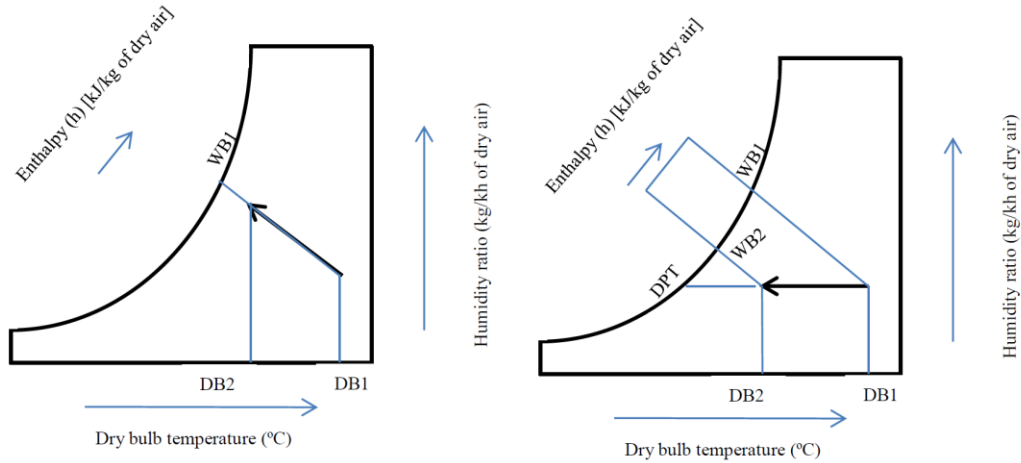


Figure 3-10 Psychrometric diagram for direct evaporative cooling (left) and indirect evaporative cooling (right)

The hybrid membrane air drying/indirect evaporative cooling can be expressed on the psychrometric chart shown in Figure 3-11(left). In the first step, i.e., air drying, the state of the air moves along a vertical line downward (from 1-2), during which the moisture content of air (i.e., the humidity) drops while the dry bulb temperature remains the same. In the second step of indirect evaporation, the state of the air moves along a horizontal line pointing left (from 2 to 3), where the humidity ratio remains the same, at the end of this line when it meets the 100% relative humidity curve (left bound of the chart), it represents the dew point temperature (DPT) for the processed air. The DBT of the air drops in the heat exchanger in this step.

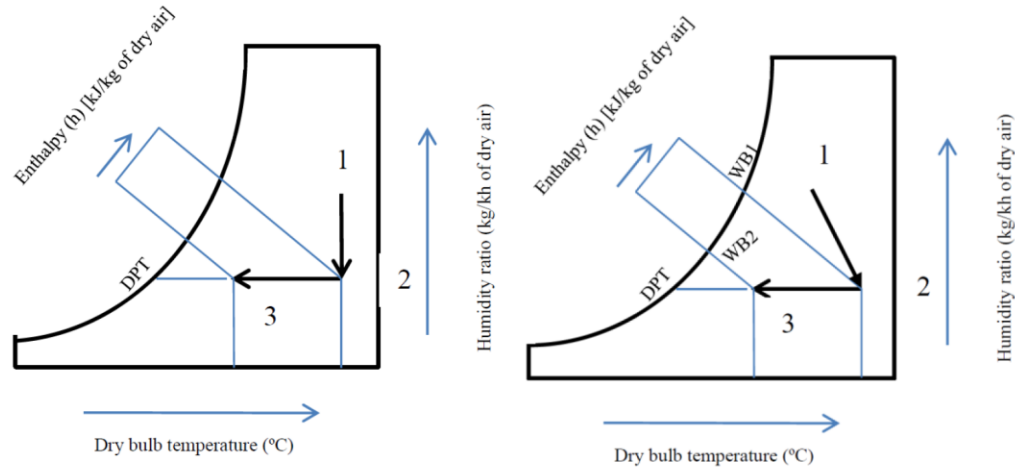


Figure 3-11 Psychrometric chart for membrane air drying direct evaporative cooling process (left) and for membrane assisted desiccant drying direct evaporative cooling process (right)

Multi-layer membrane evaporative cooling process described previously in section 3.3.2 is similar to direct evaporative cooling, it uses membrane as a physical barrier for liquid phase and evaporated water vapor phase. If assuming no heat exchange with ambience, and the system is closed, e.g., the microclimate environment underneath the impermeable protective clothes to be cooled by evaporative cooling garment, the process could be then described as adiabatic process, which follows the isenthalpic diagonal line on the psychrometric chart on the left side of Figure 3-10.

For membrane assisted desiccant cooling process described in section 3.4.3, desiccant releases heat during water absorption process, and air is heated up through membrane material by heat conduction. A psychrometric chart can be used to describe this process shown as Figure 3-11 (right). During the first step where processed air is dried by liquid desiccant, the process follows the 1-2 direction on Figure 3-11 (right), with the moisture content in the air reduce and

the DBT of air increased, and the second step is indirect evaporative cooling process which follows the horizontal line (from 2-3) line.

3.6 Conclusions

A large variety of different evaporative cooling technologies have been developed in the past decades for applications in industrial process cooling, HVAC, microclimate cooling, and other areas. They are characterized as processes harness the latent heat of water evaporation for the creation of a cooling medium, whether it is air or water. A novel approach is proposed to classify these different evaporative cooling technologies. While ambient air has been used for different evaporative cooling processes such as cooling tower, enhanced evaporative cooling by means of air dehumidification using membranes, desiccants, or the combination of membranes and desiccants could greatly increase the cooling efficiency and minimize the side effects in association with the high humidity and in some scenario the cross-contaminations inherited from ambient air evaporative cooling.

3.7 Reference

- [1] ASHRAE. ANSI/ASHRAE stand 62.1-2007, ventilation for acceptable indoor air quality. Atlanta: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. 2007.
- [2] ASHRAE. ANSI/ASHRAE standard 55-2004, thermal environmental conditions for human occupancy. Atlanta: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. 2004.
- [3] Hughes BR, Chaudhry HN, Ghani SA. A review of sustainable cooling technologies in buildings. *Renewable and Sustainable Energy Reviews* 2011;15:3112-3120.
- [4] Ge G, Abdel-Salam MRH, Besant RW, Simonson CJ. Research and applications of liquid-to-air membrane energy exchangers in building HVAC systems at University of Saskatchewan: A review. *Renewable and Sustainable Energy Reviews* 2013;26:464-479.
- [5] Zhao B, Peng N, Liang C, Yong WF, Chung T-. Hollow fiber membrane dehumidification device for air conditioning system. *Membr* 2015;5:722-738.
- [6] El-Dessouky HT, Ettouney HM, Bouhamra W. A Novel Air Conditioning System: Membrane Air Drying and Evaporative Cooling. *Chem Eng Res Design* 2000;78:999-1009.
- [7] Dai YJ, Wang RZ, Zhang HF, Yu JD. Use of liquid desiccant cooling to improve the performance of vapor compression air conditioning. *Appl Therm Eng* 2001;21:1185-1202.
- [8] Sultan M, El-Sharkawy II, Miyazaki T, Saha BB, Koyama S. An overview of solid desiccant dehumidification and air conditioning systems. *Renewable and Sustainable Energy Reviews* 2015;46:16-29.
- [9] World business council for sustainable development. Energy efficiency in buildings.
- [10] Izenzon M, Chen W, Bue G. Evaporative cooling and dehumidification garment for portable life support systems. 43rd International Conference on Environmental Systems 2013.
- [11] Kim J-, Coca A, Williams WJ, Roberge RJ. Subjective perceptions and ergonomics evaluation of a liquid cooled garment worn under protective ensemble during an intermittent treadmill exercise. *Ergonomics* 2011;54:626-635.
- [12] Nyberg KL, Diller KR, Wissler EH. Model of Human/Liquid Cooling Garment Interaction for Space Suit Automatic Thermal Control. *J Biomech Eng* 2000;123:114-120.

[13] Erkan G. Enhancing The Thermal Properties of Textiles with Phase Change Materials. Research Journal of Textile and Apparel 2004;8:57-65.

[14] Hasenöhl T. An Introduction to Phase Change Materials as Heat Storage Mediums. Dept. of Energy Sciences, Faculty of Engineering, Lund University: Lund, Sweden. 2009:1-5.

[15] Grzyll LR, Balderson WC. Development of a man-portable microclimate adsorption cooling device. Proceedings of the Intersociety Energy Conversion Engineering Conference 1997;3-4:1646-1651.

[16] Yang Y, Stapleton J, Diagne BT, Kenny GP, Lan CQ. Man-portable personal cooling garment based on vacuum desiccant cooling. Appl Therm Eng 2012;47:18-24.

[17] GJ Bom, R Foster, E Dijkstra, M Tummers. Evaporative Air-Conditioning Applications for Environmentally Friendly Cooling The World Bank: Washington, DC; 1999.

[18] Xuan YM, Xiao F, Niu XF, Huang X, Wang SW. Research and application of evaporative cooling in China: A review (I) – Research. Renewable and Sustainable Energy Reviews 2012;16:3535-3546.

[19] SJ You, WJ Zhang. Study on the metal fill-type direct evaporative air cooler. Journal of Refrigeration [in Chinese] 1994:28-31.

[20] Y Yang, X Huang, SQ Yan. Experimental research and analysis on the performance of aluminum foil packing in packed-type spray chamber. Construction Heating and Refrigeration [in Chinese] 2007:28-30.

[21] QM Zhang, PL Chen. Heat and mass transfer performance of a domestic product of sprayed corrugated media. Journal of Tongji University [in Chinese] 1995;23:648-653.

[22] Malli A, Seyf HR, Layeghi M, Sharifian S, Behraves H. Investigating the performance of cellulosic evaporative cooling pads. Energy Conversion and Management 2011;52:2598-2603.

[23] Z Wei, S Geng. Experimental research on direct evaporative cooling of organic padding. Contamination control and air-conditioning technology [in Chinese] 2009:22-26.

[24] Y Jiang, XS Zhang, YG Yin. Experimental research on direct evaporative cooling using inorganic padding. 4th seminar on new technologies of refrigeration and air conditioning [in Chinese] 2006.

[25] SS Feng, QF Liu. Research of heat and mass transfer process on foam ceramic filled surface. Contamination control and air-conditioning technology [in Chinese] 2007:4-11.

- [26] YM Xuan, X Huang, JM Wu. Performance evaluation of pads used in direct evaporative cooling air conditioning. Contamination control and air-conditioning technology [in Chinese] 2001;6-8.
- [27] JR Watt, WK Brown. Evaporative Air Conditioning Handbook. 3rd Ed. The Fairmount Press: USA; 1997.
- [28] Rey Martínez FJ, Velasco Gómez E, Herrero Martín R, Martínez Gutiérrez J, Varela Díez F. Comparative study of two different evaporative systems: an indirect evaporative cooler and a semi-indirect ceramic evaporative cooler. Energy Build 2004;36:696-708.
- [29] Duan Z, Zhan C, Zhang X, Mustafa M, Zhao X, Alimohammadisagvand B, et al. Indirect evaporative cooling: Past, present and future potentials. Renewable and Sustainable Energy Reviews 2012;16:6823-6850.
- [30] Hasan A. Indirect evaporative cooling of air to a sub-wet bulb temperature. Appl Therm Eng 2010;30:2460-2468.
- [31] D Rogdakis Emmanuel, Nik Tertipis Dimitrios. Maisotsenko cycle: technology overview and energy-saving potential in cooling systems. Energy and emission control technologies 2015;3:15-22.
- [32] Zhan C, Duan Z, Zhao X, Smith S, Jin H, Riffat S. Comparative study of the performance of the M-cycle counter-flow and cross-flow heat exchangers for indirect evaporative cooling – Paving the path toward sustainable cooling of buildings. Energy 2011;36:6790-6805.
- [33] Heidarinejad G, Moshari S. Novel modeling of an indirect evaporative cooling system with cross-flow configuration. Energy Build 2015;92:351-362.
- [34] Cui X, Chua KJ, Yang WM. Use of Indirect Evaporative Cooling as Pre-cooling Unit in Humid Tropical Climate: An Energy Saving Technique. Energy Procedia 2014;61:176-179.
- [35] Rosa Ioannou Christodoulaki, Emmanuil D. Rogdakis, I.P. Koronaki. Hybrid liquid desiccant/ vapor compression air-conditioning systems: a critical review 2008;ASME 2008 9th Biennial Conference on Engineering Systems Design and Analysis.
- [36] Kashani MMH, Dobrego KV. Effect of inlet window deflectors on the performance of a natural-draft cooling tower subjected to crosswinds. Heat Transfer Eng 2016;37:1293-1301.
- [37] Rothmaier M, Weder M, Meyer-Heim A, Kesselring J. Design and performance of personal cooling garments based on three-layer laminates. Med Biol Eng Comput 2008;46:825-832.

[38] Rother M, Barmettler J, Reichmuth A, Araujo JV, Rytka C, Glaied O, et al. Self-Sealing and Puncture Resistant Breathable Membranes for Water-Evaporation Applications. *Adv Mater* 2015;27:6620-6624.

[39] Halliday SP, Beggs CB, Sleigh PA. The use of solar desiccant cooling in the UK: a feasibility study. *Appl Therm Eng* 2002;22:1327-1338.

[40] Kessling W, Laevemann E, Peltzer M. Energy storage in open cycle liquid desiccant cooling systems. *Int J Refrig* 1998;21:150-156.

[41] Rafique MM, Gandhidasan P, Bahaidarah HMS. Liquid desiccant materials and dehumidifiers - A review. *Renewable Sustainable Energy Rev* 2016;56:179-195.

[42] Mohammad AT, Mat SB, Sopian K, Al-Abidi AA. Review: Survey of the control strategy of liquid desiccant systems. *Renewable Sustainable Energy Rev* 2016;58:250-258.

[43] Kessling W, Laevemann E, Peltzer M. Energy storage in open cycle liquid desiccant cooling systems. *Int J Refrig* 1998;21:150-156.

[44] Mujahid Rafique M, Gandhidasan P, Rehman S, Al-Hadhrami LM. A review on desiccant based evaporative cooling systems. *Renewable and Sustainable Energy Reviews* 2015;45:145-159.

[45] Woods J, Kozubal E. Combining liquid desiccant dehumidification with a dew-point evaporative cooler: A design analysis. *HVAC R Res* 2013;19:663-675.

[46] Woods J, Kozubal E. Combining liquid desiccant dehumidification with a dew-point evaporative cooler: A design analysis. *HVAC R Res* 2013;19:663-675.

[47] Srivastava NC, Eames IW. A review of adsorbents and adsorbates in solid-vapour adsorption heat pump systems. *Appl Therm Eng* 1998;18:707-714.

[48] Hamed AM, Khalil A, Kabeel AE, Bassuoni MM, Elzahaby AM. Performance analysis of dehumidification rotating wheel using liquid desiccant. *Renewable Energy* 2005;30:1689-1712.

[49] Gandhidasan P, Mohandes MA. Predictions of vapor pressures of aqueous desiccants for cooling applications by using artificial neural networks. *Appl Therm Eng* 2008;28:126-135.

[50] Rambhad KS, Walke PV, Tidke DJ. Solid desiccant dehumidification and regeneration methods - A review. *Renewable Sustainable Energy Rev* 2016;59:73-83.

[51] Zouaoui A, Zili-Ghedira L, Ben Nasrallah S. Open solid desiccant cooling air systems: A review and comparative study. *Renewable Sustainable Energy Rev* 2016;54:889-917.

[52] Al-Alili A, Hwang Y, Radermacher R. Performance of a desiccant wheel cycle utilizing new zeolite material: Experimental investigation. *Energy* 2015;81:137-145.

[53] Enteria N, Yoshino H, Satake A, Mochida A, Takaki R, Yoshie R, et al. Development and construction of the novel solar thermal desiccant cooling system incorporating hot water production. *Appl Energy* 2010;87:478-486.

[54] Panaras G, Mathioulakis E, Belessiotis V, Kyriakis N. Theoretical and experimental investigation of the performance of a desiccant air-conditioning system. *Renewable Energy* 2010;35:1368-1375.

[55] Tu R, Liu X, Jiang Y. Irreversible processes and performance improvement of desiccant wheel dehumidification and cooling systems using exergy. *Appl Energy* 2015;145:331-344.

[56] Deng J, Wang RZ, Han GY. A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Progress in Energy and Combustion Science* 2011;37:172-203.

[57] Majumdar P. Heat and mass transfer in composite desiccant pore structures for dehumidification. *Solar Energy* 1998;62:1-10.

[58] Hu LM, Ge TS, Jiang Y, Wang RZ. Performance study on composite desiccant material coated fin-tube heat exchangers. *Int J Heat Mass Transfer* 2015;90:109-120.

[59] Zheng X, Ge TS, Hu LM, Wang RZ. Development and Characterization of Mesoporous Silicate/LiCl Composite Desiccants for Solid Desiccant Cooling Systems. *Ind Eng Chem Res* 2015;54:2966-2973.

[60] Woods J. Membrane processes for heating, ventilation, and air conditioning. *Renewable and Sustainable Energy Reviews* 2014;33:290-304.

[61] Xing R, Rao Y, TeGrotenhuis W, Canfield N, Zheng F, Winiarski DW, et al. Advanced thin zeolite/metal flat sheet membrane for energy efficient air dehumidification and conditioning. *Chem Eng Sci* 2013;104:596-609.

[62] Bolto B, Hoang M, Xie Z. A review of water recovery by vapour permeation through membranes. *Water Res* 2012;46:259-266.

[63] Bui DT, Nida A, Ng K, Chua K. Water vapor permeation and dehumidification performance of poly(vinyl alcohol)/lithium chloride composite membranes. *J Membr Sci* 2016;498:254-262.

[64] Asfand F, Bourouis M. A review of membrane contactors applied in absorption refrigeration systems. *Renewable and Sustainable Energy Reviews* 2015;45:173-191.

[65] Abdel-Salam AH, Ge G, Simonson CJ. Performance analysis of a membrane liquid desiccant air-conditioning system. *Energy Build* 2013;62:559-569.

[66] Yang Y, Stapleton J, Diagne BT, Kenny GP, Lan CQ. Man-portable personal cooling garment based on vacuum desiccant cooling. *Appl Therm Eng* 2012;47:18-24.

[67] Gabino F, Belleville M-, Preziosi-Belloy L, Dornier M, Sanchez J. Evaluation of the cleaning of a new hydrophobic membrane for osmotic evaporation. *Separation and Purification Technology* 2007;55:191-197.

[68] Yang Y, Rana D, Matsuura T, Zheng S, Lan CQ. Criteria for the selection of a support material to fabricate coated membranes for a life support device. *RSC Adv* 2014;4:38711-38717.

[69] Chen Z, Rana D, Matsuura T, Yang Y, Lan CQ. Study on the structure and vacuum membrane distillation performance of PVDF composite membranes: I. Influence of blending. *Separation and Purification Technology* 2014;133:303-312.

[70] Baghbanzadeh M, Rana D, Matsuura T, Lan CQ. Effects of hydrophilic CuO nanoparticles on properties and performance of PVDF VMD membranes. *Desalination* 2015;369:75-84.

[71] Woods J, Pellegrino J, Kozubal E, Burch J. Design and experimental characterization of a membrane-based absorption heat pump. *J Membr Sci* 2011;378:85-94.

[72] Woods J, Pellegrino J, Kozubal E, Burch J. Design and experimental characterization of a membrane-based absorption heat pump. *J Membr Sci* 2011;378:85-94.

[73] Smith JM, Van Ness HC, Abbott MM. *Introduction to Chemical Engineering Thermodynamics* McGraw-Hill; 2005.

Chapter 4: Criteria for the selection of support material to fabricate coated membranes for life support device

Yifan Yang, Dipak Rana, Takeshi Matsuura, Songyuan Zheng, Christopher Q. Lan

Department of Chemical and Biological Engineering

University of Ottawa

161 Louis Pasteur Private, Ottawa, ON, K1N 6N5, Canada

4.1 Abstract

Life support device, specifically vacuum desiccant cooling device requires hydrophobic micro-porous membranes with high liquid entry pressure of water (LEP_w), high mechanical strength and large vacuum distillation flux in the temperature range of 10-30 °C. To achieve this goal, membranes were prepared by casting polyvinylidene fluoride (PVDF) on various non-woven fabric (NWF) materials using the immersion precipitation technique at the ambient temperature. Four porous polyester NWF materials were tested as the membrane support materials which were characterized by the SEM analysis and by measuring the contact angle and porosity. The PVDF coated membranes were also characterized by the SEM image analysis and LEP_w . Finally, the coated membranes were tested for vacuum membrane distillation (VMD) performance at a relatively low feed temperature of 30 °C. Results of this study revealed a significant impact of NWF materials on VMD performance. A proper NWF material lead to a much enhanced VMD flux of the PVDF coated membrane that was approximately 15 times of the unsupported PVDF membrane. These results suggest that the spongy-like layer may have strong impacts on the flux of membrane distillation. The studies provide understanding VMD phenomenon and provide new insights for development of coated membranes used for the life support device.

Key words: Vacuum membrane distillation; support material; PVDF membrane;

4.2 Introduction

Membrane technology is of great interest in diverse applications such as sea water desalination, power generation and storage, greenhouse gases removal, semiconductor technology and medicine [1]. Membrane distillation is one of the most important applications for hydrophobic membranes, such as seawater desalination [2, 3], wastewater treatment [4-6], extracting volatile organic compounds from dilute aqueous solutions [7], degassing, etc. Hydrophobic polymeric membrane are also used in various setups like evaporative cooling [8, 9] and vacuum desiccant cooling (VDC) [10]. One of the popular options for producing this type of membrane is coating the hydrophobic polymeric layer over a porous support such as non-woven fabric (NWF) for strengthened mechanical property and resilience [11]. Permeation flux, mechanical strength, stability under operating condition and fouling resistance are some of the important properties affecting performance, as well as applicability and life-span of membranes [12-15].

Many researchers have shown a great interest on optimization of the performance of the membrane with a coated layer recently and most of these works are focused on optimizing the coated layer. For instance, researchers have attempted to increase the flux by adding different non-solvent additives in the coagulation bath, adjusting the temperatures of the casting dope and coagulation bath [16], adding surface modifying macromolecules into dope solution [17], etc. However, it has been recognized that NWF not only improves mechanical strength, but other properties of NWF such as material, diameter and length of the fiber, pore size distribution, air transmission coefficient and surface roughness also play important roles in membrane performance [18]. Only a few studies have been addressed from the existing literature about the

effects of backing material on the performance of the coated membrane. A notable exception is the work done by Lohokare et al. [19] on the effect of NWF on ultrafiltration membrane performance by comparing the woven and nonwoven supports. The effects of pre-treatment of the backing material on the membrane performance were also studied by Zhang et al. [18] whereby two approaches to prepare a membrane of high rejection were proposed.

We recently reported that the hydrophobic membrane with high liquid entry pressure of water (LEP_w) (larger than 3 bar) is desirable for the application in personal cooling garment [10]. Izenson et al. [20] also reported the use of membranes of similar feature as part of their thermal and humidity control system for space suits. In their approach, they have used an expanded polytetrafluoroethylene (PTFE) laminate which can stand vacuum pressure while having sufficiently high vapor flux. Recognizing that PTFE is extremely inert as well as thermally stable, because of the nonpolar and nonreactive feature resulted from even distribution of fluorine atoms, it is however, on the other hand, difficult for anything to bond to it, and that's why PTFE (Teflon[®]) is well-known as a non-sticking and easy-to-clean product. This non-reactivity makes PTFE membrane less possible of fusing with other material, and therefore less processability for setups which require membrane to be fabricated with other material. Polyvinylidene fluoride (PVDF), on the other hand, has similar feature with PTFE (hydrophobic, thermal stable, good chemical compatibility, etc.), and also have better adaptability for fabrication process.

For this reason, PVDF is an excellent membrane material choice for life support device. Design criteria is based on human trial tests of personal cooling garment application from our previous study, the desirable water vapor flux requirement is around 0.56 L/m²h, and operating feed temperature is as low as around 30 °C, membrane is required to have high LEP (larger than

3 bar), improved water vapor flux, and improved robustness. Moreover, PVDF membrane, as a popular membrane material, has been widely studied in different applications for improved performance. Interested readers may find literatures on PVDF membranes [21]. Operating at low feed temperature (10-30 °C) for evaporative cooling purpose in life support device is relatively a new field of application, requiring for further deeper study for the new challenges. The presenting study is focused on these specific features requirement for PVDF development.

Recognizing the importance of support material that affects the performance of the coated membrane, and less studies have been reported from literature, the specific objective of this research is to investigate and understand the effect of backing materials on the morphology and vacuum membrane distillation (VMD) performance of coated PVDF membranes for life support device. However, more research is required for development of high performance membranes, which are a key component for VDC technology, improving high performance membranes with features including robustness and cost-effective purpose which will further enhance life support device development.

4.3 Experimental

4.3.1 Materials

Polyvinylidene fluoride (PVDF) (Kynar 740, Arkema Inc., Philadelphia, PA) was used as the base polymer. Dimethylacetamide (DMAc) supplied by Sigma-Aldrich of 99% purity was used as the solvent. Four non-woven fabric (NWF) polyester materials were used as the support materials for the membrane fabrication. Three of them, Hollytex[®] 3396, 3329, 3229 (Kavon

Filter Products Co., Farmingdale, NJ), were kindly provided by the National Research Council, Ottawa, ON. The forth NWF support material was supplied by the Teijin Ltd. (Osaka, Japan), and quoted by its product number E055100-85. Those support materials are coded as 3396-support (A), E055100-85-support (B), 3329-support (C), and 3229-support (D) hereafter.

4.3.2 Polymer characterization by average molecular weights measurement

The weight average molecular weight (M_w) and polydispersity index ($PDI = M_w/M_n$) of PVDF material was determined by the Younglin ACME 9000 gel permeation chromatography (GPC) in dimethyl formamide (DMF) at 40 °C with flow rate 0.5 ml/min on two polystyrene gel columns [PL gel 5 μ m 10E 4 Å columns (300x7.5 mm)] connected in series to a Younglin ACME 9000 Gradient Pump and a Younglin ACME 9000 refractive index (RI) detector. The columns were calibrated against seven poly (methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10). The M_w and PDI of Kynar[®] 740 is 410 kD and 2.34, respectively.

4.3.3 Membrane preparation

Flat sheet PVDF membrane was prepared by the immersion precipitation method [22] using the casting dope with a composition of PVDF 15 wt. % and water 1.25 wt. % in DMAc. To prepare the casting dope, PVDF, DMAc and water were mixed in a container, which was rotated at 180 rpm at 50 °C for 24 h to ensure complete dissolution of the polymer. To make an unsupported membrane, the dope was cast at room temperature over a glass plate to a thickness

of 0.25 mm, using a casting blade at a casting speed of around 6-7 cm/s, followed by immersing the cast film together with the glass plate into the coagulation bath (distilled water, ambient temperature) within 5 s. During gelation, the cast film solidified on the glass plate. The membrane was then taken out of the coagulation bath and dried at room temperature before being subjected to characterization and performance testing. This membrane is coded as PVDF-unsupported membrane.

When the membranes supported by the support materials were fabricated, a selected support material was used instead of the glass plate. The other fabrication procedure was the same as the unsupported membrane. The membranes so fabricated are coded as PVDF-3396-coated, PVDF- E055100-85-coated membrane, PVDF-3329-coated and PVDF-3229-coated, respectively.

4.3.4 Scanning electron microscopy (SEM) measurement

The top surface of both non-woven polyester support materials and PVDF coated membranes was investigated by SEM (VegaII XMU, Tescan, PA). Au/Pd alloy was used to coat the samples by sputtering. SEM images were also used to obtain the pore size for PVDF coated membranes, followed by the ImageJ analysis proposed by Gribble et al. [23] and Zhao et al. [24]. The ImageJ software (National Institute of Health, USA) was used in this study, assuming every pore is shaped like a circle [25]. Ten individual pores were chosen to calculate the pore size and the average value was recorded to minimize errors.

