

Techno-economic modelling of CO₂ capture systems for Australian industrial sources.

Author:

Ho, Minh Trang Thi

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Techno-economic modelling of CO₂ capture systems for Australian industrial sources

Minh T. Ho

UNSW



A thesis submitted in fulfilment of the requirement for the degree of
Doctor of Philosophy

School of Chemical Sciences and Engineering
The University of New South Wales
Sydney, Australia

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Abstract

Australia is recognising that carbon capture and storage (CCS) may be a feasible pathway for addressing increasing levels of CO₂ emissions. This thesis presents a preliminary economic assessment and comparison of the capture costs for different Australian CO₂ emission sources. The capture technologies evaluated include solvent absorption, pressure swing adsorption (PSA), gas separation membranes and low temperature separation.

The capture cost estimated for hydrogen production, IGCC power plants and natural gas processing is less than A\$30/tonne CO₂ avoided. CO₂ capture cost for iron production ranges from A\$30 to A\$40 per tonne CO₂ avoided. Higher costs of A\$40 to over A\$80 per tonne CO₂ avoided were estimated for flue gas streams from pulverised coal and NGCC power plants, oil refineries and cement facilities, and IDGCC synthesis gas.

Based on 2004 and 2005 EU ETS carbon prices (A\$30 to A\$45 per tonne CO₂ avoided), the cost of capture using current commercially available absorption technology may deter wide-scale implementation of CCS, in particular for combustion processes. A sensitivity analysis was undertaken to explore the opportunities for reducing costs.

The high cost for capture using solvent absorption is dependent on the energy needed for solvent regeneration and the high capital costs. Cost reductions can be achieved by using new low regeneration energy solvents coupled with recycling the waste heat from the absorption process back to the steam cycle, and using low cost “fit-for-purpose” equipment.

For membrane and PSA technologies, the capture costs are dominated by the flue gas and post-capture compressors. Operating the permeate or desorption stream under vacuum conditions provides significant cost reductions. Improvements in membrane and adsorbent characteristics such as the adsorbent loading or membrane permeability, CO₂ selectivity, and lower prices for the membrane or adsorbent material provide further cost benefits.

For low partial pressure CO₂ streams, capture using low temperature “anti-sublimation” separation can be an alternative option. Low costs could be achieved by operating under low pressures and integrating with external sources of waste heat.

Applying the cost reductions achievable with technology and process improvements reduces the capture and CCS costs to a level less than current carbon prices, making CCS an attractive mitigation option.

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Dedication

I would like to dedicate this thesis to my mother, Thi An Ho.
You are a source of endless love.

"It isn't pollution that's harming the environment. It's the impurities in our air and water that are doing it."

George W. Bush

Table of Contents

Abstract	i
Acknowledgements	iii
Dedication	iv
Table of Contents	vi
List of Figures	xi
List of Tables	xvi
List of Acronyms	xviii
Nomenclature	xx
Publications	xxv
Chapter 1. Introduction: CO₂ Capture and Storage	1
1.1 Background.....	1
1.2 Australian sources of CO ₂ emissions.....	2
1.3 CO ₂ capture technologies.....	4
1.4 Storage and utilisation	5
1.4.1 <i>Utilisation: Direct usage and materials conversion</i>	5
1.4.2 <i>Transport and storage</i>	5
1.5 Research aims	6
1.6 Outline of thesis.....	8
Chapter 2. Review of CO₂ Capture Technologies	9
2.1 Background.....	9
2.2 Absorption	10
2.2.1 <i>Chemical absorption</i>	11
2.2.2 <i>Advantages and disadvantages of chemical absorption</i>	13
2.2.3 <i>Physical absorption</i>	17
2.2.4 <i>Advantages and disadvantages of physical absorption</i>	18
2.3 Membranes	18
2.3.1 <i>Advantages and disadvantages of polymeric membranes</i>	20
2.4 Adsorption	23
2.4.1 <i>Pressure swing adsorption (PSA)</i>	26

