

DEVELOPMENT AND MODELLING OF MIXED MATRIX MEMBRANES
INCORPORATING LARGE PORE SIZE CLAY FOR GAS SEPARATION

SEYED ABDOLLATIF HASHEMIFARD

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Gas Engineering)

Faculty of Petroleum and Renewable Energy Engineering
Universiti Teknologi Malaysia

JULY 2011

**For Ahlul Bayt,
my beloved mother and father,
my wife
and my sons.**

ACKNOWLEDGEMENT

In the name of Allah, the beneficent and the merciful.

First and foremost I offer my sincerest gratitude and appreciation to my supervisor, **Prof. Ahmad Fauzi bin Ismail**, who has supported me throughout my thesis with his patience and knowledge whilst allowing me the room to work in my own way. I attribute the level of my PhD degree to his encouragement and effort and without him this thesis, would not have been completed. His cheerful presence has always created a friendly atmosphere and motivated me to work harder. One simply could not wish for a better or friendlier supervisor.

Second I am heartily thankful to my co-supervisor, **Prof. Takeshi Matsuura**, whose encouragement, guidance and scientific supports from the start to the completion of this thesis enabled me to develop an understanding of the subject in the various aspects. In one word, without answering his comments on my articles, I never could publish them.

In my daily work, I have been blessed with a friendly and cheerful group of AMTEC members. Therefore, it is a pleasure to thank all of the AMTEC members who made this thesis possible to be completed due to their direct or indirect participation.

Finally, my deepest gratitude goes to my dear father, **Seyed Abolghasem Hashemifard** whose praying on behalf of me, has always resulted in my prosperous in my lifetime. I am also thankful to my beloved wife, **Azadeh Khorram Heydarkhani**, who always gave me encouragement, reassurance and valuable support during all the difficult phases of my study. Thanks also to my lovely sons, **S. Mohammad Javad** and **S. Mohammad Reza**, as their presence always inspires me.

ABSTRACT

The objective of this study is to develop Polyetherimide (PEI) mixed matrix membranes (MMM) by incorporating large pore size fillers. This study was divided into two main parts. In the first part, the existing MMM permeation models were evaluated and based on series-parallel resistors approach, a new model has been developed. The developed model was capable to predict gas permeation for all well-known MMMs morphologies and a good agreement was achieved between the model and the experimental data from open literature. The first part was extended by proposing a morphological map which by virtue the prediction of MMMs morphologies was achievable. The second part of the work was performed to investigate the effect of incorporation of montmorillonite (MMT) and halloysite nano tubes (HNT) as large pore size filler in MMMs for gas separation. MMMs were fabricated using a dry/wet casting technique. The chemical modification of HNTs involved silylation and Ag^+ ion exchange treatment. The silylated HNTs was prepared by treating them with N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane agent. The results from thermal gravimetric analysis (TGA) and Fourier transform infra red spectroscopy (FTIR) confirmed that chemical modification on clay surface has taken place successfully. A perfect compatibility between the polymer matrix and filler was observed from field emission scanning electron microscopy (FESEM) micrographs. The outcomes showed that, 0.5% loading of silylated-HNT resulted in 27% enhancement in CO_2 permeability and 8% increase in selectivity relative to the neat polymer membrane. In order to apply the facilitated transport properties in MMMs, Ag^+ ion exchange treatment was performed because of its high affinity toward CO_2 rather than CH_4 . Results showed that silane can successfully enhance the HNTs cation exchange capacity, which led to higher concentration of Ag^+ ions in the modified HNTs. Ag^+ ion exchange exhibited about 250% enhancement in CO_2 permeability. The effect of montmorillonite nano-clay fillers on PEI MMM was also studied. The gas permeation results revealed the following order in terms of selectivity for CO_2/CH_4 separation: Cloisite 15A > general MMT > hydrophilic MMT > hydrophobic MMT > raw MMT. In conclusion, the best results were achieved at 0.5% of Cloisite 15A loading where permeability and selectivity enhancements were 24% and 28% respectively.

ABSTRAK

Tujuan kajian ini adalah untuk menghasilkan membran matrik tercampur (MMM) polieterimida (PEI) dengan memasukkan bahan pengisi berliang besar. Penyelidikan ini pada dasarnya dibahagikan kepada dua bahagian utama. Dalam bahagian pertama, model kebolehtelapan MMM yang sedia ada telah dinilai dan kemudian berdasarkan pendekatan perintang siri-selari, model baru telah dibangunkan. Model yang dibangunkan mampu untuk meramal kebolehtelapan gas untuk semua morfologi MMM yang sedia ada dan kesamaan yang baik telah dicapai di antara semua model dan data ujikaji dari literatur. Bahagian pertama ini telah dilanjutkan dengan mencadangkan plan morfologi berdasarkan kepada peramalan morfologi MMMs yang boleh dicapai. Bahagian kedua dari penyelidikan ini dijalankan untuk mengkaji pengaruh montmorillonite (MMT) dan tiub nano haloisit (HNT) sebagai bahan pengisi berliang besar dalam MMM bagi pemisahan gas. MMM telah dihasilkan dengan menggunakan teknik tuangan basah-kering. Modifikasi kimia HNTs termasuk sililasi dan rawatan pertukaran ion Ag^+ . HNT bersililasi telah dihasilkan melalui rawatan menggunakan agen silan N- β -(aminoetil)- γ -aminopropiltrimetoxi. Keputusan daripada analisis termogravimetri (TGA) dan spektroskopi inframerah penjelmaan fourier (FTIR) mengesahkan bahawa pengubahsuaian kimia pada permukaan tanah liat itu berlaku dengan jayanya. Keceriasan sempurna antara matrik polimer dan bahan pengisi dapat diperhatikan dari mikrograf mikroskopi imbasan elektron pemancaran medan (FESEM). Keputusan kajian menunjukkan bahawa penambahan 0.5% HHT bersililasi menghasilkan peningkatan 27% dalam kebolehtelapan CO_2 dan 8% peningkatan pemilihan berbanding membran polimer asal. Untuk menggunakan sifat pengangkutan dalam MMM, rawatan pertukaran ion Ag^+ telah dilakukan kerana ia mempunyai daya tarikan terhadap CO_2 lebih tinggi berbanding CH_4 . Keputusan kajian menunjukkan bahawa silan berjaya meningkatkan kapasiti tukaran kation HNT, yang turut menyebabkan peningkatan kepekatan ion Ag^+ pada HNT terubahsuai. Pertukaran ion Ag^+ menunjukkan peningkatan sekitar 250% dalam kebolehtelapan CO_2 . Pengaruh bahan pengisi tanah liat bersaiz nano, montmorillonit PEI MMM juga telah dikaji. Keputusan kebolehtelapan gas menunjukkan urutan kememilihan berikut untuk pemisahan CO_2/CH_4 : Cloisite 15A > MMT umum > hidrofilik MMT > hidrofobik MMT > MMT mentah. Kesimpulannya, hasil yang terbaik dicapai pada penambahan 0.5% Cloisite 15A di mana peningkatan kebolehtelapan dan kememilihan adalah 24% dan 28%.

	Membranes for Gas Permeation	21
2.3.2	Interphase Morphologies	24
2.3.3	Conventional Mixed Matrix Membranes	28
2.3.3.1	Dense Flat Sheet Mixed Matrix Membranes	31
2.3.3.2	Asymmetric and Composite Mixed Matrix Membranes	34
2.3.3.2.1	Asymmetric Flat Sheet Mixed Matrix Membranes	35
2.3.3.2.2	Asymmetric Hollow Fiber Mixed Matrix Membranes	37
2.3.4	Parameters and factors influencing Mixed Matrix Membrane performance	40
2.3.4.1	Suitable Combination of Polymer/Inorganic Filler	41
2.3.4.2	Particles Size	43
2.3.4.3	Particle Precipitation and Agglomeration	44
2.3.4.4	Pore Blockage and Chain Rigidification Morphologies	45
2.3.5	Coupling Methods to Hinder Interfacial Defects	46
2.3.5.1	Low Tg Polymers	46
2.3.5.2	High Tg Polymers	46
2.3.5.3	Chemical Surface Modification Of Filler Particles	47
2.3.5.4	Utilizing Hydrophobic Phases for Both Organic and Inorganic Media	49
2.3.5.5	Priming Technique	49
2.3.5.6	Sizing Technique	50
2.3.5.7	Low Molecular-Weight Additive (LMWA)	50
2.3.5.8	Utilizing Copolymers	51
2.3.5.9	Heat Treatment or Annealing of Pre-	

	Fabricated MMMs	51
	2.3.6 Ion Exchange Method	52
3	RESEARCH METHODOLOGY	54
3.1	Research Design	54
3.2	Development of the MMMs permeability Model	54
3.2.1	Models for MMMs Gas Permeation	55
3.2.2	Development of the New Theoretical Model	58
3.2.3	Development of the Morphological map	58
3.3	Experimental Studies	59
3.3.1	Material Selection	59
3.3.1.1	Polymer	59
3.3.1.2	Solvents	60
3.3.1.3	Non-solvent	61
3.3.1.4	Fillers	61
3.3.1.5	Coupling Agent	62
3.3.2	Silylation of HNTs	62
3.3.3	Ag ⁺ Ion Exchange Treatment of the HNTs	65
3.3.4	Dope Formulation	65
3.3.5	Dope Preparation	67
3.3.6	Fabrication of the Flat Sheet Matrix Mixed Membranes	68
3.3.7	Solvent Exchange and Post-treatment	69
3.3.8	Membranes Coating	70
3.3.9	Membrane Characterization Methods	71
3.3.9.1	Fourier Transform Infra Red Spectroscopy (FTIR)	71
3.3.9.2	Thermo Gravimetric Analysis (TGA)	71
3.3.9.3	Differential Scanning Calorimetric (DSC)	72
3.3.9.4	Field Emission Scanning Electron Microscopy (FESEM)	72
3.3.9.5	Energy Dispersive X-Rays (EDX)	73
3.3.9.6	X-Ray Diffraction (XRD)	73
3.3.9.7	Constant Pressure Gas Permeation Test	73

4	PREDICTION OF GAS PERMEABILITY IN MIXED MATRIX MEMBRANES USING THEORETICAL MODELS	76
4.1	Introduction	76
4.2	Gas Permeation Models	78
4.3	Parameters Needed to Evaluate the Models	81
4.4	Formulation to Calculate Inorganic Permeability	82
4.5	Estimation of Diffusivity	86
4.5.1	NaA Diffusivity	86
4.5.2	NaX Diffusivity	90
4.6	Estimation of Solubility	92
4.7	Estimation of Permeability	94
4.8	Results and Discussions	95
4.9	Conclusions	99
5	A NEW THEORETICAL GAS PERMEABILITY MODEL USING RESISTANCE MODELING FOR MIXED MATRIX MEMBRANE SYSTEMS	101
5.1	Introduction	101
5.2	Theory of the Proposed Model	104
5.2.1	Mixed Matrix Membrane Element Description	104
5.2.2	Developing the New Model Using Resistance Modeling Approach	107
5.3	Results and Discussions	113
5.3.1	Prediction of the Proposed Model	113
5.3.2	Comparison Between the Proposed Model and the Experimental Data	118
5.4	Conclusions	126
6	DEVELOPMENT OF A MORPHOLOGICAL DIAGRAM FOR MIXED MATRIX MEMBRANE INCORPORATED WITH LARGE PORE SIZE FILLERS FOR GAS SEPARATION: HALLOYSITE NANOTUBES (HNT) AS FILLER	128

6.1	Introduction	128
6.2	Halloysite Structure	130
6.3	Results and Discussion	132
6.3.1	Estimation of Halloysite Nanotubes Permeability	132
6.3.2	Expected Mixed Matrix Membranes Morphologies	135
6.4	Conclusion	147
7	MIXED MATRIX MEMBRANE INCORPORATED WITH LARGE PORE SIZE HALLOYSITE NANOTUBES (HNT) AS FILLER FOR GAS SEPARATION	149
7.1	Introduction	149
7.2	AEAPTMS for Preparation of silylated HNT	152
7.3	Fabrication of Asymmetric Flat Sheet Mixed Matrix Membrane	153
7.4	Results and Discussion	154
7.4.1	Unmodified HNTs	154
7.4.1.1	Characterization of Mixed Matrix Membranes	154
7.4.1.1.1	Field Emission Scanning Electron Microscope of Mixed Matrix Membranes	154
7.4.1.2	Permeation Test Results	156
7.4.1.2.1	Effects of Dope Preparation Factors on the Mixed Matrix Membranes	156
7.4.2	Silylated HNTs	161
7.4.2.1	Characterization of Silylated HNTs	161
7.4.2.1.1	Field Emission Scanning Electron Microscope	161
7.4.2.1.2	Fourier Transform Infrared	162
7.4.2.1.3	X-Ray Diffraction	165
7.4.2.1.4	Thermal Gravimetry Analysis	166
7.4.2.2	Characterization of Mixed Matrix Membranes	168