As well, the surface roughness of the support NWF material was investigated with the aid of the ImageJ software, following the approach discussed by Banerjee et al. [26]. The

micrographs were taken at 100× for backing materials and 15k× for the PVDF coated membranes; it has been proved by Banerjee et al. [26] that different magnifications of the micrographs provide similar results.

4.3.5 Porosity measurement

The porosity of the support NWF materials was measured by the pre-described methods [27]. As the NWF polyester support materials are quite hydrophobic, water did not enter the pores, hence instead of water uptake, dimethylsulfoxide (DMSO) uptake tests were performed to calculate porosity. The swelling effect caused by DMSO to the pore structures were considered to be minor in this case. The support material was immersed in DMSO for 24 h to complete the wetting process. The weight of the support sample was measured before (dry) and after wetting with DMSO. The porosity can be calculated by the following equation:

$$\varepsilon (\%) = \frac{\text{Total pore volume}}{\text{Total sample volume}} = \frac{(m_s - m_d)}{A * L * \rho} \quad (4.1)$$

Where m_s and m_d are the weight of the wet and the dry sample, respectively.

The thickness of the support material was measured by a digital micro-meter before immersion into DMSO. Five measurements were conducted for each type of support material to minimize the experimental error.

4.3.6 Contact angle measurement for calculation of surface energy

The contact angle of the support materials and the PVDF coated membranes was measured by using A VCA Optima Surface Analysis System (AST Products Inc., Billerica, MA). The measurement was done by dropping 0.2 μL of liquid on the sample surface by using a micro-syringe (Hamilton Co., Reno, NV). Contact angles of ten randomly chosen locations were recorded and the average value was calculated to eliminate experimental errors.

Three liquids of different polar/nonpolar properties were used to measure the contact angel for the purpose of calculating the surface energy. The three liquids are deionized water, ethylene glycol (EG) and diiodomethane (DIM).

The surface free energy of the solid γ_s , was calculated, for each support material, by the Van Oss-Chaudhury-Good method proposed by Van Oss et al. [27] According to their method, γ_s is divided into two components, one includes the long-range interactions called the Lifshitz-van der Waals component (γ_s^{LW}), and the other contains the short-range interactions (acid-base) called the acid-base component (γ_s^{AB}). The equation is as followed:

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2(\gamma_s^+ \gamma_s^-)^{\frac{1}{2}} \quad (4.2)$$

It is noted that γ_s^{AB} is further divided into γ_s^+ and γ_s^- , the Lewis acid and Lewis base component.

In order to calculate the surface free energy, the following Young-Dupré equation is used [28].

$$(1 + \cos \theta)\gamma_L = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_s^+\gamma_L^-} + 2\sqrt{\gamma_s^-\gamma_L^+} \quad (4.3)$$

Where θ is the contact angle, γ 's have already been defined except for the subscript L which is for liquid.

The method to obtain the surface energy components γ_S^{LW} , γ_S^+ and γ_S^- of a given membrane is as follows. From the experimental contact angle data for three different liquids (water, EG and DIM) three simultaneous equations are written by using equation (4.3). In the equation numerical values are known for $(\gamma_L, \gamma_L^{LW}, \gamma_L^- \text{ and } \gamma_L^+)$ as summarized in Table 4-1. Then, the three simultaneous equations can be solved in terms of three unknowns: γ_S^{LW} , γ_S^+ and γ_S^- . As for the PVDF coated membranes, only the contact angle of water was measured.

Table 4-1 Van Oss, Chaudhury and Good Surface Tension Parameters of Liquids used in this Study

Liquid properties (mJ/m ²)	Water	Ethylene Glycol	Diiodomethane
γ_L	72.8	48	50.8
γ_L^{LW}	21.8	29	50.8
γ_L^+	25.5	1.92	0
γ_L^-	25.5	47	0

4.3.7 Liquid entry pressure of water (LEP_w) measurement

Membranes for the vacuum desiccant cooling device need to be operated under vacuum with concerns of potentially large local pressure. Therefore, the liquid entry pressure (LEP_w) of

the VDC membrane is a governing parameter for it. The membrane with LEP_w lower than 3 bar is considered as a failure in this study. LEP_w was measured for all the PVDF coated and unsupported membranes using the LEP_w test set-up. The membrane cell was a stainless steel filter holder with a reservoir of 200 ml and an effective membrane area of 13.1 cm^2 .

A dry membrane sample was placed on a sintered metal plate which was at the lower end of the membrane cell, and the liquid reservoir was filled with water. Compressed gas (nitrogen) was supplied to the reservoir from the nitrogen cylinder, and the pressure was increased by using a precision pressure regulator at a speed of 2 psi per 10 min until water started to flow continuously from the testing cell outlet. At this point, the LEP_w value was read from the pressure gauge. For each membrane sample, three measurements were made and the average value was recorded.

4.3.8 Permeation flux measurement by vacuum membrane distillation (VMD) setup

The equipment used for VMD consists of a cylindrical permeation cell with a feed chamber of about 300 mL wrapped with a heating tape for temperature control in a range of 22 to 35 °C. The temperature was measured by inserting a thermocouple to the feed chamber. The membrane was mounted to the bottom of the feed chamber. The vacuum was applied to the permeated side of the membrane via two cold traps. The permeate line was switched from cold trap 1 to cold trap 2 to collect the condensate after the system reached steady state in about 30 min. The feed side and the permeate side pressure were maintained at atmospheric pressure and 0.038 bar, respectively. The permeate flux was calculated by:

$$J = \frac{W}{At} \quad (4.4)$$

Where J , in unit of $\frac{kg}{m^2h}$ is the evaporation flux; W , in unit of kg, is the mass of vapor condensed in the trap 2; A , in unit of m^2 , is the membrane area; t , in unit of h, is the operation time.

4.4 Results and discussion

The SEM top view and the two-dimensional pixel brightness graph of the four NWF materials are shown in Figure 4-1. From the figure it is observed that the fibers of the NWF material 3396 (coded as A in Figure 4-1) are flattened and most densely packed. The fiber diameter of 3396-support is the largest among all, and E055100-85-support (coded as B in Figure 4-1) appears to have the smallest fiber diameter while those of 3329-support (coded as C in Figure 4-1) and 3229-support (coded as D in Figure 4-1) are in between.

The intensities of pixels along a line drawn on the NWF material surface are shown at the right side of Figure 4-1, representing brightness intensity vs. distance. Looking at the figure, 3396-support (A) and E055100-85-support (B) are clearly distinguished from 3329-support (C) and 3229-support (D) by the following two features: (i) The average of the pixel brightness is higher for 3396-support (A) and E055100-85-support (B); The average pixel intensities of A, B, C, and D are 130, 130, 70, and 70, respectively; and (ii) The peaks of 3329-support (C) and 3229-support (D) are broader and reach the bottom (Gray value = 0) more frequently than 3396-support (A) and E055100-85-support (B), meaning that the void spaces of 3329-support (C) and 3229-support (D) are larger and penetrate deeply to the bottom.

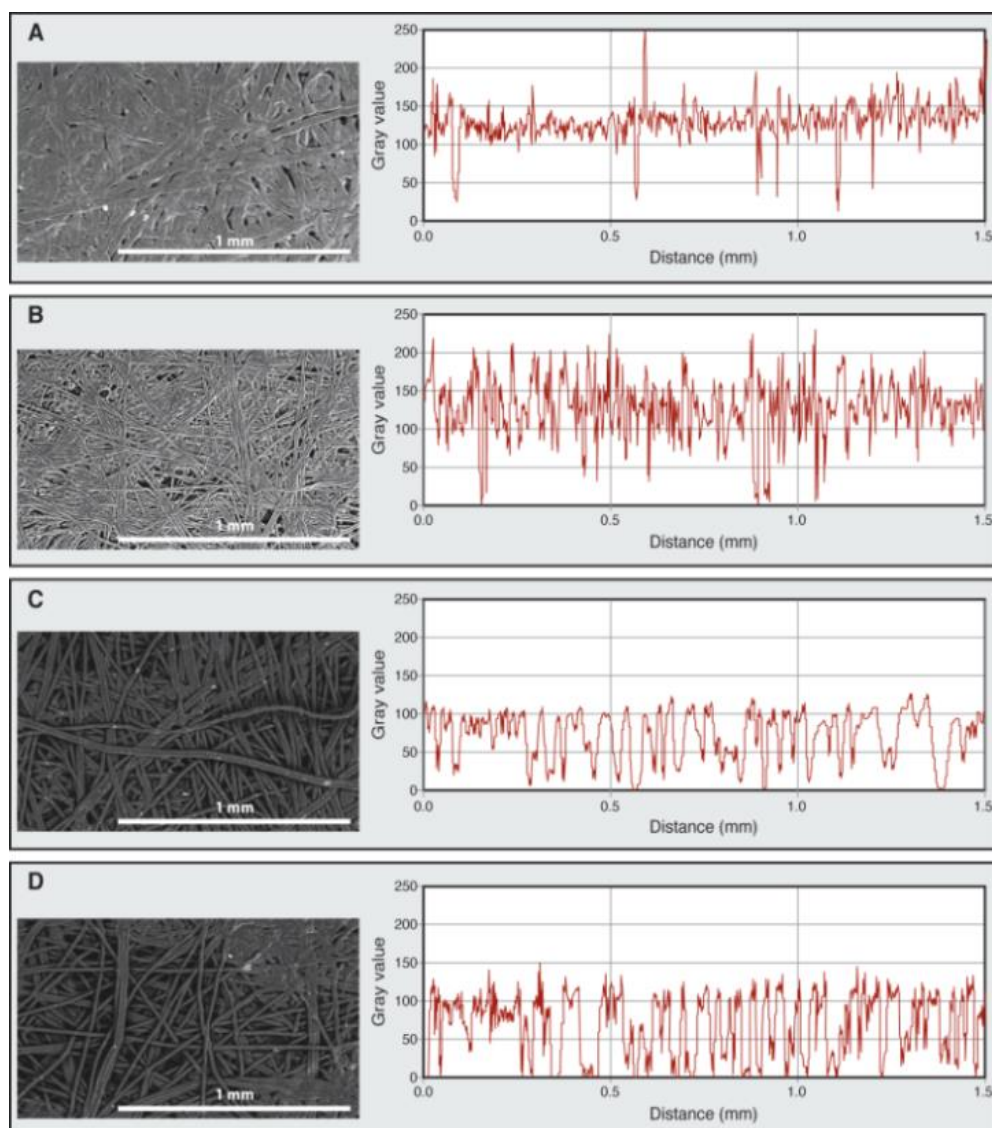


Figure 4-1 Top SEM images for 3396-support (A), E055100-85-support (B), 3329-support (C), 3229-support (D), and the line profiles.

The contact angle data are plotted in Figure 4-2. It seems that 3396-support (A) and E055100-85-support (B) are remarkably different from the other two NWF materials with smaller contact angle for water and larger contact angle for diiodomethane (DIM). Since water is the most polar and DIM is the least polar liquid among the liquids used for the contact angle

measurement, the above results indicate that the surface of 3396-support (A) and E055100-85-support (B) are less polar.

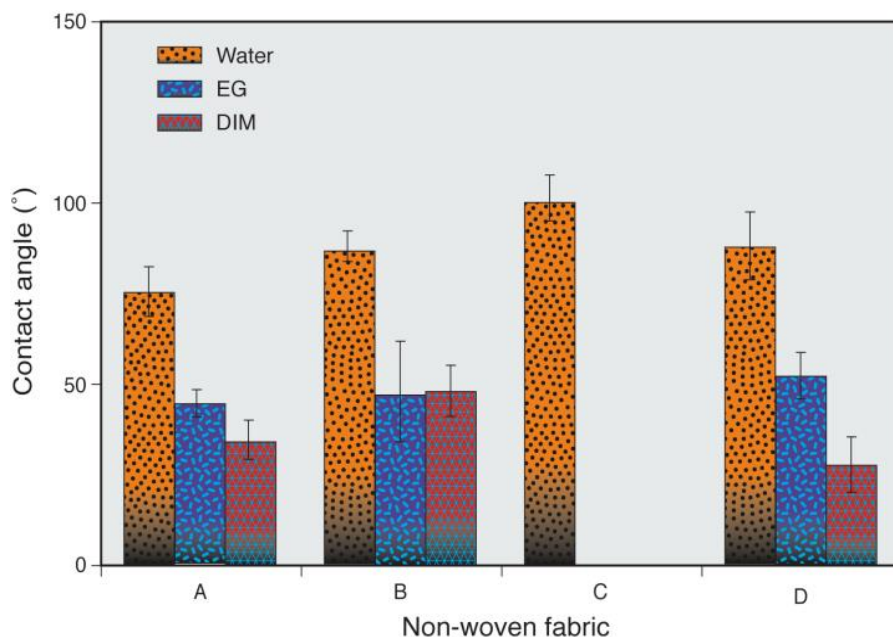


Figure 4-2 Contact angles for water, ethylene glycol (EG), and diiodomethane (DIM) on four non-woven fabric materials. (Contact angles for EG and DIM on non-woven fabric material C are both zero.)

The calculated surface energies are summarized in Table 4-2. The NWF 3396-support (A) and E055100-85-support (B) have the two lowest values among all the NWF materials. Since the contact angle is largely affected by the surface morphology [29], it is currently unknown if the surface energy represents the chemistry or the morphology of the NWF material. It can however be said the low surface energy enabled the wetting of the NWF material surface by DMAc, which is known to be a polar solvent.

Table 4-2 Thickness, porosity, surface energy, and work of adhesion results for four support NWF materials.

NWF material	A	B	C	D
Thickness ($\times 10^{-4}$ m)	1.85	0.87	1.51	1.28
Porosity (%)	11.56 ± 0.80	34.00 ± 6.28	47.15 ± 4.80	18.92 ± 0.85
Surface energy (mJ/m^2)	44.23	37.46	53.53	48.15

The SEM images of the coated PVDF membrane top view are given in Figure 4-3. The surface of the PVDF-3329-coated membranes has developed some micro-cracks as can be observed clearly in Figure 4-3 C. These SEM images can be used to evaluate the pore size using the ImageJ software [23-25]. The results presented in Table 4-3 show that the pore sizes of all the studied membranes were about 0.1 μm .

The water contact angles are shown in Table 4-3 for all PVDF-coated membranes together with that of the unsupported PVDF membrane. The contact angles of PVDF-3396-coated (A-coated) and PVDF-E-055100-85-coated (B-coated) membrane and the unsupported membrane had similar contact angles, which were larger than that of the PVDF-3329-coated (C-coated) and PVDF-3229-coated (D-coated) membrane. These results suggest that the support materials did not have significant impact on the A-coated and B-coated membranes. However, it affected the surface properties of the C-coated and D-coated membranes. This observation coincidence with the observation that some casting solution passed through the entire thickness of the support material in the fabrication of the C-coated and the D-coated membranes whereas in the case of the A-coated and B-coated membranes, casting solution did not pass through the

entire thickness of the support material. It appears that the significant penetration of casting solution in fabrication of C-coated and D-coated membrane resulted in higher roughness of the membrane surface, which led to lower contact angles according to Wenzel's equation [30]. On the other hand, the limited penetration of casting solution in the fabrication of A-coated and B-coated membranes allowed the making of A-coated and B-coated membranes with surface properties very similar to the supported membrane. This is consistent with the observation that extremely small LEP_w (less than 1 bar) was obtained with C-coated and D-coated membrane, which were confirmed by SEM images to have defects such as micro-cracks and pinholes. The significant penetration of casting solution through the C-support and D-support can be attributed to their surface unevenness, which is characterized by wide and deep valleys with thick fibers in the NWF. Thus the rough surface decreased the contact angle accordingly to Wenzel's equation, which predicts the contact angle on a rough surface would be smaller than on a smooth surface for the same material [30]. Nevertheless, it should be cautioned that the error ranges involved in the contact angles were large and the difference between the contact angles of composite membrane cast on different NWF materials may not be significant. It should be noted that although PVDF is a hydrophobic material, the contact angles of PVDF membranes were less than 90° . While this seems to contradict the intuitive thinking that the contact angle of a hydrophobic material should be equal or larger than 90° , however it is consistent with the observation of many other researchers [31-34]. For instance, the contact angle of UF membrane prepared from 19 wt. % PVDF using DMAc solvent by phase inversion method was reported to be 83.64° [33]. Similarly, the contact angle was 78° for a UF membrane prepared from 16 wt. % PVDF using DMF solvent by phase inversion method [34].

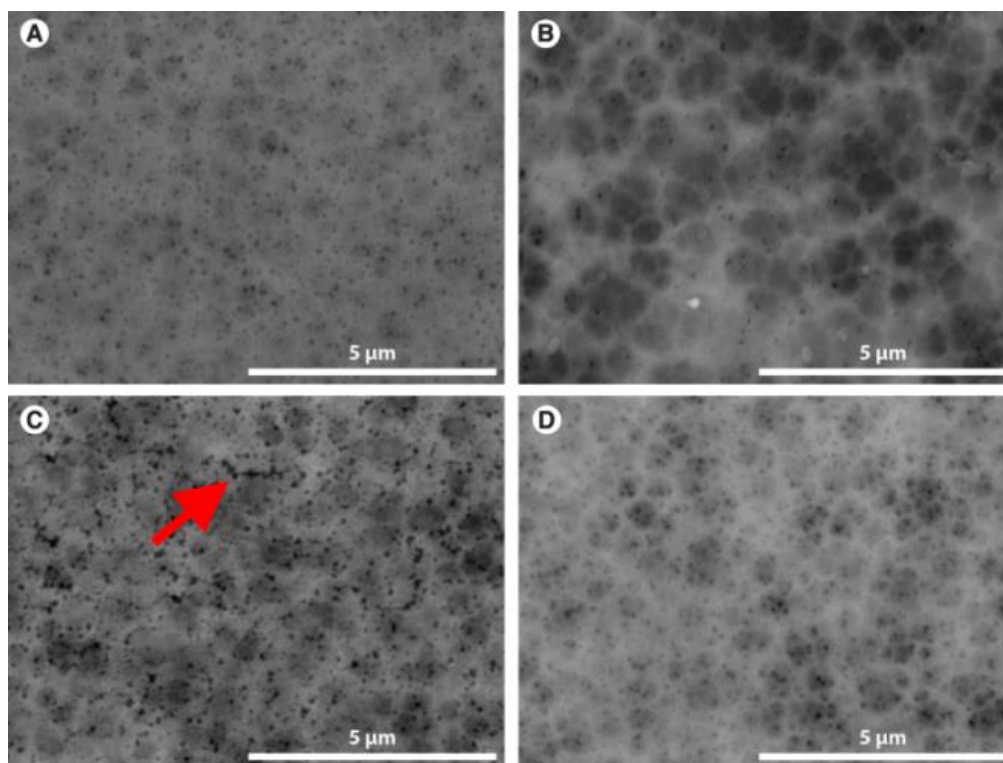


Figure 4-3 Top SEM images for PVDF coated membranes and unsupported membrane. (A: PVDF-3396 coated; B: PVDF-E055100-85 coated; C: PVDF-3329 coated; and D: PVDF-3229 coated membrane.)

The VMD vapor fluxes are shown in Figure 4-4 for A-coated, B-coated and the unsupported membrane. The other two coated PVDF membranes (i.e., C-coated and D-coated) were unable to be used for VMD due to their low LEP_w values (less than 1 bar). The obtained vapor fluxes were $0.263 \text{ L/m}^2\text{h}$ and $1.2325 \text{ L/m}^2\text{h}$ for A-coated and B-coated membrane, respectively, at the feed temperature of 30°C . It is worth noting that the B-coated membrane exhibited a much higher flux (4.7 times higher at the feed temperature of 30°C) than A-coated membrane in the entire temperature range tested, i.e., from $25\text{--}35^\circ\text{C}$. This can be attributed to the smaller thickness and larger porosity of the B-support, as listed in Table 4-2, resulting in less resistance to the vapor transport than A-support.

Table 4-3 Contact angle, LEPw, and VMD flux of the PVDF coated membranes.

Membrane	A-coated	B-coated	C-coated	D-coated	Unsupported
Pore size (μm)	0.092 ± 0.015	0.11 ± 0.019	0.14 ± 0.013	0.09 ± 0.019	N/A
Water contact angle ($^{\circ}\text{C}$)	81.1 ± 4.2	87.7 ± 7.7	78.9 ± 8.7	78 ± 3.6	81.4 ± 13.8
LEP _w	74	70	4.5	9.5	70
Flux at 30 $^{\circ}\text{C}$ (L/m ² h)	0.263 ± 0.028	1.2325 ± 0.107	N/A	N/A	0.08 ± 0.317

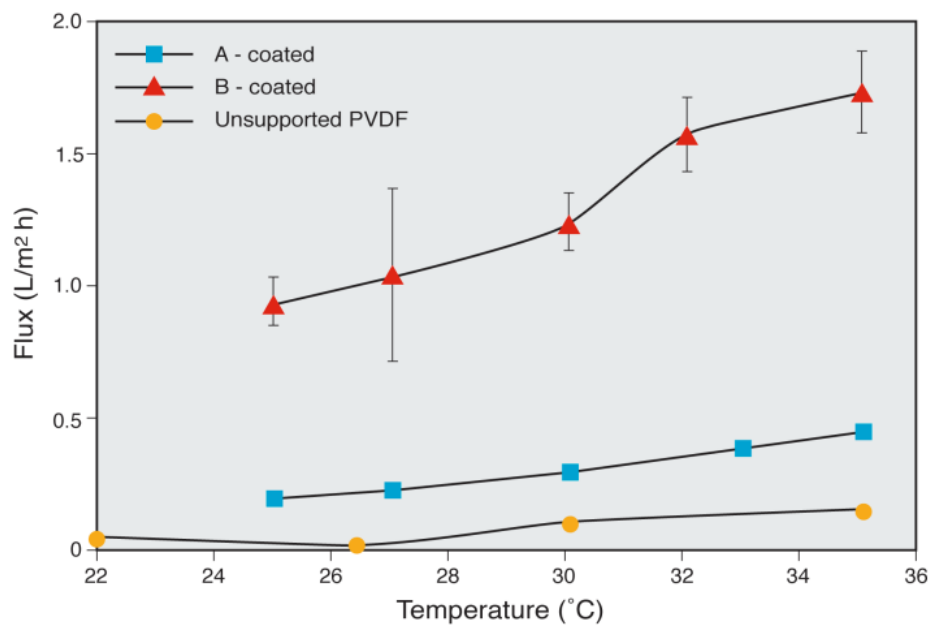


Figure 4-4 Vapor flux of A-coated, B-coated, and unsupported PVDF membrane.

It is worth noting that the unsupported membrane had a much lower VMD flux in the temperature range of 25-35 °C (Figure 4-4) in comparison with both the A-coated and B-coated membranes. For instance, at 30 °C, the unsupported membrane had a flux of 0.08 L/m²h, which was only one third of the flux of the A-coated membrane (0.263 L/m²h), and 6.5% of the B-coated membrane (1.2325 L/m²h). These results strongly indicate that properly selected NWF material could improve the structure of the coated membrane layer and therefore the overall VDM performance. One of such improvements could be that the pores of the supported membrane may not shrink as much as that of the unsupported membrane during the drying process in membrane fabrication due to the anchoring effects of the NWF material, minimizing pore size reduction.

B-coated membrane has significantly improved the fluxes comparing to the A-coated membrane. This could be explained by the NWF physical properties data shown in Table 4-2. B-support has less than half of the thickness comparing to that of A-support, which can enhance the flux by reducing the travelling distance for diffusing molecules. The B-support also has roughly three times the porosity than that of the A-support, and higher porosity means more pore channels open for diffusion, hence higher flux [35].

4.5 Conclusion

Membranes were fabricated by coating a thin-layer of PVDF via the immersion precipitation technique on four NWF materials to be used for VMD. The properties of the coated PVDF membranes depend largely on those of the NWF materials. A poor choice of NWF material selection may result in insufficient LEP_w due most likely to the formation of defective

pores on the coated layer that may lead to the formation of micro-cracks. For the choice of proper NWF materials the following three requirements have to be satisfied: (i) The NWF material surface is smooth; (ii) The NWF material should be thin; (iii) The porosity of the NWF material is large, and (iv) The NWF material has relatively low surface energy. The water vapor flux of the PVDF membrane coated on the E055100-85 (B) NWF material was 1.2325 L/m²h, which was more than four times as high as that coated on 3396 (A) NWF, and was 15 times more than that of unsupported PVDF membrane.

This study helps to develop a guideline for choosing a proper NWF support material for fabricating a hydrophobic PVDF membrane for life support VDC garment, which requires high LEP_w (over 3 bar) with high vapor flux, high mechanical strength and better processability. The flux of B-coated membrane is more than twice as much as the permeation flux (0.56 L/m²h) desired for the life support device, which will significantly benefit the design of life support device by increasing the cooling performance. Processability is also improved significantly by the use of NWF for the backing material. At the same time, in contrast to conventional thinking that the membrane skin-layer is the limiting factor governing the flux of membrane distillation, these results suggest that the sponge-like layer of membrane, which is adjacent to the NWF, might also be a major contributing to mass transfer resistance in the supported membrane. Future studies in this regard are therefore warranted given the scarce information of the effects of sponge-layer structure on the performance of distillation membrane.

Acknowledgements

Financial supports by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Institute of Health Research (CIHR). We would like to thank the Arkema Inc. (Philadelphia, PA) for the gift of polyvinylidene fluoride (Kynar[®]) polymer.

4.6 Reference

- [1] a) M. Tanaka and E. Sackmann, *Nature* 2005, 437, 656 ; b) C. C. Striemer, T. R. Gaborski, J. L. McGrath and P. M. Fauchet, *Nature* 2007, 445, 749; c) H. B. Park, B. D. Freeman, Z.-B. Zhang, M. Sankir and J. E. McGrath, *Angew. Chem. Int. Ed.* 2008, 47, 6019; d) M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas and A. M. Mayes, *Nature* 2008, 452, 301; e) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.* 2010, 49, 6058; f) M. Elimelech and W. A. Phillip, *Science* 2011, 333, 712; g) B. E. Logan and M. Elimelech, *Nature* 2012, 488, 313; h) M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Science* 2013, 339, 303; i) K. Celebi, J. Buchheim, R. M. Wyss, A. Droudian, P. Gasser, I. Shorubalko, J.-I. Kye, C. Lee and H. G. Park, *Science* 2014, 344, 289.
- [2] G. C. Sarti, C. Gostoli and S. Matulli, *Desalination* 1985, 56, 277.
- [3] M. Khayet, J. I. Mengual and T. Matsuura, *J. Membr. Sci.* 2005, 252, 101.
- [4] S. Rosenberger, U. Krüger, R. Witzig, W. Manz, U. Szewzyk and M. Kraume, *Water Res.* 2002, 36, 413.
- [5] P. Le-Clech, V. Chen and T. A. G. Fane, *J. Membr. Sci.* 2006, 284, 17.
- [6] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen and R. Leysen, *Environ. Prog.* 2003, 22, 46.
- [7] S. Bandini, A. Saavedra and G. C. Sarti, *AIChE J.* 1997, 43, 398.
- [8] H. T. El-Dessouky, H. M. Ettouney and W. Bouhamra, *Chem. Eng. Res. Des.* 2000, 78, 999.
- [9] D. W. Johnson, C. Yavuzturk and J. Pruis, *J. Membr. Sci.* 2003, 227, 159.
- [10] Y. Yang, J. Stapleton, B. T. Diagne, G. P. Kenny and C. Q. Lan, *Appl. Therm. Eng.* 2012, 47, 18.
- [11] M. Khayet and T. Matsuura, *Membrane Distillation: Principles and Applications*, Elsevier, Amsterdam, 2011, Ch. 6.