2.4.2	<i>Advantages and disadvantages of PSA</i>	27
2.5	Low-temperature separation	31
2.5.1	<i>Advantages and disadvantages of low temperature separation</i>	33
2.6	Novel CO ₂ capture options	35
2.7	Measuring the cost of CO ₂ avoided	37
2.7.1	<i>CO₂ avoided and CO₂ injected</i>	37
2.7.2	<i>Energy penalty</i>	38
2.8	Reported costs of CO ₂ capture	38
2.8.1	<i>Capture costs for pulverised coal and advanced power plants</i>	39
2.8.2	<i>Capture costs for industrial sources</i>	42
2.9	Conclusion: Understanding the cost of CO ₂ development	44
Chapter 3.	Techno-economic Model Development	46
3.1	Overview	46
3.2	Defining the system boundary	46
3.3	Process model	46
3.3.1	<i>Configuring the process model</i>	47
3.3.2	<i>Process equations</i>	48
3.3.3	<i>Model outputs</i>	53
3.4	Cost model	53
3.4.1	<i>Configuring the cost model</i>	54
3.4.2	<i>Cost outputs and equations</i>	55
3.5	Evaluating CO ₂ capture from Australian CO ₂ emission sources	61
3.5.1	<i>Economic assumptions</i>	64
3.5.2	<i>Processing assumptions for Chapters 5 to 7</i>	64
3.5.3	<i>Processing assumptions for Chapter 8</i>	65
Chapter 4.	Chemical Absorption	68
4.1	Overview	68
4.2	CO ₂ capture using chemical absorption solvents	68
4.2.1	<i>Introduction</i>	68
4.2.2	<i>Chemical absorption process</i>	69
4.2.3	<i>Assumptions</i>	70
4.2.4	<i>Chemical absorption model</i>	71
4.3	Baseline results for commercial solvents	76
4.3.1	<i>Comparison with other studies</i>	79

4.4	Reducing the capture cost.....	80
4.5	Effect of solvent improvement	81
4.5.1	<i>Regeneration energy requirements</i>	<i>81</i>
4.5.2	<i>The impact of recent solvent developments.....</i>	<i>81</i>
4.5.3	<i>Developing new low regeneration energy solvents.....</i>	<i>83</i>
4.5.4	<i>Reducing solvent replacement costs.....</i>	<i>90</i>
4.5.5	<i>Synopsis – “low cost solvent” for CO₂ capture</i>	<i>92</i>
4.6	Effect of process improvements	94
4.6.1	<i>Steam and waste-heat utilisation.....</i>	<i>94</i>
4.6.2	<i>Innovative stripper design.....</i>	<i>95</i>
4.7	Effect of reducing the unit cost for capital	97
4.7.1	<i>Efficient packing material.....</i>	<i>97</i>
4.7.2	<i>“Fit for purpose” equipment.....</i>	<i>98</i>
4.8	Conclusion.....	100
Chapter 5.	Gas Separation Membranes.....	101
5.1	Overview	101
5.2	CO ₂ capture using polymeric membrane technology	101
5.2.1	<i>Introduction.....</i>	<i>101</i>
5.2.2	<i>Membrane process</i>	<i>102</i>
5.2.3	<i>Assumptions.....</i>	<i>104</i>
5.2.4	<i>Membrane models</i>	<i>104</i>
5.2.5	<i>Model parameters and outputs.....</i>	<i>107</i>
5.3	Baseline results for commercial membranes	107
5.3.1	<i>Comparison with other studies.....</i>	<i>110</i>
5.3.2	<i>Changes in capture cost with increasing CO₂ recovery.....</i>	<i>111</i>
5.4	Recent membrane development.....	112
5.5	Reducing the capture cost.....	114
5.5.1	<i>Pressure differential.....</i>	<i>115</i>
5.5.2	<i>Vacuum membrane systems.....</i>	<i>117</i>
5.5.3	<i>Baseline results for vacuum permeate conditions.....</i>	<i>119</i>
5.5.4	<i>Reducing the costs of membrane units</i>	<i>122</i>
5.5.5	<i>Reducing the CO₂ compressor costs</i>	<i>124</i>
5.5.6	<i>Synopsis – “low-cost membrane systems”</i>	<i>130</i>
5.6	Conclusion.....	134