7.4.2.2.1	Field Emission Scanning Electron Microscope	168
7.4.2.2.2	Differential Scanning Calorimetry	169
7.4.2.3	Permeation Test Results	170
7.4.2.3.1	Effect of Silane Agent on MMMs Separation Properties	170
7.4.2.3.2	Effect of Silane Concentration on MMM Separation Properties	
7.4.2.3.3	Effect of S2-HNT Loading on MMM Separation Properties	173
7.5	Conclusion	176
		178
8	FACILITATED TRANSPORT EFFECT OF Ag⁺ ION EXCHANGED HALLOYSITE NANOTUBES ON THE PERFORMANCE OF POLYETHERIMIDE MIXED MATRIX MEMBRANE FOR GAS SEPARATION	180
8.1	Introduction	180
8.2	Results and Discussion	182
8.2.1	Characterization of Modified HNTs	182
8.2.1.1	Field Emission Scanning Electron Microscope	182
8.2.1.2	Fourier Transform Infrared	184
8.2.1.3	X-Ray Diffraction	185
8.2.1.4	Thermal Gravimetry Analysis	186
8.2.1.5	Energy Dispersive X-Rays	189
8.2.2	Characterization of MMMs	190
8.2.2.1	Field Emission Scanning Electron Microscope	190
8.2.2.2	Differential Scanning Calorimetry	191
8.2.2.3	Permeation Test Results	192
8.3	Conclusion	196

9	EFFECTS OF MONTMORILLONITE NANO-CLAY FILLERS ON PEI MIXED MATRIX MEMBRANE FOR CO₂ REMOVAL	198
9.1	Introduction	198
9.2	Structure and Chemical Formula of MMT	199
9.3	Results and Discussion	201
9.3.1	Characterization of MMTs Using Fourier Transform Infrared Spectrometer	201
9.3.2	Characterization of MMTs Using X-Ray Diffraction	203
9.3.3	Characterization of MMTs Using Thermal Gravimetric Analysis	205
9.3.4	Characterization of MMMs Using Differential Scanning Calorimetry	209
9.3.5	Field Emission Scanning Electron Microscope of Mixed Matrix Membranes	209
9.3.6	Gas Permeation Results	211
9.3.6.1	Effect Of Different MMTs on MMM Performance	211
9.3.6.2	Effect of Cloisite 15A Loading On MMM Performance	214
9.4	Conclusion	215
10	GENERAL CONCLUSION AND RECOMMENDATIONS	217
10.1	General Conclusion	217
10.2	Recommendations	218
	REFERENCES	220
	Appendices A-E	243-250

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Molecular weight and kinetic diameter (\AA) of different gases applied in Gas separation via membrane technology.	15
2.2	Required parameters and nested application of the Maxwell model(Moore and Koros, 2005).	26
2.3	MMM permeability and selectivity: prediction vs. experimental at 35 °C (Mahajan and Koros, 2000; Mahajan and Koros, 2002b).	30
2.4	Typical inorganics applied in MMMs.	32
2.5	Chemical composition and pore specification of some more widely utilized zeolites.	33
2.6	Major advances of MMMs.	36
3.1	Physical, mechanical and thermal properties of PEI (GE plastic).	60
3.2	Physical and chemical properties of NMP (Merck).	61
4.1	Permeance and Ideal selectivity for zeolite NaA membrane.	82
4.2	Diffusivity of Nitrogen in NaA Zeolite.	87
4.3	Diffusivity of Oxygen in NaA Zeolite.	88
4.4	Diffusivity of Carbon Dioxide in NaA Zeolite.	88
4.5	Diffusivity of Methane in NaA Zeolite.	89
4.6	Diffusivity of gases in Zeolite NaA.	90
4.7	Diffusivity of gases in Zeolite NaX.	91
4.8	Adsorption isotherm parameters for gases in Zeolite NaA and	

	NaX.	93
4.9	Permeability of gases in Zeolite NaA and NaX.	94
4.10	Morphology of collected MMM's.	97
4.11	Models fitted parameters for rigidified region.	98
4.12	Standard deviation and percentage of average absolute relative error.	99
5.1	Specification of cases 1 to 7.	119
6.1	Estimated Knudsen number, molecular, Knudsen, Poiseuille and total diffusion coefficient for CO ₂ and CH ₄ through HNT at 25 °C.	134
6.2	Details of the experimental data utilised to examine the predicted morphologies.	138
6.3	The parameters used for model predictions.	139
7.1	Details of four protocols to fabricate PEI/HNT MMMs.	154
7.2	Relation between the cases and the morphologies.	160
7.3	Positions and assignments of the IR vibrations bands.	163
7.4	Glass transition temperature of the fabricated neat PEI membrane and PEI /S2-HNT MMMs.	170
8.1	Positions and assignments of the IR vibrations bands.	185
8.2	The surface elemental composition of raw HNTs and silylated HNTs before and after the Ag-ion exchange treatment measured by EDX.	190
8.3	Glass transition temperature for neat PEI membrane, original, Ag-ion exchanged and AEAPTMS-modified HNT MMM samples .	191
9.1	Positions and assignments of the IR vibrations bands.	202
9.2	Glass transition temperature of the fabricated neat PEI membrane and 1%MMTs/PEI MMMs.	209

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Schematic of membrane gas separation.	11
2.2	Diagram of different gas separation mechanism in membrane technology.	12
2.3	Upper-bound diagram for CO ₂ /CH ₄ selectivity and CO ₂ permeability for different polymeric membranes (Robeson, 2008) (the red circles belongs to 1991 and the blue circles were added later in 2008).	19
2.4	Schematic diagram of a Mixed Matrix Membrane (MMM).	20
2.5	Five main morphologies concerned with MMMs proposed by Moore and Koros (2005) for Ultem [®] MMM. Solid and open circles show the predicted values for 35 vol.% and 15 vol.% 4A respectively.	24
2.6	MMMs separation and permeation properties along with the Robeson, 1991 upper-bound diagram (Merkel et al., 2002; He et al., 2002; Merkel et al., 2003a).	30
2.7	The commonly applied technique to fabricate dense flat sheet mixed matrix membranes.	33
2.8	Typical cross sectional view of a MMM hollow fibre.	37
2.9	Typical schematic of a dual-layer spinning system.	39
2.10	n-C ₄ /C ₅ selectivity vs. n-C ₄ permeability in: AF2400/fumed silica MMMs (18, 30, and 40 wt%); PMP/fumed silica MMMs (15, 25, 40, and 45 wt%); PTMSP/fumed silica MMMs (30, 40, and 50 wt%) (Merkel et al., 2003a).	43
2.11	Details of particle migration to MMMs top surface cast at high temperatures (Mahajan et al., 2002).	45
2.12	Schematic of the chemical reaction between APDEMS and	

	zeolite surface (Liet al., 2006).	48
2.13	Comparison of O ₂ permeability and O ₂ /N ₂ permselectivity of PES/zeolite A mixed matrix membranes using different type of zeolite A before and after the silylation (Liet al., 2006).	49
2.14	Comparison of CO ₂ /CH ₄ permselectivity of PES/zeolite mixed matrix membranes using original and modified (Ag ⁺ ion-exchanged) zeolite NaA as dispersed phase (Liet al., 2006).	53
3.1	Research design for the theoretical and modeling studies.	55
3.2	Research design for experimental studies.	56
3.2	Research design for experimental studies (Continued).	57
3.3	Molecular formula of polyetherimide.	60
3.4	Chemical structure of AEAPTMS.	62
3.5	Schematic representation of silylation of HNT by AEAPTMS.	63
3.6	Hydrogen bonding (broken lines) between PEI and S-HNTs.	64
3.7	Schematic of silylation of HNTs.	65
3.8	Dope viscosity versus polymer concentration for PEI .	67
3.9	Schematic of the dope preparation steps.	68
3.10	Process steps for dry/wet casting.	68
3.11	Schematic of flat sheet membrane MMMs fabrication.	69
3.12	Schematic for membrane coating process steps.	71
3.13	Schematics diagram of pure gas permeation testing system.	75
4.1	The steps leading to inorganic permeability.	84
4.2	The morphology diagram for MMM containing zeolite NaA Moore and Koros (2005).	95
4.3	Bar diagram exhibits standard deviation and percentage of average absolute relative error for the models.	100
5.1	BCC structure considered for particle distribution in MMM.	104
5.2	Unit cell of BCC structure considered for particle distribution in MMM.	105

5.3	Side (a) and top (b) view of the half BCC unit cell where a cylindrical particle is placed.	106
5.4	Penetrant gas flow path through MMM element for void in MMM morphology.	108
5.5	Penetrant gas flow path through MMM element for rigidified MMM morphology.	111
5.6	Effect of dispersed filler permeability ratio and filler loading on relative permeability for ideal MMM.	114
5.7	Effect of dispersed filler permeability ratio and filler loading on relative permeability for rigidified MMM.	115
5.8	Effect of dispersed filler permeability ratio and filler loading on relative permeability for leaky MMM.	115
5.9	Effect of dispersed filler permeability ratio and filler loading on relative permeability for void in MMM.	116
5.10	Effect of dispersed filler permeability ratio and interphase thickness to particle diameter ratio on relative permeability for rigidified and void in MMM.	116
5.11	Effect of dispersed filler permeability ratio and interphase permeability ratio on MMM relative permeability.	117
5.12	Effect of filler loading and interphase permeability ratio on MMM relative permeability.	118
5.13	Model prediction of relative permeability and selectivity versus experimental data for MPD-BPADA-Zeolite NaA MMM for O ₂ /N ₂ gas separation.	122
5.14	Model prediction of relative permeability and selectivity versus experimental data for Matrimid-Zeolite NaA MMM for O ₂ /N ₂ gas separation.	122
5.15	Model prediction of relative permeability and selectivity versus experimental data for (BAPB-BPADA)-Zeolite NaA MMM for O ₂ /N ₂ gas separation.	123
5.16	Model prediction of relative permeability and selectivity versus experimental data for Ultem-Zeolite NaA MMM for O ₂ /N ₂ gas separation.	124
5.17	Model prediction of relative permeability and selectivity versus experimental data for Matrimid-CMS MMM for	

	CO ₂ /CH ₄ gas separation.	125
5.18	Model prediction of relative permeability and selectivity versus experimental data for Matrimid-CMS MMM for O ₂ /N ₂ gas separation.	125
5.19	Model prediction of relative permeability and selectivity versus experimental data for Polyethesulfone-Zeolite NaA MMM for O ₂ /N ₂ gas separation.	126
6.1	TEM micrographs of the three main morphologies of halloysite from New Zealand: (a) spheroidal (Opotiki); (b) short-tubes (Te Puke); and (c) large-tubes (Matauri Bay) (Joussein et al., 2005).	131
6.2	Schematic diagrams of (a) the crystalline structure of halloysite-(10 Å), and (b) the structure of a halloysite nanotube (Yuan et al., 2008).	132
6.3	Schematic illustration of expected morphologies of MMMs HNT/PEI across dense selective skin layer; Case I) Ideal, Case II) Void (yellow colored space surrounding the filler is the void), Case III) Rigidification (blue colored spece shows the rigidified region), Case IV) Blocking (black tips shows the blocked patrs) and Case V) Blocking + void.	137
6.4	Relationship between MMM ideal morphology (Case I) and transport properties for large pore size fillers.	139
6.5	Relationship between MMM voids morphology (Case II) and transport properties for large pore size fillers.	140
6.6	Relationship between MMM rigidified morphology (Case III) and transport properties for large pore size fillers.	142
6.7	Relationship between MMM pore blocking morphology (Case IV) and transport properties for large pore size fillers.	143
6.8	Relationship between MMM pore blocking-void morphology (Case V) and transport properties for large pore size fillers.	145
6.9	Asymmetric MMM versus dense symmetric MMM .	146
6.10	Comparison between the small pore size fillers MMMs morphology diagram (gray arrows along with gray italic words) proposed by Moore and Koros (2005) to the large pore size fillers MMMs morphology diagram proposed in the present work (stripped area along with black bold words) (The illustration can be observed in full colour online).	147