- [12] A. Alpatova, E. Kim, X. Sun, G. Hwang, Y. Liu and M. Gamal El-Din, *J. Membr. Sci.* 2013, 444, 449.
- [13] C. Feng, K. C. Khulbe, T. Matsuura, R. Gopal, S. Kaur, S. Ramakrishna, and M. Khayet, *J. Membr. Sci.* 2008, 311, 1.
- [14] M. Nasir, H. Matsumoto, T. Danno, M. Minagawa, T. Irisawa, M. Shioya and A. Tanioka, *J. Polym. Sci. Polym. Phys. Ed.* 2006, 44, 779.
- [15] M. Liu, J. Sun, Y. Sun, C. Bock and Q. Chen, *J. Micromech. Microeng.* 2009, 19, 035028.
- [16] Y. Wang, B. Shi and X. Li, *Polym. Eng. Sci.* 2013, 53, 1614.
- [17] a) H. Mahmud, J. Minnery, Y. Fang, V. A. Pham, R. M. Narbaitz, J. P. Santerre and T. Matsuura, *J. Appl. Polym. Sci.* 2001, 79, 183; b) D. Rana and T. Matsuura, *Chem. Rev.* 2010, 110, 2448; c) D. Rana, Y. Kim, T. Matsuura and H. A. Arafat, *J. Membr. Sci.* 2011, 367, 110; d) Y. Kim, D. Rana, T. Matsuura and W.-J. Chung, *Chem. Commun.* 2012, 48, 693; e) J. A. Prince, D. Rana, G. Singh, T. Matsuura, T. Jun Kai and T. S. Shanmugasundaram, *Chem. Eng. J.* 2014, 242, 387; f) D. Rana, R. M. Narbaitz, A.-M. Garand-Sheridan, A. Westgate, T. Matsuura, S. Tabe and S. Y. Jasim, *J. Mater. Chem. A* 2014, 2, 10059.
- [18] J. Zhang, Z. Wang and W. Li, *Desalin. Water Treat.* 2014, DOI: 10.1080/19443994.2013.831786.
- [19] H. R. Lohokare, Y. S. Bhole and U. K. Kharul, *J. Appl. Polym. Sci.* 2006, 99, 3389.
- [20] M. Izenzon, W. Chen and G. Bue, 43rd International Conference on Environmental Systems, Vail, CO, 14-18 July, 2013.
http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20130011144_2013010796.pdf
- [21] a) K. Y. Wang, T.-S. Chung and M. Gryta, *Chem. Eng. Sci.* 2008, 63, 2587; b) S. Bonyadi, T. S. Chung and R. Rajagopalan, *AIChE J.* 2009, 55, 828; c) H. Fan and Y. Peng, *Chem. Eng. Sci.* 2012, 79, 94; d) D. Hou, G. Dai, J. Wang, H. Fan, L. Zhang and Z. Luan, *Sep. Purif. Technol.* 2012, 101, 1; e) H. Savoji, D. Rana, T. Matsuura, S. Tabe and C. Feng, *Sep. Purif. Technol.* 2013, 108, 196; f) G. Kang and Y. Cao, *J. Membr. Sci.* 2014, 463, 145; g) A. Figoli, S. Simone, A. Criscuoli, S. A. Al-Jlil, F. S. Al-Shabouna, H. S. Al-Romaih, E. Di Nicolò, O. A. Al-Harbi and E. Drioli, *Polymer* 2014, 55, 1296.

- [22] T. Matsuura, *Synthetic Membranes and Membrane Separation Processes*, CRC Press, Boca Raton, FL, 1994.
- [23] C. M. Gribble, G. P. Matthews, G. M. Laudone, A. Turner, C. J. Ridgway, J. Schoelkopf and P. A. C. Gane, *Chem. Eng. Sci.* 2011, 66, 3701.
- [24] S. Zhao, Z. Wang, J. Wang and S. Wang, *Ind. Eng. Chem. Res.* 2014, 53, 11468.
- [25] Image J. Available from: <http://rsb.info.nih.gov/ij/>, accessed: July, 2014.
- [26] S. Banerjee, R. Yang, C. E. Courchene and T. E. Connors, *Ind. Eng. Chem. Res.* 2009, 48, 4322.
- [27] M. Khayet and T. Matsuura, *Ind. Eng. Chem. Res.* 2001, 40, 5710.
- [28] C. J. Van Oss, M. K. Chaudhury and R. J. Good, *Chem. Rev.* 1988, 88, 927.
- [29] H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, *Science* 2003, 299, 1377.
- [30] R. N. Wenzel, *Ind. Eng. Chem.* 1936, 28, 988.
- [31] L. Yan, Y. S. Li and C. B. Xiang, *Polymer* 2005, 46, 7701.
- [32] X. Cao, J. Ma, X. Shi and Z. Ren, *Appl. Surf. Sci.* 2006, 253, 2003.
- [33] F. Liu, N. A. Hashim, Y. Liu, M. R. M. Abed and K. Li, *J. Membr. Sci.* 2011, 375, 1.
- [34] J. Ma, Y. Zhao, Z. Xu, C. Min, B. Zhou, Y. Li, B. Li and J. Niu, *Desalination* 2013, 320, 1.
- [35] X. Shao, D. Dong, G. Parkinson and C.-Z. Li, *J. Mater. Chem. A* 2014, 2, 410.

**Chapter 5: The heat and mass transfer of vacuum
membrane distillation: effect of active layer
morphology with and without support material**

Yifan Yang, Dipak Rana, Takeshi Matsuura, Christopher Q. Lan

Department of Chemical and Biological Engineering

University of Ottawa

161 Louis Pasteur Private, Ottawa, ON, K1N 6N5, Canada

5.1 Abstract

This research aims to the analysis of the heat and mass transfer in vacuum membrane distillation (VMD), specifically for a dead-end feed set-up. The influence of support material for the supported membrane on VMD performance was identified. A mathematical model was proposed to evaluate the membrane/feed interface temperature, membrane tortuosity, membrane mass transfer coefficient, and temperature polarization coefficient (TPC). The model was solved by an excel solver based on experimental results of feed temperature, system pressure and the evaporative fluxes. The SEM images showed that the thickness of unsupported membrane was reduced by 42% after the VMD test. Pore shrinkage and tortuosity increase were also expected during this pore collapsing process. On the other hand, the cross-sectional views of the supported membranes did not show significant changes. These results show that the support material can help prevent the membrane pore channel structure from collapsing during the VMD experiment. TPC is close to unity at low feed temperatures. However, it decreases with an increase of evaporation flux as the feed temperature increases, or a high flux supported membrane is applied.

Keywords: vacuum membrane distillation; heat transfer; mass transfer; supported membrane; temperature polarization coefficient

5.2 Introduction

Vacuum membrane distillation (VMD) is a separation process for various aqueous solution treatments. The downstream of VMD is maintained under vacuum conditions, while vapor is thermally driven through a porous hydrophobic membrane. The applications of VMD can be grouped into three major processes based on the feed types, the single component transport process, the binary component transport process and the multicomponent transport process [1]. Evaporative cooling devices are one of the relatively new applications of VMD membranes [2]. It is a single component transport process, in which only the water vapor evaporates and transports through the membrane, while the liquid water as the single component feed, is kept outside of the membrane pore due to its high membrane hydrophobicity. The cooling effect is achieved due to the latent heat of evaporation required for water to evaporate, while the membrane serves as the physical barrier between liquid water and the desiccant pad. The reported evaporative cooling devices mostly have a dead-end design for the water distribution pads (feed chamber) instead of a continuous system for most of the common VMD aqueous solution separation applications [2-4]. Since evaporative cooling has different configuration from the traditional VMD setup, specific heat and mass transfer modelling needs to be performed for further design and optimization.

Practically, a supported membrane has enhanced mechanical strength than an unsupported membrane, which gives the supported membrane a higher durability and preference in the common VMD membrane applications. The desired support material needs to be highly porous, resistant to chemicals and pH variations, and durable. A common choice for membrane support is non-woven fabrics made of polyester. Even though polyester supports have been

widely used, and the effects of the support material on the membrane performance for vacuum membrane distillation have been reported by a few researchers [5-10], there are by far no literature reports performing heat and mass transfer modelling on supported membranes to mathematically reveal the impacts of the support material.

The objective of this study is to investigate the heat and mass transfer through a VMD membrane in a dead-end feed set-up for a single component (water) transport process in a temperature range of 23 to 35 °C. This temperature range was chosen based on the temperatures used in evaporative cooling devices. Membrane flux data is analyzed to reveal the effects of support materials on the performance of supported poly (vinylidene fluoride) (PVDF) membranes.

5.3 Mass transfer

In a VMD process, a feed solution, usually an aqueous solution, is brought into contact with one side of a micro-porous hydrophobic membrane while the vacuum is applied on the permeate side. The pore is filled with vapor since no liquid enters the pore due to the high hydrophobicity of the membrane material. Thus, the vapor is driven through the membrane pore by the difference in the partial pressure of the water vapor between two sides of the membrane. The transport process in VMD is divided into the following three steps: 1) transport from the feed bulk to the membrane surface (feed side); 2) transport through the membrane pores from the feed to the permeate side; 3) transport from the membrane surface (permeate side) to the condenser surface. Usually, the first and the third steps are ignored in the VMD of pure water, for the reason that diffusion inside the pores of the vapor molecules at the feed/membrane

interface is favored, and also the mass transfer resistance is neglected on the permeate side due to vacuuming.

Thus, the VMD flux, J ($\text{kg/m}^2 \text{ s}$), can be given in analogy to Fick's law as:

$$J = J_m = K_m(p_m - p_v) \quad (5.1)$$

Where J_m is the flux through the membrane, K_m ($\text{kg/m}^2 \text{ s Pa}$) is the membrane mass transfer coefficient, and p_m and p_v are the partial water vapor pressure (Pa) at the membrane surface on the feed side and the permeate side, respectively. In VMD, p_v is maintained at vacuum. p_m depends on the temperature, T_m (K), at the membrane surface (feed side) and can be given by the Antoine equation as:

$$p_m(T_m) = \exp\left(23.1964 - \frac{3816.44}{T_m - 46.13}\right) \quad (5.2)$$

Transport mechanisms for mass transfer across the membrane involve molecular diffusion. The Knudsen diffusion, and viscous flow, depending on the Knudsen number, Kn . In VMD, molecular diffusion is considered negligible since only a trace amount of air is present within the pores. Knudsen number (Kn), is defined as the ratio of the mean free path, λ (m) of the transported molecule to the membrane characteristic length, also known as pore diameter, r (m), providing a guideline of which mechanism is active inside the membrane pore. The mean free path can be calculated by equation (5.3).

$$\lambda = \frac{k_B T}{\sqrt{2} \pi p d_p^2} \quad (5.3)$$

where k_B (J/K), T (K) and p (Pa) are the Boltzmann constant, absolute temperature, and average pressure within the membrane pore, respectively, and d_p (m) is the collision diameter of the transporting molecule. In particular, T_m and $(p_m + p_v)/2$ can be used for T and p in VMD and this rule is maintained throughout this article, unless they are specified otherwise.

When $K_n > 10$ or $d < 0.1\lambda$, the mean free path of water molecules is large compared to the membrane pore size, which means the molecule-pore wall collisions are dominant over molecule-molecule collision [11-14]. This flow regime is known as Knudsen diffusion. When $K_n < 0.01$ or $d > 100\lambda$, the mean free path of the molecule is negligible compared to the pore size, the molecule-molecule collisions will dominate and a viscous flow exists in the membrane pores. The intermediate region in between $0.01 < K_n < 10$ is considered as the transition region. In the slip flow region, the no-slip boundary condition is no longer true, a layer of about one mean free path thickness, known as the Knudsen layer, starts to become dominant between the bulk of the fluid and the wall surface. And within the transition flow region, both the Knudsen diffusion and viscous flow occur in parallel, the mass transfer coefficient are additive, it can be represented by equation (5.4).

$$K_m = K_{knudsen} + K_{viscous} \quad (5.4)$$

Furthermore, the following equations are known for $K_{Knudsen}$ and $K_{viscous}$ [12]:

$$K_{knudsen} = \frac{2}{3} \frac{r\epsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}} \quad (5.5)$$

$$K_{viscous} = \frac{r^2 \epsilon M p}{8 \tau \delta \mu R T} \quad (5.6)$$

Where $\epsilon(-)$, $\tau(-)$, $r(m)$ and $\delta(m)$ are membrane porosity, pore tortuosity, pore radius and thickness, respectively. M (18.02 kg/kmol) is the molecular weight of water, μ (Pa s) is viscosity of water vapor, R (8.314 x 10³ J/kmol K) is the universal gas constant.

The mean free path, λ , was in the range of 6.53-6.75×10⁻⁷ m when system pressure is around 3 kPa. Considering the pore diameter of about 0.1 μm, this indicates that the transport in the membrane pore takes place in the transition region. Then, combining equations (5.4), (5.5) and (5.6):

$$K_m = K_{knudsen} + K_{viscous} = \frac{2}{3} \frac{r\epsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}} + \frac{r^2 \epsilon M p}{8 \tau \delta \mu R T} = A \sqrt{\frac{1}{T}} + B \frac{1}{T} \quad (5.7)$$

Further,

$$\frac{K_m}{\sqrt{\frac{1}{T}}} = A + B \sqrt{\frac{1}{T}} \quad (5.8)$$

Hence the plot of $K_m/\sqrt{1/T}$ vs $\sqrt{1/T}$ would result in a linear relationship, the intercept and slope of which are $\frac{2}{3} \frac{r\epsilon}{\tau\delta} \sqrt{\frac{8M}{\pi R}}$ and $\frac{r^2 \epsilon M p}{8 \tau \delta \mu R}$, respectively. (Strictly speaking, the second term of equation (5.8) is not necessarily proportional to $\sqrt{1/T}$ but a little bit more complicated function

of T , because p and μ are temperature dependent. However, if $\frac{K_m}{\sqrt{1/T}}$ remains constant in a studied range of T , as will be shown later, it is justifiable to ignore the second term).

5.4 Heat transfer

The heat transfer in a VMD process can also be split into three steps. 1) From the feed bulk to the membrane surface (feed side) through the liquid boundary layer; 2) through the membrane; 3) from the membrane surface (permeate side) to the condenser surface. The third step is ignored in the VMD due to low heat conductions at a pressure near vacuum.

The heat transfer in the first step is given by:

$$Q_f = h_f (T_f - T_m) \quad (5.9)$$

Where $Q_f(\text{W/m}^2)$ and $h_f(\text{W/m}^2 \text{ K})$ are the heat flux through and heat transfer coefficient at the liquid boundary layer, and $T_f(\text{K})$ is the temperature of the feed bulk.

For a dead-end feed chamber without forced convection (stirring), convection within the feed chamber can be treated as natural convection, and the feed heat transfer coefficient, h_f , can be calculated from the correlations between Nusselt (N_u), Prandtl (P_r) and Grashof (G_r) dimensionless numbers, i.e.,

$$N_u = \frac{h_f L_c}{k} \quad (5.10)$$

Where L_c (m) is the characteristic length and k (W/m K) is thermal conductivity of the fluid; N_u is given as [5]:

$$N_u = 0.53(P_r \cdot G_r)^{0.25} \text{ for } 10^3 < (P_r \cdot G_r) < 10^6 \quad (5.11a)$$

$$N_u = 0.13(P_r \cdot G_r)^{0.33} \text{ for } 10^6 < (P_r \cdot G_r) < 10^{12} \quad (5.11b)$$

P_r and G_r are given by:

$$P_r = \frac{c_p \mu}{k} \quad (5.12)$$

$$G_r = \frac{L_c^3 \rho^2 g \beta (T_f - T_m)}{\mu^2} \quad (5.13)$$

Where C_p (J/kg K), μ (Pa s), ρ (kg/m³), and β (1/K) are heat capacity, viscosity, density and volume thermal expansion of liquid water, respectively, and g is the acceleration by gravity (9.8 m/s²).

In the second step, Q_m (W/m²), heat flux through the membrane, is given by:

$$Q_m = J_m \Delta H_{evap} \quad (5.14)$$

Where ΔH_{evap} is the heat of evaporation (2400kJ/kg, mean value for the tested temperature range) of water.

At steady state Q (W/m²), the total heat flux, is given by:

$$Q = Q_f = Q_m \quad (5.15)$$

Furthermore, the temperature polarization coefficient (TPC) is defined as:

$$\text{TPC} = \frac{T_m}{T_f} \quad (5.16)$$

TPC is used to measure the effect of heat transfer through a boundary layer to total heat transfer resistance of the system. When the thermal boundary layer resistance is reduced, the temperature difference between the feed bulk and the membrane surface becomes close to each other and, consequently, TPC approaches unity.

5.5 Experimental

VMD experimental data reported in our earlier communication is used in this work for a further theoretical analysis [6]. Briefly, the VMD experiments were carried out with a cylindrical permeation cell, without stirring, with a feed chamber of about 300 mL wrapped with a heating tape for temperature control in a range of 23 to 35°C. The feed side and the permeate side pressures were maintained at atmospheric pressure and 0.038 bar, respectively. The permeate flux was calculated by:

$$J = \frac{W}{At} \quad (5.17)$$

where J (kg/m² s) is the flux, W (kg) is the weight of water collected in the condensor through membrane area A (m²) in time t (s).

Three membranes were used for VMD experiments. Two of them, designated as A-supported and B-supported are PVDF membranes coated on the nonwoven fabric backing materials Hollytex[®] 3396 (Kavon Filter Products Co., Farmingdale, NJ) and E055100-85 (Teijin Ltd., Osaka, Japan), respectively. The third one, designated as an unsupported membrane, is a PVDF membrane cast without any backing material. All the three tested membranes were cast using the same formula of polymeric solution. Details of the membrane preparation and specifications are given elsewhere [6].

5.6 Results and discussions

5.6.1 VMD experimental results

The flux data obtained from the VMD experiments are summarized in Table 5-1.

Table 5-1VMD experimental results.

Unsupported		A-supported		B-supported	
Temperature (°C)	Flux (kg/m ² h)	Temperature (°C)	Flux (kg/m ² h)	Temperature (°C)	Flux (kg/m ² h)
23	0.04	25	0.19	25	0.93
27	0.02	27	0.23	27	1.03
30	0.10	30	0.26	30	1.23
35	0.14	33	0.39	32	1.57
		35	0.45	35	1.73

5.6.2 Solution of mass and heat transfer equations

The mass and heat transport equations are used for the theoretical analysis of the VMD experimental data as follows.

- 1) The heat flux Q_f is calculated from equation (5.14) and (5.15) using experimental flux data J .
- 2) The mass transfer coefficient K_m and the temperature at the membrane surface T_m are the only unknowns in equations (5.1) and (5.9), and therefore they can be calculated simultaneously, by the aid of equations (5.2) and (5.10) to (5.13). The numerical values required for the calculations are provided in Table 5-2.

Table 5-2 Constants used in heat and mass transfer analysis.

Symbol	Value	Unit
C_p	4179	J/kg K
$^{\dagger}\mu$	0.00001	Pa.s
k	0.598	W/mK
ρ	998	kg/m ³
g	9.8	m/s ²
L_c	0.17	m
β	0.000207	1/K

† Calculated value at 30°C and system vacuum pressure.

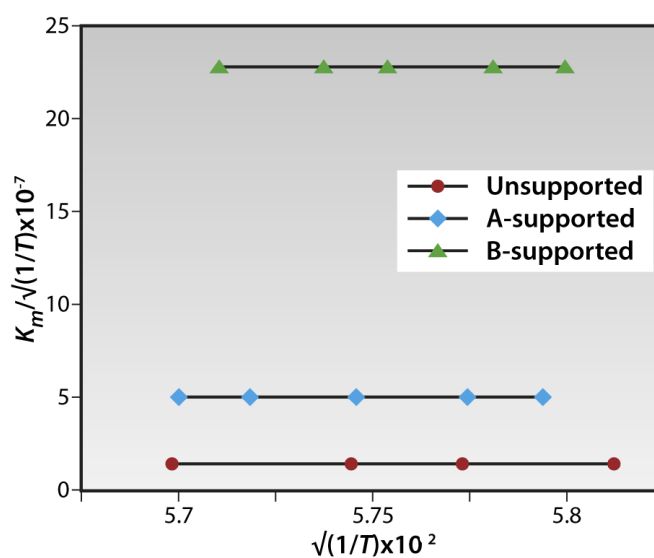
It should be noted that h_f depends on T_m according to equations (5.10), (5.11) and (5.13). An h_f value was calculated to be 1315 W/m² K by rigorous iteration using $T_f = 303$ K (30 °C) and the physical properties of water listed in Table 5-2. The latter h_f value was then used consistently throughout the work together with equations (5.1) and (5.9) to obtain K_m and T_m . This approximation, though not rigorous, can be justified since the flux is low due to the low feed temperature and the difference between T_f and T_m is very small for every experiment. The K_m and T_m values obtained are summarized in Table 5-3.

Table 5-3 Calculation of Km and Tm for three membranes at different operating condition.

Unsupported			A-supported			B-supported		
Feed Temperature (K)	$K_m \times 10^9$ (kg/m ² s Pa)	T_m (K)	Feed Temperature (K)	$K_m \times 10^8$ (kg/m ² s Pa)	T_m (K)	Feed Temperature (K)	$K_m \times 10^7$ (kg/m ² s Pa)	T_m (K)
296.15	8.00	296.13	298.15	2.85	298.05	298.15	1.27	297.68
300.15	7.95	300.14	300.15	2.84	300.03	300.15	1.26	299.63
303.15	7.91	303.10	303.15	2.82	303.02	303.15	1.26	302.53
308.15	7.84	308.08	306.15	2.81	305.95	305.15	1.25	304.35
			308.15	2.80	307.92	308.15	1.25	307.27

5.6.3 Membrane characterization parameters

Figure 5-1 exhibits $K_m/\sqrt{1/T}$ vs $\sqrt{1/T}$ plot, with $T=T_m$, for each membrane. All plots resulted in horizontal straight lines, indicating that the mass transfer in the membrane is dominated by the Knudsen diffusion.

Figure 5-1 Plot of $K_m/\sqrt{1/T}$ versus $\sqrt{1/T}$.

From the average $K_m/\sqrt{1/T}$, $r\epsilon/\tau\delta$ was obtained. Further, membrane porosity, ϵ , pore size, r , both the membrane coating layer thickness and overall thickness, δ , are listed in Table 5-4.

Table 5-4 Membrane parameters used in the experimental validation.

Unsupported				A-supported PVDF				B-supported PVDF			
ϵ^*	$\delta^\wedge$	δ^a	$\perp$ Pore	ϵ^*	$\delta^\wedge$	δ^a	$\perp$ Pore	ϵ^*	$\delta^\wedge$	δ^a	$\perp$ Pore
(-)	(μm)	(μm)	radius (nm)	(-)	(μm)	(μm)	radius (nm)	(-)	(μm)	(μm)	radius (nm)
0.68	48	48	10	0.21	31	185	46	0.51	23	87	55

* Porosity includes both coated and support layer

$\wedge$ Thickness represents that of the coating layer obtained from the SEM cross-sectional image

^a Thickness includes both coated and support layer

$\perp$ Pore size was obtained by the analysis of the surface SEM images [6]

Figure 5-2 shows the cross-sectional SEM images of the three membranes. In the figure comparison of the coating layer thickness (For the case of an unsupported membrane, the thickness of the cast membrane.) is made between before and after the VMD experiment. This figure indicates that after VMD the unsupported membrane thickness has decreased 42% while for the two supported membranes the thickness of the coated layer was practically unchanged. This observation clearly shows that support materials successfully help the coating layer maintain the pore channel structure during vacuuming, and therefore the pore size and tortuosity

of the supported membrane can be considered unchanged throughout the VMD experiment. As the unsupported membrane was compressed during the test, the associated pore size shrinkage and apparent tortuosity enlargement were expected during the VMD experiment. The calculated theoretical tortuosity by applying the membrane porosity, pore size and thickness (given in Table 5-4) are listed Table 5-5. Due to the stable pore channel structures of the two supported membrane, their calculated tortuosity should be reasonably accurate. On the other hand, the unsupported membrane should have different values before and after VMD experiments due to the significant pore collapsing phenomena. Table 5-5 shows the tortuosity data calculated from the $\frac{r\varepsilon}{\tau\delta}$ values (also given in Table 5-5) with ε , r and τ (given in Table 5-4). It should be noted that τ of the unsupported membrane corresponds to the membrane after the VMD experiment. In Table 5-5, the unsupported membrane has the largest tortuosity and smallest characteristic parameter value among the three membranes, indicating the collapse of the channel structure.

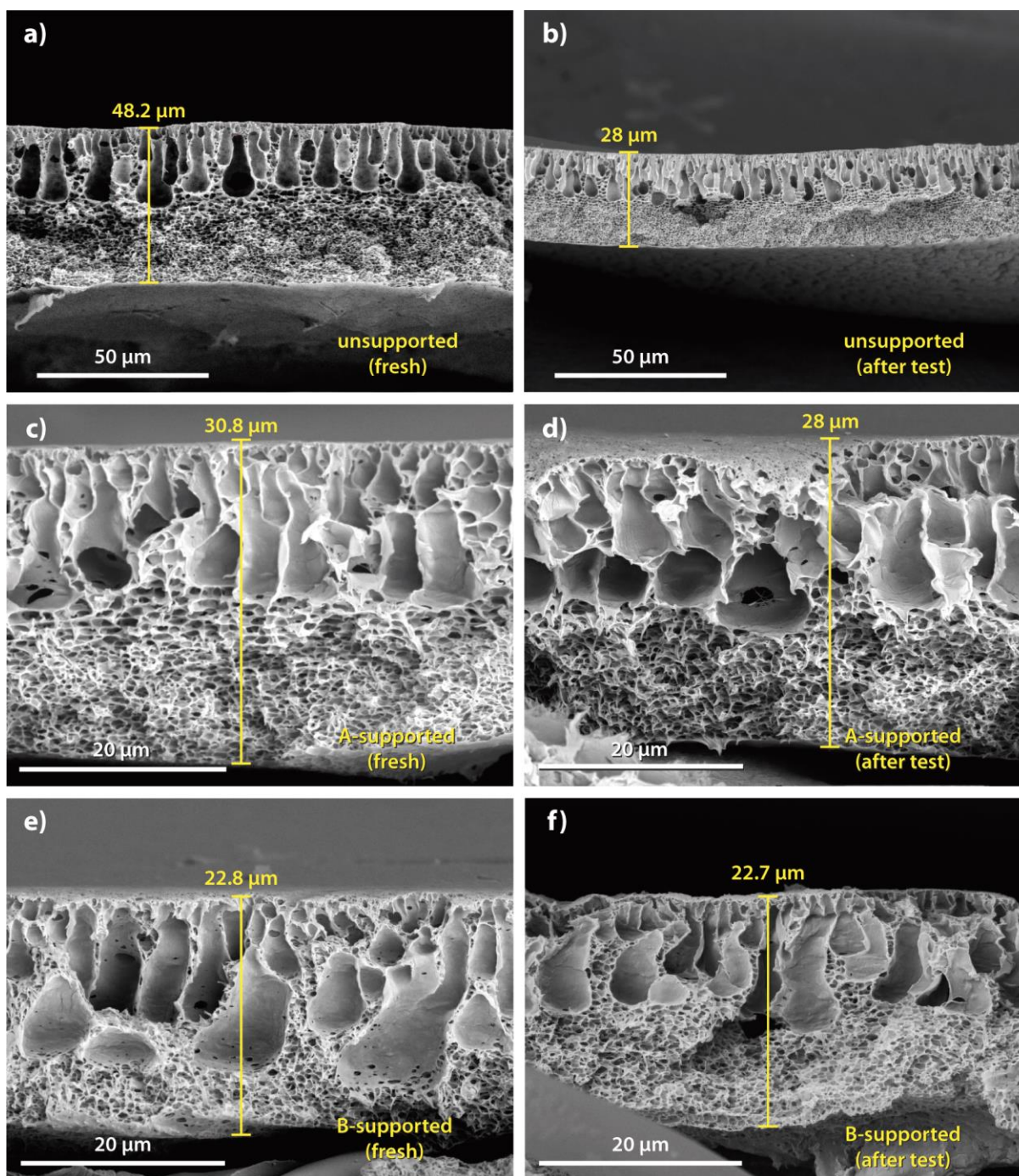


Figure 5-2 Membrane coating layer thickness comparison among fresh and after tests membranes by cross-sectional SEM imaging: (a) Unsupported fresh, (b) Unsupported after test, (c) A-supported fresh, (d) A-supported after test, (e) B-supported fresh, and (f) B-supported after test.