Chapter 6. Pressure Swing Adsorption.....	136
6.1 Overview	136
6.2 CO ₂ capture using pressure swing adsorption	136
6.2.1 Introduction.....	136
6.2.2 The PSA cycle.....	137
6.2.3 Assumptions.....	139
6.2.4 PSA model	140
6.2.5 Outputs from the PSA model	143
6.3 Baseline results for commercial adsorbents	143
6.3.1 Comparison with other studies.....	146
6.4 Reducing the capture cost.....	146
6.4.1 Effect of adsorbent characteristics.....	146
6.4.2 Adsorbent working capacity and selectivity.....	147
6.4.3 The effect of recent adsorbent development for PSA CO ₂ capture	149
6.4.4 Reducing the cost of the CO ₂ compressor.....	152
6.4.5 Reducing the cost of the adsorption units	156
6.4.6 Effect of process improvements.....	158
6.4.7 Effect of adsorption step time.....	163
6.4.8 Synopsis – “low cost PSA systems”	165
6.5 Conclusion.....	167
Chapter 7. Low Temperature CO₂ Capture.....	169
7.1 Overview	169
7.2 Low temperature CO ₂ anti-sublimation process	169
7.2.1 Introduction.....	169
7.2.2 Processing and economic assumptions	171
7.2.3 Low temperature separation model.....	174
7.2.4 Model parameters and outputs.....	176
7.3 Baseline results and comparison with literature	176
7.4 The effect of processing parameters on the capture cost	178
7.4.1 Refrigeration pressure	178
7.4.2 Maximising the heat transfer of the lean waste gas	181
7.4.3 Utilising the waste energy of an external source	184
7.5 Conclusion.....	185
Chapter 8. CO₂ Capture from Industrial Sources	187

8.1	Overview	187
8.2	Introduction	187
8.3	Method.....	189
8.3.1	<i>Processing assumptions</i>	189
8.3.2	<i>Process modelling</i>	190
8.3.3	<i>Economic assumptions</i>	190
8.4	Power generation	191
8.4.1	<i>Economic results for post-combustion capture</i>	192
8.4.2	<i>Economic results for pre-combustion capture</i>	197
8.5	Hydrogen production.....	201
8.6	Natural gas processing.....	203
8.7	Iron and steel production	206
8.8	The petrochemicals industry.....	214
8.9	Cement production	216
8.10	Comparison of CO ₂ capture technologies for different industries.....	218
8.11	Application of technology learning and equipment cost reductions.....	219
8.12	Conclusion.....	221
Chapter 9.	Variability and uncertainties in CCS economics	224
9.1	Overview	224
9.2	Introduction	224
9.3	The impact of methodological assumptions	225
9.3.1	<i>The reference point</i>	225
9.3.2	<i>Impact of different energy sources</i>	227
9.3.3	<i>Other methodological parameters</i>	233
9.3.4	<i>Economic variability</i>	235
9.4	Conclusion.....	238
Chapter 10.	Conclusion	239
Chapter 11.	References.....	247
APPENDICES		264

List of Figures

Figure 1-1 Capture and Storage/Utilisation of CO ₂ emissions.....	2
Figure 1-2 Stationary sources of CO ₂ in Australia.....	3
Figure 2-1 Characteristic solvent loading of chemical and physical solvents.....	11
Figure 2-2 Adsorption of CO ₂ onto a solid adsorbent.....	19
Figure 2-3 Adsorbent loading as modelled by Langmuir Equation and Henry's Law.....	24
Figure 2-4 Schematic of a membrane module.....	25
Figure 2-5 CO ₂ phase diagram.....	33
Figure 3-1 Typical layout of post-processing CO ₂ capture.....	47
Figure 3-2 CO ₂ capture using a post combustion system.....	60
Figure 3-3 CO ₂ capture using a pre combustion system in power plants.....	62
Figure 3-4 Oxyfuel combustion in power plants.....	62
Figure 4-1 Process flow diagram for the chemical absorption process.....	69
Figure 4-2 Total energy requirement for chemical absorption with MEA, KS1 and FG Plus solvents.....	78
Figure 4-3 Breakdown of operating cost for MEA, KS1 and FG Plus solvents.....	78
Figure 4-4 Breakdown of the capital investment for MEA, KS1 and FG Plus solvents.....	78
Figure 4-5 Capture cost and thermal energy for regeneration as a function of solvent working capacity where 1) the rich solvent loading is varied and 2) lean solvent loading is varied.....	85
Figure 4-6 Thermal regeneration energy and capture cost at two different solvent prices; \$1.5/kg and \$5/kg, as a function of solvent concentration.....	87
Figure 4-7 Capture cost (o) and thermal regenerator energy (o) as a function of solvent heat of reaction.....	89
Figure 4-8 Capture cost as a function of solvent losses at solvent prices: A\$1.5/kg , A\$5/kg and A\$10/kg.....	90
Figure 4-9 Variation in capture cost with increasing solvent working capacity at two solvent losses: 1.6 and 0.5 kg/tonne CO ₂ captured, and two heat of reactions.....	92
Figure 4-10 Integrating heat from the chemical absorption process with the boiler water for the power plant steam cycle.....	94
Figure 4-11 Multipressure stripper with 5°C temperature approach and vapour recompression (Rochelle et al. 48].....	96
Figure 4-12 Capture cost for MEA and the new solvent, and the absorber height as a function of increasing mass transfer rates and packing efficiency.....	98