7.1	Schematic representation of silylation of HNT and AEAPTMS.	152
7.2	FESEM micrographs of PEI/HNT MMMs cross sectional view using different protocols at magnification of 10,000×. Note the magnification for (d) is 6000×.	155
7.3	FESEM micrographs of PEI/HNT MMMs plan view using different protocols at magnification of 10,000×.	156
7.4	Effect of the four protocols on 1.0%HNT MMM CO ₂ permeability at 15 bar.	156
7.5	Effect of the four protocols on 1.0%HNT MMM CO ₂ /CH ₄ selectivity at 15 bar.	158
7.6	Effect of the four protocols on 1.0%HNT MMM O ₂ permeability.	159
7.7	Effect of the four protocols on 1.0%HNT MMM O ₂ /N ₂ selectivity.	159
7.8	Movement of experimental points on the membrane performance map as a result of different dope preparation protocols, all of the samples contain 1.0%HNT.	160
7.9	FESEM micrographs of (A) HNT, (B) S2-HNT, and (C) S4-HNT. Top and bellow images magnification are 10,000× and 25,000× respectively.	162
7.10	FTIR spectra (4000-500 cm ⁻¹) for HNT, S2-HNT, and S4-HNT at room temperature.	164
7.11	XRD patterns for HNT, S2-HNT, and S4-HNT at room temperature.	165
7.12	TG and DTG curves of original and AEAPTMS -modified halloysite samples; A) HNT, B) S2-HNT and C) S4-HNT.	167
7.13	FESEM micrographs of S-HNT MMMs cross sectional view using protocol 50-5-4, a) 1.0% S2-HNT, b) 0.5% S2-HNT and c) 1.0% S4-HNT at magnification of 7,000×, 3,500× 5,000× respectively.	169
7.14	The effect of HNT and S2-HNT incorporation and dope preparation protocol on the gas permeability of MMM, all of the samples contain 1.0% filler.	171
7.15	The effect of HNT and S2-HNT incorporation and dope preparation protocol on the permeability ratio of MMM, all of	

	the samples contain 1.0% filler.	171
7.16	Movement of experimental points on the membrane performance map as a result of silane incorporation and different dope preparation protocols, all of the samples contain 1.0% filler.	173
7.17	Effect of AEAPTMS concentration on PEI/S-HNT MMM CO ₂ permeability using protocol 50-5-4, all of the MMMs contains 1.0% filler.	174
7.18	Effect of AEAPTMS concentration on S-HNT MMMs CO ₂ /CH ₄ selectivity using protocol 50-5-4, all of the MMMs contains 1.0% filler.	175
7.19	Movement of experimental points on the membrane performance map as a result of increase in silane concentration.	176
7.20	Effect of S2-HNT loading on S2-HNT MMM CO ₂ permeability and CO ₂ /CH ₄ selectivity using protocol 50-5-4.	177
7.21	Movement of experimental points on the membrane performance map as a result of increase in filler loading.	178
8.1	FESEM images of (a) HNT, (b) Ag-HNT, (c) S-HNT, (d) S-Ag-HNT and (e) Ag-S-HNT. The images magnification are 25,000×.	183
8.2	FTIR spectra (4000-500 cm ⁻¹) for HNT, S-HNT, Ag-HNT and S-Ag-HNT at room temperature.	184
8.3	XRD patterns for HNT and Ag-HNT at room temperature.	186
8.4	TG and DTG curves of original, Ag-ion exchanged and AEAPTMS-modified halloysite samples: A)HNT, B)Ag-HNT, C)S-Ag-HNT and D)Ag-S-HNT.	188
8.4	TG and DTG curves of original, Ag-ion exchanged and AEAPTMS-modified halloysite samples: A)HNT, B)Ag-HNT, C)S-Ag-HNT and D)Ag-S-HNT (Continued).	189
8.5	FESEM micrographs of modified HNT MMMs cross sectional view using protocol 50-5-4, a) 1.0% S-HNT, b) 1.0% S-Ag-HNT and c) 1.0% Ag-S-HNT at magnification of 7,000×, 7,000× 3,300× respectively.	191
8.6	Effect of different protocols along with fillers loading on modified HNT MMMs CO ₂ permeability.	194

8.7	Effect of different protocols along with fillers loading on modified HNT MMMs CH ₄ permeability.	194
8.8	Effect of different protocols along with fillers loading on modified HNT MMMs CO ₂ /CH ₄ selectivity.	195
8.9	Effect of different loadings shown on the membrane performance map.	196
9.1	Schematic diagrams of the crystalline structure of MMT.	200
9.2	FTIR spectra (3500-500 cm ⁻¹) for Raw MMT, General MMT, Cloisite 15A, Hydrophobic MMT and Hydrophilic MMT at room temperature.	203
9.3	XRD patterns for the MMT samples at room temperature.	204
9.4	TG and DTG curves of MMT samples; A) Raw MMT, B) General MMT, C) Cloisite 15A, D) Hydrophobic MMT and E) Hydrophilic MMT.	206
9.4	TG and DTG curves of MMT samples; A) Raw MMT, B) General MMT, C) Cloisite 15A, D) Hydrophobic MMT and E) Hydrophilic MMT (continued).	207
9.5	FESEM micrographs cross sectional view of different 1.0% MMT MMMs, a) Raw MMT, b) General MMT, c) Cloisite 15A, d) Hydrophobic MMT and e) Hydrophilic MMT.	210
9.6	Effect of various MMTs on 1.0%MMT/PEI MMM CO ₂ permeance.	212
9.7	Effect of various MMTs on 1.0%MMT/PEI MMM CO ₂ /CH ₄ selectivity.	212
9.8	Effect of Cloisite 15A loading on PEI/Cloisite 15A MMM CO ₂ permeance and CO ₂ /CH ₄ selectivity.	215

LIST OF SYMBOLS

ROMAN LETTERS

a, b, c	-	MMM element dimensions
A	-	Membrane area
$AARE$	-	Average absolute relative error
d	-	Particle diameter or height or number density
D	-	Diffusivity
E	-	Diffusion activation energy
J	-	Gas flux
k	-	Langmuir adsorption coefficient or constant or Knudsen number
l	-	Membrane thickness,
m		Mass of gas molecule
M	-	Molecular weight
n	-	Parameter in Frenlich –Lungmuir Model
NDP	-	Number of data points
p	-	Gas pressure
P	-	Permeability
q		Amount of gas saturated in adsorbant
Q	-	Gas volumetric flow rate
r		Pore radius
R	-	Gas universal constant or Permeance resistance
S	-	Gas solubility in membrane or inorganic, or parameter
t		Interphase thickness or measured time
T	-	Absolute temperature
u	-	Parameter in the developed model
V	-	Gas volume

x	-	Diffusion distance dimension
Z	-	Gas compressibility factor
$\%AARE$		Average absolute relative errors
$\%ARE$	-	Percentage of absolute relative erroe
$\%RE$	-	Percentage of relative error

GREEK LETTERS

α	-	Permselectivity
β	-	Ratio of the interphase permeability to the polymer permeability
δ	-	Ratio of the interphase radius to the particle radius, particle size
Δ	-	Difference in pressure
ε	-	Porosity
ϕ	-	Filler loading
ϕ'		Dimension parameters in developed model
γ	-	Ratio of the interphase thickness to the particle radius
η	-	Gas viscosity
λ	-	Permeability ratio or Gas mean free path
μ	-	Number density
θ	-	Site occupancy of gas molecules in adsorbant
ρ	-	Density,
σ	-	Standard deviation or molecular size
δ	-	Gas kinetic diameter
τ	-	Tortuosity

SUPERSCRIPTS

Cal	-	Calculated
Exp	-	Experimental
i	-	Interphase

SUBSCRIPTS

<i>B</i>	-	Boltzmann
<i>d</i>	-	Dispersed phase
<i>f</i>	-	Feed side
<i>i</i>	-	Interphase or gas component
<i>j</i>	-	Gas component or counter
<i>K</i>	-	Knudson
<i>L</i>	-	Downstream pressure
<i>m</i>	-	Polymer matrix or molecular property
<i>M</i>	-	Molecular weight, Maximum filler loading
<i>O</i>	-	Upstream pressure
<i>p</i>	-	Permeate side or Poiseuille
<i>r</i>	-	Relative
<i>S</i>	-	Inorganic phase in the combined inorganic and interphase phase
$0, \infty$	-	Different diffusivity
<i>1,2</i>	-	Penetrant gas through membrane
<i>I,II,III</i>	-	Element different regions

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	List of publications	243
B	Dope preparation calculations	245
C	Measured CO ₂ permeability and CO ₂ /CH ₄ selectivity of fabricated raw-HNT/PEI MMMs and modified-HNT/PEI MMMs at 25 °C by applying different protocols	246
D	Measured CO ₂ permeability and CO ₂ /CH ₄ selectivity of fabricated Ag-HNT/PEI MMMs at 25 °C by applying different protocols	248
E	Measured CO ₂ permeability and CO ₂ /CH ₄ selectivity of fabricated different nano clay-MMT/PEI MMMs at 25 °C	250

CHAPTER 1

INTRODUCTION

1.1 Research Background

Membranes are used industrially for separation purposes and gas separation is a particularly attractive area because of their potential energy savings compared with more conventional separation techniques. Like any process, their application is closely linked to economic aspects such as energy costs, but also costs associated with the system itself. Membrane economics is closely related to their transport properties, permeability and selectivity. Permeability determines the productivity of the separation, and selectivity determines the efficiency of separation. The application potential of membranes is determined by the polymeric layers or composite structures which separate gaseous mixtures such as nitrogen /oxygen for air separation, CO₂ separation from natural gas and hydrogen separation, areas which form the backbone of membrane technology research.

Nowadays, natural gas is the fastest growing primary energy source in the world and its applications are expected to increase by 70 % between 2001 and 2025 (Energy Information Administration, 2005). Natural gas is a very versatile feedstock, since it can be converted into a variety of products such as methanol, synthesis gas (CO/H₂), and synthetic crude oil and diesel via Fisher-Tropsch technology. From many points of view, methane is a perfect fuel for these purposes. It is available in most populated areas, impurities can be easily separated and among the hydrocarbons, it has the highest heating value relative to the amount of CO₂

produced. On the other hand, natural gas is a cleaner burning fuel compared to coal or fuel oils for power plants and home heating.

As worldwide demand increases, even those gas fields with high concentrations of CO_2 must be developed. The natural gas CO_2 content must be reduced to a specific level in order to increase the heating value and to reduce the effect of corrosion in process equipment in the presence of water (formation of carbonic acid). Acid gases, including CO_2 and H_2S , are known as contaminants in natural gas and biogas. On one hand, CO_2 causes a decline in natural gas and biogas heating value and on the other hand, H_2S is a very poisonous, polluting and corrosive ingredient. The removal of these acid gases becomes very important. Present approaches to separate off-gas impurities and to increase its heating value have been basically limited to physicochemical methods such as chemical separation, adsorption, cryogenic separation, as well as membrane separation technology. Chemical techniques are principally based on absorption at high pressure (in water, 30% solution of potassium carbonate, solution of monoethylenamine, etc.). Adsorption is based on the sorptivity of impurities in which a suitable adsorbent material plays a vital role (Astarita, 1983). Amine absorption is a conventional process in the acid gas removal market. High costs, solvent regeneration and operational issues are major problem in the absorption process. Thus, the application of membranes for gas separation may be preferred in many cases provided that they could maintain good implementation in the presence of corrosive feed streams. On the other hand, there are also economically significant benefits in constructing hybrid membrane-amine systems. (Rao and Rubin, 2002).

1.2 Problem Statement

Penetration through membranes in which filler has been embedded, known as mixed matrix membranes (MMMs), has already been investigated theoretically as well as experimentally since the 1960s. Theoretically, there is a demand for an equation that describes the permeability of the composite membrane as a function of the permeability of the matrix phase and the filler phase, along with the amount of filler. The equivalent for this problem in dielectrics has been studied extensively.

(Bouma *et al.*, 1997). Nearly all of the present models are derived from other systems i.e. electrical or thermal systems, while a model based purely on MMM physical geometry is highly required. Moreover, almost all of the present models are not able to predict the MMMs permeability directly in one step.