Table 5-5 The calculated tortuosity and the membrane characteristic parameter, $\frac{r\epsilon}{\tau\delta}$, from proposed model.

	Unsupported	A-supported	B-supported
Tortuosity (-)	51	5.3	7.3
Membrane characteristic parameter, $\frac{r\epsilon}{\tau\delta} (\times 10^{-6})$	2.8	9.9	43.7

5.6.4 Calculation of TPC

Temperature polarization coefficient (TPC) was calculated using the T_m values given in Table 5-3 in equation (5.16) and the results are shown in Figure 5-3. The figure shows that TPC decreases from low to high temperatures and from unsupported of the lowest flux to B-supported of the highest flux. Therefore, TPC tends to decrease with an increase in flux.

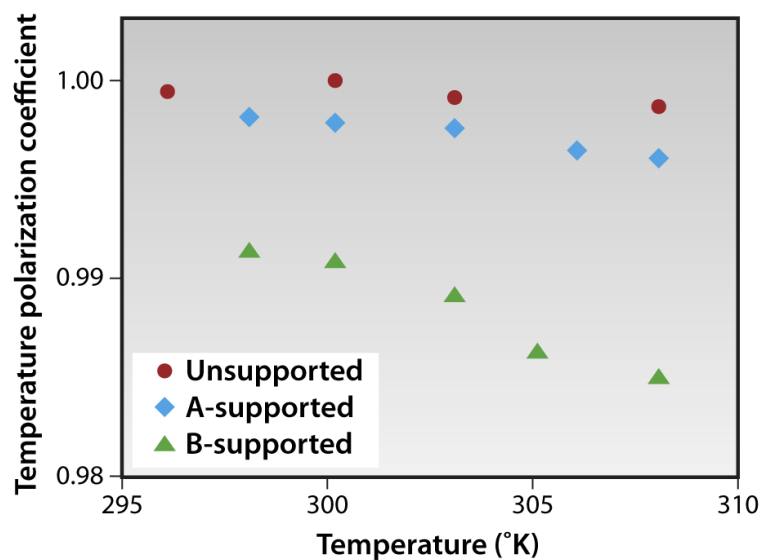


Figure 5-3 Feed temperature effect on temperature polarization coefficient.

5.7 Conclusion

In this study, the heat and mass transfer of the supported vacuum membrane distillation (VMD) membrane in the dead-end set-up for a single component (water) transport process are analyzed. With the model proposed, the membrane mass transfer coefficient K_m and the membrane surface temperature T_m and theoretical membrane tortuosity were calculated. The tortuosity could be calculated more accurately for the supported membranes than the unsupported membrane, since the membrane structure, especially the thickness, changed considerably for the unsupported membrane during the VMD experiment. As a result, the unsupported membrane had a much higher tortuosity value and a much lower characteristic parameter than the supported membrane. The cross-sectional SEM images were examined to validate the pore collapsing phenomena. The effect of support material for vapor transport was identified, that is, for the same casting solution as coating layers, supports helped to prevent the membrane coating layer to maintain the pore structure during the VMD test. Temperature polarization coefficients (TPC) were also calculated for the membranes. It was found that TPC is close to unity at low feed temperatures adopted in this work, but decreases with an increase of evaporation flux as feed temperature increases.

Acknowledgements

Financial supports by the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. We would like to thank the Arkema Inc. (Philadelphia, PA) for the gift of polyvinylidene fluoride (Kynar[®]) polymer.

5.8 Reference

- [1] C. Chiam, R. Sarbatly, Vacuum membrane distillation processes for aqueous solution treatment - A review, *Chem. Eng. Process.* 74 (2013) 27–54.
- [2] Y. Yang, J. Stapleton, B.T. Diagne, G.P. Kenny and C.Q. Lan, Man-portable personal cooling garment based on vacuum desiccant cooling, *Appl. Therm. Eng.* 47 (2012) 18–24.
- [3] M. Izenson, W. Chen, G. Bue, Reduced volume prototype spacesuit water membrane evaporator: A next-generation evaporative cooling system for the advanced extravehicular mobility unit portable life support system, 43rd Int. Conf. on Environmental Systems, Am. Inst. Aeronautics & Astronautics, Vail, CO, July 15-18, 2013, doi: 10.2514/6.2013-3440.
- [4] J.V. Makinen, I. Anchondo, G.C. Bue, C. Campbell, A. Colunga, Evaporative cooling and dehumidification garment for portable life support systems, 43rd Int. Conf. on Environmental Systems, Am. Inst. Aeronautics & Astronautics, Vail, CO, July 15-18, 2013, doi: 10.2514/6.2013-3442.
- [5] S.K.S. Boetcher, *Natural Convection from Circular Cylinders*, Springer, Cham, Switzerland, 2014.
- [6] Y. Yang, D. Rana, T. Matsuura, S. Zheng, C.Q. Lan, Criteria for the selection of support material to fabricate coated membranes for life support device, *RSC Adv.* 4 (2014) 38711–38717.
- [7] Z. Chen, D. Rana, T. Matsuura, Y. Yang, C.Q. Lan, Study on the structure and vacuum membrane distillation performance of PVDF composite membranes: I. Influence of blending, *Sep. Purif. Technol.* 133 (2014) 303–312.
- [8] Z. Chen, D. Rana, T. Matsuura, D. Meng, C.Q. Lan, Study on the structure and vacuum membrane distillation performance of PVDF composite membranes: I. Influence of molecular weight, *Chem. Eng. J.* 276 (2015) 174–184.
- [9] J. Zhang, Z. Wang, W. Li, The effects of pretreatment condition of non-woven fabrics on the PVC-co-PVAc-OH membrane performances, *Desalin. Water Treat.* 52 (2014) 7507–7519.
- [10] S. Zhao, L. Wardhaugh, J. Zhang, P.H.M. Feron, Condensation, re-evaporation and associated heat transfer in membrane evaporation and sweeping gas membrane distillation, *J. Membr. Sci.* 475 (2015) 445–454.

- [11] G. Karniadakis, A. Beskok, N. Aluru, *Microflows and Nanoflows: Fundamentals and Simulation*, Interdiscip. Appl. Math. Ser., Vol. 29, Springer, New York, NY, 2005.
- [12] M. Khayet, T. Matsuura, *Membrane Distillation: Principles and Applications*, Elsevier, Amsterdam, The Netherlands, 2011, pp. 134-136.
- [13] T. Matsuura, *Synthetic Membrane and Membrane Separation Processes*, CRC Press, Boca Raton, FL, 1993.
- [14] M. R. Qtaishat, T. Matsuura, Modeling of pore wetting in membrane distillation compared with pervaporation, in: A. Basile, A. Figoli, M. Khayet (Eds.), *Pervaporation, Vapor Permeation and Membrane Distillation: Principles and Applications*, Elsevier, Amsterdam, The Netherlands, 2015, Ch. 13, pp. 385-413.

Chapter 6: Development of solid super desiccants based on polymeric superabsorbent hydrogel composite

Yifan Yang, Dipak Rana, Christopher Q. Lan

Department of Chemical and Biological Engineering

University of Ottawa

161 Louis Pasteur Private, Ottawa, ON, K1N 6N5, Canada

6.1 Abstract

A solid super desiccant was developed based on the concept of impregnating a super liquid hygroscopic agent in a superabsorbent polymer to take advantage of the vast vapor absorption capacity of the hygroscopic agent and the liquid withholding capacity of the superabsorbent polymer. The maximum hygroscopic salt loading was determined based on different salt concentrations in sodium polyacrylate. The newly developed desiccant showed a vapor absorption capacity of $276\pm 20\%$, which is superior in comparison to that of conventional solid desiccants such as silica gel, activated alumina and molecular sieves. Thus they have great potential in applications requiring solid desiccants such as desiccant cooling, air conditioning, storage of moisture sensitive materials, and dehydration of natural gas.

Key words: solid desiccant; sodium polyacrylate; SAP; hydrogel; lithium chloride;

6.2 Introduction

Desiccants are a group of hygroscopic substances that can attract water-vapor molecules via adsorption or absorption. Desiccants have numerous industrial applications, for example, in oilfields (natural gas dehydration), heating, ventilation, the air conditioning (HVAC) industry (energy-saving desiccant-aided cooling systems and desiccant dehumidification wheel), and in electronics, pharmaceutical formulations, diagnostic reagents storage and delivery, etc. Based on the physical state, there are two types of desiccants, liquid desiccant and solid desiccant. Examples of typical liquid desiccants are concentrated aqueous solutions of hydroscopic salts (i.e. calcium chloride or lithium chloride solutions) and glycols, etc. The vapor pressure of a liquid desiccant solution is proportional to the temperature and is inversely proportional to the desiccant concentration. Liquid desiccants, in general, have a much higher capacity than solid desiccants. For instance, a lithium chloride solution is a popular choice for liquid desiccant air conditioning because of its great humidity capture capacity. As an illustrative example, aqueous LiCl solution can still absorb water vapor at a concentration of 10% (w/w) at 30 °C and 90% relative humidity (RH), implying a water vapor absorption capacity of 10 g water/g LiCl [1, 2]. Liquid desiccants have found numerous applications [3, 4]. One of the liquid desiccant systems is the Advantix Systems (Sunrise, FL), which uses a 40% lithium chloride solution as the desiccant. It has been proven to be an energy-saving, air quality improving, low maintenance cooling and dehumidification method.

Nevertheless, liquid desiccants, mostly lithium chloride solutions, are not applicable in many scenarios. For instance, desiccant cooling is designed for personal heat mitigation. A safer desiccant is required, specifically toxic-free. Therefore, solid desiccants are preferred due to their

dryness, and simplicity of their structure [5]. Solid desiccants are favoured in many other scenarios over liquid ones for their ease of operation, simplicity of device, and chemical inertness [6]. In contrast, liquid desiccants are usually corrosive, difficult to handle, and require complicated systems.

Most commonly encountered conventional solid desiccants are silica gel, activated alumina, molecular sieves, and activated carbon. Further, certain synthetic polymers have also been recognized as great desiccant options. For instance, various polymers and proteins were studied in terms of water vapor adsorption at a temperature of 25 °C, and the carboxyl groups presented a strong affinity with the adsorbed water [7, 8].

Unlike liquid desiccants, which absorb water molecules into the entire volume of the solution, solid desiccant relies on the adsorption of vapor molecules onto their surface to retain moisture. As a result, solid desiccants are inherently of low vapor adsorption capacity in comparison to liquid desiccants.

In the 1960's, researchers developed cross-linked polyacrylamide which can absorb liquid water up to 15-75 times its own weight and retained the water under pressure at about 2.5 psi. In the 1970's, the Agricultural Research Administration of US (Northern Regional Res. Lab. (NRRL), Bureau of Agricultural and Industrial Chemistry, Peoria, IL) developed a new material that can absorb more than 10^3 times its weight in water and was called a super absorbent polymer (SAP). Since then, this type of polymer, which has great water retention ability, has been widely used in disposable diapers and in agriculture industries.

We hypothesized that the superb liquid holding capacity of SAP, could be exploited in combination with superior vapor absorption capacity of liquid desiccants to create a super solid

desiccant. Since sodium polyacrylate has been proven to be a great water retention agent, and also a decent moisture absorption material, further optimization in order to develop a super solid desiccant seems feasible theoretically. With the motivation of developing a super solid desiccant that is highly efficient, non-corrosive and easy to regenerate, we have proposed the use of a superabsorbent hydrogel composite (SHC), a material that is based on sodium polyacrylate, with the impregnation of a hygroscopic agent (lithium chloride), as a novel solid desiccant material. SHC takes advantages of both, the great absorption capacity of lithium chloride and the large liquid-holding property of SAP. Moreover, commercial sodium polyacrylate is available at around \$10 per kilogram, which is comparable in price to the commercial silica gel. This newly developed desiccant has shown big potential in applications in oilfields, HVAC industries, etc.

6.3 Experimental

6.3.1 Materials

The cross-linked sodium polyacrylate, sodium salt of poly (acrylic acid) with partial sodium salt-*graft*-poly (ethylene oxide), powder (granular) was purchased from Sigma-Aldrich Inc., with a particle size reported to be 90-850 μm . The chemical structure of cross-linked sodium polyacrylate is shown in Figure 6-1. The anhydrous lithium chloride (99% purity) was purchased from the same source. All the above mentioned chemicals were used without any further treatment.

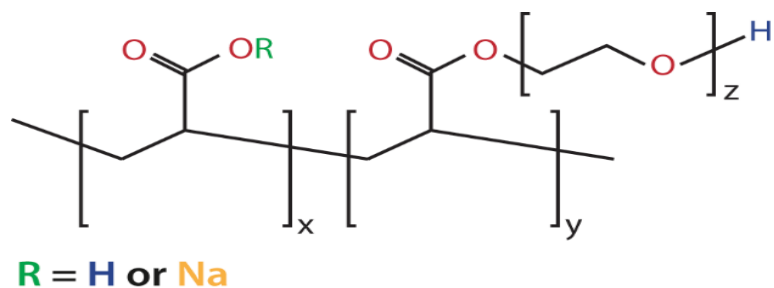


Figure 6-1 The chemical structure of cross-linked sodium polyacrylate.

6.3.2 Preparation of superabsorbent hydrogel composite desiccant

The superabsorbent hydrogel composite (SHC) is formed by soaking sodium polyacrylate powder with a pre-determined lithium chloride solution, and then rinsed with distilled water. The resulting gel was dried in the oven to form the final desiccant. Different concentrations of lithium chloride solutions were prepared. These are 1, 2, 2.5, 3, 4, 5 mol/L. 3 grams of sodium polyacrylate powder were weighed and added slowly into a flask with a magnetic stirrer, which contained 100 ml of the solution. The mixture was stirred for another 5 minutes before being transferred into a programmable shaker (180 rpm, 25 °C) to incubate for 1 h. Excess liquid was filtered out with mesh fabric and then, the flask was refilled with a fresh LiCl solution. This step in the shaker was repeated as needed for a complete ion exchange. At the end of the ion exchange process, the resulting gel mixture was again filtered out. A volume of 300 ml of deionized water was added into the flask to rinse the LiCl impregnated polymers. The mixture was kept in the shaker for 1 h and this step was repeated one more time to ensure complete rinsing. The final gel was filtered out and transferred onto a piece of glass plate to form a thin layer of gel film. The plate together with the gel film was placed inside a gravity convection oven (Model 18EG, Precision Scientific Inc., Buffalo, NY) at 80 °C to dry for 24 h.

6.3.3 Methods of characterization

6.3.3.1 Vapor absorption performance

Vapor absorption tests were performed inside a programmable water bath (Model 1225, VMR Int., Radnor, PA) with a cover, shown in Figure 6-2. The water bath was preheated to allow the water temperature to be stabilized at 26 °C. The air temperature inside the water bath is maintained at 25±0.2 °C and the relative humidity is stabilized at 99%. 0.5 grams of the sample was put into a pre-weighed petri-dish, and then the loaded dish weight was recorded. The loaded dish was kept on a rack which was half-immersed under water within the water bath. The total dish weight was recorded every hour from the 1st h to the 4th h, along with the 24 h final dish weight. The absorption capacities were defined as the absorbed vapor amount per unit mass of dry desiccant sample, which can be calculated by the following formula:

$$\text{Absorption Capacity } \left(\frac{\text{g}}{\text{g}} \right) = \frac{(W_f - W_i)}{W_d} \quad (6.1)$$

Where W_f is the dish weight at a specific time interval (1-h, 2-h, etc.) , W_i is the initial dish weight with the dry sample loaded, W_d is the dry sample weight.

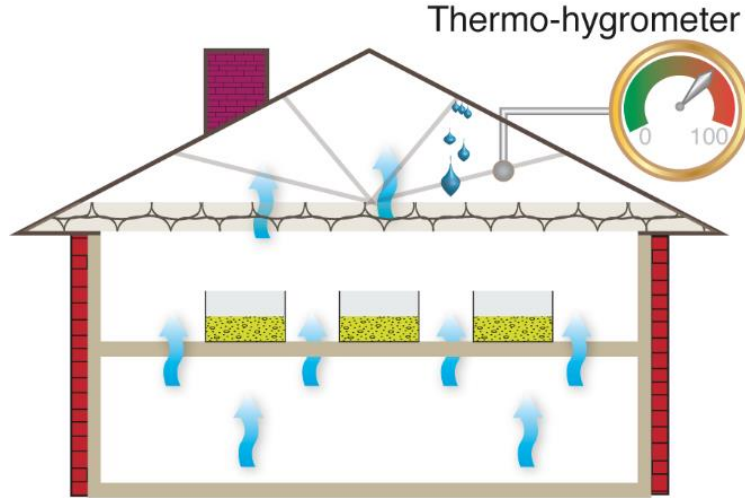


Figure 6-2 Schematic diagram for vapor absorption test within water bath.

6.3.3.2 Swelling measurements for different concentrations of LiCl solution

The pre-weighed 0.1 grams of dry SAP was put into a teabag, where the opening of the teabag was closed with staples. The loaded teabag was weighed before immersion in large amount of LiCl solution (100 ml). After allowing 24 h to reach its equilibrium swelling state, the swollen SHC within the wet teabag was taken out of the solution and hung up for 1 h to remove the excess water [9]. The teabag was finally dried by using a paper towel before measuring the final weight and the resulted swollen gel weight is repeatable. The equilibrium solution absorption amount was calculated by using the following equation:

$$Q_{eq} = \frac{W_2 - W_1}{W_1} \quad (6.2)$$

Where Q_{eq} is the swelling capacity, defined as grams of solution per gram of dry SAP, W_1 and W_2 are the mass of sample before and after swelling, respectively.

6.3.3.3 Surface morphology of the SHC desiccant

The dry SAP was measured by X-ray diffraction (XRD) and the surface morphologies of dry SHC samples with different loadings were examined by scanning electron microscopy (SEM) with a Vega-II XMU with Oxford Inca Energy (Tescan Inc., Warrendale, PA) at 20 kV. Prior to taking images, graphite was used to sputter-coat the samples and the images were taken at magnifications ranging from 60× to 5000×. The qualitative surface elemental information was analysed by the SEM coupled energy dispersive X-ray (EDX) spectroscopy.

6.3.3.4 Surface area measurement

The specific surface areas of dry sodium polyacrylate powder and dry SHC samples were determined by nitrogen adsorption and desorption at 77 K using a physisorption analyzer (Model ASAP 2020, Micromeritics Instrument Corp., Norcross, GA). The surface area was calculated using the Brunauer-Emmett-Teller (BET) method that was applied to the adsorption data in the relative pressure (P/P_0) range of 0.05–0.20.

6.3.3.5 Lithium and sodium ion concentration measurement in SHC gel mixture leachates

Lithium and sodium ion concentration in the leachates from each round of gel / solution mixing steps were measured by Varian (Agilent Technologies Inc., Santa Clara, CA) Vista Pro Inductively Coupled Plasma Emission Spectrometry (ICP-ES). This information can reveal ion exchange rates at each stage and the total ion exchange capacity of the sodium polyacrylate

being studied. The 1st sample was taken from the leachate of 1 h gel preparation and then, 100 ml of fresh 2.5 M LiCl solution was used to replace the previous batch of leachate. The flask containing new gel mixtures were put into the shaker at the same condition for another hour of preparation. The 2nd equilibrium ion concentration sample was then taken from this batch of leachate and samples were collected until the 5th equilibrium. The measured sodium ion amounts from the 5 samples were added up as the total sodium ion exchange capacity of the sodium polyacrylate used in this study. Ion exchange efficiency is defined as amount of sodium ion in the leachate divided by the total sodium ion exchange capacity. The data analysis was based on results of 3 replicates.

6.4 Results and discussion

6.4.1 Effect of LiCl solution concentration on SAP swelling capacity

The swelling capacity (g of weight gain / g of dry SAP) of SAP and LiCl loading (mmol of LiCl / g of dry SAP) were plotted vs LiCl concentration in Figure 6.3. Results showed that the SAP swelled less when the concentration of LiCl solution increased. This is reasonable because the Na⁺ density on the matrices of the SAP was constant. As a result, when the concentration of the LiCl solution increases, the osmotic pressure difference between the liquid phase inside the SAP and that outside of it would decrease, resulting in reduced swelling of SAP.

Figure 6.3 also shows that a 2.5 M LiCl solution led to the largest LiCl retention in SAP, which can be potentially beneficial because of the larger moisture retention for the resulting SHC desiccant. The existence of a LiCl concentration at which a maximum LiCl retention was obtained was due to the fact that the amount of LiCl retained in the gel, which equals the amount

of solution absorbed at equilibrium multiplies the solution concentration. When low concentrations of LiCl solution was used for swelling, little LiCl was contained in the relatively large volume of solution absorbed. On the other hand, when the LiCl concentration was high (i.e., 3 M or higher in this study), the reduced volume of solution absorbed by the SAP led to less LiCl retention despite of the relatively high LiCl concentration.

The swelling behaviour of ionic hydrogel such as SAP is a result of a balance between the elastic energy of the SAP network and the osmotic pressure difference between the liquid phase inside the gel matrices and that outside of it. The elastic term is described by the Flory expression derived from an assumption of Gaussian chain distributions, and in an electrolytic solution, the osmotic pressure is associated with the molarity of the solution and temperature.

Liquid absorption by polymer can be described by the Flory theory for an ionic network [10].

$$Q^{5/3} = \left(\frac{1}{2} * \frac{i}{V_u} * \frac{1}{2S} \right) + \left(\frac{X_1}{2V_1} * \frac{V_0}{v} \right) \quad (6.3)$$

Where Q is the maximum swelling ratio of SAP, i is the electronic charge on the polymer structure per polymer unit, V_u is the polymer repeating unit volume, S is the ionic strength of solution, X_1 is the thermodynamic parameter of polymer with solvent (expressed by Flory-Huggins parameter), V_1 is the molar volume of solvent, in a real network, V_0 is the unswollen polymer volume, and v is the effective number of chains. These parameters in the equation formed a balance of the swelling which can be further defined as follows: the first term in the equation represents the ionic strength on both polymer structures and in the solution, the

second term is the affinity of network with solvent and $\frac{V_0}{v}$ is the cross-linking density. This equation shows that the water absorption power results mainly from the osmotic pressure, the polymer's affinity of water, and the cross-linking density of the network [10].

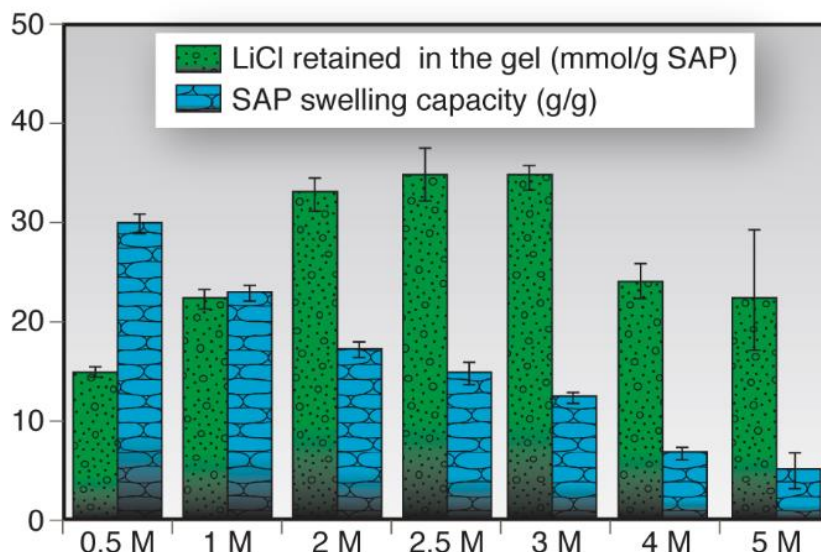


Figure 6-3 SAP swelling capacities and LiCl retained amount with respect to the molarity of LiCl solution.

The osmotic pressure dependency is through i / S , which is the electronic charge on the polymer structure per polymer unit versus ionic strength of solution. When the solution is more concentrated or solution contains ion with more charges, the swelling capacity of the particular polymer decreased due to raised ionic strength of the solution. The affinity of water and polymer in this case is referring to the water affinity of the hydrophilic group on the polymer chain, more specifically carboxylate and carboxylic acid groups in this system (as shown in Figure 6-1).

By recognizing the mechanism of hydrogel swelling, based on the same polymer structure, the affinity of the water and the polymer and cross-linking density of the network

remain the same. The swelling capacity is directly affected by the osmotic pressure. Thus, decreasing the ionic strength, more specifically, decreasing the concentration of the LiCl solution for this system, can increase the polymer swelling capacity (liquid retention). We can see that there is a trade-off for an higher amount of liquid retention which requires a low solution concentration and more LiCl amount trapped inside of SAP which generally prefers a higher solution concentration. Figure 6-3 has shown the optimum solution concentration for the maximum LiCl retention within SHC.

6.4.2 Effect of lithium chloride content on SHC vapor absorption performance

Lithium and sodium are both alkali metals, and have the same electric charge, +1. The cation radius of lithium is smaller than that of sodium as lithium is from period 2 and sodium is from period 3. Lithium ion therefore has a greater charge density, and can attract water molecules more effectively than sodium ions. Thus, theoretically, both lithium ions on the polymer chain, which were part of the SAP matrices after ion exchange with Na^+ , and lithium chloride crystals, which were impregnated inside the SAP matrices, will benefit from the moisture absorption of SHC.

Vapor absorption experiments on the different loading of SHC were tested with a sample preparation based on a 1 time of solution / SAP equilibrium. As shown in Figure 6-4, 2.5 M SHC has the largest 24 h moisture absorption capacity compared to the other loading of SHC. The results followed the same trend as the LiCl solution retained in the SAP gel in Figure 6-4, meaning that the larger the amount of LiCl absorbed on the polymer, the greater the moisture absorption ability of the final SHC. The retained LiCl solution in the gel became a salt crystal

after drying and staying on the SHC surface. The crystal acts like the separate moisture absorbent on the polymer, which further increases the capacity.

It is worth noting that more LiCl salt outside of the polymer did not always positively affect the SHC performance. When large amounts of free lithium chloride crystals absorb moisture, a layer of concentrated LiCl solution film is slowly formed around the SHC, and this is hardly absorbed by the SHC due to its high osmotic pressure. This layer of free LiCl solution becomes more and more diluted and corrosive, and is harmful to the equipment. Therefore, a rinsing step as the last step of SHC preparation is important to ensure that the resulting desiccant is non-corrosive and therefore ease of operation.

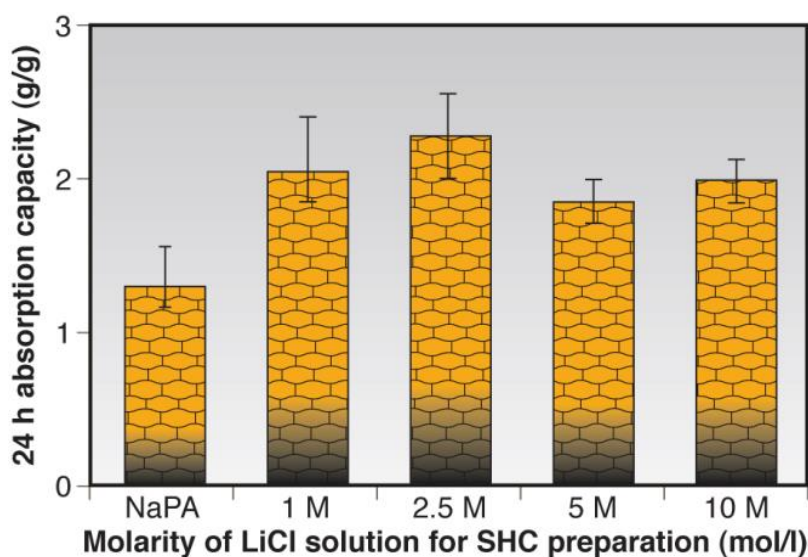


Figure 6-4 24 h absorption capacity versus molarity of LiCl solution for SHC preparation (1-h equilibrium duration).