Figure 4-13 Effect of reducing unit production cost of absorbers/regenerators for MEA or a new solvent, costed as multiple or single absorption train.....	99
Figure 5-1 Single-stage membrane system (SMS).....	102
Figure 5-2 Two-stage cascade membrane systems (TCMS), the dotted line represents the retentate recycle for the TSCM-RR process.....	103
Figure 5-3 Total energy requirement for SMS, TCMS and TCMS-RR layouts.....	109
Figure 5-4 Breakdown of the capital investment for SMS, TCMS and TCMS-RR layouts	110
Figure 5-5 Changes in capture cost and CO ₂ permeate purity with changes in CO ₂ recovery..	111
Figure 5-6 Capture cost as a function of feed pressure for SMS layout.....	115
Figure 5-7 Breakdown of the major equipment costs for the SMS layout at three feed pressures: 4, 8 and 15 bar,.....	117
Figure 5-8 Simplified diagram of SMS with permeate vacuum conditions.....	119
Figure 5-9 Breakdown of equipment costs for a high pressure feed and vacuum membrane systems.....	121
Figure 5-10 Breakdown of operating costs for a high pressure feed and vacuum membrane systems.....	120
Figure 5-11 Capture cost as a function of membrane price for the high pressure feed SMS, and vacuum membrane systems: SMS, TCMS and TCMS-RR.....	123
Figure 5-12 Capture cost as a function of CO ₂ permeability for the vacuum membrane systems: SMS, TCMS and TCMS-RR.....	124
Figure 5-13 Effect on permeate CO ₂ purity with changes in the CO ₂ /N ₂ selectivity at pressure ratios of 0.01 to 0.1 (in 0.01 increments).....	126
Figure 5-14 Effect on permeate CO ₂ purity with increasing CO ₂ /N ₂ selectivity for the two-stage membrane layouts.....	127
Figure 5-15 Capture cost as a function of CO ₂ /N ₂ selectivity for the high pressure feed SMS and vacuum membrane systems: SMS and TCMS.....	128
Figure 5-16 Capture cost as a function of pressure ratio for the PPO membrane and the new development membrane when 1Pp is constant at held constant at 0.05 bar and Pf is constant at 1.5 bar.....	130
Figure 5-17 Capture cost as function of improved membrane characteristics at two membrane prices: A\$13/m ² and A\$66/m ² , and two CO ₂ /N ₂ selectivities: 40 and 250.....	131

Figure 5-18 Capture cost with changes in CO ₂ permeability for the TCMS-RR configuration at CO ₂ /N ₂ selectivity of 40 and different membrane prices: A\$13/m ² , A\$27/m ² , A\$40/m ² , A\$53/m ² , A\$66/m ²	132
Figure 5-19 Membrane characteristics and price combinations to achieve a cost of A\$30 per tonne CO ₂ avoided for the SMS, TCMS and TCMS-RR process layouts.....	133
Figure 6-1 Simplified flow diagram of a pressure swing adsorption (PSA) process.....	137
Figure 6-2 Four-step Skarstrom cycle.....	138
Figure 6-3 A typical concentration profile of the light component and direction of travel along the adsorber bed for a PSA process.....	139
Figure 6-4 Short-cut PSA model.....	141
Figure 6-5 Total energy requirement for the VSA and PSA processes.....	145
Figure 6-6 Breakdown of the capital investment for the VSA and PSA processes.....	145
Figure 6-7 Breakdown of annual operating cost for the VSA and PSA processes.....	145
Figure 6-8 Comparison of an adsorbent's working capacity for CO ₂ with a linear and non-linear isotherm.....	148
Figure 6-9 Effect of feed pressure on CO ₂ product purity and capture cost.....	154
Figure 6-10 Effect of desorption/evacuation pressure on CO ₂ recovery, purity and capture cost.....	155
Figure 6-11 Effect on CO ₂ purity with changes in the adsorbent CO ₂ /N ₂ selectivity at a pressure ratio of 0.05.....	156
Figure 6-12 Changes in CO ₂ capture cost and adsorber volume with increasing CO ₂ adsorbent working capacity at three CO ₂ /N ₂ selectivities: 50, 100 and 500.....	157
Figure 6-13 Seven-step PSA cycle.....	158
Figure 6-14 CO ₂ purity, CO ₂ recovery, and CO ₂ capture cost for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE.....	159
Figure 6-15 Breakdown in equipment item cost for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE.....	160
Figure 6-16 Breakdown of operating cost for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE.....	160
Figure 6-17 The performance of the PSA process shown as CO ₂ purity and CO ₂ recovery, and CO ₂ capture cost for the Skarstrom cycle and a PSA cycle with product purge.....	162
Figure 6-18 Capture cost, CO ₂ purity and recovery as a function of the percentage of CO ₂ product purged.....	163