Membrane materials possessing high selectivity for carbon dioxide/(methane or nitrogen) have been proposed, using both organic (e.g. polymeric materials) and inorganic (e.g. ceramic materials) membranes. At present, the application of commercial membranes is governed by polymeric membranes. Current studies have pointed to the development of polymeric membranes as well as their applications. The separation properties of the inorganic materials locate far from the polymeric membranes which indicates their superiority based on the upper-bound diagram (Singh and Koros, 2000; Feuters and Centeno, 1999; Kim *et al.*, 2004; Park *et al.*, 2004; Tin *et al.*, 2004). Although outstanding enhancement in gas separation performance of the membranes over the last few decades had been achieved, much development is still needed if membrane performance surpassing the trade-off boundary is considered as the key target. Likewise, the current utilization of inorganic membranes seems to be limited because of the unclear issues in terms of preparing membranes with defect-free structures, the economic aspects, along with the handling problem (Saracco *et al.*, 1999; Caro *et al.*, 2000). In order to achieve this goal, and to provide an acceptable substitute, an economically viable membrane with outstanding properties beyond the upper-bound limit, should be proposed using novel techniques. MMM, one of the most recent advances in membrane morphology development is comprised of a polymeric matrix and inorganic phases, representing the latest generation of membranes. MMMs or hybrid membranes have inorganic fillers such as zeolite, carbon molecular sieve or carbon nanotubes with excellent gas separation properties embedded into the matrix of a prospective polymer (Duval *et al.*, 1994; Gur, 1994 and Anson *et al.*, 2004). The composite material would have permeation properties surpassing the upper-bound while retaining the attractive economics and relative ease of processing a polymeric material (Jia *et al.* 1991; Jiang *et al.*, 2004a; Huang *et al.*, 2006 and Jiang *et al.*, 2006b). However, among the attempts to develop MMM, there is some successful work that can jump the upper bound, but there is still a long distance to go before mass production and

industrialization of this category of membranes. Therefore, developing new MMMs with the aid of novel fillers and polymers in conjunction with the use of novel coupling agents is highly required.

The majority of membranes used in natural gas dehydration or CO₂ removal application have been made from cellulose acetate and polysulfone, which provide a CO₂/CH₄ selectivity around 15 to 20. Membranes with high CO₂/CH₄ selectivities (>35) would be very beneficial to minimize the loss of CH₄ and other hydrocarbons in the permeate stream, thereby maximizing recovery of CH₄ and other hydrocarbons in the product or retentate stream. For N₂ removal from N₂/CH₄ gas mixture Teflon AF2400 (Pinnau and Toy, 1996; Robeson, 2008) and polyimide (Wang *et al.*, 2008; Robeson, 2008) offer a selectivity of 1.3 and 4.43 respectively. As can be seen, membrane with higher selectivities are required (>10) to minimize the CH₄ loss. Hydrocarbon loss in the permeate stream can incur significant processing cost because of the loss of product gas that could otherwise be sent down the pipeline. Currently, hydrocarbon losses are typically greater than 5 % for natural gas CO₂ removal application using existing membranes. Such high losses are not economically favorable in comparison to conventional amine process where hydrocarbon loss is negligible. Therefore, more selective along with more permeable membranes are required to effectively compete with traditional process. Now for the purpose to achieve higher selectivity, using polymers having higher performance in terms of selectivity and permeability such as: Polyimide (i.e. Matrimid 5218) because of high cost is not economically applicable; therefore developing MMMs to achieve higher selectivity and permeability but not at the cost of the increase in expenses is one of the researchers interests.

1.3 Objectives of the Study

The preceding sections outlined the current challenges which must be overcome before MMMs can be used for commercial application. Therefore, based on the problem statement, the objectives of this study are as follows:

1. To develop a new theoretical model to predict gas permeability for mixed matrix membrane.
2. To conduct functionalization and characterization of clay i.e. Montmorillonite and Halloysite nano-tubes using coupling agent .
3. To perform transition metal ion exchange treatment on halloysite nano tubes to study the facilitated transport effects on mixed matrix membranes performance.
4. To characterize and evaluate the performance of mixed matrix membrane membranes for CO₂/CH₄ separation.

1.4 Scopes of the Study

In order to achieve the abovementioned objectives, the following scopes of works were drawn:

1. Studying and evaluating the existing theoretical models.
2. Developing a new model to predict the MMMs permeability and the MMMs penetration flow path across MMMs.
3. Functionalization of clay nan-otubes using N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) as a coupling agent.
4. Fabricating of mixed matrix membrane using polyetherimide and functionalized Halloysite nano-tubes clay.
5. Fabricating of mixed matrix membrane using polyetherimide and five types of Montmorillonite (raw MMT, Cloisite 15 A, general MMT, hydrophilic MMT and hydrophobic MMT) nano-particles clay.
6. Conducting Ag⁺ ion exchange treatment of Halloysite nano-tubes to enhance CO₂ solubility selectivity, hence the final MMMs permselectivity.
7. Membrane characterization using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infra Red spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA),

Differential Scanning Calorimetric (DSC), Energy dispersive X-rays (EDX), viscometry and constant pressure permeation test.

8. Proposing a morphological map and modeling of MMMs transport properties applying large pore size fillers.
9. Performance evaluation of each functionalized or synthesized clay nano-tubes mixed matrix membrane for the purification of natural gas.

1.5 Thesis Organization

This thesis describes the development of PEI/MMMs incorporated with large pore size halloysite nano-tubes (HNTs) for gas separation both theoretically and experimentally, which is divided into 10 chapters.

Chapter 1 presents background of the study, problem statement, objectives and scopes of the researches. Chapter 2 discusses the different aspects of MMMs along with their challenges for gas separation in details. In addition, current status of the techniques is critically presented. The research methodology of the developed permeability model for MMMs system along with the MMMs fabrication and characterizations are described in details in Chapter 3.

The gas permeability in MMMs using theoretical models and their comparison with the published experimental data are extensively discussed in Chapter 4. The models considered are: Maxwell model modified Maxwell model, Lewis-Nielsen model, modified Lewis-Nielsen model and Felske model. Chapter 5 discusses the development of a new theoretical model based on resistance modeling approach to predict mixed matrix membrane performance. The expected morphologies for MMMs comprising large pore size fillers are investigated in Chapter 6. Halloysite nanotube (HNT) was employed as a representative of large pore size fillers to interpret the morphologies.

Chapter 7 investigates the gas separation and transport properties of asymmetric mixed matrix membranes fabricated from polyetherimide (PEI); Ultem 1000 incorporated with raw and modified HNTs as filler. The modified HNTs; S-HNTs were prepared by treating HNTs with N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane (AEAPTMS). In Chapter 8, the facilitated transport effect of Ag⁺ ion exchanged HNTs as filler on the gas separation performance of asymmetric mixed matrix membranes are discussed. Three protocols were performed: (i) S-HNT MMM (no Ag⁺ ion exchange treatment), (ii) S-Ag-HNT MMM (first Ag⁺ ion exchanging and then silylation of HNTs), and (iii) Ag-S- HNT MMM (first silylation and then Ag⁺ ion exchanging of HNTs). The effect of montmorillonite (MMT) nano-clay fillers on polyetherimide (PEI) mixed matrix membrane for carbon dioxide removal has been studied in Chapter 9. Five different types of MMT nano-clays including unmodified and industrially modified clays were used as filler to fabricate asymmetric flat sheet MMM via a dry/wet phase inversion technique. The five types of clay used were: raw MMT, Cloisite 15A, general MMT, hydrophobic MMT and hydrophilic MMT.

The general conclusions drawn from this research and some recommendations proposed for future study are presented in Chapter 10.

REFERENCES

- Abanades, J. C., Rubin, E. S., and Anthony, E. J. (2004). Sorbent cost and performance in CO₂ capture systems. *Industrial and Engineering Chemistry Research*. 43(13): 3462–3466.
- Aboudheir, A., Tontiwachwuthikul, P., and Idem, R. (2006). Rigorous model for predicting the behavior of CO₂ absorption into AMP in packed-bed absorption columns. *Industrial and Engineering Chemistry Research*. 45(8): 2553-2557.
- Adamsa, R., Carsona, C., Warda, J., Tannenbaum, R., Koros, W. (2010). Metal organic framework mixed matrix membranes for gas separations, *Micropor. Mesopor. Mater.* 131: 13-20.
- Adoor, S. G. Sairam, M., Manjeshwar, L. S., Raju, K. V. S. N., and Aminabhavi, T. M. (2006). Aminabhavi, Sodium montmorillonite clay loaded novel mixed matrix membranes of poly(vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane. *J. Membr. Sci.* 285: 182-195.
- Ahn, H., Moon, J. H., Hyun, S. H., and Lee, C. H. (2004). Diffusion Mechanism of Carbon Dioxide in Zeolite NaA and CaX Pellets. *Adsorption*. 10:111–128.
- Ahn, J. Chung, W. J. Pinnau, I. and Guiver, M.D. (2008). Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation, *J. Membr. Sci.* 314: 123-133.
- Al-Juaied, M., and Rochelle, G. T. (2006). Absorption of CO₂ in aqueous diglycolamine. *Industrial and Engineering Chemistry Research*. 45(8): 2473–2482.
- Anand, M., Langsam, M., Rao, M. B., and Sircar, S. (1997). Multicomponent gas separation by selective surface flow (SSF) and polytrimethylsilylpropyne (PTMSP) membranes. *J Membr Sci.* 123:17–25.

- Anson, M., Marchese, J., Garis, E., Ochoa, N., and Pagliero, C. (2004). ABS copolymer-activated carbon mixed matrix membrane for CO₂/CH₄ separation. *J Membr Sci.* 243:19–28.
- Aroon, M. A., Ismail, A. F., Montazer-Rahmati, M. M., and Matsuura, T. (2010a). Effect of raw multi wall carbon nanotubes on morphology and separation properties of polyimide membranes. *Sep. Sci. Technol.* 45: in press.
- Aroon, M. A., Ismail, A. F., Montazer-Rahmati, M. M., and Matsuura, T. (2010b). Effect of chitosan as a functionalization agent on the performance and separation properties of polyimide/multi-walled carbon nanotubes mixed matrix flat sheet membranes, *J. Membr. Sci.* doi:10.1016/j.memsci.2010.08.023.
- Aroon, M. A., Ismail, A. F., Montazer-Rahmati, M. M., and Matsuura, T. (2010c). Performance studies of mixed matrix membranes for gas separation: A review. *Sep. Purif. Technol.* 75: 229–242.
- Aroon, M. A., Ismail, A. F., Montazer-Rahmati, M. M., and Matsuura, T. (2010d). Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent. *Sep. Purif. Technol.* 72 :194–202.
- Astarita, G.D., W. Savage and A. Bisio, (1983), *Gas treating with chemical solvents*, John Wiley and Sons, New York.
- Atdlhan, S. *Molecular Dynamics Simulation of Montmorillonite and Mechanical and Thermodynamic Properties Calculations*. Master of science thesis. Texas A&M University. 2007.
- Auerbach , S. M., Carrado, K. A., and Dutta , P. K. (2005). *Handbook of Zeolite Science and Technology*. New York: Taylor and Francis e-Library.
- Baron, J. D., Roof, J. G., and Wells, F. W. (1959). Viscosity of nitrogen, methane, ethane, and propane at elevated temperature and pressure. *J. Chem. Eng. Data* 4: 283-288.
- Barsema, J., Balster, J., Jordan, V., Vegt, N. van der, and Wessling, M. (2003). Functionalized carbon molecular sieve membranes containing Ag nanoclusters. *J Membr Sci.* 219: 47–57.
- Bello, A., and Idem, R. O. (2006). Comprehensive study of the kinetics of the oxidative degradation of CO₂ loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during