From Figure 6-4, it can also be observed that the absorption capacity increased slightly from 5 M SHC to 10 M SHC. This could imply that the ion exchange degree also affected

moisture absorption ability. A 10 M LiCl solution, which is an almost saturated LiCl solution, can exchange the largest amount of Li^+ onto the polymer chain at equilibrium conditions compared to a lower concentration solution. However, for 10 M SHC, it retained the least amount of LiCl solution within the polymer structure during SHC formation. Overall, the active lithium ions or lithium chloride salts on the 10 M SHC is still less compared to the others (especially 2.5 M SHC). For similar reasons, the 1 and 5 M SHC, either have a lesser degree of ion exchange or they retained less amounts of LiCl crystal on the polymer, resulting in a less moisture absorption performance.

The 2.5 M SHC shows the best performance with Figure 6-4 revealing the impact of ion exchange degree on the moisture absorption capacity. This led to the concerns about ion exchange rate limiting factors, with these two factors being studied. One is equilibrium duration and the other is number of equilibrium.

6.4.3 Effects of equilibrium duration on the ion exchange degree

Equilibrium duration is referred to as the step where the solution / SAP was stirred inside the shaker. This stirring duration can affect the ion exchange degree depending on the ion exchange rate. Thus, the effects of equilibrium duration were tested based on the vapor absorption tests for 2.5 M SHC. This stirring period was extended from 1 to 4 h for the sample preparation. The vapor absorption capacities for the SHC prepared, were done using both 1 h equilibrium and 4 h equilibrium, and were compared with the results shown in Figure 6-5. No significant differences were observed between the two, since the rinsing step was performed following the same procedure and the freest LiCl salts were removed. Therefore, the similarity of

vapor absorption results shows the similarity of the ion exchange degree on the polymer chain. We further concluded that 1 h preparation of SAP soaking with LiCl solution would be sufficient for ion exchange to reach equilibrium. As such, 4 h preparation was not necessary.

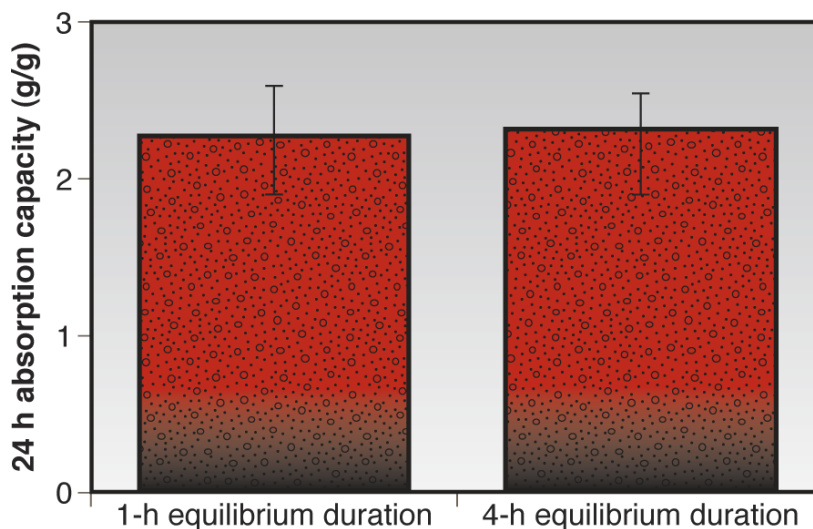


Figure 6-5 24 h absorption capacity comparisons for 1-h and 4-h equilibrium durations.

6.4.4 Effects of the number of equilibrium steps on vapor absorption performance

Repeating the solution/gel equilibrium step with fresh LiCl solution can further push the completion of ion exchange. By replacing the leachate from the previous step, the sodium ion has been removed out of the system. As a result, more lithium ion is transferred onto the polymer. This should benefit the vapor absorption capacity of SHC, since the lithium ion has a higher hydration power due to its high charge density compared to sodium ion. SHC with different numbers of equilibrium were prepared, i.e., 1 - equilibrium, 2 - equilibrium, 3 - equilibrium, 5 - equilibrium, vapor absorption tests were performed and the absorption data is listed in Figure 6-6.

SAP vapor absorption data was also plotted as a baseline for comparison. The 24 h absorption for SAP without further treatment is measured as 1.31 g of vapor per gram of SAP. For different numbers of equilibrium preparation, the higher the equilibrium number, the higher the vapor absorption capacity. The slope for each type of SHC increases as well when a higher number of equilibrium is achieved. It is interesting to note that the 3-equilibrium SHC has a similar vapor absorption curve to that for 5-equilibrium SHC, meaning that the ion exchange might be completed by the end of 3-equilibrium. This hypothesis needs to be further proven by ICP-ES results.

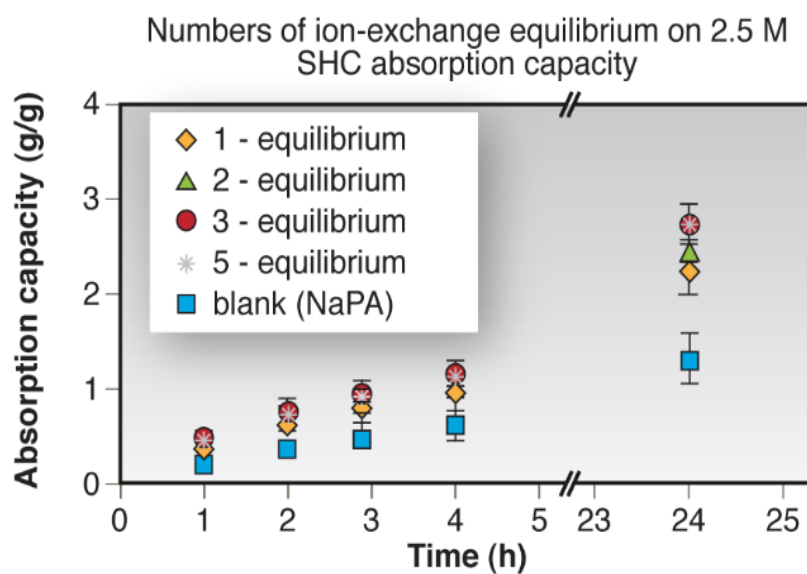


Figure 6-6 Vapor absorption performance with 2.5 M SHC prepared by different numbers of ion-exchange equilibrium.

The relative ion exchange degree is calculated based on the ICP-ES results. The sodium ion amount from the leachates of different equilibrium runs was summarized to calculate the total ion exchange capacity for sodium polyacrylate.

Total exchangeable sodium ion on SAP =

$$\frac{\sum_1^5 \text{sodium ion amount}_i \frac{mg}{23 \left(\frac{g}{mol} \right)}}{\text{amount of treated SAP (g)}} = 0.86 \frac{mmol}{g \text{ of SAP}} \quad (6.4)$$

The relative ion exchange degrees were then calculated by using the sodium ion amount from each batch of equilibrium divided with the total ion exchange capacity. The calculation is summarized in the following equation:

$$\text{Relative ion exchange degree}_i = \frac{\text{sodium ion amount}_i}{\sum_1^5 \text{sodium ion amount}_i} \quad (6.5)$$

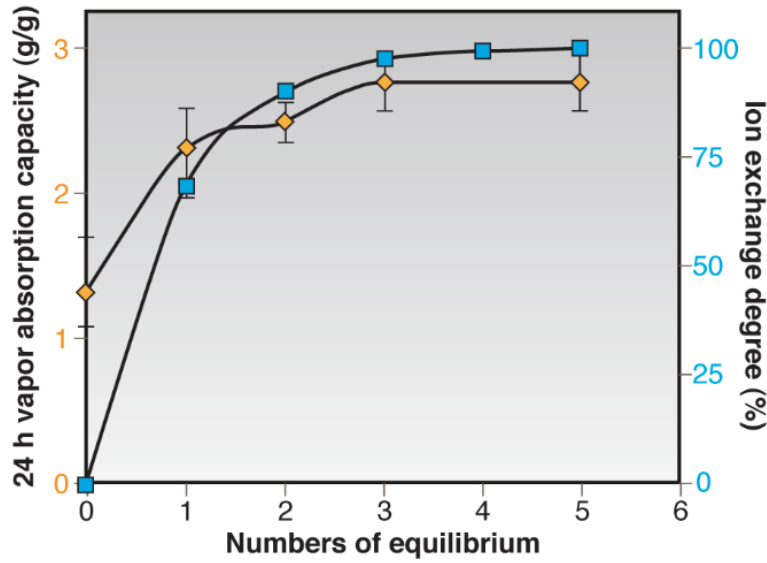


Figure 6-7 24 h vapor absorption capacity and ion exchange degree with respective to the numbers of equilibrium.

From the grey curve shown in Figure 6-7, we can see that the ion exchange degree reaches a plateau after the 3rd equilibrium, reaching 97.2% of ion exchange degree at the 3rd

equilibrium. This trend is maintained for the 24 h moisture absorption tests from different equilibrium degrees of SHC samples. The 5th equilibrium showed the same 24 h moisture absorption capacity as that of the 3rd equilibrium SHC, and these are the largest results of all 5 tests. The sodium polyacrylate sample was tested at the same condition as the control. The reason for this is because more numbers of equilibrium pushed the ion exchange to the Li^+ favour direction on the polymer, and more Li^+ on the polymer chain can help attract more vapor, resulting in a better desiccant performance.

The morphologies of the SHC under different equilibrium conditions were measured by SEM-EDX. Figure 6-8 lists the SEM images for 2.5 M 1-equilibrium, 2.5 M 3-equilibrium and 2.5 M 5-equilibrium SHC at a magnification of 60 $\times$. These images clearly showed that the amount of salt crystals (white dots) on the polymer surface decreased when the number of equilibrium increased. To better understand this phenomenon, an elemental analysis was performed by EDX to confirm the crystal content. The EDX results are listed in Figure 6-9.

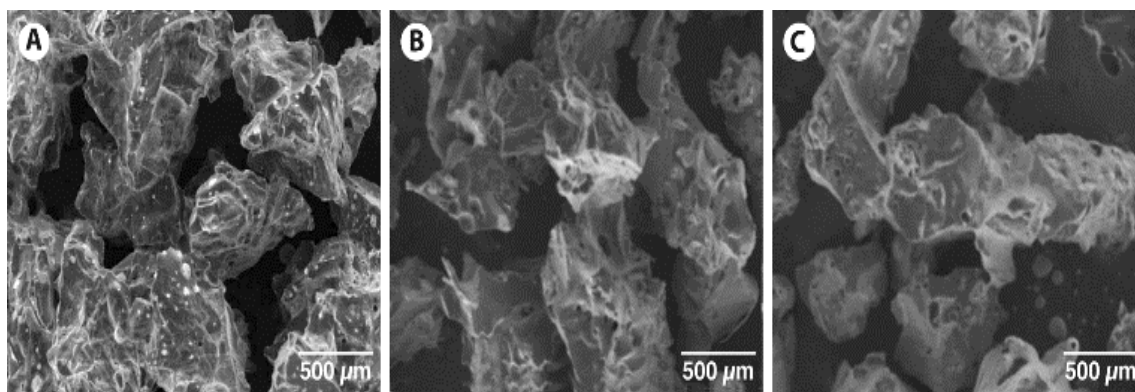


Figure 6-8 SEM images for (A) 2.5 M 1-eq), (B) 2.5 M 3-eq SHC and (C) 2.5 M 5-eq SHC (magnification 60 $\times$).

The top images of Figure 6-9 are the SEM images for the corresponding SHC at a magnification of 5000X. The actual detecting spots are highlighted in the images, and the bottom images are the EDX peaks showing elements detected from the selected spot. It was found that most of the crystal shown in Figure 6-9A was made of sodium chloride, which had a perfect cubic crystal shape. The crystals found on Figures 6-9 B and 6-9 C are mainly made of lithium chloride. It is noted that lithium is not detectable by EDX due to its small atomic size. However, the peaks show high levels of chlorine and zero cation. Based on the fact that only lithium and sodium ion exist in the system, it can be therefore concluded that the crystal is made of lithium chloride.

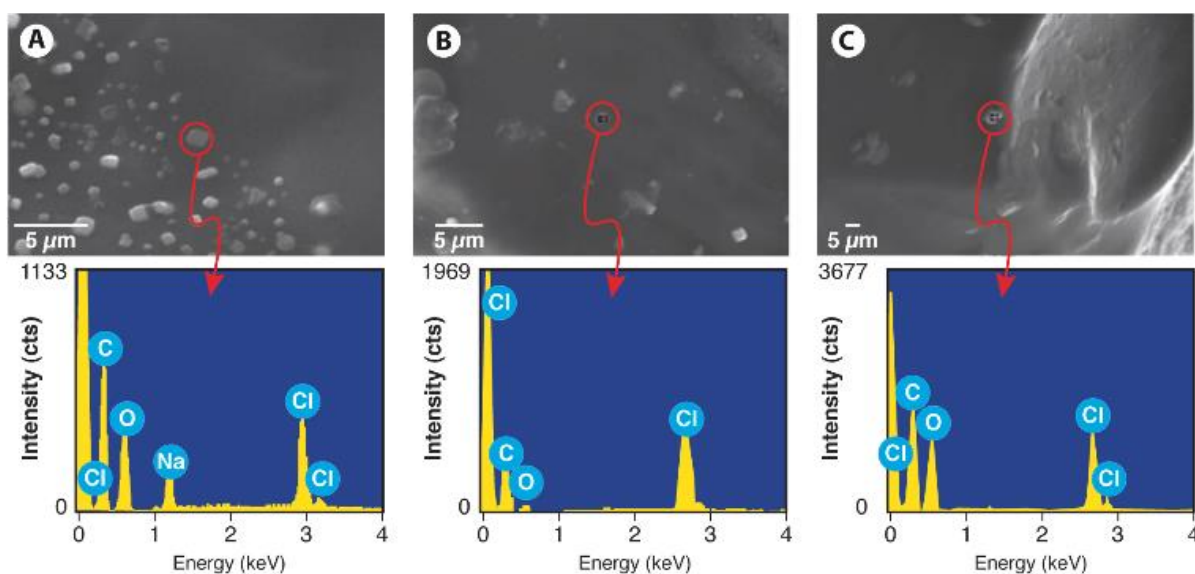


Figure 6-9 SEM-EDX elemental analysis results for (A) 2.5 M 1-eq, (B) 2.5 M 3-eq and (C) 2.5 M 5-eq.

Another interesting fact from the SEM images shown in Figure 6-9, is that the shape of the crystals found on the surface of 3-equilibrium (Figure 6-9 B) and 5-equilibrium (Figure 6-9 C)

SHC are not the perfect cubic shape as those found in 1-equilibrium (Figure 6-9 A). These deformed crystals are all detected as lithium chloride while those cubic shaped crystals found in the Figure 6-9 A are sodium chloride. The deformation of lithium chloride crystals may be due to the hygroscopic nature of lithium chloride salt. It has a higher affinity for moisture compared with sodium chloride. Therefore, under the same sample preparation period before the SEM measurement, the lithium chloride attracted slight amount of moisture and slowly deformed. This also explains another observation from Figure 6-9, that it seems to have more crystals on Figure 6-9B comparing to Figure 6-9 C, this doesn't mean that 3-equilibrium has more lithium chloride crystals than 5-equilibrium, it is again due to the trace amount of sodium chloride on the surface of Figure 6-9 B (cubic shaped crystals found on the bottom right of Figure 6-9 B). The observed less crystals on Figure 6-9 C surface is due to the fast moisture capture from the lithium chloride crystal during sample preparation, the ICP-ES results have confirmed that 5-equilibrium has more completed sodium removal comparing to 3-equilibrium, and therefore Figure 6-9 C should contain slightly more lithium chloride crystal comparing to Figure 6-9 B. This phenomenon also leads to another conclusion that by performing more equilibrium steps, less sodium ion exists within the system. This leaves more space for lithium chloride crystals to be attached on the polymer surface, thus further improving the vapor absorption capacity.

6.4.5 Performance comparison with common solid desiccant

Bakass et al. measured the vapor absorption capacity of different polymers and concluded that SAPs have weak surfaces (lower than 10 m²/g) and are nonporous [11]. The surface area measured in this study is by BET for SAP is 3.5±0.06 m²/g, and the 3-equilibrium SHC has

4.6±0.08 m²/g of surface area. These results confirm that the SAP has a small surface area compared to other common solid desiccants, and by impregnating lithium chloride salts on SAP, the resulting SHC surface area has increased due to salt crystal formation on the polymer surface. The adsorption isotherms of water vapor on a SAP surface follows type III isotherms at an ambient temperature with hysteresis phenomena. The absorption capacity of sodium polyacrylate has been tested by Zhang et al. [12], and the monomer concentration, dosage of initiator and reaction temperature effects on the moisture absorption capacity have been systematically investigated. Moisture absorbing capacities of sodium polyacrylate have shown a better performance compared to conventional solid desiccants, such as silica gel and molecular sieve. The optimum moisture capacity of sodium polyacrylate from Zhang's research group reached 1.01 g/g.

To better evaluate the proposed solid desiccant, the physical properties and performances of a few common solid desiccants were researched in literature. Silica gel, a generic name for a gel manufactured from sulphuric acid and sodium silicate, has a high water capacity in that it can adsorb up to 45% of its own weight in water. It is easier to regenerate and it costs less than a molecular sieve. Activated alumina, a hydrated form of aluminium oxide (Al₂O₃), is the least expensive adsorbent for gas dehydration can produce a dew point below -105.56 °C if applied properly and less heat is required to regenerate than molecular sieves. However, molecular sieves give lower outlet water dew points. Molecular sieves are the most versatile adsorbent because they can be manufactured for a specific pore size, depending on the application and are capable of dehydration for less than 0.1 ppm water content. It is the most expensive adsorbent but offers

greater dehydration and requires higher temperatures for regeneration. These are alkaline and are subject to attack by acids. Table 6-1 has listed the common desiccant physical properties.

The cost of commercial sodium polyacrylate is around \$10 per kilogram, which is comparable to the commercial silica gel price, considering that the lithium chloride chemical is more expensive, a more detailed cost analysis was performed. By performing ICP-ES tests, we measured the amount of Na in the leachate solution, the total amount of Na removed from SAP is 0.85 mmole per gram of SAP, and this amount of lithium ion is expected to be on the polymer chain. The amount of LiCl obtained by the gel swelling shown in Figure 6.3 (2.5 M) is 34.6 mmole per gram of SAP that is 1.5 g of LiCl per g of SAP, this amount can be considered as the amount of LiCl crystals trapped inside of SAP. The cost of the analytical grade of lithium chloride purchased from Sigma-Aldrich Inc. is \$0.15 per gram (\$368 per bottle of 2.5 kg), this chemical cost can be greatly reduced when approaching it to a non-analytical grade source. Therefore, by this proposed modification on sodium polyacrylate, the resulted SHC has doubled the vapor absorption capacity with reasonable amount of cost during preparation.

Table 6-1 Comparisons of physical properties with common solid desiccants.

	Silica gel	Activated alumina	Molecular sieves	SAP [¶]	SHC [¶]
Surface area (m ² /g) [‡]	600-800	200-300	600-700	3.5±0.06	4.6±0.08
Pore diameter (Å) ¹³	10-90	15	3,4,5,10	Non-porous	Non-porous
Static adsorption at RH 100% ¹⁴	38%	36-42%	23%	131±27%	276±20%
Regeneration temperature (°C) ¹⁵	100	120-260	175-315	N/A	<80

[‡]Data reported from Sigma-Aldrich; [¶]data were obtained from this study.

It is noted that adding LiCl can double the vapor absorption of SAP, which is significant considering that the conventional solid desiccant has the capacity only around 40% of its own weight (shown in Table 6-1). Furthermore, the vapor absorption capacity reported is 24 h absorption instead of equilibrium capacity. As shown in Figure 6-6, the new desiccant was still absorbing vapor after 24 h and the gap between the desiccants and the SAP would become much larger if we push the vapor absorption to equilibrium. The much larger rate of vapor absorption by the desiccant than the SAP provides another important advantage.

There is an important concern in terms of potential LiCl leaching, since this new developed solid desiccant has great potential in various health related applications, for example, life support vacuum desiccant cooling device [16], in which three-layer structure including water reservoir, spacer and solid desiccant layer are encapsulated inside of an air-tight bag, water evaporation which can be initiated through vacuuming provides cooling. LiCl solution leaching from desiccant can potentially damage the device and eventually irritates the body skin. Other

applications like the compact space cooling unit, also has similar safety concern. Thus solid desiccants are required to not only be efficient but also safe to handle (non-corrosive). The rinsing step as the last step for SHC gel preparation is designed to remove all the freest LiCl outside of SHC gel so that the desiccant will stay solid (gel) with the multiple absorption-desorption cycles, and therefore is safe to the environment and equipment.

6.5 Conclusions

A new desiccant made from superabsorbent polymer (SAP), which was impregnated with 2.5 M LiCl solution in sodium polyacrylate, has been developed. It is clear that the impregnated SAP shows double the amount of vapor absorption capacity compared with the SAP without treatment. The 24 h absorption capacity can reach 2.76 ± 0.2 g/g at 99% relative humidity and 25 °C air temperature. Moreover, the appropriate impregnating concentrations of 2.5 M were determined based on the equilibrium water vapor absorption performance. Polymer based solid desiccants have the potential of being regenerated below 80 °C and can maintain long-term stability through thousands of absorption-desorption cycles. The proposed modified SAP impregnated with LiCl salts, has shown a great vapor capacity and thus reveals its great potential for larger scale drying applications, such as those required in natural gas dehydration and heating, ventilation, and the air conditioning applications.

Acknowledgement

Financial supports by the Natural Sciences and Engineering Research Council of Canada (NSERC).

6.6 Reference

- [1] E. F. Johnson and M. C. Molstad, *J. Phys. Chem.*, 1951, **55**, 257.
- [2] S. K. Chaudhari and K. R. Patil, *Phys. Chem. Liq.*, 2002, **40**, 317.
- [3] W. Kessling, E. Laevemann, M. Peltzer, *Int. J. Refrig.*, 1998, **21**, 150.
- [4] S. H. Won and W. Y. Lee, *Heat Recov. Syst. CHP*, 1991, **11**, 41.
- [5] J. Kim, S. Kato, B. Park, *J. Environ. Eng. (Japan)*, 2014, **79**, 99.
- [6] Y. Yang, J. Stapleton, B. T. Diagne, G. P. Kenny, C. Q. Lan, *Appl. Therm. Eng.*, 2012, **47**, 18.
- [7] G. Wang, B. Dou, J. Wang, W. Wang, Z. Hao, *RSC Adv.*, 2013, **3**, 20523.
- [8] C. D. Teng, M. H. Zarrintan, M. Groves, *Pharm. Res.*, 1991, **8**, 191.
- [9] F. Hua and M. Qian, *J. Mater. Sci.*, 2001, **36**, 731.
- [10] W. A. Laftah, S. Hashim, A. N. Ibrahim, *Polym. Plast. Technol. Eng.*, 2011, **50**, 1475.
- [11] M. Bakass, J. P. Bellat, A. Mokhlisse, G. Bertrand, *J. Appl. Polym. Sci.*, 2006, **100**, 1450.
- [12] C. Zhang, W. Zhang, Z. Pan, X. Zhang, J. Liu, C. Yue, *Sci. China Ser. B: Chem.*, 2009, **52**, 1000.
- [13] R. A. Hubbard and J. M. Campbell, *Hydrocarbon Eng.*, 2000, **5**, 71, 76.
- [14] Van Air Systems, <http://airvacuumprocess.com/wp-content/uploads/2014/07/Adsorbent-desiccant.pdf> 2009.
- [15] Drytech Inc., <http://www.drytechinc.com/types-of-desiccant.html> 2015.
- [16] Y. Yang, D. Rana, T. Matsuura, S. Zheng, C. Q. Lan, *RSC Adv.*, 2014, **4**, 38711.

Chapter 7: Development of membrane-based desiccant fiber for vacuum desiccant cooling

Yifan Yang, Dipak Rana, Christopher Q. Lan, Takeshi Matsuura

Department of Chemical and Biological Engineering

University of Ottawa

161 Louis Pasteur Private, Ottawa, ON, K1N 6N5, Canada

7.1 Abstract

A novel hydrophobic membrane-based desiccant fiber (MDF) was developed by loading lithium chloride into hydrophobic hollow fiber membranes. The MDF thus made was then tested for vapor absorption under controlled conditions. Furthermore, a MDF pad, which was made by weaving MDF into a piece of garment, was built into a laboratory vacuum desiccant cooling (VDC) setup, which included the MDF pad as the desiccant layer and a cooling towel saturated with water as the water reservoir, to test the cooling effects at atmospheric pressure and vacuum of 25 inches of Hg. Results indicate that MDF is suitable for applications such as in VDC. Mass and heat transfer of vapor absorption by MDF were also analysed.

KEYWORDS: membrane-based desiccant fiber; vacuum desiccant cooling; hollow fiber membrane; hybrid desiccant; heat and mass transfer; vapor absorption

7.2 Introduction

Desiccant cooling and desiccant dehumidification are technologies that have been extensively researched in recent years for their energy saving and environmental friendly features. This is based on the reliability and simplicity provided by their configurations and the desiccant materials ability to be regenerated with low temperature heat, solar energy, biomass heat, or any waste heat source.[1-5]

Physically, desiccants could be in either liquid or solid state. The most common liquid desiccants include aqueous solutions of hygroscopic salts such as lithium chloride, calcium chloride, and lithium bromide [6, 7]. They are of large vapor absorption capacity and a low vapor saturation pressure compared to solid desiccants. However, their corrosive nature complicates the system to handle them and makes the maintenance cost high [8]. Solid desiccants such as silica gel, molecular sieve, zeolites, etc., can adsorb vapor fast due to large surfaces and are chemically inert, which allows them to be used with simple devices. A polymer, such as hydrogel, is also a great candidate to be a solid desiccant. Hydrogel composite as super solid desiccant was reported by Yang et al. to be one of the competitive solid desiccant options that provide great absorption capacity [9]. However, they still have relatively less absorption capacity when compared to a liquid desiccant [4]. Both liquid and solid desiccants are used in diverse desiccant cooling systems [10].

Desiccant cooling can be a stand-alone cooling method or a supplement to traditional vapor compression air conditioning technology [8]. One of the typical arrangements is called the desiccant wheel, which consists of a slow rotating wheel (8-10 revolutions/h) impregnated or coated with solid desiccant [10-12]. Conventional liquid desiccant cooling systems can be

classified into direct contact and indirect contact systems. Drawbacks of direct contact liquid desiccant cooling include difficulties to prevent the dust in the air stream from contaminating the desiccant solution, and the entrainment of desiccant solution droplets in the air streams as well [10, 13, 14]. Hence, studies have been carried out to investigate the potential of indirect liquid desiccant cooling, which typically involves the circulation of liquid desiccants in membrane-based systems using membranes to separate the liquid desiccants from the air streams [2, 10, 15-17]. It was reported that the liquid desiccant cooling system can potentially reduce 50 to 90% of energy usage even when compared to top-tier commercial vapor cycle products [17-20]. For example, Eldeeb et al. [18] developed a heat and moist transfer ceiling panel for better indoor humidity control with the assistance of a semi-impermeable porous flat-sheet membrane. Simulation results showed a reduced energy cost under different city environments when compared with various commercial HVAC systems [21]. Mahmud et al. [22] proposed a run-around membrane energy exchanger (RAMEE) system consisting of one liquid-to-air membrane energy exchanger in the supply air duct and another one in the exhaust air duct. The system employed flat sheet membranes and was designed to run continuously in a cross-flow pattern at ambient pressure. Tubular membrane [23] and hollow fiber membrane based liquid desiccant air dehumidification systems have also been studied to operate under atmospheric conditions [24].