Figure 6-19 Effect of the adsorption step time on the CO ₂ purity, CO ₂ recovery, and capture cost.....	164
Figure 6-20 Capture cost with changes in CO ₂ adsorbent working capacity at CO ₂ /N ₂ selectivity and purge (%) combinations of 200/0, 140/5, 100/10 and 80/15.....	165
Figure 6-21 Adsorbent characteristics and price combinations to achieve a cost of A\$30/tonne CO ₂ avoided at CO ₂ /N ₂ selectivity and purge combinations of 200/0%, 140/5%, 100/10% and 80/15%.....	166
Figure 7-1 Schematic of CO ₂ recovery by anti-sublimation.....	170
Figure 7-2 Simplified diagram of the baseline conditions for the low temperature separation.....	172
Figure 7-3 Temperature-pressure diagram for CO ₂	172
Figure 7-4 Percentage breakdown of capital cost, operating cost and energy consumption for the low temperature separation.....	178
Figure 7-5 Changes in the capture cost with increasing refrigeration pressure when a gas-lock is used and when no gas-lock is used.....	179
Figure 7-6 Energy consumption [total, compression, refrigeration and expansion] for low temperature separation at different refrigeration pressures.....	179
Figure 7-7 Effect of flue gas inlet temperature on capture cost at refrigeration pressures of 5.5 bar and 1 bar, when a gas-lock is used and when no gas-lock is used.....	182
Figure 7-8 Schematic of “Case A”.....	182
Figure 7-9 Comparison of the capital cost breakdown for the baseline case and Case A.....	183
Figure 7-10 Utilisation of the LNG gasification for low temperature CO ₂ capture.....	183
Figure 8-1 Comparison of capture costs for Australian pulverised coal power plants.....	193
Figure 8-2 Comparison of capture costs for current and advanced NGCC power plants.....	195
Figure 8-3 Comparison of capture costs for IGCC and IDGCC power plants.....	198
Figure 8-4 Schematic of the hydrogen production process compared to an IGCC power plant.....	201
Figure 8-5 Comparison of capture costs for different CO ₂ feed concentrations.....	205
Figure 8-6 Process flow diagram of CO ₂ capture by converting a conventional blast furnace with a water shift reaction.....	207
Figure 8-7 Comparison of different CO ₂ capture costs and options for iron production.....	213
Figure 8-8 Comparison of capture costs for oil refineries.....	215
Figure 8-9 CO ₂ capture costs for cement production flue gas.....	217
Figure 8-10 Lowest capture cost option for different Australian industrial sources.....	218
Figure 9-1 Schematic of options A and B for CO ₂ capture from a power plant.....	228

Figure 9-2 Schematic of options C1, C2 and C3 for CO ₂ capture from a power plant.....	228
Figure 9-3 The capture cost for different power sources [renewable, NGCC and IGCC] as a function of the price of purchased electricity compared to case C1.....	232
Figure 9-4 Sensitivity of capture cost due to processing and economic assumptions; discount rate, energy cost, plant operating capacity, capital cost and project life.....	234
Figure 9-5 Range cost uncertainties for the baseline MEA case study.....	237