- CO₂ absorption from flue gases. *Industrial and Engineering Chemistry Research*. 45(8): 2569-2579.
- Bhardwaj, V., Macintosh, A., Sharpe, I.D., Gordeyev, S.A., and Shilton, S.J. (2003). Polysulfone hollow fiber gas separation membranes filled with submicron particles. *Ann NY Acad Sci*. 984:318–28.
- Boom, J. P. (1994). Transport through zeolite filled polymeric membranes. Ph. D. Thesis, The Netherlands: University of Twente.
- Boroglu, M. S., and Gurkaynak, M. A. (2010). Fabrication and characterization of silica modified polyimide–zeolite mixed matrix membranes for gas separation properties. *Polym. Bull*. 66: 463-478.
- Bos, A., Punt, I. G., Wessling, M., and Strathmann, H. (1998). Plasticization-resistant glassy polyimide membrane for CO₂/CH₄ separations. *Sep Purif Technol*. 14:27–39.
- Bos, A., Punt, I., Strathmann, H., and Wessling, M. (2001). Suppression of gas separation membrane plasticization by homogeneous polymer blending. *AIChE J*. 47:1088–93.
- Bouma, R. H. B., Checchetti, A., Chidichimo, G., Drioli, E. (1997). Permeation through a heterogeneous membrane: the effect of the dispersed phase, *J. Membr. Sci*.128:141-149.
- Brindley G.W. and Brown G.(1980). *Crystal Structures of Clay Minerals and their X-ray Identification*. London: Mineralogical Society.
- Broyles, N.S., Verghese, K.N.E., Davis, S.V., Davis, H. Li, Lesko, J.J., and Riffle, J. (1998). Fatigue performance of carbon fiber/vinyl ester composites: the effect of two dissimilar polymeric sizing agents, *Polymer*. 39:3417–3424.
- Bruggeman, D. A. G. (1935). Berechnung Verschiedener Physikalischer Konstanten Von Heterogenen Substanzen. I. Dielektrizitätskonstanten Und Leitfähigkeiten Der Mischkörper Aus Isotropen Substanzen. *Ann. Phys*. 24:636-679.
- Busetto, L., Cassani, M. C., Femoni, C., Macchioni, A., Mazzoni, R., and Zuccaccia, D. (2008). Synthesis, molecular structures and solution NMR studies of N-heterocyclic carbene–amine silver complexes. *J. Organomet. Chem*. 693: 2579–2591.
- Cabasso, I., Klein, E., and Smith, J. K. (1977). Polysulfone hollow fibers. II. Morphology. *J Appl Polym Sci*. 21:165–80.

- Cao, D.V., Mohr, R.J., Rao, M.B., and Sircar, S. (2000). Self-Diffusivities of N₂, CH₄, and Kr On NaAZeolite Pellets by Isotope Exchange Technique, *J. Phys. Chem. B.* 104:10498–10501.
- Caro, J., Noack, M., Kolsch, P., and Schaefer, R. (2000). Zeolite membrane-state of their development and perspective. *Micropor Mesopor Mater.* 38:3–24.
- Carrado, K.A., Xu, L.Q., Csencsits, R., and Muntean, J.V. (2001). Use of organo- and alkoxy-silanes in the synthesis of grafted and pristine clays. *Chem. Mater.* 13: 3766-3773.
- Cavenati, S., Grande, C. A., and Rodrigues, A. E. (2006). Removal of Carbon Dioxide from Natural Gas by Vacuum Pressure Swing Adsorption. *Energy Fuels* 20:2648-2659.
- Chang, T. S., and Kafchinski, E. R. (1997). The Effects of Spinning Conditions on Asymmetric 6FDA/6FDAM Polyimide Hollow Fibers for Air Separation. *J. Appl. Polym. Sci.* 65: 1555–1569.
- Chen, X., Yang, W., Lie, J., and Lin, L. (2005). Synthesis of zeolite NaA membrane with high permeance under microwave radiation on mesoporous-layer-modified macroporous substrates for gas separation. *J. Membr. Sci.* 255:201-211.
- Chiou, J. S., Maeda, Y., and Paul, D. R. (1987). Gas permeation in polyethersulfone. *J Appl Polym Sci.* 33:1823–1828.
- Chow, W. S., and Neoh, S. S. (2009). Dynamic mechanical, thermal, and morphological properties of silane-treated montmorillonite reinforced polycarbonate nanocomposites. *J. Appl. Polym. Sci.* 114: 3967–3975 .
- Choy, J.H., Kwak, S. Y., Han, Y. S., and Kim, B. W. (1997). New organo-montmorillonite complexes with hydrophobic and hydrophilic functions. *Mate. Lett.* 33: 143-147.
- Chung, T. S., Chan, S.S., Wang, R., Lu, Z., and He, C. (2003). Characterization of permeability and sorption in Matrimid/C60 mixed matrix membranes. *J Membr Sci* . 211:91–9.
- Chung, T. S., Jiang, L. Y., Li, Y., and Kulprathipanja, S. (2007). Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog. Polym. Sci.* 32:483–507.

- Chung, T. S., Kafchinski, E. R., Vora, R. H. (1994). Development of a defect-free 6FDA durene asymmetric hollow fibers and its composite hollow fibers. *J Membr Sci.* 88:21–36.
- Churchman, G.J. and Carr, R.M. (1975). The definition and nomenclature of halloysites. *Clays and Clay Miner.* 23: 382-388.
- Churchman, G.J., Davy, T.J., Aylmore, L.A.G., Gilkes, R.J., and Self, P.G. (1995). Characteristics of fine pores in some halloysites. *Clay Miner.* 30: 89-98.
- Clarizia, G., Algieri, C., and Drioli, E. (2004). Filler–polymer combination: a route to modify gas transport properties of a polymeric membrane. *Polymer.* 45:5671–81.
- Clarizia, G., Algieri, C., Regina, A., and Drioli, E. (2008). Zeolite-based composite PEEK-WC membranes: Gas transport and surface properties. *Micropor. Mesopor. Mater.* 115:67–74.
- Clausi, D. T. and W. J. Koros, "Formation of defect-free polyimide hollow fiber membranes for gas separations", *J. Membr. Sci.*, 167, 79-89 (2000).
- Coady, A., and Davis, J. (1982). CO₂ recovery by gas permeation. *Chem Eng Prog.* 78: 43-49.
- Cong, H., Zhang, J., Radosz, M., and Shen, Y. Sh. (2007). Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4- phenylene oxide) for gas separation., *J. Membr. Sci.* 294: 178-185.
- Cong, H., Zhang, J., Radosz, M., Shen, Y. (2007). Carbon nanotube composite membranes of brominated poly(2,6-diphenyl-1,4-phenylene oxide) for gas separation. *J. Membr. Sci.* 294: 178–185.
- Damle, A. S., and Dorchak, T. P. (2001). Recovery of carbon dioxide in advanced fossil energy conversion processes using a membrane reactor. *Journal of Energy and Environment Research.* 1(1): 77–89.
- Defontaine, G., Barichard, A., Letaief, S. Feng, C., Matsuura, T., And Detellier, C. (2010). Nanoporous polymer – Clay hybrid membranes for gas separation, *J. Colloid Interf. Sci.* 343: 622–627.
- Duval, J. M., Folkers, B., Mulder, M. H. V., Desgrandchamps, G., and Smolders, C. A. (1993). Adsorbent filled membranes for gas separation. Part 1. Improvement of the gas separation properties of polymeric membranes by incorporation of microporous adsorbents. *J Membr Sci.* 80:189–98.

- Duval, J.M. (1995). Adsorbent filled polymeric membranes. PhD thesis. The Netherlands: University of Twente.
- Ekiner, O. M., and Vassilatos, G. (1990). Polyaramide hollow fibers for hydrogen/methane separation—spinning and properties. *J Membr Sci.* 53:259–73.
- Ekiner, O. M., Kulkarni, S.S. (2003). Process for making hollow fiber mixed matrix membranes: US patent 6663805.
- Energy Information Administration, 2004, annual energy outlook with projection to 2025, U.S. department of energy
- Ersolmaz, S. B. T., Senorkyan, L., Kalaonra, N., Tatlier, M., and Senatalar, A.E. (2001). n-Pentane/i-pentane separation by using zeolite–PDMS mixed matrix membranes. *J Membr Sci.* 189:59–67.
- Fauth, D. J., Frommell, E. A., Hoffman, J. S., Reasbeck, R. P., and Pennline, HW. (2005). Eutectic salt promoted lithium zirconate: Novel high temperature sorbent for CO₂ capture. *Fuel Processing Technology.* 86(14-15): 1503–1521.
- Felske, J. D. (2004). Effective thermal conductivity of composite spheres in a continuous medium with contact resistance. *Int. Heat Mass Transfer.* 47:3453–3461.
- Feuters, A. B., and Centeno, T. A. (1999). Preparation of supported carbon molecular membranes. *Carbon.* 37:679–84.
- Fouda, A., Chen, Y., Bai, J. and Matsuura, T. (1991). Wheatstone bridge model for the laminated polydimethylsiloxane/polyethersulfone membrane for gas separation. *J. Membrane Sci.* 64: 263-271.
- Freeman, B., and Pinnau, I. (1997). Separation of gases using solubility-selective polymer. *Trends Polym Sci.* 5: 167–73.
- Freeman, B., and Pinnau, I. (1999). Polymer membrane for gas and vapor separations: chemistry and material science. Washington, DC: American Chemical Society.
- Fritzsche, A. K., Cruse, C. A., Kesting, R. E., and Murphy, M. K. (1990). Polysulfone hollow-fiber membranes spun from Lewis acid:base complexes. Part II. The effect of Lewis acid-to-base ratio on membrane structure. *J Appl Polym Sci.* 39:1949–56.

- Fritzsche, A., and Kurz, J. (1990). The separation of gases by membranes, in: Handbook of industrial membrane technology porter MC, editor. William Andrew Publishing. 559-593.
- Funk, C. V., and Lloyd, D. R. (2008). Zeolite-filled microporous mixed matrix (ZeoTIPS) membranes: Prediction of gas separation performance , J. Membrane Sci. 313: 224–231.
- Goff, G. S., and Rochelle, G. T. (2006). Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO₂ capture processes. Industrial and Engineering Chemistry Research. 45(8): 2513–2521.
- Gonzo, E.E., Parentis, M.L., and Gottifredi, J.C. (2006). Estimating models for predicting effective permeability of mixed matrix membranes. J. Membr. Sci. 277:46-54.
- Gorgojo, P., Uriel, S., Tellez, C., and Coronas, J. (2008) .Development of mixed matrix membranes based on zeolite Nu-6(2) for gas separation, Micropor. Mesopor. Mater. 115 :85–92.
- Gray, M. L., Soong, Y., Champagne, K. J., Pennline, H., Baltrus, J. P., Stevens, R. W., Khatri, R. Jr., Chuang, S. S. C., and Filburn, T. (2005). Improved immobilized carbon dioxide capture sorbents. Fuel Processing Technology. 86(14-15): 1449–1455.
- Guan, H. M., Chung, T. S., Huang, Z., Chng, M. L., and Kulprathipanja, S. (2006). Poly (vinyl alcohol) multilayer mixed matrix membranes for the dehydration of ethanol-water mixture. J Membr Sci. 268:113–122.
- Guiver, M. D., Robertson, G. P., Dai, Y., Bilodeau, F., Kang, Y. S., and Lee, K. J. (2003). Structural characterization and gas-transport properties of brominated Matrimid polyimide. J Polym Sci: Polym Chem . 40:4193–204.
- Gur, T. M. (1994). Permselectivity of zeolite filled polysulfone gas separation membranes, J. Membr. Sci. 93: 283-289.
- Gur, T. M. (1994) Permselectivity of zeolite filled polysulfone gas separation membranes. J. Membr. Sci. 93:283-289.
- Hashemifard, S.A., Ismail, A.F., Matsuura, T. (2010). A new theoretical gas permeability model using resistance modeling for mixed matrix membrane systems. J. Membr. Sci. 350: 259–268.