In another interesting development, vacuum desiccant cooling (VDC), was shown to be effective for personal cooling in our previous studies [25, 26]. This VDC system is designed to operate under vacuum, which provides three major advantages: 1) the mass transfer resistance to the transportation of water vapour molecules from the water surface in the cooling layer is reduced; 2) heat transfer from the hot desiccant layer to the cold water layer is minimized; and furthermore, 3) the impact of ambient conditions to cooling performance is minimized since the

influence of the ambience is limited to the heat dissipation and therefore the temperature of the desiccant layer only. As a matter of fact, the driving force of mass transfer is the water vapor saturation pressure at the temperature of the towel layer minus the saturation vapor pressure at the desiccant surface, either of which are directly dependent of the ambient conditions. It was demonstrated experimentally that the first generation VDC had a cooling capacity of approximately 370 W/m^2 under an ambient temperature of 37°C and a VDC personal cooling garment covering 0.4 m^2 torso area was more effective than a commercial ice pad cooling garment in mitigating the thermal stress of human subjects in an environment of 40°C and 50% relative humidity (RH).

However, the first generation VDC relied on desiccant layers made of lithium chloride (LiCl) powders, which became an aqueous solution after absorbing sufficient amounts of vapor. The complexity of the desiccant layer structure, which was required to prevent LiCl leakage, was one of the major factors that made the first generation VDC bulky, not reusable, and easily breakable. There is, therefore, a great interest in developing desiccants with large capacity, fast kinetics, and easy processing in the context of VDC for personal cooling. In this study, the concept of a novel membrane-based desiccant fiber (MDF) was proven for the first time. Experiments were also carried out to verify the feasibility of its application as the desiccant of choice for a VDC garment, among other potential applications.

7.3 Materials and methods

7.3.1 Materials

Two types of polytetrafluoroethylene (PTFE) hollow fiber membranes specified in Table 7-1 were used because of their inertness to the effects of corrosive LiCl solution and the high thermal stability. Cross-sectional, inner surface and outer surface SEM images of the two studied membrane are shown in Figure 7-1. Lithium chloride supplied by Sigma-Aldrich Inc. was used as the desiccant for its superior vapor absorption capacity.

Table 7-1 Hollow fiber membrane specifications.

Hollow fiber designation	A	B
Manufacturer	Puresea Spring Membrane Technology Co., China	
Mean pore size (μm)	0.3	
Max pore size (μm)	0.6	
Porosity (%)	46	
Weight (g)	0.80	1.30
Internal diameter (d_i , mm)	0.42	0.70
Outer diameter (d_o , mm)	1.04	1.34
Surface area based on membrane log-mean radius $\times 10^{-3}$ (m^2/m)	2.11	3.10
Internal volume (mL/m)	0.14	0.39

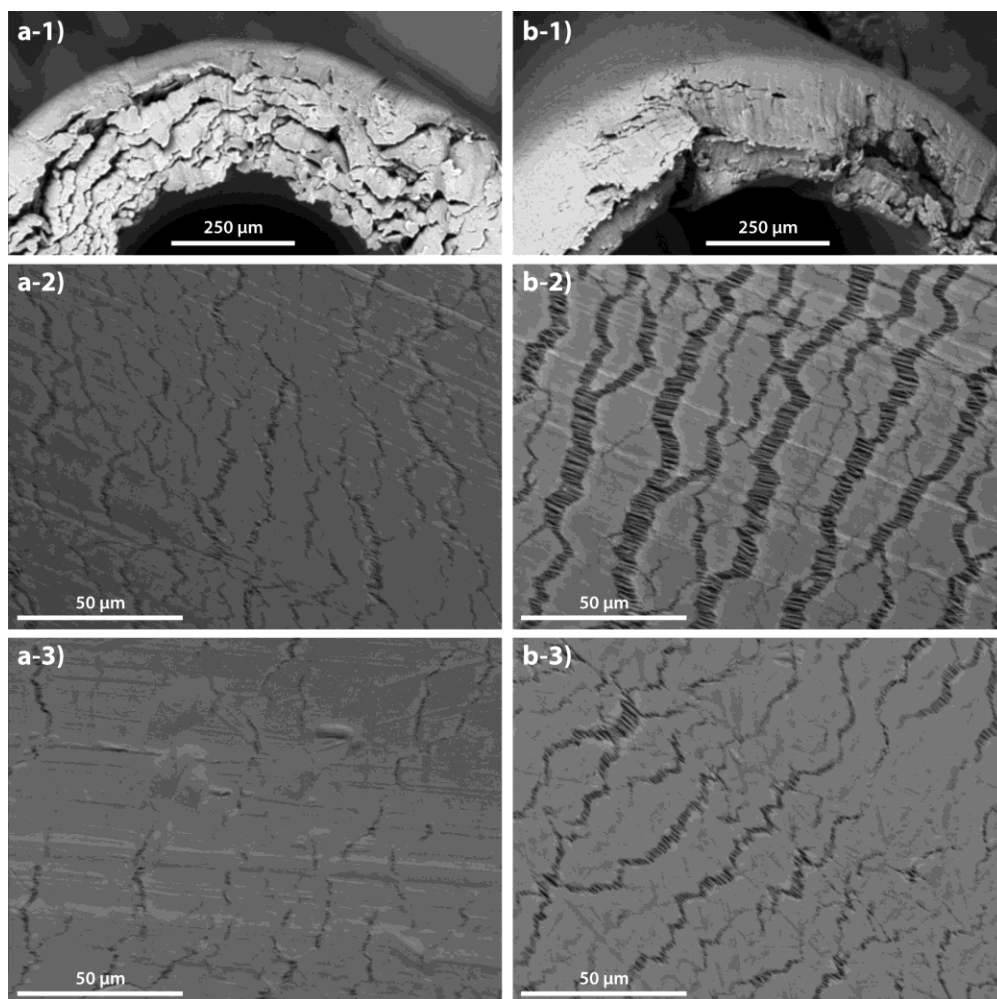


Figure 7-1 Hollow fiber A: a-1, a-2 and a-3 are cross sectional, inside surface and outside surface morphology; hollow fiber B: b-1, b-2 and b-3 are cross sectional, inside surface and outside surface morphology.

7.3.2 Preparation of membrane-based desiccant fiber (MDF)

Hollow fiber (HF) membrane was cut into a desired length (e.g., 1 m) and dried completely before weighing. The weight of the dry HF was recorded as W_{HF} . An aqueous LiCl solution of predetermined concentration was injected into the lumen of the HF, followed by sealing of both ends of the HF by heat sintering. The concentration of the aqueous LiCl solution,

called hereafter the loading solution concentration, was varied as specified in the related texts in the range of 5 to 25 wt.%. The loaded HF was then dried in an oven at 105°C overnight to ensure dehydration of LiCl. The LiCl loaded HF is hereafter called MDF. The weight of the MDF, W_0 , was measured before installing it in the vapor absorption test device or being woven to make MDF pads. Used MDF was regenerated in an oven at 110°C overnight.

7.3.3 Vapor absorption test at ambient pressure for MDF

A vapor absorption test was conducted inside the water bath (programmable VWR Model 1225, Zhejiang Dongda Environment Engineering Co., China) with a lid. The schematic of the test device is shown in Figure 7-2. The temperature of water in the bath was set at 26°C to ensure constant air temperature and humidity within the water bath, $25 \pm 0.2^\circ\text{C}$ and 99%, respectively while the ambience had a temperature of $23 \pm 2^\circ\text{C}$ and a relative humidity of 40-60%. Thermometer and hygrometer were used to monitor the temperature and humidity of the inside space above the water surface inside the water bath, which displayed no significant fluctuation during the testing period. The MDF was placed in the test device for vapor absorption and kept there for 4 h or until the LiCl solution began to leak due to MDF breakage due to vapour over-absorption. In the meantime, the MDF was taken from the test device every 30 min for weighing. The MDF weight is called W_t , where the subscript t indicates the length of the time of MDF's exposure to the humid air. At least 3 replicates were performed for each MDF.

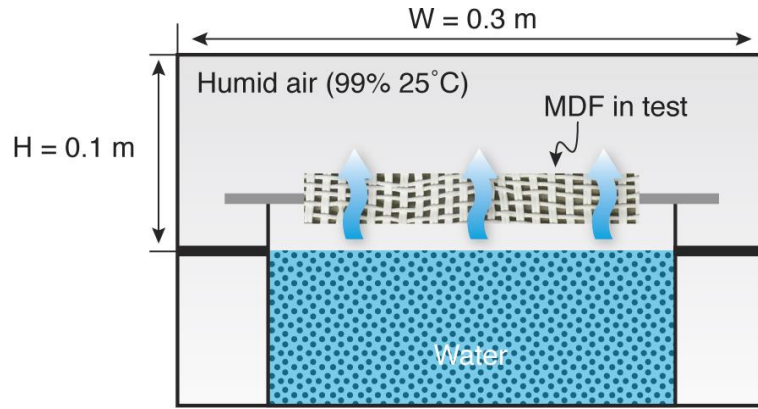


Figure 7-2 Schematics of vapor absorption test device.

The work duration of MDF is defined as the absorption time it takes for small liquid droplets to appear on the surface of MDF after dry MDF is subjected to a particular set of conditions of absorption. In this study, these conditions were absorption at 99% RH and 25°C. The appearance of liquid droplets is determined by careful visual inspection. The choice of 99% RH is to avoid condensation of saturated vapor on the MDF surface while simulating the environment of intended application, i.e., the skin surface of a wearer, which is typically saturated with vapor due to sweat evaporation.

The 2 h absorption capacity, AC_{2h} , is defined as the mass of vapor absorbed by a unit mass of dry MDF at a given condition (i.e., 99% RH and 25°C) during a time period of two hours, (i.e. $t = 2$ in the following equation.)

$$AC = \frac{w_t - w_0}{w_0} \quad (7.1)$$

W_0 and W_t are the weights of MDF at the beginning and the time when leakage occurs in an absorption experiment, respectively.

The 2 h length absorption capacity, LAC_{2h} , is defined as the mass of vapor absorbed by a unit length of dry MDF (L) at a given condition (i.e., 99% RH and 25°C) during a time period of two hours (i.e. $t = 2$ in the following equation).

$$LAC = \frac{W_t - W_0}{L} \quad (7.2)$$

The absorption capacity of MDF is defined as the mass of vapor absorbed by a unit mass of dry MDF at a given condition (e.g., 99% RH and 25°C) when the concentration of the loading LiCl solution is restored inside the MDF. Since any absorption beyond this would very likely lead to leakage of solution from inside the MDF, this is the maximum amount of vapor that could be absorbed by a unit of mass of MDF without risking leakage. This quantity was calculated using equation (7.3):

$$Absorption\ capacity = \frac{V_{hf} * \rho * (1 - C)}{W_0} \quad (7.3)$$

Where V_{hf} is the internal volume of the hollow fiber, ρ is the density of the loading solution, and C is the LiCl concentration (weight fraction) of the loading solution. V_{hf} of a given membrane is estimated according to its length and internal diameter.

The length absorption capacity was calculated according to the absorption capacity of a given MDF using equation (7.4).

$$Length\ absorption\ capacity = \frac{V_{hf} * \rho * (1 - C)}{L} \quad (7.4)$$

7.3.4 Preparation of MDF pad

Desiccant pads were made by weaving MDF into a pad with a dimension of 40 cm × 50 cm (Figure 7-3). The MDF was made by loading 22 wt.% LiCl aqueous solution to PTFE hollow fibre membranes with an ID of 0.7 mm. A total of a 120-meter length of MDF fibres were weaved into each pad, which had a weight of 145±2 g each. A total of 10.5±0.3 g LiCl was loaded with the MDF at a loading rate of 0.071 g LiCl/g MDF.

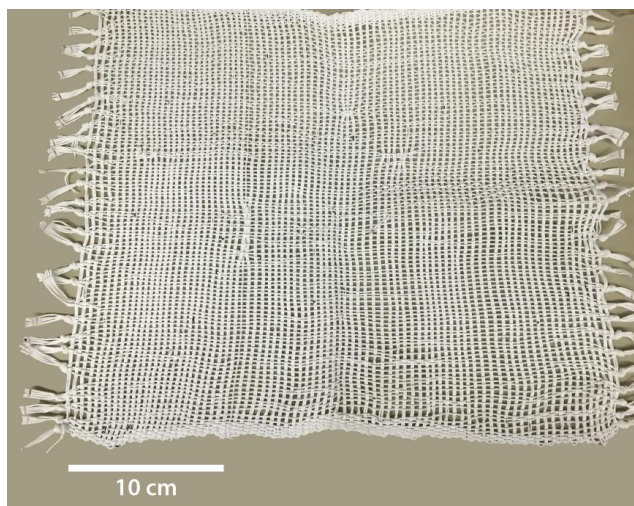


Figure 7-3 Weaved MDF pad by loom.

7.3.5 Vacuum vapor absorption test for MDF pad

A single MDF pad, as described in Section 7.3.4, was folded into four layers and used as the desiccant pad. A cooling towel (Endura Cool, Mission Athletecare™, NY), which was folded into three layers and soaked with 50 g of distilled water, was employed as the water reservoir. A vacuum desiccator (Pyrex 3120, Cole-Parmer), which was connected to a vacuum pump (WZ-07061-11, Cole-Parmer) that could generate a theoretical maximum vacuum of 29-inches of Hg, was used to house the desiccant layer and the water reservoir. The desiccator is a 3.8-liter vessel

made of borosilicate glass (Pyrex) with a conic cover that ends in a cylindrical form where a Pyrex rugged stopcock was installed. The stopcock had a tube connection of 10 mm OD (outside diameter), which allowed thick vacuum tubing to connect the desiccator and the pump. To maintain a tight contact between the detachable parts of the vacuum desiccator during an operation, vacuum grease was put on the edges of the vessel; and also on the stopcock and the cylindrical top part of the cover, opposite from each other. A liquid nitrogen cold trap was installed between the desiccator and the vacuum pump in order to retain water vapor to prevent damaging the vacuum pump. A glass vacuum valve was installed on the tubing connecting the vacuum pump and the desiccator.

Before a VDC test, the initial weights of a dried desiccant pad and a cooling towel (Endura Cool, Mission Athletecare™, NY) soaked with 50 g of distilled water were measured with a balance and recorded. Then, the cooling towel was placed at the bottom of the desiccator, and the desiccant pad was placed on the perforated plate of the desiccator before putting the lid of desiccator back and sealing the system. The vacuum pump was then turned on to allow the system to reach the desired vacuum degree. This typically took approximately 5 minutes, before turning it off. The weights of the cooling towel and desiccant pad were measured and recorded every 15 mins, and the whole system was re-evacuated every time after weighing the samples, requiring the opening of the desiccator lid. After the absorption test, the desiccant pad was regenerated in a conventional oven (Precision Model 18EG at 105°C) for 12 h. VDC experiments were carried out at atmospheric pressure and a vacuum of 25 inches of Hg.

7.4 Results and discussion

7.4.1 Time-course profile of vapor absorption at ambient pressure

Figure 7-4 depicts the time course profiles of vapor absorption with MDF made of PTFE hollow fibres of 0.42 and 0.70 mm, respectively, by loading with LiCl solutions of varied concentrations. As shown in Table 1, the internal volume of the 0.70 mm membrane was 0.39 ml/m, 2.78 times that of the 0.42 mm membrane (i.e., 0.14 ml/m). As a result, about 2.78 times the amount of LiCl could be loaded on to a 0.70 mm membrane in comparison to the 0.42 mm membrane when the same loading solution concentration was used (Table 7-2). Quite reasonably, absorption of vapor was much faster with the 0.70 mm MDF than with the 0.42 MDF. For the same membrane, as also shown in Figure 7-4, vapor absorption improved with the increase in loading LiCl concentration. It is worth noting, however, that membrane leakage would happen if too much vapor was absorbed. This is because the PTFE hollow fibre membrane, although capable of holding water and aqueous solution due to its hydrophobic nature, cannot hold the liquid if the pressure inside in the membrane is increased beyond the liquid entrance pressure (LEP) of the membrane. As can be seen from Figure 7-4, leakage occurred at 2.0 and 3.5 h with 0.42 mm MDF when the loading solution was 20 and 15%, respectively (Figure 7-4a). For the 0.70 mm MDF, leakage occurred at 1.5, 2.5 and 3.5 h in the absorption process when the loading solution concentration was 25, 22, and 20%, respectively. Small liquid droplets would appear on the MDF surfaces when leakage happened. Leakage is defined as the appearance of sweat, i.e., small liquid droplets of LiCl aqueous solution, at the MDF surface. Leakage is the consequence of the increase of the volume of the LiCl aqueous solution inside the MDF hollow fibre membrane as a result of vapor absorption.

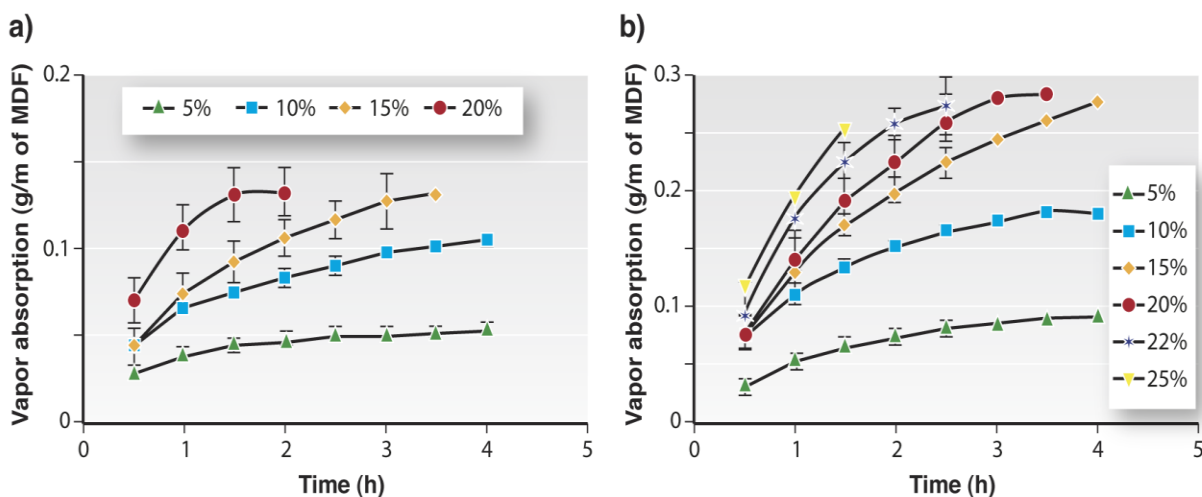


Figure 7-4 Vapor absorption of MDF with an ID of (a) 0.42 mm and (b) 0.70 mm when loaded with LiCl aqueous solution of different concentrations. (Absorption tests stopped at the point when sweat was detected at the MDF surface if the last data point was at 3.5 h or less).

Table7-2 Summary of key parameters of MDF made of two different membranes with varied loading LiCl solution concentrations.

Loading solution concentration (w/v)		5%	10%	15%	20%	22%	25%
Loading solution density (g LiCl/ml)		1.01	1.03	1.05	1.08	1.09	1.10
Length LiCl Loading (mg LiCl/m MDF)	ID 0.42 mm	7	14	22	30		
	ID 0.70 mm	20	40	61	83	92	106
Mass LiCl loading (mg LiCl/ g MDF)	ID 0.42 mm	8	16	24	33		
	ID 0.70 mm	16	32	48	64	71	81
Absorption capacity (mg vapor/g MDF)	ID 0.42 mm	151	144	138	131		
	ID 0.70 mm	303	288	273	258	252	243
Length absorption capacity (mg vapor/m MDF)	ID 0.42 mm	134	129	125	120		
	ID 0.70 mm	371	358	345	332	326	318
2 h Absorption capacity (mg vapor/ g MDF)	ID 0.42 mm	50	90	120	140		
	ID 0.70 mm	60	120	160	170	200	210
2 h Length absorption capacity (mg vapor/m MDF)	ID 0.42 mm	50	80	110	130		
	ID 0.70 mm	70	150	200	230	260	270
Work duration (h)	ID 0.42 mm	>24	>24	3.5-4.0	2.0-2.5		
	ID 0.70 mm	>24	>24	4.0-4.5	3.0-3.5	2.0-2.5	1.5-2.0

The leakage of corrosive LiCl onto the outside of the MDF would not only cause the loss of absorption capacity but, more seriously, contamination of equipment or irritation to the skin of the wearer if the MDF is to be used for making personal cooling garments. The time at which leakage occurs defines the maximum period of time the MDF could be used before regeneration.

Table 7-2 summarizes some key parameters of MDF made from PTFE hollow fibre membranes with two different IDs, i.e., 0.42 and 0.70 mm at varied LiCl loadings. The loading of LiCl was varied because 1) membranes of different ID would have been able to be loaded with different volumes of LiCl solution for a unit length and 2) for the same membrane, the concentration of loading LiCl solution would determine the total amount of LiCl to be loaded per unit length of membrane (g LiCl/m MDF). Furthermore, since different membranes have different weights per unit length, the LiCl loading on the basis of weight (g LiCl/g MDF) also varied accordingly.

As shown in Table 7-2, the length LiCl loading (grams of LiCl loaded to per meter of MDF) and the mass LiCl loading (grams of LiCl loaded per gram of MDF) increased proportionally with the concentration of loading LiCl solution for the same membrane. Furthermore, the LiCl loading was much larger with the 0.7 mm membrane than with the 0.42 mm membrane when the same loading solution was applied, due to the much larger volume of solution that could be loaded with the former. Quite logically, both the 2 h length of vapor absorption capacity (grams of vapor absorbed per metre of MDF in 2 h) and the 2 h mass absorption capacity (i.e., grams of vapor absorbed per gram of MDF in 2 h) followed similar trends.

It should be pointed out that the absorption capacity, is defined as the amount of vapor to be absorbed by a unit mass of MDF when the LiCl solution inside the fibre is the same as the loading LiCl solution which decreased with the increase of the concentration of loading LiCl solution when the loading solution concentration was restored inside the MDF. This is reasonable because the higher the concentration of the loading solution, the less portion of water in the solution when the volume of the loading solution was fixed as the internal volume of a given MDF. It is important to notice that, when the vapor absorption approaches the absorption capacity, the volume of the LiCl solution inside the membrane would also approach the original loaded volume. If the absorption is continuous beyond this point, the volume of solution would become larger than the internal volume of the MDF and leakage might occur. The membranes used in this study were hydrophobic microporous hollow fibers, which could withhold water or aqueous solution when the transmembrane pressure was smaller than the liquid entrance pressure of water or the solution, respectively. Since a small increase of liquid volume would cause a dramatic increase of pressure inside a confined compartment such as the lumen of MDF, the solution inside a MDF would leak out through the micro membrane pores if the absorption exceeded the absorption capacity. It is, therefore, recommended that the vapor to be absorbed by MDF is kept lower than its absorption capacity. In other words, MDF should be regenerated before the maximum absorption capacity is reached to avoid possible leakage. If necessary, it is recommended to load the MDF with a LiCl aqueous solution of 10 wt% or less to minimize the risk of leakage even during a long time work period.

As also shown in Table 7-2, the working duration of MDF for both IDs was more than 24 h when the loading solution concentration was 10 wt% or lower. This can be explained by the fact that LiCl aqueous solution at a concentration of 10 wt% or less has a very small affinity for

vapor, and the absorption of vapor occurred at a much reduced rate before the absorption capacity was reached. On the other hand, for the MDF with a loading LiCl concentration of 20 wt% or higher, the work duration was limited to 3 h or less.

It should be pointed out, that although the LiCl inside fresh or newly regenerated MDF is usually solid, it soon becomes an aqueous solution after vapor absorption starts. It is, therefore, more appropriate to classify MDF as a novel liquid desiccant. It should also be pointed out that much larger absorption capacities of long work duration could be achieved by using a hollow fiber membrane of larger internal diameter. MDF, therefore, offers a range of versatile desiccants whose use could be custom designed for different applications. The large membrane surface also allows quick absorption kinetics using the MDF.

7.4.2 Suitability of MDF for application in a VDC

As discussed earlier, researchers have studied this specific subject extensively and have developed several membrane assisted liquid desiccant dehumidification/ cooling systems recently. These studies included very different configurations. Air flow and desiccant flow can be in a hexagonal parallel membrane channel (HPMC) modified counter flow setup [27], a counter flow setup [28], or a cross flow setup [29, 30], etc., which are all continuous systems. These systems, however, usually require relatively large and heavy equipment such as circulation pumps, piping, valves, regeneration units, air blowers, etc. Therefore, most of the conventional membrane desiccant systems are not suitable for personal VDC application because these are oversize and overweight [30].

The aforementioned personal VDC garment developed in our group consists of four main components: a desiccant layer, a spacer, a water layer, and an outer bag [26]. This VDC garment is designed to operate in a batch mode with initialization by a vacuum pump in the beginning and able to operate for a given period of time free of electricity or any moving parts before the desiccant layer is regenerated and the water reservoir recharged. In this way, the advantages associated with a continuous membrane-based liquid desiccant dehumidification/cooling system are traded for a batch mode lightweight and man-portable system. The desiccant for such a system needs to satisfy the following conditions: 1) sufficiently large vapor absorption capacity to support the VDC for a given work period (typically 1-4 h) with a limited weight; 2) easy to handle in the context of VDC; 3) easily to regenerate; and 4) safe, flexible and comfortable to wear.

In comparison with the aforementioned desiccant pad, which is essentially made of LiCl powder capsuled in a fabric bag, the MDF utilizes microporous hydrophobic hollow fiber membranes to house LiCl and provide the surface for vapour absorption. As demonstrated in this study, these MDF could be easily woven into a desiccant pad that is flexible, robust and conveniently regenerable. As a result, MDF can make the VDC reusable, simple structured, and significantly miniaturized, as the woven MDF pad has very large contact surface for effective absorption. Its great flexibility would allow easy processing and regeneration and also provide comfort to wearers.

In the current study, a MDF pad was woven to verify its flexibility and processability in the context of VDC fabrication. A garment-like MDF pad as shown in Figure 7-3 and is perfect for this purpose. As discussed before, the leakage could be prevented by controlling the loading

LiCl to be 10 wt.% or lower. In addition and as noted previously, the capacity of MDF is determined by the inner diameter (ID) of the hollow fibre membrane, which could be varied according to the need. For instance, as shown in Table 7-2, a MDF of 0.7 mm ID is loaded with 10% LiCl solution, containing an absorption capacity and length absorption capacity of 288 and 358 mg/m, respectively. If we double the ID to 1.4 mm, which is easily achievable, then the capacities will be quadrated to 1.152 and 1.432 mg/m, respectively, when other conditions remain the same. Furthermore, to verify the suitability the MDF pad as the desiccant layer in a VDC, a laboratory VDC setup was designed and tested with a MDF pad to simulate the desiccant layer, with a cooling towel soaked with distilled water as the water layer, a perforated plate as the spacer, and the vacuum desiccator as the outer bag to house water evaporation/vapor absorption. In comparison to an actual VDC garment, this device provided the convenience of vacuum control as well as measurements of water evaporation and vapor absorption. However, the distance between the MDF pad and cooling towel was too large to be representative of the scenario in a VDC garment, where these two layers are to be separated from each other by a thin separator. Nevertheless, the data obtained were able to demonstrate the feasibility of the MDF in applications such as VDC.