List of Tables

Table 1-1 Order of magnitude estimates for worldwide capacity of CO ₂ sinks (Herzog et al., 1997)	6
Table 2-1 Summary of the advantages and disadvantages of CO ₂ capture systems	10
Table 2-2 CO ₂ capture costs for power plants	40
Table 2-3 CO ₂ capture costs for industrial installations.....	44
Table 3-1 Capital cost model parameter and nominal values	57
Table 3-2 Equipment capital costing	58
Table 3-3 Operating cost equations	59
Table 3-4 General capital and operating costing methods for power plants.....	61
Table 3-5 Baseline economic assumptions	64
Table 3-6 Flue gas composition of power generation facilities	65
Table 3-7 Flue gas compositions and characteristics of different CO ₂ emission sources	67
Table 4-1 Processing conditions for CO ₂ chemical absorption.....	71
Table 4-2 Processing equations for the chemical absorption model.....	73
Table 4-3 Economic results for CO ₂ capture using chemical absorption	76
Table 4-4 Comparison of capture cost for MEA, 5MK+/2.5PZ and aqueous ammonia.....	82
Table 4-5 Capture costs for different solvents with process heat integration	95
Table 4-6 Capture costs for the different stripper scenarios examined in Rochelle and Jassim (2005).	97
Table 5-1 Physical properties of commercially available membranes.....	104
Table 5-2 CO ₂ capture costs of single and two-stage membrane systems	108
Table 5-3 Properties of the development membranes extracted from TIPS database.....	113
Table 5-4 Comparison of capture cost for membrane technology under vacuum conditions...	119
Table 6-1 Physical and processing conditions for PSA process	140
Table 6-2 Economic results for CO ₂ capture using pressure swing adsorption	144
Table 6-3 Processing and physical properties of new adsorbents.....	150
Table 7-1 Economic results for CO ₂ capture using anti-sublimation technology	177
Table 7-2 Effect on capture cost for Case A by integrating the refrigeration unit with gasifying LNG.....	185
Table 8-1 Capture costs for pulverised coal power plants	192
Table 8-2 Capture costs for NGCC power plants	195
Table 8-3 CO ₂ capture costs for new IGCC and IDGCC power plants	198
Table 8-4 Capture costs for hydrogen production	202

Table 8-5 Capture costs for natural gas processing for low, medium and high CO ₂ concentration feed gases	205
Table 8-6 Capture costs for iron production blast furnace flue gas	209
Table 8-7 CO ₂ capture costs for the converted synthesis gas of a blast furnace	211
Table 8-8 CO ₂ capture costs for Corex iron production flue gas	212
Table 8-9 Capture costs for CO ₂ recovery from an oil refinery flue gas	214
Table 8-10 Capture costs for cement production flue gas	216
Table 9-1 Cost of CO ₂ avoided for an IGCC compared to a PC and NGCC power plants	226
Table 9-2 Capture cost for IGCC power plant with capture as a function of different reference points	226
Table 9-3 Key costs for cases A, B1, C, C2, C3 and reference power plant	230
Table 9-4 Baseline economic assumptions	234
Table 9-5 Cost model parameter, nominal values and data range	236

List of Acronyms

ABS	Australian Bureau of Statistics
AGO	Australian Greenhouse Office
Capex	Capital costs
CCS	CO ₂ Capture and Storage
CEPCI	Chemical Engineering Plant Cost Index
CO2CRC	The Australian Cooperative Research Centre for Greenhouse Gas Technologies
COE	Cost of electricity
DEA	Diethanolamine
DOE	Department of Energy
DP	Depressurisation
ECBM	Enhanced Coal Bed Methane
ESAA	Electricity Supply Association of Australia
EOR	Enhanced Oil Recovery
EU ETS	European Union Emissions Trading Scheme
FGD	Flue Gas Desulphurisation
FOM	Fixed Operational and Maintenance
GDP	Gross Domestic Product
GHG	Greenhouse Gas
IEA GHG	International Energy Agency Greenhouse Gas R&D Programme
IDGCC	Integrated Coal-Drying Gasification Combined Cycle
IGCC	Integrated (coal) Gasification Combined Cycle
LHP	Loss Hydrocarbon Product
LNG	Liquefied Natural Gas
MDEA	Methyl-diethanolamine
MEA	Monoethanolamine
MMSCF	Million square cubic feet
NGCC	Natural Gas Combined Cycle
NPV	Net Present Value
Opex	Operating costs
PAI	Poly-amido-imides
PC	Pulverised Coal