- Hasse, D. J., Kulkarni, S. S., Corbin, D. R., and Patel, A.N. (2003). Mixed matrix membranes incorporating chabazite type molecular sieves: US patent 6626980
- He, Z., Pinnau, I., and Morisato, A. (2002). Nanostructured poly (4-methyl-2-pentyne)/silica hybrid membranes for gas separation. *Desalination*. 146:11–5.
- Heide, W. (2002). Production of Acid-modified Potassium Zeolite 3A by Cation Exchange of Sodium Zeolite 4A. European Patent No. DE10107819.
- Hill, T. (1956). Surface diffusion and thermal transpiration in fine tubes and pores. *J Chem. Phys.* 25; 730-745.
- Hillock, A. M.W., Miller, S. J., and Koros, W. J. (2008). Crosslinked mixed matrix membranes for the purification of natural gas: Effects of sieve surface modification. *J. Membr. Sci.*314:193-199.
- Ho, W., and Sirkar, K. (1992). *Membrane handbook*. New York: Van Nostrand Reinhold.
- Ho, W., and Dalrymple, D. (1994). Facilitated transport of olefins in Ag-containing polymer membranes. *J Membr Sci.* 91: 13–25.
- Hope, E. W., and Kittrick, J. A. (1964). Surface tension and the morphology of halloysite. *Am. Mineral.* 49: 859-866.
- Huang, A., and Yang, W. (2008). Enhancement of zeolite NaA membrane properties through organic cation addition. *Sep. Purif. Technol.* 61:175-181
- Huang, H. Y., Yang, R. T., Chinn, D., and Munson, C. L. (2003). Aminegrafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas. *Industrial and Engineering Chemistry Research*. 42(12): 2427–2433.
- Huang, Z. Li, Y. Wen, R. Teoh, M.M. Kulprathipanja, S. (2006) Enhanced gas separation properties by using nanostructured PES-zeolite 4A mixed matrix membranes, *Journal of Applied of Polymer Science*. 101, 3800-3805
- Hughes, R. W., Lu, D. Y., Anthony, E. J., and Macchi, A. (2005). Design, process simulation and construction of an atmospheric dual fluidized bed combustion system for in situ CO₂ capture using high-temperature sorbents. *Fuel Processing Technology*. 86(14-15): 1523–1531.
- Husain, S., and Koros, W. J. (2005). *In mixed matrix hollow fibers for gas separation*. Providence, RI: North American Membrane Society.

- Hwang, S. T., and Kammermeyer, K. (1975). *Membrane Separations*. New York: Wiley-Interscience.
- Idem, R., Wilson, M., Tontiwachwuthikul, P., Chakma, A., Veawab, A., Aroonwilas, A., and Gelowitz, D. (2006). Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the university of regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant. *Industrial and Engineering Chemistry Research*. 45(8): 2414–2420.
- Ismail, A. F., Kusworo, T. D., Mustafa, A. (2008a). Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Amino silane agent. *Journal of Membrane Science* .319:306–312.
- Ismail, A. F., Lai, P. Y. (2003). Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. *Separation and Purification Technology*.33:127-143.
- Ismail, A. F., Rahim, R. A., Rahman, W. A. W. A. (2008b). Characterization of polyethersulfone/Matrimid® 5218 miscible blend mixed matrix membranes for O₂/N₂ gas separation. *Separation and Purification Technology*.63:200–206.
- Jassim, M. S., and Rochelle, G. T. (2006). Innovative absorber/stripper configurations for CO₂ capture by aqueous monoethanolamine. *Industrial and Engineering Chemistry Research*. 45(8): 2465–2472.
- Jawad, M. (1989). Future for desalination by reverse osmosis. *Desalination*. 72: 23-28.
- Jia, M., K.-V. Peinemann, and R.-D. Behling. (1991) Molecular Sieving Effects of Zeolite-Filled Silicone Rubber Membranes in Gas Permeation. *Journal of Membrane Science*, 57:289-296.
- Jia, M., Peinemann, K. V., and Behling, R. D. (1991). Molecular sieving effect of the zeolite-filled silicone rubber membranes in gas permeation. *J Membr Sci*. 57:289–292.
- Jia, M., Peinemann, K. V., and Behling, R. D. (1992). Preparation and characterization of thin-film zeolite–PDMS composite membranes. *J Membr Sci*. 73:119–128.

- Jiang, L. Y. (2006). Fabrication and characterization of composite membranes for gas separation. PhD thesis. Singapore: National University of Singapore.
- Jiang, L. Y., Chung, T.S., Kulprathipanja, S. (2006b) Fabrication of mixed matrix hollow fibers with intimate polymer-zeolite interface for gas separation, *AIChE* 52, 2898.
- Jiang, L. Y., Chung, T. S., and Kulprathipanja, S. (2006a). An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation. *J Membr Sci.* 276:113–25.
- Jiang, L. Y., Chung, T. S., and Kulprathipanja, S. (2006c). A novel approach to fabricate mixed matrix hollow fibers with superior intimate polymer/zeolite interface for gas separation. *AIChE J.* 52:2898–908.
- Jiang, L. Y., Chung, T. S., Cao, C., Huang, Z., and Kulprathipanja, S. (2005). Fundamental understanding of nano-sized zeolite distribution in the formation of the mixed matrix single- and duallayer asymmetric hollow fiber membranes. *J Membr Sci.* 252:89–100.
- Jiang, L.Y., Chung, T.S., and Rajagopalan, R. (2007). Matrimid®/MgO mixed matrix membranes for pervaporation. *AIChE J.* 53 : 1745-1757.
- Jiang, L.Y., T.S. Chung, D.F. Li, C. Cao and S. Kulprathipanja, (2004a) Fabrication of Matrimid/polyethersulfone dual-layer hollow fiber membranes for gas separation”, *Journal of Membrane Science*, 240, p. 91.
- Joussein, E. Petit, S., Churchman, J., Theng, B., Righi, D., and Delvaux, B. (2005). Halloysite clay minerals - a review, *Clay Miner.* 40: 383-426.
- Karger, J., and Ruthven, D. M. (1992). Diffusion in zeolites and oihier microporous maierials. New York: Wiley.
- Karger, J., and Ruthven, D. M. (1992). Diffusion in Zeolites and Other Microporous Solids. New York: Wiley-Interscience.
- Karniadakis, G. E., Beskok, A., and Aluru, N. (2005). Microflows–fundamentals and simulations. Springer, New York.
- Karniadakis, G.E., Beskok, A., and Aluru, N. (2005). Microflows–fundamentals and simulations. New York: Springer.
- Karode, S.K., Patwardhan, V.S., and Kulkarni, S.S. (1996). An improved model incorporating constriction resistance in transport through thin film composite membranes , *J. Membrane Sci.* 114: 157-170.

- Kautz, C. Q., and Ryan, P. C. (2003). The 10 Å to 7 Å halloysite transition in a tropical soil sequence, Costa Rica. *Clays Clay Miner.* 51: 252–263.
- Kesting, R. E., Fritzsche, A. K., Cruse, C. A., and Moore, M. D. (1990). The second-generation polysulfone gas-separation membrane. II. The relationship between sol properties, gel macrovoids, and fiber selectivity. *J Appl Polym Sci.* 40:1575–82.
- Kesting, R., and Fritzsche, A. (1993). *Polymeric gas separation membranes*. New York: Wiley.
- Kim, S., and Marand, E. (2008). High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix, *Micropor. Mesopor. Mater.* 114 : 129–136.
- Kim, S., Chen, L., Karl, J. J., and Eva, M. (2007). Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment, *J. Membr. Sci.* 294: 147-158.
- Kim, S., Pechar, T. W., and Marand, E. (2006). Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation presented at the international congress on membranes and membrane processes (ICOM), Seoul, Korea, 21–26 August 2005. *Desalination* 192: 330-339.
- Kim, S., Pechar, T.W., and Marand, E. (2006). Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation, *Desalination* 192:330–339.
- Kim, Y. K., Lee, J. M., Park, H. B., and Lee, Y. M. (2004). The gas separation properties of carbon molecular sieve membranes derived from polyimides having carboxylic acid groups. *J Membr Sci.* 235:139–46.
- Knowles, G. P., Delaney, S. W., and Chaffee, A. L. (2006). Diethylenetriamine[propyl(silyl)]-functionalized (DT) mesoporous silicas as CO₂ adsorbents. *Industrial and Engineering Chemistry Research.* 45(8): 2626–2633.
- Kobayashi, Y., Katakami, H., Mine, E., Nagao, D., Konno, M., and Liz-Marza, L. M. (2005). Silica coating of silver nanoparticles using a modified Stober method. *J. Colloid Interf. Sci.* 283: 392–396.
- Kohyama, N., Fukushima, K., and Fukami, A. (1978). Observation of the hydrated form of tubular halloysite by an electron microscope equipped with an environmental cell. *Clays and Clay Miner.* 26: 25-40.

- Koros, W. J., and Flemming, G. K. (1993). Membrane-based gas separation. *J Membr Sci* . 83:1–80.
- Koros, W. J., Wallace, D., Wind, J. D., Miller, S. J., Bickel, C. S., and Vu, D. Q. (2004). Crosslinked and crosslinkable hollow fiber mixed matrix membrane and method of making the same: US patent 6755900.
- Koros, W.J. (1991). Gas Separation, in: *Membrane Separation Systems -Recent Developments and Future Directions* Baker RW. William Andrew Publishing.
- Kovvali, A., Chen, H., and Sirkar, K. K. (2000). Dendrimer Membranes: A CO₂-Selective Molecular Gate. *J Am Chem Soc*. 122: 7594-7595.
- Krishna, R. (1990). Multicomponent surface diffusion of adsorbed species. A description based on the generalized Maxwell-Stefan diffusion equations. *Chem. Engng Sci*. 45:1779-1791
- Krishna, R. (1993). A unified approach to the modelling of intraparticle diffusion in adsorption processes. *Gas Sep. Pur.* 7:91-104.
- Krishna, R., and Wesselingh, J. A. (1997). The Maxwell-Stefan Approach to Mass Transfer *Che. Eng. Sci*. 52: 861-911.
- Kulkarni, S. S., David, H. J., Corbin, D. R., and Patel, A. N. (2003). Gas separation membrane with organosilicon-treated molecular sieve: US patent 6580860.
- Kumar, R., and Ruthven, D.M. (1979). Chromatographic Study of the Diffusion of N₂, CH₄ and Binary CH₄-N₂ Mixtures in NaA Molecular Sieve. *Can J. Chem. Engg*. 57:342–348.
- Kumar, S. A., Yuelong, H., Yumei, D., Le, Y., Kumaran, M.G., and Thomas, S. (2008). Gas transport through nano poly(ethylene-co-vinyl acetate) composite membranes, *Ind. Eng. Chem. Res*. 47: 4898–4904.
- Kusworo, T. D., Ismail, A. F., Mustafa, A., Matsuura, T. (2007). Dependence of membrane morphology and performance on preparation conditions: the shear rate effect in membrane casting. *Sep. Purif. Technol*. 61:249–257.
- Loeb, S., and Sourirajan, S. (1964): US3133132.
- Lee, K. H., and Hwang, S. T. (1986). The transport of condensable vapors through a microporous Vycor glass membrane. *J Colloid Interf. Sci*. 110: 544-555.
- Lequerica, M. C., Baena, M. J., and Espinet, P. (2008). Ionic metallomesogens derived from silver(I) bis-amine complexes: Structure and mesogenic behaviour. *Inorganica Chimica Acta* 361: 2270–2278.

- Lewis, T. B. Nielsen, L. E. (1970). Dynamic Mechanical Properties of Particulate-Filled Composites, *J. Appl. Polym. Sci.* 14:1449-1471.
- Li, Y. (2006). Development of mixed matrix membranes for gas separation application. PhD Thesis. Singapore: National University of Singapore.
- Li, Y., Cao, C., Chung, T. S., and Pramod, K. P. (2004). Fabrication of dual-layer polyethersulfone (PES) hollow fiber membranes with an ultrathin dense-selective layer for gas separation, *J. Membr. Sci.* 245: 53–60.
- Li, Y., Chung, T. S., and Huang, Z. (2006). Dual-layer polyethersulfone (PES)/BTDA-TDI/MDI co-polyimide (P84) hollow fiber membranes with a submicron PES–zeolite beta mixed matrix dense-selective layer for gas separation. *J Membr Sci.* 277:28–37.
- Li, Y., Chung, T. S., and Kulprathipanja, S. (2007a). Novel Ag⁺-zeolite/polymer mixed matrix membranes with a high CO₂/CH₄ selectivity. *AIChE J.* 53:610–6.
- Li, Y., Chung, T. S., and Xiao, Y. (2008). Superior gas separation performance of dual-layer hollow fiber membranes with an ultrathin dense-selective layer. *J. Membr. Sci.* 325: 23–27.
- Li, Y., Chung, T. S., Cao, C., and Kulprathipanja, S. (2005). The effects of polymer chain rigidification, zeolite pore size and pore blockage on polyethersulfone (PES)–zeolite A mixed matrix membranes. *J Membr Sci.* 260:45–55.
- Li, Y., Guan, H. M., Chung, T. S., and Kulprathipanja, S. (2006). Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)–zeolite A mixed matrix membranes. *J Membr Sci.* 275:17–28.
- Li, Y., Krantz, B., and Chung, T.S. (2007b). A Novel Primer to Prevent Nanoparticle Agglomeration in Mixed Matrix Membranes. *AIChE J.* 53 : 2470-2475.
- Lin, H., and Freeman, B.D. (2005). Materials selection guidelines for membranes that remove CO₂ from gas mixtures. *J. Mol. Struct.* 739: 57-74.
- Liu, C., Mcculloch, B., Wilson, S. T., Benin, A. I., and Schott, M. E. (2009). Metal organic framework-polymer mixed matrix membranes. us 7637983.
- Liu, P., and Zhao, M. (2009). Silver nanoparticle supported on halloysite nanotubes catalyzed reduction of 4-nitrophenol (4-NP). *Appl. Surf. Sci.* 255: 3989–3993.
- Loeb, S., Sourirajan, S. (1962). Sea water demineralization by means of an osmotic membrane. *Adv Chem Ser.* 38:117–32.