Figure 7-5 shows (a) the impacts of vacuum on the time-course profiles of water evaporation of the cooling towel, and (b) the temperatures of both the desiccant pad and the cooling towel when a VDC setup was tested in a sealed desiccator. As shown in Figure 7-5a, the amount of water evaporation every 15 minutes was always higher at 25 inches of Hg than at atmospheric pressure. This was expected because the vacuum would enhance the water evaporation and also reduce the resistance to mass transfer of vapor molecules from the cooling towel surface to the desiccant surface.

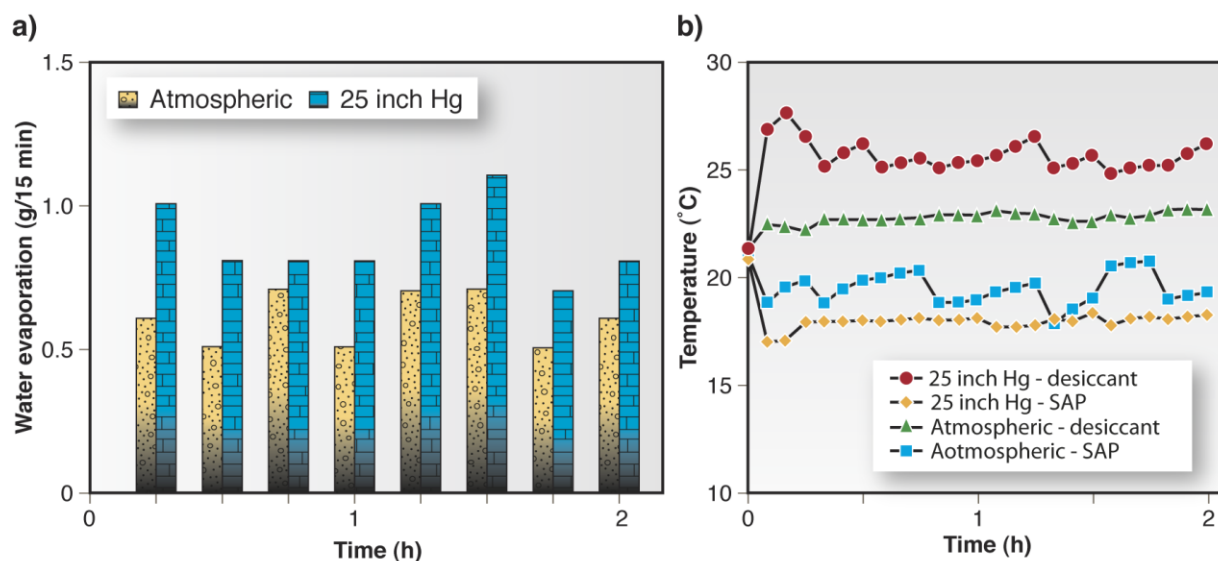


Figure 7-5 (a) The time-course profiles of water evaporation of the cooling towel layer and (b) the temperatures of both the cooling tower and desiccant layers of a VMD lab setting at different vacuum degrees (i.e., atmospheric pressure and 25 inches of Hg).

It is also worth noting that the water evaporation, although fluctuating from time to time, was stable in the range of 0.7 – 1.0 g per 15 minutes at 25 inches of Hg vacuum and 0.5 – 0.7 g every 15 minutes at atmospheric pressure during the entire course of 2 h of experimentation, indicating that the desiccant pad was far from being saturated.

It should be mentioned that the water evaporation from the cooling towel was slightly but constantly higher than the vapor absorption from the desiccant pad in all the VDC tests. This can be explained by the fact that vapor molecules would be lost to the desiccator space, tubing, and the vacuuming process as well.

As shown in Figure 7-5b, for the test at 25 inches of Hg vacuum, the temperature of the desiccant pad increased in the beginning of the experiments but reached the highest temperature within 5 minutes. The desiccant pad temperature then remained stable at around 26°C throughout the 2 h test, with minor fluctuations. This indicates that the heat generation of the desiccant pad

due to vapor absorption quickly reached a balance with the heat dissipation to the surroundings. Likewise, but in opposite direction, the temperature of the cooling towel decreased quickly in the beginning and reached the lowest temperature within 5 minutes. The temperature was then stabilized at around 18°C, which is a temperature suitable for personal cooling, throughout the test with minor fluctuations. In other words, a temperature difference of approximately 8°C was maintained between the desiccant pad and the cooling towel within the VDC structure under the specified conditions. For the test at atmospheric pressure, similar trends were observed but the temperatures of the desiccant pad and the cooling towel were maintained at approximately 23 and 20°C, respectively, representing a temperature difference of about 3°C.

The desiccant layer heated up due to the release of the heat of absorption, which is composed of heat of condensation and heat of dilution. As a result, the temperature of the desiccant layer was higher than the ambient as soon as of the vapour absorption started. It is worth noting that the desiccant layer will be facing the ambience while the cooling towel side the skin of wearer in the practical application of a VDC garment. Consequently, the heat from the desiccant side will have minimum impact on the wearer due to the thermal insulation provided by the vacuum gap separating the cooling towel from the desiccant pad. Furthermore, as long as the MDF pad is replaced before it reaches a pre-determined degree of saturation, the system will be able to provide a relatively consistent cooling performance.

The much larger temperature difference that could be achieved at 25 inches of Hg, in contrast to atmospheric pressure, reflects the larger water evaporation from the cooling towel and vapor absorption by the desiccant pad due to reduced mass transfer resistance at vacuum. It can

also be partially attributed to the improved thermal insulation between the hot desiccant pad and the cold cooling towel due to the existence of vacuum

The PTFE membrane used for MDF is very strong mechanically and inert chemically. Comparing to the first generation VDC system [26], the MDF desiccant fiber can be leakage proof within certain limitation. For instance, according to the experimental results, the following precautions could be taken to prevent over-absorption of vapour, which is the cause of leakage: 1) use a loading LiCl aqueous solution of 10 wt% or less, which would the resulting MDF to work for more than 24 h without leakage; 2) strictly limit the actually work period to be significantly shorter than the theoretical work period.

7.4.3 Mass and heat transfer analysis in vapor absorption process by MDF

As shown in Figure 7-6, the mass/vapor transfer direction is from the outside to the inside of the MDF fiber due to a partial pressure difference. On the other hand, the direction of the heat of absorption released in the process of vapor absorption is from the inside to the outside of the MDF fiber. The analysis is performed at steady state. Mass transfer resistance is mainly due to the membrane layer, and therefore is assumed as constant in the following calculation.

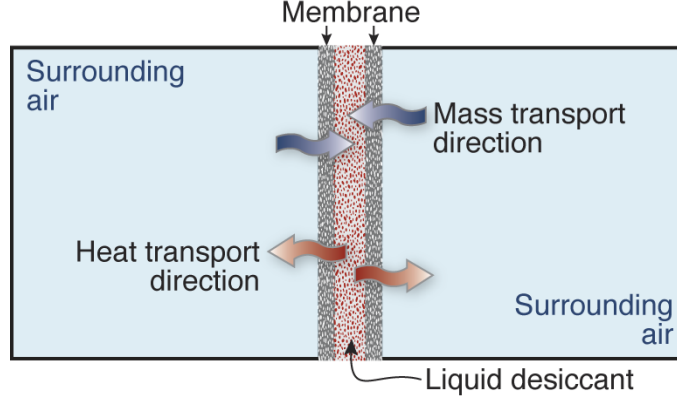


Figure 7-6 Schematic illustration of a heat and mass transfer model in the hollow fiber membrane.

7.4.3.1 Mass transfer

We assume the mass transfer resistance is mainly due to the membrane, therefore the rate of vapor absorption by MDF is given by:

$$\frac{w_t - w_0}{t} = K_m A_{log} (P_{\infty} - P_{sol}) \quad (7.5)$$

Where A_{log} is the membrane area based on the logarithmic mean hollow fiber diameter, K_m is the mass transfer coefficient of vapor. P_{∞} is the partial vapor pressure in the surrounding air corresponding to 99% saturation at 25°C, which can be calculated by Antoine's equation to be 3.14 kPa. P_{sol} is the vapor pressure in equilibrium with the LiCl solution in MDF. It can be calculated as a function of the weight fraction of LiCl in the solution, ω , and the temperature of the LiCl solution, T_{sol} by the following equations (7.6-7.10) [32].

$$P_{sol}(\omega, T_{sol}) = \pi * P_{water}(T_{sol}) = \pi_{25} * f(\omega, T_{sol}) * P_{water}(T_{sol}) \quad (7.6)$$

$$f(\omega, T_{sol}) = A + B * T_r \quad (7.7)$$

$$A = 2 - \left(1 + \left(\frac{\omega}{\pi_0}\right)^{\pi_1}\right)^{\pi_2} \quad (7.8)$$

$$B = \left(1 + \left(\frac{\omega}{\pi_3}\right)^{\pi_4}\right)^{\pi_5} - 1 \quad (7.9)$$

$$\pi_{25} = 1 - \left(1 + \frac{\omega}{\pi_6}\right)^{\pi_7} - \pi_9 \exp\left(\frac{-(\omega-0.1)^2}{0.005}\right) \quad (7.10)$$

Where Tr is the reduced temperature and π_1 to π_9 are constants, the values of which are cited from the literature [32]. The value of ω , the concentration of LiCl of the aqueous solution inside MDF at time t , was determined by the following equation:

$$\omega = \frac{W_0 - W_{HF}}{W_t - W_{HF}} \quad (7.11)$$

The mass transfer coefficient, K_m (g/m² s Pa), is given by equation (7.12). The first term is the Knudsen diffusion coefficient, $K_{knudsen}$. The second term is the viscous flow coefficient, $K_{viscous}$. The dominant mass transfer machnism can be determined by the calculation of the Knudsen number, Kn , which is the ratio of the mean free path of transporting molecules, i.e. water molecules, to the pore diameter, d . The mean free path for water vapor molecules can be calculated by equation (7.13). When $Kn > 10$ or $d < 0.1 \lambda$, the mean free path of water molecules is large compared to the membrane pore size, which means the molecule-pore wall collisions are dominant over molecule-molecule collision. This flow regime is known as the Knudsen diffusion.

When $K_n < 0.01$ or $d > 100 \lambda$, the mean free path of the molecule is much smaller than the pore size, the molecule-molecule collisions will dominate and the mass transfer in the membrane pores is by the viscous flow. When $0.01 < K_n < 10$, the mass transport is in the transition region.³³ Based on the maximum pore size of 0.6 μm , K_n is 0.22; Hence, it belongs to the transition region.

$$K_m = K_{knudsen} + K_{viscous} = \frac{2}{3} \frac{r\varepsilon}{\tau\delta} \sqrt{\frac{8M}{\pi RT}} + \frac{r^2 \varepsilon M p}{8\tau\delta\mu RT} \quad (7.12)$$

Where ε (-), τ (-), r (m) and δ (m) are membrane porosity, pore tortuosity, pore radius and thickness, respectively. M (18.02 kg/kmol) is the molecular weight of water, μ (Pa s) is viscosity of water vapor and R (8.314 x 10³ J/kmol K) is the universal gas constant.

$$\lambda = \frac{k_B T}{\sqrt{2} \pi p d_p^2} \quad (7.13)$$

Where k_B (J/K), T (K) and p (Pa) are the Boltzmann constant, absolute temperature, and average pressure within the membrane pore, respectively, and d_p (m) is the collision diameter of the transporting molecule (2.641 Å for water molecule). At 1 bar and 25°C, $\lambda = 1.311 \times 10^{-7}$ m.

7.4.3.2 Heat transfer

When the vapor transported through the membrane is absorbed by the LiCl solution, heat of absorption (= heat of condensation h_c (2400 J/g (water)) + heat of dilution, h_d (380 J/g (water))) is released. This heat generation is balanced out by the increase in the sensible heat of LiCl solution and heat dissipation through the membrane, to the ambient environment (99%, 25°C). Hence the heat transfer is given by equation (7.14).

$$\frac{W_t - W_0}{t} (h_c + h_d) = \frac{W_t - W_0}{t} C_p (T_{sol} - T_{\infty}) + U A_{log} (T_{sol} - T_{\infty}) \quad (7.14)$$

C_p is the specific heat capacity of water (4.18 J/g K). U (W/m²K) is the overall heat transfer coefficient, A_{log} (m²) is the contact area for mass and heat transfer, and T_{sol} and T_{∞} are the temperature of the lithium chloride solution in MDF and the temperature of the surrounding air, respectively.

Comparing the left side and the first term of the right side of equation (7.14), the minimum amount of water absorbed in 2 h was 0.05 g, evolving 139 J. On the other hand, the maximum amount of absorbed water was 0.25 g, when the temperature was increased within 2 h by 20 K. Therefore, the maximum increment in the sensible heat is 21 J. Judging from this conservative estimation, it is safe to ignore the first term of the right side of equation (7.14). In other words, most of the heat released by vapor absorption by LiCl solution is dissipated to the surrounding air.

Based on the assumption of the constant overall mass transfer coefficient U , an attempt is made to obtain the U value by the following steps.

For a given LiCl loading concentration of 5 wt%,

- 1) K_m is calculated by equation (7.12) for 298.2 K.
- 2) From the slope of the absorbed amount of vapor W_t between time 0 and 0.5 h, $\frac{W_t}{t}$ is calculated.
- 3) P_{sol} is calculated by equation (7.6). This P_{sol} is considered to represent the solution vapor pressure prevailing between 0 and 0.5 h.
- 4) ω is calculated for 0 and 0.5 h by equation (7.11) and averaged. This ω is considered to represent the concentration of LiCl solution inside the MDF between time 0 and 0.5 h.
- 5) Using the P_{sol} and ω , obtained at step 3 and 4, respectively, T_{sol} is calculated using equations (7.6) to (7.10). This T_{sol} is considered to represent the LiCl solution temperature between 0 and 0.5 h.
- 6) Then U is calculated by equation (7.14) ignoring the first term of the right side of the equation.
- 7) Steps 1) to 6) are repeated for the time intervals (0.5 to 1.0 h), (1.0 to 1.5 h) and (1.5 to 2.0 h).
- 8) The U values obtained by the above steps are then averaged.
- 9) Steps 1) to 8) are repeated for the other LiCl loading concentrations and all the resulting U values are compared.

7.4.3.3 Heat transfer coefficient at different LiCl loadings

Figure 7-7 shows that, U increased significantly from 1.0 to 2.3 W/m²K when LiCl loading increased from 5 to 10 wt.% LiCl loading and then U levels off. This is likely due to the higher T_{sol} at the higher LiCl loading, which leads to the decrease in solution viscosity and as a consequence, an increase in heat transfer coefficient. Indeed, when T_{sol} is calculated by equation (11), using the average of all U values recorded in Figure 7-7. T_{sol} increases with an increase in LiCl loading as shown in Figure 7-8.

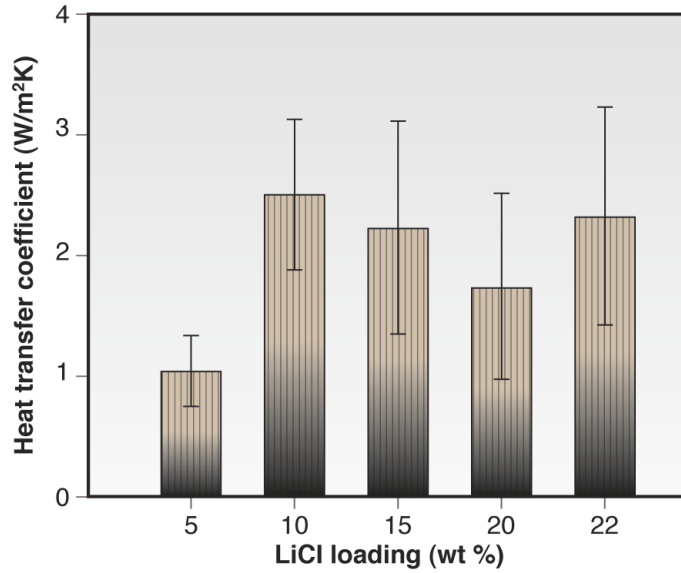


Figure 7-7 Average heat transfer coefficient changes with LiCl loading.

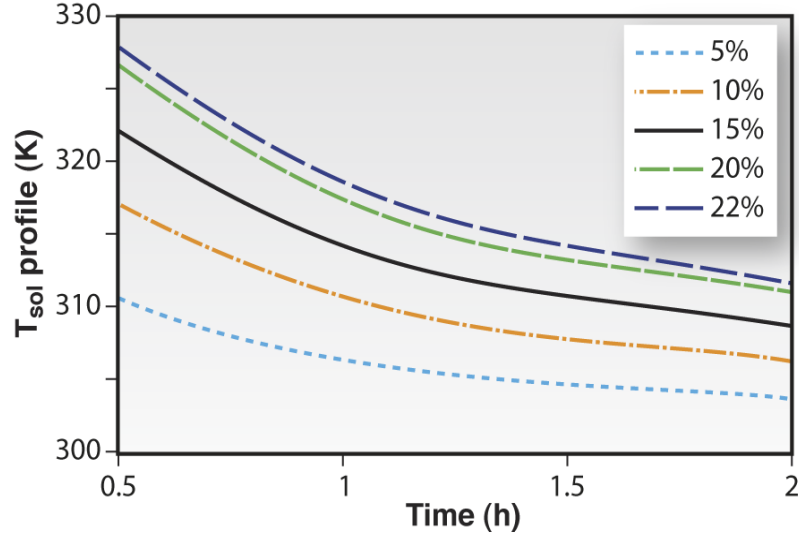


Figure 7-8 Solution temperature profile changes with LiCl loading.

The viscosity of Newtonian fluids is affected by temperature, pressure and concentration in the case of solutions. For liquids, Ling and Dybbs [34] suggested that viscosity changes are inversely proportional to temperature T . Thus, higher LiCl loading leads to higher T_{sol} , and smaller viscosity means reduced heat transfer resistance, resulting in higher heat transfer coefficients.

7.4.3.4 Prediction at different ambient relative humidity at 25 °C for 22%

An attempt was then made to predict the absorption performance (g water absorbed /m of MDF) for a given LiCl loading of 22 wt.% at different ambient RHs. In the above mentioned Figure 7-7, U scatters, even for a given LiCl loading of 22 wt.%, in a wide range, which is caused by the change of U with the vapor absorption time. Therefore, U versus natural logarithm

time (h) was plotted and a linear correlation was found between Ln time and U , as shown in Figure 7-9. U versus T_{sol} was also plotted in Figure 7-10.

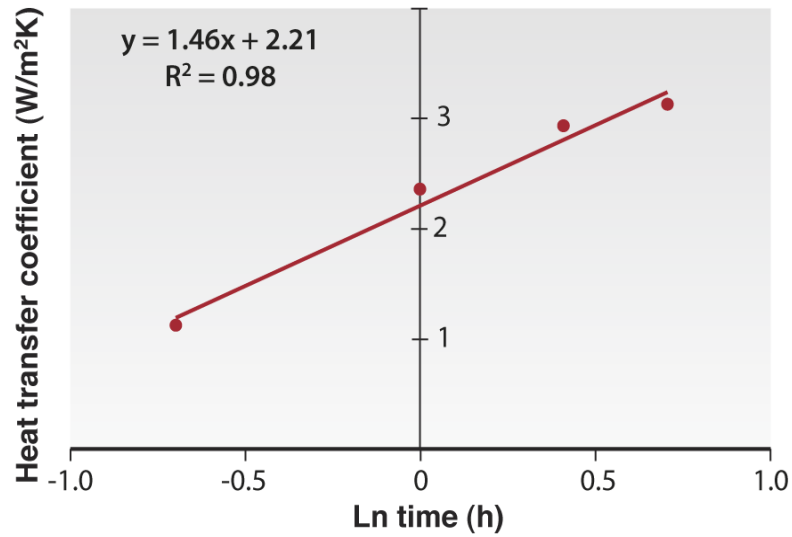


Figure 7-9 Heat transfer coefficient change with time for 22 wt.% 0.7 mm MDF.

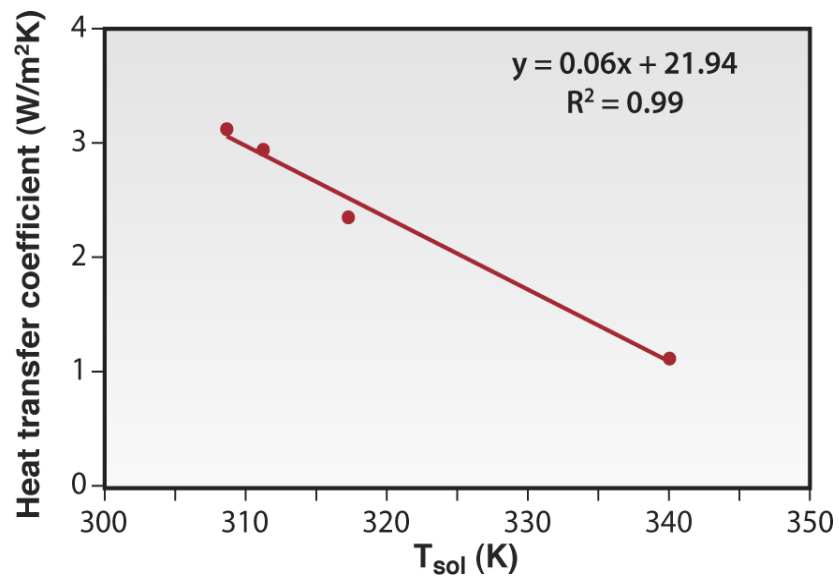


Figure 7-10 Heat transfer coefficient changes with solution temperature for 22 wt.% 0.7 mm MDF.

One might ask why U increases while the T_{sol} decreases with time. The reason is that the solution viscosity as well as U is in fact the function of not only T_{sol} but also LiCl concentration which decreases as a larger amount of water is absorbed with time. The U relationship with time on the linear correlation line from Figure 7-9 was then used to predict the absorption capacity at different ambient relative humidity ($U = 1.46 \cdot \ln(T) + 2.21$). This is assuming that U is only the function of LiCl loading (fixed to 22 wt.%) and absorption time without dependence upon the ambient RH. The results of the calculation are shown in Figure 7-11.

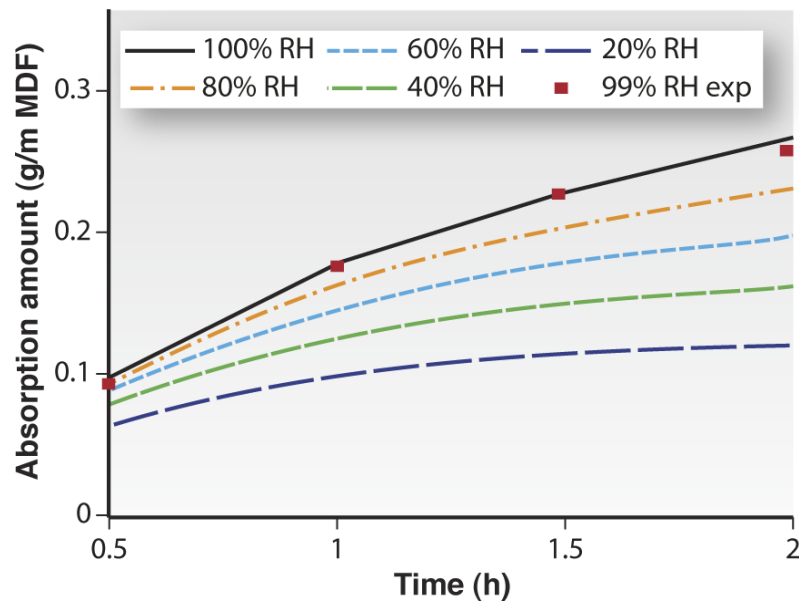


Figure 7-11 Absorption amount prediction for 22 wt.% loading 0.7 mm MDF at different ambient relative humidity.

It is worth noting that, absorption under lower ambient relative humidity leads to a smaller driving force as described by equation (7.5), therefore decreasing the absorption rate, and

as a consequence, decreasing the T_{sol} . The relationship found in Figure 7-10 was based on 99% RH experimental results, which has the highest T_{sol} among other RH tests, suggesting the lowest U values. Thus, the MDF absorption amount prediction shown in Figure 7-11 is the minimum absorption amount in the corresponding RH.

7.5 Conclusions

A novel desiccant, MDF, was developed by loading hydrophobic hollow fiber membranes with LiCl aqueous solution of appropriate concentrations, and then shown to be suitable for applications such as in VDC, which has great potential for applications such as personal cooling. MDF was able to absorb large quantities of vapor under different conditions. For instance, the 2 h absorption capacity and vapor absorption capacity of a MDF made by loading 0.7 mm ID hollow fiber with 22 wt.% LiCl solution were 200 mg/g MDF and 251.6 mg/g MDF, respectively. The capacity could be further increased by using hollow fiber of a larger internal diameter.

The desiccant pad was tested as the desiccant layer in a laboratory VDC setup together with a cooling towel as the water reservoir. Results indicate that, when a vacuum of 25 inches of Hg was applied, the cooling towel could be maintained at a temperature of around 18°C, which is ideal for personal cooling, while the desiccant pad temperature was maintained at around 26°C. On the other hand, the same VDC operating under atmospheric pressure would only be able to maintain a cooling towel temperature of 20°C and a temperature difference of 3°C, reflecting a scenario of much a lower level of thermal insulation.

It is fair to expect a reduction of cooling effect of the VDC garment made of MDF with time, as the aqueous desiccant LiCl solution ability to absorb water vapor decreases due to its temperature rise and dilution of capsuled solution according to both the experimental data showing in Fig. 4 and the predicted data depicted in Figure 7-11. Nevertheless, due to the excellent thermal insulation provided by the vacuum, which separates the desiccant layer and the cooling towel in a VDC pad, the desiccant temperature would not have direct impact on the cooling performance of VDC, which is primarily relied on the cold water contained in the cooling towel due to continuous water evaporation. The reduction of cooling performance could be avoided by more frequent regeneration of the MDF pad or use of MDF of larger capacity, which are to be tailored according the actual need of particular applications.

Studies with VDC garments made of MDF pads as the desiccant layer and water absorption towel as the water reservoir with human subject tests are under way in our lab. Further studies with MDF made of hollow fibre membranes of different materials and larger internal diameters are warranted.

■ Nomenclature

AC	Mass of vapor absorbed by a unit mass of dry MDF at a given condition
A_{log} (m ²)	Membrane area based on logarithmic mean hollow fiber diameter
C_p (kJ/kg*K)	Specific heat capacity of water (4.18 J/g K)
h_c (kJ/kg)	Heat of condensation
h_d (kJ/kg)	Heat of dilution
K_m (g/m ² skPa)	Mass transfer coefficient of vapor
LAC	Mass of vapor absorbed by a unit length of dry MDF (L) at a given condition
P_{∞} (kPa)	Partial vapor pressure in the surrounding air corresponding to 99% saturation at 25°C (3.14 kPa)
P_{sol} (kPa)	Partial vapor pressure in equilibrium with the LiCl solution in MDF
t (h)	Operation time during test
T_{air} (K)	Temperature of ambient air
T_{sol} (K)	Temperature of the lithium chloride solution inside of MDF
U (W/m ² K)	Overall heat transfer coefficient

V_{hf}	Internal volume of the hollow fiber
W_0, W_t (g)	Weights of MDF at the beginning and the time when leakage occurs in an absorption experiment, respectively
<i>Greeks</i>	
ω (wt %)	Concentration of LiCl of the aqueous solution inside MDF at time t
ρ (kg/m ³)	Density of the loading solution
λ (m)	Mean free path for water vapor molecules

■ Acknowledgement

Hollow fiber membranes provided by Dr. Zhaohui Wang from Department of Chemical Engineering, Nanjing Tech University, China, is gratefully acknowledged.