PE	Pressure equalisation
PI	Polyimide
ppm	Parts per million
PPO	Poly-phenylene-oxide
PSA	Pressure Swing Adsorption
SMS	Single-stage Membrane System
SOA	State of the art
TCMS	Two-stage Cascade Membrane System
TSA	Temperature Swing Adsorption
VOM	Variable Operational and Maintenance
VSA	Vacuum Swing Adsorption

Nomenclature

A_1	Empirical correction factor for solvent flowrate
A_2	Empirical correction factor for number of absorber trains
A_{cross}	Absorber cross-sectional area (m^2)
$A_{\text{Heat exchanger}}$	Total heat exchanger area (m^2)
A_i	Henry's constant for component i (mol/kg)
A_{Membrane}	Total membrane are (m^2)
B_i	Langmuir' constant for component i (1/bar)
C_{Absorber}	Cost of absorber (\$)
$C_{\text{Adsorbent}}$	Cost of adsorbent (\$)
$C_{\text{Adsorber Shell}}$	Cost of adsorber shell (\$)
$C_{\text{CO}_2 \text{ Drying}}$	Cost of CO_2 drying unit (\$)
$C_{\text{Compressor}}$	Cost of compressor (\$)
C_{Cooling}	Annual Cost of cooling water (\$)
C_{Energy}	Annual Cost of energy (\$)
C_{Expander}	Cost of expander (\$)
C_{FGD}	Cost of FGD unit (\$)
C_{Fuel}	Annual costs for fuel consumption (\$)
$C_{\text{Heat Exchanger}}$	Cost of heat exchanger (\$)
C_{LHP}	Annual cost of loss hydrocarbon product (\$)
$C_{\text{Liquefaction}}$	Cost of CO_2 liquefaction (\$)
$C_{\text{Membrane housing}}$	Cost of membrane housing (\$)
$C_{\text{Membrane material}}$	Cost of membrane material (\$)
$C_{\text{O\&M}}$	Annual fixed and variable costs (\$)
$C_{\text{Refrigeration}}$	Cost of refrigeration (\$)
$C_{\text{Regenerator}}$	Cost for regeneration unit
$C_{\text{Replacement}}$	Annual Cost of replacing chemicals/adsorbents/membranes etc. (\$)
$C_{\text{Vacuum pump}}$	Cost of vacuum pump (\$)
Capex	Total capital costs (\$)
Carbon intensity	Carbon intensity of fuel source (GJ/kg)
COE	Cost of electricity (\$/MWh)
$C_{p\text{TEG}}$	Specific heat of TEG (2.784 kJ/kgK)

C_{Solvent}	Solvent concentration (g-moles/L)
d_{ABS}	Absorber diameter (m)
ΔP_{lm}	Log mean of partial pressure of CO ₂ (kPa)
d_{shell}	Adsorber shell diameter (m)
ΔT_{lm}	Log mean temperature difference (K)
F_i	Flowrate of the i th stream (m ³ /s)
f_a	Wetting factor
$F_{\text{chemical I}}$	Annual flowrate of chemical i (kg)
F_{CO_2}	Flowrate of CO ₂ recovered (kg CO ₂ recovered/hr)
$F_{\text{Cooling water}}$	Total annual flowrate of cooling water (kg)
F_f	Feed flow rate (kmol/s)
f_i	Amount of the i th component in the feed (mole)
F_{LHP}	Annual flowrate of loss hydrocarbon product (kg)
F_p	Permeate flow rate (kmol/s)
F_r	Retentate flow rate (kmol/s)
H_{ABS}	Absorber height (m)
$H_{\text{Condenser}}$	Enthalpy of steam leaving the low pressure turbine to the condenser (kJ/kg)
H_{LP}	Enthalpy of low pressure steam (kJ/kg)
$h_{\text{operating hours}}$	Number of annual operating hours (hr)
H_{Reboiler}	Enthalpy of water at reboiler temperature (kJ/kg)
$k_{\text{chemical I}}$	Unit cost of chemical I (\$/kg)
k_{Cooling}	Unit cost for cooling water (\$/kg)
k_{Drying}	Unit cost for drying (\$/kg CO ₂ recovered/hr)
k_{Energy}	Unit cost for purchased energy (\$/MWh)
k_{Expander}	Unit cost for an expander (\$/MW)
k_{FGD}	Unit cost for FGD (\$/kg flue gas/hr)
k_{Fuel}	Unit cost for fuel source (\$/GJ)
$k_{\text{Heat Exchanger}}$	Unit cost for heat exchangers (\$/MW)
$k_{\text{Natural Gas}}$	Unit cost of natural gas (\$/GJ)
$k_{\text{Liquefaction}}$	Unit cost for liquefaction (\$/kg CO ₂ recovered/hr)
k_{Membrane}	Unit cost for membrane material (\$/m ²)
$k_{\text{Power plant}}$	Reference cost for a power plant (\$)
$k_{\text{Refrigeration}}$	Unit cost for refrigeration (\$/MW)
$k_{\text{Regenerator}}$	Unit cost for regenerator (\$/kg CO ₂ recovered/hr)