- MacKenzie, A., Granatstein, D. L., Anthony, E. J., and Abanades, J. C. (2007). Economics of CO₂ capture using the calcium cycle with a pressurized fluidized bed combustor. *Energy and Fuel*. 21: 920–926.
- Mahajan, R. (2000). Formation, characterization and modeling of mixed matrix membrane materials. PhD thesis. University of Texas at Austin.
- Mahajan, R., and Koros, W. J. (2002b). Mixed matrix membrane materials with glassy polymers. Part II. *Polym. Eng. Sci.* 42:1432-1441.
- Mahajan, R., and Koros, W. J. (2000). Factors controlling successful formation of mixed-matrix gas separation materials. *Ind Eng Chem Res.* 39:2692–2696.
- Mahajan, R., and Koros, W. J. (2002a). Mixed matrix membrane materials with glassy polymers. Part I, *Polym. Eng. Sci.* 42:1420-1431.
- Mahajan, R., Burns, R., Schaeffer, M., and Koros, W. J. (2002). Challenges in forming successful mixed matrix membranes with rigid polymeric materials. *J Appl Poly Sci.* 86:881–890.
- Mahajan, R., Koros, W.J., and Thundiyil, M. (1999). Mixed matrix membranes: Important and challenging!. *Membr. Tech.* 105: 6-8.
- Manovic, V., and Anthony, E. J. (2007). Steam reactivation of spent CaO-based sorbent for multiple CO₂ capture cycles. *Environmental Science and Technology*, 41: 1420–1425.
- Maroto-Valer M M, Fauth D J, Kuchta M E, Zhang Y, Andresen J M, 2005. Activation of magnesium rich minerals as carbonation feedstock materials for CO₂ sequestration. *Fuel Processing Technology.* 86: 1627–1645.
- Maxwell, J. C. (1954). *A Treatise on Electricity and Magnetism*, Dover Publications, New York.
- Mazur, W., and Chan, M. (1982). Membranes for natural gas sweetening and CO₂ enrichment. *Chem Eng Prog.* 78: 38-43.
- McCaig, M. S., and Paul, D. R. (1999). Effect of UV cross-linking and physical aging on the gas permeability of the thin glassy polyacrylate films. *Polymer.* 40:7209–25.
- McLeary, E.F., Jansen, J.C., and Kapteijn, F. (2006). Zeolite based films, membranes and membrane reactors: Progress and prospects. *Micropor. Mesopor. Mater.* 90:198-220.
- Meier, W. M., and Olson, D. H. (1992). *Atlas of zeolite structure types*, 3rd ed. London: Butterworths.

- Mellini, M., Fuchs, Y., Viti, C., Lemaire, C., and Linar `Es J. (2002). Insights into the antigorite structure from Mössbauer and FTIR Spectroscopies. *Eur. J. Mineral.* 14: 97–104.
- Merkel, T. C., Freeman, B. D., Spontak, R. J., He, Z., and Pinnau, I. (2002). Ultrapermeable, reverse-selective nanocomposite membranes. *Science.* 296:519–22.
- Merkel, T. C., He, Z., Pinnau, I., Freeman, B. D., Meakin, P., and Hill, A. J. (2003b). Effect of nanoparticles on gas sorption and transport in poly (1-trimethylsilyl-1-propyne). *Macromolecules.* 36: 6844–55.
- Merkel, T.C., He, Z., Pinnau, I., Freeman, B.D., Meakin, P., and Hill, A.J. (2003a). Sorption and transport in poly (2,2-bis(trifluoromethyl)- 4,5-difluoro-1,3-dioxole-co-tetrafluoro-ethylene) containing nanoscale fumed silica. *Macromolecules.* 36:8406–14.
- Miller, S. J., Munson, C. L., Kulkarni, S. S., and Hasse, D. J. (2002). Purification of p-xylene using composite mixed matrix membranes: US patent 6500233.
- Moaddeb, M., and Koros, W. J. (1997). Gas transport properties of thin polymeric membranes in the presence of silicon dioxide particles. *J Membr Sci.* 125:143–63.
- Mohr, R.J., Vorkapic, D., Rao, M. B., and Sircar, S. (1999). Pure and Binary Gas Adsorption Equilibria and Kinetics of Methane and Nitrogen on NaZeolite by Isotope Exchange Technique. *Adsorption* 5:145-158.
- Moore, T. T., and Koros, W. J. (2005). Non-ideal effects in organic–inorganic materials for gas separation membranes. *J. Mol. Struct.* 739:87–98.
- Moore, T. T., Mahajan, R., Vu, D. Q., and Koros, W. J. (2004). Hybrid membrane materials comprising organic polymers with rigid dispersed phases. *AIChE J.* 50:311–321.
- Moore, T.T., and Koros, W.J. (2007). Gas sorption in polymers, molecular sieves, and mixed matrix membranes, *J. Appl. Polym. Sci.* 104: 4053-4059.
- Mulder, M. (1996). *Basic principles of membrane technology.* Dordrecht: Kluwer Academic Publisher.
- Mustafa, A., Kusworo, T.D., Busairi, A. Ismail, A.F., and Budiyo, P. (2010). The Effect of Functionalization Carbon Nanotubes (CNTs) on the Performance of PES-CNTs Mixed Matrix Membrane. *Internat. J. of Sci. and Eng.* 1:15-20.

- Nagumo, R., Takaba, H., Suzuki, S., and Nakao, S. (2001). Estimation of inorganic gas permeability through an MFI-type silicalite membrane by a molecular simulation technique combined with permeation theory. *Microporous and Mesoporous Materials*. 48:247-254.
- Pal, R. (2007). New models for thermal conductivity of particulate composites. *J Reinf Plast Compos*. 26:643–651.
- Pal, R. (2008). Permeation models for mixed matrix membranes. *J. Colloid Interface Sci*. 317:191–198.
- Pandey, P., and Chauhan, R.S. (2001). Membranes for gas separation, *Prog. Polym. Sci*. 26:853-893.
- Parfitt, R.L., and Wilson, A.D. (1985). Estimation of allophane and halloysite in three sequences of volcanic soils, New Zealand. *Geoderma*. 29: 41-57.
- Park, H. B., Kim, Y. K., Lee, J. M., Lee, S. Y., and Lee, Y. M. (2004). Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes. *J Membr Sci*. 229:117–27.
- Paul, D. R., and Kemp, D. R. (1973). The diffusion time lag in polymer membranes containing adsorptive fillers. *J Polym Sci: Polym Phys*. 41:79–93.
- Paul, D., and Yampol'skii, Y. (1994). *Polymeric gas separation membranes*. Boca Raton, FL: CRC Press.
- Pechar, T. W., Kim, S., Vaughan, B., Marand, E., Tsapatsis, M., and Jeong, H. K. (2006). Fabrication and characterization of polyimide–zeolite L mixed matrix membranes for gas separation. *J Membr Sci*. 277:195–202.
- Pechar, T. W., Tsapatsis, M., Marand, E., and Davis, R. (2002). Preparation and characterization of a glassy fluorinated polyimide zeolite-mixed matrix membrane. *Desalination*. 146: 3–9.
- Pechar, T.W., Kim, S., Vaughan, B., Marand, E., Baranauskas, V., and Riffle, J. (2006). Preparation and characterization of a poly (imide siloxane) and zeolite L mixed matrix membrane. *J Membr Sci*. 277:210–8.
- Perez-Rodriguez, J. L., Carrera, F., Poyato, J., and Pérez-Maqueda, L. A. (2002). Sonication as a tool for preparing nanometric vermiculite particles, *Nanotechnology* 13: 382–387.
- Pesek, S. C., and Koros, W. J. (1993). Aqueous quenched asymmetric polysulfone membranes prepared by dry/wet phase separation. *J Membr Sci*. 81:71–88.

- Petropoulos, J. H. (1985). A Comparative Study of Approaches Applied to the Permeability of Binary Composite Polymeric Materials. *J. Polym. Sci., Polym. Phys. Ed.* 23:1309-1324.
- Phillips, P. (1912). The Viscosity of Carbon Dioxide: Proceedings of the Royal Society of London. Series A, 87: 48-61.
- Pinnau, I., and Toy, L. G.(1996). Gas and vapor transport properties of amorphous perfluorinated copolymer membranes based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene, *J. Membr. Sci.* 109:125.
- Pinnau, I., and Freeman, B. (1990). Membrane formation and modification: overview. Washington, DC: American Chemical Society.
- Pinnau, I., and He, Z. (2001). Filled superglassy membrane: US Patent 6,316,684 .
- Pinnau, I., and Koros, W. J. (1991). Structures and gas separation properties of asymmetric polysulfone membranes made by dry, wet, and dry/wet phase inversion. *J Appl Polym Sci.* 43:1491–502.
- Plate, N., and Yampol'skii, Y. P. (1994). Relationship between structure and transport properties for high free volume polymeric materials, in: *Polymeric Gas Separation Membranes*. Baton Rouge: CRC Press. 115-208.
- Podall, H. (1971). Recent advances in reverse osmosis membranes for desalination. *Chem Eng Prog.* 67: 260-266.
- R. Baker. (2004). *Membrane Technology and Applications*. (2nd Ed.) West Sussex: Wiley.
- Rafizah, W. A. W., Ismail, A. F. (2008). Effect of carbon molecular sieve sizing with poly(vinyl pyrrolidone) K-15 on carbon molecular sieve–polysulfone mixed matrix membrane. *J. Membr. Sci.*307:53–61.
- Raman, V., and Abbas, A. (2008). Experimental investigations on ultrasound mediated particle breakage, *Ultrason. Sonochem.* 15: 55–64.
- Rao, A. B., and Rubin, E. S. (2002). A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control, *Environ Sci Technol.* 36:4467–4475.
- Rao, M. B., and Sircar, S. (1996). Performance and pore characterization of nanoporous carbon membranes for gas separation. *J Membr Sci.* 110:109–18.
- Reeves, G. M., Sims, I., and Cripps, J. C. (2006). *Clay materials used in construction*. London: Geological Society of London.