■

7.6 References

- [15] Woods, J.; Kozubal, E. Combining Liquid Desiccant Dehumidification with a Dew-point Evaporative Cooler: A Design Analysis. *HVAC R. Res.* **2013**, *19*, 663–675.
- [16] Bassuoni, M. M. Experimental Performance Study of a Proposed Desiccant Based Air Conditioning System. *J. Adv. Res.* **2014**, *5*, 87–95.
- [17] Huang, S.; Zhang, L. Researches and Trends in Membrane-based Liquid Desiccant Air Dehumidification. *Renew. Sust. Energ. Rev.* **2013**, *28*, 425–440.
- [18] Sultan, M.; El-Sharkawy, I. I.; Miyazaki, T.; Saha, B. B.; Koyama, S. An Overview of Solid Desiccant Dehumidification and Air Conditioning Systems. *Renew. Sust. Energ. Rev.* **2015**, *46*, 16–29.
- [19] Abdel-Salam, A. H.; Ge, G.; Simonson, C. J. Performance Analysis of a Membrane Liquid Desiccant Air-Conditioning System. *Energy Build.* **2013**, *62*, 559–569.
- [20] Liu, X. H.; Jiang, Y.; Yi, X. Q. Effect of Regeneration Mode on the Performance of Liquid Desiccant Packed Bed Regenerator. *Renew. Energ.* **2009**, *34*, 209–216.
- [21] Wang, X.; Cai, W.; Lu, J.; Sun, Y.; Ding, X. Heat and Mass Transfer Model for Desiccant Solution Regeneration Process in Liquid Desiccant Dehumidification System. *Ind. Eng. Chem. Res.* **2014**, *53*, 2820–2829.
- [22] Daou, K.; Wang, R. Z.; Xia, Z. Z. Desiccant Cooling Air Conditioning: A Review. *Renew. Sust. Energ. Rev.* **2006**, *10*, 55–77.
- [23] Yang, Y.; Rana, D.; Lan, C. Development of Solid Super Desiccants Based on a Polymeric Superabsorbent Hydrogel Composite. *RSC Adv.* **2015**, *5*, 59583–59590.
- [24] MujahidRafique, M.; Gandhidasan, P.; Rehman, S.; Al-Hadhrami, L. A Review on Desiccant Based Evaporative Cooling Systems. *Renew. Sust. Energ. Rev.* **2015**, *45*, 145–159.
- [25] Madhiyanon, T.; Adirekrut, S.; Sathitruangsak, P.; Soponronnarit, S. Integration of a Rotary Desiccant Wheel into a Hot-Air Drying System: Drying Performance and Product Quality Studies. *Chem. Eng. Process.* **2007**, *46*, 282–290.
- [26] Harshe, Y. M.; Utikar, R. P.; Ranade, V. V.; Pahwa, D. Modeling of Rotary Desiccant Wheels. *Chem. Eng. Technol.* **2005**, *28*, 1473–1479.

- [27] Zadpoor, A. A.; Nikooyan, A. A. Development of an Improved Desiccant-Based Evaporative Cooling System for Gas Turbines. *J. Eng. Gas Turb. Power* **2009**, *131*, 034506 (5 pp).
- [28] Rey Martínez, F. J.; Velasco Gómez, E.; Herrero Martín, R.; Martínez Gutiérrez, J.; Varela Diez, F. Comparative Study of Two Different Evaporative Systems: An Indirect Evaporative Cooler and a Semi-Indirect Ceramic Evaporative Cooler. *Energy Build.* **2004**, *36*, 696–708.
- [29] Woods, J.; Pellegrino, J.; Kozubal, E.; Burch, J. Design and Experimental Characterization of a Membrane-Based Absorption Heat Pump. *J. Membr. Sci.* **2011**, *378*, 85–94.
- [30] Zhao, B.; Peng, N.; Liang, C.; Yong, W. F.; Chung, T.-S. Hollow Fiber Membrane Dehumidification Device for Air Conditioning System. *Membranes* **2015**, *5*, 722–738.
- [31] National Renewable Energy Laboratory. Energy Saving A/C Conquers All Climates. **2010**, <http://tinyurl.com/NREL2010>.
- [32] Eldeeb, R; Fauchoux, M; Simonson, C. J. Applicability of a Heat and Moisture Transfer Panel (HAMP) for Maintaining Space Relative Humidity in an Office Building using TRNSYS. *Energy Build.* **2013**, *66*, 338–345.
- [33] Qi, R; Lu, L. Energy Consumption and Optimization of Internally Cooled/Heated Liquid Desiccant Air-Conditioning System: A Case Study in Hong Kong. *Energy* **2014**, *73*, 801–808.
- [34] Kim, M; Yoon, D; Kim, H; Jeong, J. Retrofit of a Liquid Desiccant and Evaporative Cooling-Assisted 100% Outdoor Air System for Enhancing Energy Saving Potential. *Appl. Therm. Eng.* **2016**, *96*, 441–453.
- [35] Fauchoux, M. T.; Simonson, C. J.; Torvi, D. Tests of a Novel Ceiling Panel for Maintaining Space Relative Humidity by Moisture Transfer from an Aqueous Salt Solution. *ASTM Int.* **2009**; *6(4)*, 1–10.
- [36] Mahmud, K; Mahmood, G. I.; Simonson, C. J.; Besant, R. W. Performance Testing of a Counter-Cross-Flow Run-Around Membrane Energy Exchanger (RAMEE) System for HVAC Applications. *Energy Build.* **2010**; *42*, 1139–1147.

- [37] Keniar, K.; Ghali, K.; Ghaddar, N. Study of Solar Regenerated Membrane Desiccant System to Control Humidity and Decrease Energy Consumption in Office Spaces. *Appl. Energy J.* **2015**, *138*, 121–132.
- [38] Ouyang, Y.-W.; Zhang, L.-Z., Conjugate Heat and Mass Transfer in a Skewed Flow Hollow Fiber Membrane Bank Used for Liquid Desiccant Air Dehumidification. *Int. J. Heat Mass Transfer* **2016**, *93*, 23–40.
- [39] Yang, Y.; Rana, D.; Matsuura, T.; Zheng, S.; Lan, C. Criteria for the Selection of a Supported Material to Fabricate Coated Membranes for a Life Support Device. *RSC Adv.* **2014**, *4*, 38711–38717.
- [40] Yang, Y.; Stapleton, J.; Diagne, B. T.; Kenny, G. P.; Lan, C. Q. Man-Portable Personal Cooling Garment Based on Vacuum Desiccant Cooling. *Appl. Therm. Eng.* **2012**, *47*, 18–24.
- [41] Huang, S.-M.; Hong, Y.; Qin, F. G. F. Fluid Flow and Heat Transfer in Hexagonal Parallel-Plate Membrane Channels (HPMC): Effects of the Channel Heights and Fluid Parameters. *Appl. Therm. Eng.* **2016**, *93*, 8–14.
- [42] Lu, H.; Lu, L.; Luo, Y.; Qi, R. Investigation on the Dynamic Characteristics of the Counter-Current Flow for Liquid Desiccant Dehumidification. *Energy* **2016**, *101*, 229–238.
- [43] Abdel-Salam, M.; Besant, R. W.; Simonson, C. J. Design and Testing of a Novel 3-Fluid Liquid-to-Air Membrane Energy Exchanger (3-Fluid LAMEE). *Int. J. Heat Mass Transfer* **2016**, *92*, 312–329.
- [44] Huang, S.-M.; Zhong, Z.; Yang, M. Conjugate Heat and Mass Transfer in an Internally-Cooled Membrane-Based Liquid Desiccant Dehumidifier (IMLDD). *J. Membr. Sci.* **2016**, *508*, 73–83.
- [45] Abdel-Salam, A.; Simonson, C. J. State-of-the-art in Liquid Desiccant Air Conditioning Equipment and Systems. *Renew. Sust. Energ. Rev.* **2016**, *58*, 1152–1183.
- [46] Conde, M. R. Properties of Aqueous Solutions of Lithium and Calcium Chlorides: Formulations for use in Air Conditioning Equipment Design. *Int. J. Therm. Sci.* **2004**, *43*, 367–382.
- [47] Khayet, M.; Matsuura, T. Membrane Distillation: Principles and Applications. In: *Membrane Distillation: Principles and Applications*, Elsevier Science, Amsterdam, The Netherlands; **2011**, pp. 134–136.

- [48] Ling, J. X.; Dybbs, A. Forced Convection over a Flat Plate Submersed in a Porous Medium: Variable Viscosity Case. *Am. Soc. Mech. Eng. Paper # 87-WA/HT-23*, ASME Winter Annual Meeting, Boston, MA, December **1987**, pp. 13–18.

Chapter 8: Conclusions and recommendations for second generation vacuum desiccant cooling garment

8.1 Conclusions

This PhD thesis project targets on developing innovative membranes and desiccants that are suitable for use in a novel technology, vacuum desiccant cooling, for application in personal cooling garment, which was previously developed in our lab. VDC is a novel microclimate cooling method to provide thermal comfort for personnel who have to work in hot and humid environments or have to wear impermeable protective clothing during work. It had features of being environmental friendly (no CFCs), energy efficient, light and compact, etc., and showed great potential for being used in various applications. However, the 1st generation VDC garment had some technical challenges and which limited its commercialization. The problems arise mainly from the following three prospects. Firstly, the hydrophobic PTFE membrane used in 1st generation garment was fragile and had poor processability, which could lead to garment failure by water leakage. Secondly, although solid lithium chloride powder had a good vapor absorption capacity to ensure sufficient cooling efficiency, it was soluble in water and became corrosive after a large amount of water vapor was absorbed. The corrosive solution can damage the garment, and cause the desiccant solution leakage raising safety issue for the wearers. Thus both the first and second problems are associated with the potential water/solution leakage, which lead to poor robustness and reusability of the 1st generation VDC garment.

Chapter 2 and chapter 3 review the requirement and design trend for microclimate cooling garment, as well as membrane aided desiccant cooling technology and its application in microclimate cooling field. The main design concerns are summarized, to set a guideline for the following phases of study, and eventually the 2nd generation VDC garment design.

Among hydrophobic membranes other than PVDF, Teflon was considered first. However, it was soon discarded because of its poor adhesiveness to most of other surfaces. The choice of polyvinylidene fluoride (PVDF) seemed more appropriate because of its sufficiently high hydrophobicity, low thermal conductivity, and large options for solvents, etc. Another requirement for the membrane to be used in the membrane aided cooling is high mechanical strength. It was hence decided to use a non-woven fabric (NWF) made of polyester as the backing material on which the PVDF layer was coated. There are, however, a number of different NWFs, and the criteria of the choice among those were totally unknown. Therefore, it was decided to establish those criteria by conducting detailed characterization studies with respect to four different commercial NWFs, for which fiber diameter, packing density, surface roughness, surface tension, thickness, pore size and porosity were determined as the characterization parameter. The membranes were fabricated by casting the polymer dope 15% Kynar 740 PVDF, 1.25% distilled water and as 83.75% of DMAc on top of the NWFs at the ambient conditions. Resulted composite membranes had very different pore sizes, porosities and LEP_{ws} , but their water contact angles were very similar. Interestingly, 3396-coated membrane (meaning the PVDF dope was coated on top of backing material coded NWF 3396) showed vapor flux over 3 times more than that of PVDF membrane without backing material at 30 °C, while E055100-85-coated membrane exhibited about 15 times more vapor flux. Furthermore,

LEP_w of both 3396- and E055100-85-coated membrane was as high as 70 psi, which value seemed high enough for the VDC applications.

Based on the results from membrane characterization and VMD experiments, the proper selection criteria for the NWF to be used as the support material for the VDC application were identified, i.e. NWF should satisfy the following four requirements, 1) smooth surface and 2) thinness, 3) large porosity and 4) low surface energy.

To further understand the effect of NWF on the VDC membrane performance, heat and mass transfer were studied. According to a proposed mathematical model, the membrane/feed interface temperature, membrane tortuosity, membrane mass transfer coefficient, and temperature polarization coefficient (TPC) were evaluated from the VMD experimental data. The cross-sectional images of the coated membranes with different NWFs were taken by SEM to show the influence of NWF visually. The images showed that the thickness of the PVDF layer was reduced by 42% after VMD tests, when the layer was not supported by NWF, whereas the thickness was well maintained when it was supported. Since the thickness of the unsupported membranes reduced considerably, pore shrinkage and tortuosity increases were expected to occur due to the collapsing of the pores. Indeed, according to the mass transfer analysis, the tortuosity of the unsupported membrane increased significantly resulting in an increase in mass transfer resistance, while the supported membrane with properly chosen NWFs could enhance the VMD flux by maintaining the initial pore structure. The proposed transport model also enables the simulation of the membrane performance for many other operating conditions.

Thus, applying the newly developed method, membranes of better mechanical strength and processability with enhanced vapor flux could be fabricated. These membranes could further enhance the VDC garment performance by preventing the water leakage.

The development of a novel desiccant, which is nontoxic, easy to handle and regenerate, is another technical challenge. Two approaches were adopted to address this issue.

Based on the literature reviews of the existing solid desiccant options, a novel super solid polymer based desiccant has been developed in chapter 6. The hypothesis involves in the development was that enhanced water absorption could be achieved by impregnating hydrogel with lithium chloride powder. Such a desiccant can remain in solid state during the vapor absorption to ensure the prevention of leakage that is caused by dissolution of lithium chloride in the absorbed water. The maximum salt loading was determined experimentally using sodium polyacrylate as the hydrogel. The super absorbent polymer (SAP) based desiccant so developed showed a vapor absorption capacity of $276 \pm 20\%$ when it was exposed to an ambient condition of 100% RH and 25 °C for 24 h. The latter absorption capacity is higher than any of conventional solid adsorbent desiccants such as silica gel, activated alumina and molecular sieves, thus, ensuring its superior potential in the applications in desiccant cooling, and portable VDC garment with a number of advantages such as enhanced absorption capacity, safe handling, and easier regeneration, etc. However, it suffered also several disadvantages when used in practical application, i.e., the desiccant swelled significantly by absorbing water vapor and its slipperiness made it hard to stay on a flat surface (desiccant pad) without detachment during multiple absorption/ regeneration cycles. Different mounting method of SAP based desiccant needed to be developed for ease of application.

Hence, another desiccant option was developed in this thesis based on confinement of the desiccant in hollow fibers. In this approach, aqueous desiccant solution was loaded into hydrophobic hollow fibers, both ends of the hollow fibers were sealed and then the fibers were dried. The desiccant could remain solid during the vapor absorption, which could prevent the crossover contamination between treated air and desiccant solution. Experiments are performed with PTFE hollow fibers of different internal diameters using varying lithium chloride concentrations to prove that the design concept is indeed feasible. It was found that the vapor absorption rate could be even more improved by selecting proper loading for membrane based desiccant fiber (MDF). Theoretical models have been established considering both heat and mass transfer to predict the vapor absorption flux through the hollow fiber membrane under different operating conditions. The model validity was proved by the results of the experiments conducted with a single fiber. As presented in chapter 7, vapor absorption capacity of 0.18 g of vapor per gram of MDF was achieved for the first hour absorption. With a 0.4 m² body coverage surface, this MDF can take 194 gram of vapor, allowing a potential cooling capacity of 324 W/m².

8.2 Recommendations for 2nd generation vacuum desiccant cooling garment

Finally, by solving the membrane and desiccant challenges, three design proposals can be suggested for second generation VDC garments, including both continuous and non-continuous vacuum configurations. A super absorbent polymer based fabric was used as a water reservoir to store water, as well as absorbing sweat from skin directly. Flat-sheet membrane developed from chapter 4 was used as physical barrier to separate liquid water/sweat and evaporated vapor. Air

stream dehumidification could be achieved by SAP based super solid desiccant studied in chapter 6. MDF developed from chapter 7 were woven into several 0.2 m^2 patches as desiccant pads for VDC garment. Preliminary results for MDF patches were also presented in chapter 7.

By suggesting the promising design approaches with technical challenges solved from this PhD project, it has successfully paved the way for the fabrication of 2nd generation VDC garment to be more efficient, robust, durable and wearer-friendly microclimate cooling technology. The next phase of study will be fabricating the three proposed VDC garments, and performing the human trial tests. Cooling capacity, total weight, flexibility, reusability and cost factor will be compared among each other, as well as other commercial cooling garments.

8.2.1 Introduction of first generation VDC garment design concept

VDC technology has been proven to be used as efficient, energy-saving portable microclimate cooling method, and can provide more comfort for wearer. The concept of VDC garment can be briefly described in Figure 8-1, VDC pad is composed of four major components, a water layer, a spacer, a desiccant layer and an outer bag. A microporous hydrophobic membrane with a sufficiently large liquid entrance pressure of water (LEP_w , 3.0 bar or larger) is used to separate the liquid water in the cooling (water) layer from the vapor in the gap created by the vacuum evaporation in the spacer.

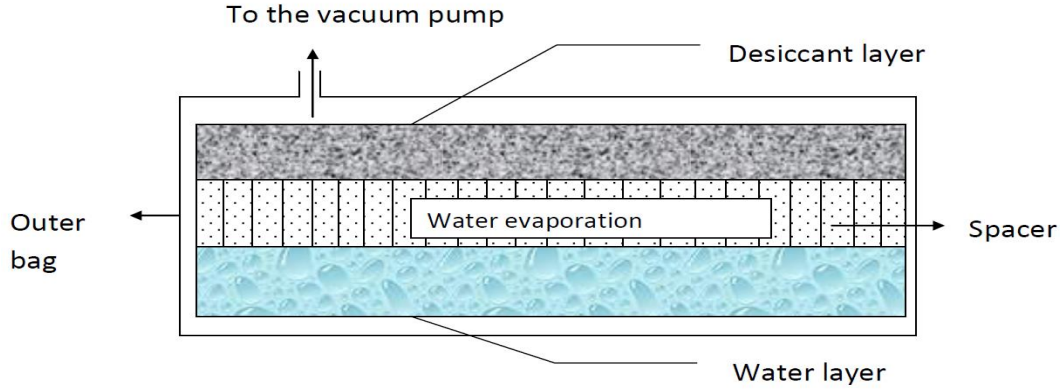


Figure 8-1 Schematic diagram of the structure of a VDC pad

In operation, the VDC pad is initialized by vacuuming the pad using a high-performance vacuum pump to reduce the pressure to 1.0-inch mercury (3.386 kPa) or less, which is close or lower than the saturation vapor pressure of water at 25 °C (3.166 kPa). The vacuum pump is then detached and the vacuum inside the sealed VDC pad maintained by sufficient vapor adsorption by the desiccants in the sorption (desiccant) layer. Since power is required for the short initialization period only, which is in the range of 3 to 5 minutes, a VDC device is practically an unpowered cooling system. This feature of it, in combination with the large latent heat of water evaporation, makes it an attractive personal cooling technology that could be made light, portable, efficient and with reasonably long working period.

Assume that the internal heat exchange between the water layer and the desiccant layer is negligible; the cooling capacity, Q (W) of a VDC pad can be estimated as the rate of latent heat of water evaporation using the following equation

$$Q = JA\Delta H_v \quad (8.1)$$

Where J is the evaporation flux ($\text{g/m}^2\text{s}$), A is the area of evaporation surface (m^2), ΔH_V is the latent heat of water evaporation (J/g).

This first generation VDC garment has great cooling performance tested by human trials, however, some technical challenges have limited its cooling performance and reliability. In this project, solving the two major challenges are the primary focus. The challenges can be briefly described here. First, the commercial PTFE (Teflon) membrane used in the 1st generation prototype was fragile and non-sticky. Consequently, it was very difficult to fabricate VDC pads, which often failed due to water leakage. Second, the desiccant used in the 1st generation VDC pads was lithium chloride powder, which has high water affinity, but becomes corrosive after absorbing water vapor to become aqueous solution. This raised safety concerns to both the wearer and the equipment which the wearer carries or operate.

With the results from chapter 4 to chapter 7, flat-sheet hydrophobic membrane with enhanced mechanical strength and improved vapor flux has been successfully developed, two options for solid desiccant have also been developed which can both be used in the future VDC garment designs to ensure lithium chloride solution leakage free. By combining these developments from previous studies, a few options of 2nd generation VDC garment designs can be done conceptually, and their pros and cons are discussed in the following section.

8.2.2 Design proposals of second generation VDC garments

Three proposals of 2nd generation VDC garments have been made in this chapter, and are referred as proposal A, proposal B and proposal C. First of all, as shown in Figure 8-2, water reservoir is made of commercially available super absorbent cooling towel saturated with water.

A saturated cooling towel is designed to contact directly to skin for three purposes. First of all, it can provide instant cooling effect utilizing its basic function as cooling towel. Secondly, it can release water continuous as a water reservoir. Thirdly, it can absorb sweat when necessary to provide comfort for the wearer and facilitate sweat evaporation. A supported flat-sheet hydrophobic membrane, which was developed in chapter 4, is followed right after the water reservoir to serve as physical barrier for water/sweat and prevent it from passing through directly without evaporation. The spacer is made of an empty hollow fiber weaved pad to provide air and water vapor path, the spacer's outlet is connected to the miniature vacuum pump. An impermeable wet suit is followed with the spacer to cover the entire treated area of the body to provide an air barrier.

An airtight fitting is required on the wet suit for the tubing from the spacer to connect with the portable miniature vacuum pump. The pump is on continuous to provide a negative pressure with garment and facilitate water evaporation. A desiccant column is installed in line between the wet-suit outlet and vacuum pump to absorb the evaporated water vapor for pump protection. It is filled with SAP-based desiccant developed from chapter 6. This design is super compact, light, and the thickness is only around 1 cm. Garment is made of a soft towel, flexible membrane, weaved pad-form hollow fiber membrane and wetsuit, which ensure the entire VDC garment to be flexible and comfort to wear. This design proposal is called 2nd generation of VDC garment proposal A. Schematic diagram is shown in Figure 8-2.

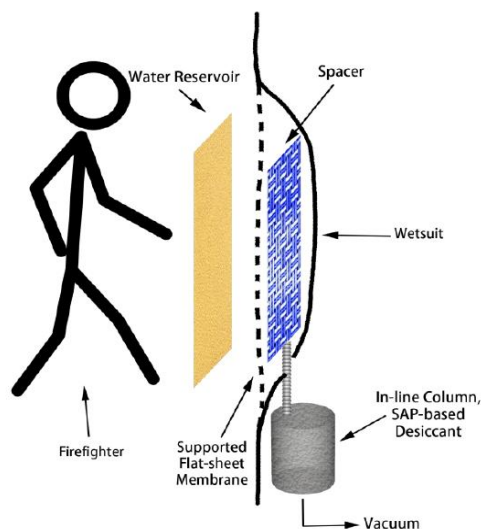


Figure 8-2 2nd generation VDC garment proposal A

Secondly, an option of VDC garment utilizing the new developed MDF from chapter 7 is also proposed. The basic structure is similar like proposal A. Instead of using a flat-sheet membrane, proposal B uses a spacer directly after the water reservoir. Schematic diagram was shown in Figure 8-2, since the spacer is made of hydrophobic hollow fiber membrane, it can serve as a physical barrier to prevent water from going through, and also providing the air/ vapor path. By separating the water reservoir with desiccant pad physically, the spacer prevents the heat transfer from the hot desiccant pad to the cool water reservoir, and helped maintain the cooling effect of the VDC garment. The spacer is also connected to a miniature vacuum pump to ensure the negative pressure internal environment. Desiccant pad made of weaved MDF pad is used after the spacer. The wet suit is again covering the entire treated area as air barrier. This 2nd generation of VDC garment proposal B has the same level of flexibility, compactness and lightness with proposal A. Different design may have different cooling performance based on the

heat and mass transfer resistance from water reservoir to the desiccant side. To better determine the effectiveness of these two proposals, human trial tests are required for more accurate analysis.

Before making the prototypes, weaved MDF pad need to be prepared in lab. Loom is employed to make large area of pad. Taking the 1st generation VDC garment human trial test as reference, the targeting body area for cooling in this study is 0.4 m².

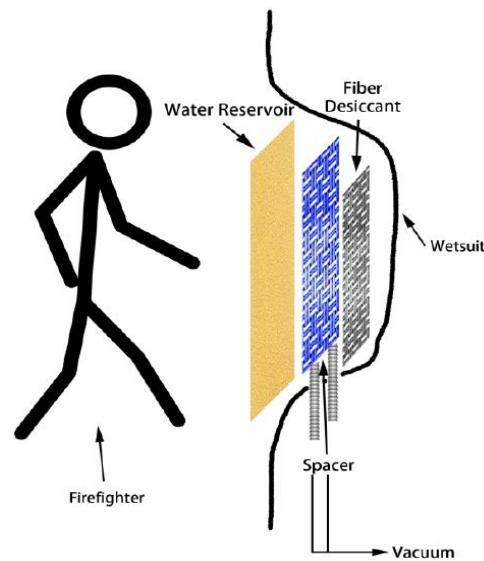


Figure 8-3 2nd generation VDC garment proposal B

These previous two proposals are both applying negative pressure directly on the skin surface, its feasibility is based on Stanford researchers current study called “cooling glove”. In their research, vacuum is applied on skin surface, while cooling liquid is directly circulating around hand. They have claimed that by directly applying vacuum on skin can fast achieve cooling effect by fasten the blood flow from body to skin surface, and efficiently cools core body temperature to comfort zone.

However, due to lack of human trial reports, there are still concerns regarding to the long-term safety issue of exposing skin under vacuum for extended period (the desired VDC garment working duration is set to be 2 hours in this project), the third option of 2nd generation of VDC garment is therefore proposed shown in Figure 8-4. A sealed outer bag is used similarly like 1st generation described in Figure 8-1. Vacuum is maintained within the bag, the advantages of this design is that, after initialization period which allow the system pressure to reach the desired vacuum degree, it can run without continuous power supply. The thickness of the garment does not change comparing to the previous proposal A and B, therefore maintaining as flexible and light. The cons, at the meantime, is that by sealing cooling towel within outer bag, it can no longer absorb body sweat during the run, which reduces the potential cooling effect of VDC garment. In terms of wearer's thermal comfort, the generated sweat from body cannot be naturally removed by sweat evaporation due to skin coverage from impermeable VDC garment or protective clothes, body sweating process is therefore slowed down, limiting the body natural cooling mechanism.

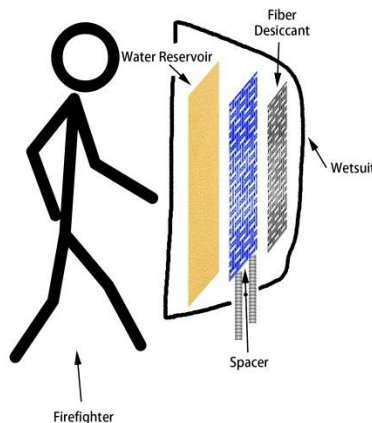


Figure 8-4 2nd generation VDC garment proposal C

Since MDF pad bench scale absorption tests under vacuum from chapter 7 have demonstrated to be working efficiently at vacuum degree higher than 20-inch Hg with 3-layers MDF pad, proposal C can be built by taking reference of these results. The thickness of hollow fiber membrane based spacer need to be tested. The actual cooling performance for the above mentioned proposals need to be tested through human trials. 2nd generation VDC garment performance will then be analyzed with other microclimate cooling garments in terms of cooling capacity, cooling duration, power consumption, total weight, flexibility, portability and wearer's thermal comfort, etc. The robustness and reusability of 2nd generation will be tested and compared among three proposals and as well as with 1st generation VDC garment.

Overall, this PhD project is targeting on the development of robust and reusable 2nd generation VDC garments. Membrane and desiccant for VDC garment have been improved through different phases of the study. Challenges have also come along during the development process from both equipment availability and technical failures of ion exchange resin matrix based desiccant development step. Thanks to those challenges that I have faced during this PhD project, I was able to think deeper and view the subject from different angles. This training process showed me the nature of academic research work, and made me stronger while addressing each problem one after another. I appreciate this challenge that has provided me with an opportunity to learn so much and enhanced my life to a new level. I will continue working in the research field where I am eager to solve more problems in the future.