- Reid, B. D., Ruiz-Trevino, F. A., Musselman, I. H., Balkus, K. J., and Ferraris, J. P. (2001). Gas Permeability Properties of Polysulfone Membranes Containing the Mesoporous Molecular Sieve MCM-41. *Chem. Mater.*, 13: 2366-2373.
- Rhim, H., and Hwang, S. T. (1975). Transport of capillary condensate. *J Colloid Interf. Sci.* 52: 174-181.
- Robertso, I.D.M., and Eggleton, R.A. (1991). Weathering of granitic muscovite to kaolinite and halloysite and plagioclase-derived kaolinite to halloysite. *Clay Clay Miner.* 39: 113-126.
- Robeson, L.M. (2008). The upper bound revisited. *Journal of Membrane Science.* 320: 390-400
- Robeson, L.M. (1991). Correlation of separation factor versus permeability for polymeric membranes. *J Membr Sci.* 62:165-85.
- Rojey, A. R., Deschamps, A., Grehier, A., and Robert, E. (1990). Process for separation of the constituents of a mixture in the gas phase using a composite membrane: US patent 4925459.
- Ruthven, D. M. (2001). Short Communication: Diffusion of Simple Molecules in NaA Zeolite. *Adsorption* 7:301-304.
- Ruthven, D. M. Farooq, S., and Knaebel, K. S. (1994). *Pressure Swing Adsorption*. New York: VCH Publishers.
- Ruthven, D. M., and Derrah, R. I. (1975). Diffusion of monoatomic and diatomic gases in 4A and 5A zeolites. *J Chem Soc: Faraday Trans.* 71:2031-7.
- Rynders, R. M., Rao, M. B., and Sircar, S. (1997). Isotope Exchange Technique for Measurement of Gas Adsorption Equilibria and Kinetics. *AIChE J.* 43:2456-2470.
- Saracco, G., Neomagus, H. W. J. P., Versteeg, G. F., and Van, S. W. P. M. (1999). High-temperature membrane reactor: potential and problems. *Chem Eng Sci.* 54:1997-2017.
- Scholes, C. A., Kentish, S. E., and Stevens, G. W. (2008). Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications. *Recent Patents on Chemical Engineering.* 1: 52-66.
- Schoofs, G. R. (1992). Fire and Explosion Hazards Induced By Repressurization of Air Driers. *AIChE J.* 38:1385-1394.
- Sebastian, J., Pillai, R. S., Peter, S. A., and Jasra, R. V. (2007). Sorption of N₂, O₂, and Ar in Mn(II)-Exchanged Zeolites A and X Using Volumetric

- Measurements and Grand Canonical Monte Carlo Simulation. *Ind. Eng. Chem. Res.* 46:6293-6302.
- Sen, D., Kalipçilar, H., and Yilmaz, L. (2007). Development of polycarbonate based zeolite NaA filled mixed matrix gas separation membranes. *J. Membr. Sci.* 303:194-203.
- Sen, D., Kalipçilar, H., and Yilmaz, L. (2006). Development of zeolite filled polycarbonate mixed matrix gas separation membranes. *Desalination* 200:222-224.
- Sen, D., Kalipçilar, H., and Yilmaz, L., (2007). Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes, *J. Membr. Sci.* 303 :194–203.
- Sheffel, J.A., and Tsapatsis, M. A. (2007). Model for the performance of microporous mixed matrix membranes with oriented selective flakes, *J. Membr. Sci.* 295: 50-70.
- Shilton, S. J. and Bell, G. (1996)The deduction of fine structural details of gas separation hollow fibre membranes using resistance modeling of gas permeation, *Polymer* 37: 485-492.
- Shu, S., Husain, S., and Koros, W. J. (2006). Formation of nanoscale morphology on zeolite surface for enhanced interfacial interaction in mixed matrix membranes. Chicago, IL: North American Membrane Society.
- Singer, A., Zarei, M., Lange, F.M., and Stahr, K. (2004). Halloysite characteristics and formation in the northern Golan Heights, *Geoderma*, 123: 279-295.
- Singh, A. S., and Koros, W. J. (2000). Air separation properties of flat sheet homogeneous pyrolytic carbon membranes. *J Membr Sci.* 174:177–88.
- Singh, B. (1996). Clays and Clay Minerals, why does halloysite roll? a new model. *Clays Clay Miner.* 44: 191- 196.
- Singh, B., and Gilkes, R. J. (1992). An electron optical investigation of the alteration of kaolinite to halloysite. *Clays Clay Miner.* 40: 212–229.
- Singh, B., and Mackinnon, I. D. R. (1996). Experimental transformation of kaolinite to halloysite. *Clays Clay Miner.* 44: 825-834.
- Sircar, S., Rao, M. B., and Tharon, C. M. A. (1999). Selective surface flow membranes for gas separation. *Sep Sci Technol.* 34: 2081–93.
- Sirkar, K.K., Kovvali, S., and Chen, H. (2003): WO03008070.

- Song, C. (2006). Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catalysis Today*. 115: 2–32.
- Spillman, R. (1989). Economics of gas separation by membranes. *Chem Eng Prog*. 85: 41.
- Spillman, R., Sherwin M. (1990). Gas separation membranes:the first decade. *Chem Technol*. 20:378–408.
- Stern, S. (1994). Polymers for gas separations: the next decade. *J Membr Sci*. 94:1–65.
- Stern, S. A., M. Y. Yamamoto, and H. Clair (1989). Structure/permeability relationships of polyimide membranes.Applications to the separation of gas mixtures. *J. Polym. Sci. Pol. Phys.*, 27(9): 1887–1909.
- Stewart, C., and Hessami, M. (2005). A study of methods of carbon dioxide capture and sequestration—the Sustainability of a photosynthetic bioreactor approach. *Energy Conversion and Management*. 46: 403–420.
- Strathman, H. (1981). Membrane separation process. *J Membr Sci*.9:121–89.
- Suer, M. G., Baç, N., and Yilmaz, L. (1994). Gas permeation characteristics of polymer-zeolite mixed matrix membranes. *J. Membr. Sci*. 91: 277-86.
- Suer, M.G., Bac, N., and Yilmaz, L. (1994). Gas permeation characteristics of polymer-zeolite mixed matrix membranes. *J Membr Sci*. 91:77–86.
- Sun, P., Grace, J. R., Lim, C. J., and Anthony, E. J. (2007). Removal of CO₂ by Ca-based sorbents in the presence of SO₂. *Energy and Fuels*. 21: 163–170.
- Taizo, K., Tooru, N., Isao, T., and Wataru, I. (1993). Manufacture of Zeolite 3A from Zeolite 4A. European Patent No. JP5147926.
- Takahashi, S., and Paul, D. R. (2006). Gas permeation in poly(ether imide) nanocomposite membranes based on surface-treated silica. Part 1: Without chemical coupling to matrix. *Polymer* 47: 7519-7534.
- Tantekin-Ersolmaz, S.B. (2000). Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membrane. *J Membr Sci*. 175:285–8.
- Tazaki, K. (1982). Analytical electron microscopic studies of halloysite formation processes: morphology and composition of halloysite. *Developments in Sedimentology*. 35: 573-584

- Teramoto, M., Matsuyama, H., Yamashiro, T., and Katayama, Y. (1986). Separation of ethylene from ethane by supported liquid membranes containing silver nitrate as a carrier. *J Chem Eng Jpn.* 19: 419–424.
- Tin, P.S., Chung, T. S., Kawi, S., and Guiver, M. D. (2004). Novel approaches to fabricate carbon molecular sieve membranes based on chemical modified and solvent treated polyimides. *Micropor Mesopor Mater.* 73:151–60.
- van de Voorde, M., Tavenier, Y., Martens, J., Verleist, H., Jacobs, P., and Baron, G. (1990). In *Gas Separation Technology*. Amsterdam: E.V. Vansant and R. Dewolfs (Eds.), Elsevier.
- Vankelecom, I. F. J., Broeck, S. V. D., Mercks, E., Geerts, H., Grobet, P., and Yutterhoeven, J. B. (1996). Silylation to improve incorporation of zeolites in polyimide films. *J Phys Chem.* 100:3753–8.
- Vankelecom, I. F. J., Mercks, E., Luts, M., Uytterhoeven, J. B. (1995). Incorporation of zeolite in polyimide membranes. *J Phys Chem.* 99:13187–92.
- van't Hof, J. A., Reuvers, A. J., Boom, R. M., Rolevink, H. H. M. and Smolders, C.A. (1992). Preparation of Asymmetric Gas Separation Membranes with High Selectivity by a Dual-bath Coagulation Method. *J. Membr. Sci.* 70:17-30.
- Villaluenga, J.P.G., Khayet, M., Lopez-Manchado, M.A., Valentin, J.L., Seoane, B., and Mengual, J.I. (2007). Gas transport properties of polypropylene/clay composite membranes. *Eur. Polym. J.* 43: 1132–1143
- Vu, D. Q., Koros, W. J. and Miller, S. J. (2003b). Mixed matrix membranes using carbon molecular sieves. II. Modeling permeation behavior. *J Membr Sci.* 211:335-348.
- Vu, D. Q., Koros, W. J., and Miller, S. J. (2003a). Mixed matrix membranes using carbon molecular sieves. I. Preparation and experimental results. *J Membr Sci.* 211:311–334.
- Vu, D. Q., Koros, W. J., and Miller, S. J. (2003c). Effect of condensable impurity in CO₂/CH₄ gas feeds on performance of mixed matrix membranes using carbon molecular sieves. *J Membr Sci.* 221:233–9.
- Wang, D., Li, K., Teo, W. K. (1997). Gas Permselection Properties in Silicone-Coated Asymmetric Polyethersulfone Membranes. *J Appl Polym Sci.* 66(5): 837–846.

- Wang, D.L., Li, K., and Teo, W.K. (1996). Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems. *J Membr Sci.* 115:85–108.
- Wang, H., Holmberg, B.A., and Yan, Y. (2002). Homogeneous polymer–zeolites nano composite membranes by incorporating dispersible template-removed zeolite nanoparticles. *J Mater Chem.* 12:3640–3.
- Wang, L., Cao, Y., Zhou, M., Ding, X., Liu Q., and Yuan,Q. (2008). The gas permeation properties of 6FDA-2,4,6-trimethyl-1,3-phenylenediamine (TMPDA)/1,3-phenylenediamine (mPDA) copolyimides, *Polym. Bull.*60:137.
- Watson, E. S., O'Neill, M. J., Justin, J. and Brenner, N. (1964). A differential scanning calorimeter for quantitative thermal analysis. *Analy. Chem.* 36: 1233–1238.
- Wunderlich, B. (1990). Differential Thermal Analysis. In *Thermal Analysis* (pp. 123–218). New York: Academic Press.
- Xu, .Z, Wang, J., Chen, W., and Xu, Y. (2001). Separation and fixation of carbon dioxide using polymeric membrane. In *Proceedings of 1st National Conference on Carbon Sequestration.* 2001. Washington DC.
- Xu, X. C., Yang, W. S., Liu, J., and Lin, L. W. (2001). Synthesis of NaA zeolite membrane from clear solution, *Micropor. Mesopor. Mater.* 43:299–301.
- Xu, X., Song, C, S., Andresen, J. M., Miller, B. G., and Scaroni, A. W. (2002). Novel polyethyleneimine-modified mesoporous molecular sieve Of MCM-41 type as adsorbent for CO₂ capture. *Energy and Fuels.* 16: 1463–1469.
- Yamamoto, K., Otsuka, H., and Takahara, A. (2007). Preparation of Novel Polymer Hybrids from Imogolite Nanofiber. *Polymer Journal.* 39(1):1–15.
- Yamasaki, A. (2003). An overview of CO₂ mitigation options for global warming – Emphasizing CO₂ sequestration options. *Journal of Chemical Engineering of Japan.* 36(4): 361–375.
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B. Bland, A. E. and Wright, I. (2008). Progress in carbon dioxide separation and capture: A review. *Journal of Environmental Sciences* 1:2014–27
- Yang, J., Hsiue, and G. Selective (1997). Olefin permeation through Ag(I) contained silicone rubber-graft-poly(acrylic acid) membranes. *J Membr Sci.* 126: 139–149.

- Yong, H. H., Park, H. C., Kang, Y. C., Won, J., and Kim, W. N. (2001). Zeolite-filled polyimide membrane containing 2,4,6-triaminopyrimidine. *J. Membr. Sci.* 188:151-163.
- Yoshitake, H., Yokoi, T., and Tatsumi, T. (2003). Adsorption of chromate and arsenate by amino-functionalized MCM-41 and SBA-1. *Chemistry of Materials.* 15: 4536–4538.
- Yuan, P., Southon, P. D., Liu, Z., Green, M. E. R., Hook, J. M. Antill, S. J., and Kepert, C. J. (2008). Functionalization of halloysite clay nanotubes by grafting with γ -aminopropyltriethoxysilane. *J. Phys. Chem. C.* 112: 15742–15751.
- Yucel, H. and Ruthven, D.M. (1980). Diffusion in NaA Zeolite: Study of the Effect of Crystal Size. *J. Chem. Soc. Faraday Trans. I.* 76:60–70.
- Zah, J., Krieg, H. M., and Breytenbach, J. C. (2007). Single gas permeation through compositionally different zeolite NaA membranes: Observations on the intercrystalline porosity in an unconventional, semicrystalline layer. *J. Membr. Sci.* 287:300-310.
- Ziegler, K., Hsieh, J.C.C., Chadwick, O.A., Kelly, E.F., Hendricks, D.M., and Savin, S.M. (2003). Halloysite as a kinetically controlled end product of arid-zone basalt Weathering, *Chem. Geol.* 202: 461-478.
- Zimmerman, C. M., Singh, A., and Koros, W. J. (1997). Tailoring mixed matrix composite membranes for gas separations. *J. Membr. Sci.* 137:145–154.