$k_{\text{Vacuum pump}}$	Unit cost for vacuum pump (\$/pump)
k_{Absorber}	Unit cost for one absorber train (\$/train)
$k_{\text{Adsorbent}}$	Unit cost for adsorbent (\$/kg)
$k_{\text{Compressor}}$	Unit cost for a compressor (\$/MW)
K_{Ga}	Mass transfer coefficient (kmols/m ³ -hr-kPa)
k_i	Amount of component i in the bulk-gas (mole)
LHV_i	Lower heating value of fuel source (fraction)
l_{shell}	Length of the adsorber shell (m)
L_{Solvent}	Solvent flowrate (kmol/s)
$n(\text{CO}_2)$	Amount of CO ₂ recovered (kg-mol/s)
$N_{\text{Absorber trains}}$	Number of adsorber trains
$N_{\text{Absorber trains}}$	Number of absorber trains
n_{CO_2}	Fraction of CO ₂ recovered
Opex	Total annual operating cost (\$)
P_i^*	Permeability of component i across the membrane (Barrer)
P_{abs}	Absorber pressure (bar)
P_{ads}	Adsorption pressure (bar)
p_{CO_2}	Partial pressure of CO ₂ (bar)
P_{des}	Desorption pressure (bar)
P_f	Pressure on feed side (bar)
p_i	Amount of component i in the adsorbent (mole)
P_i	Partial pressure of component i (bar)
P_{In}	Compressor/expander inlet pressure (bar)
P_{out}	Compressor/expander outlet pressure (bar)
P_p	Pressure on permeate side (bar)
$P_{\text{refrigeration}}$	Pressure in the refrigeration unit (bar)
p_{subCO_2}	Partial pressure of CO ₂ at sublimation (bar)
P_{Total}	Total electrical power (MW)
$Q_{\text{Dehydration}}$	Thermal duty for dehydration (MW)
$Q_{\text{Heat Exchanger}}$	Thermal heat exchanger duty (MW)
$Q_{\text{Regenerator}}$	Thermal heat duty for reboiler (MW)
$Q_{\text{condenser}}$	Duty due to solvent condenser reflux (MW)
$q_{m,I}$	Adsorbent capacity for component I (mol/kg)
Q_{rebTEG}	TEG reboiler heat duty (kW)
$Q_{\text{vap_H}_2\text{O}}$	Latent heat of vapourisation of water (kJ/kmol)

R	Universal gas constant (J/mol/K)
r	Ratio of C_p to C_v
s_i	Amount of component i in the expelled gas (mole)
Size	Gross output of power from the power plant (MW)
T	Temperature (K)
T_{abs}	Temperature of the absorber (K)
$T_{\text{condenser}}$	Temperature of condensing steam (K)
T_{In}	Temperature of flue gas into refrigeration unit (K)
T_o	Temperature of environmental heat sink (K)
$T_{\text{sublimation}}$	Temperature for sublimation
U	Overall heat transfer coefficient ($\text{W/m}^2 \text{ K}$)
V_{void}	Void volume of adsorbent inside the vessel (m^3)
W_{ABS}	Total energy consumption for the absorption system (MW)
W_{ads}	Amount of adsorbent weight (kg)
W_{Blower}	Work for the flue gas blower (MW)
$W_{\text{Compressor}}$	Expansion power (MW)
$W_{\text{Dehydration}}$	Work for dehydration (MW)
$W_{\text{Expansion}}$	Work for compression (MW)
$W_{\text{Low temperature}}$	Total energy consumption of the low temperature system (MW)
W_{Membrane}	Total energy consumption of the membrane system (MW)
$W_{\text{Power Plant}}$	Net output of the power plant (MW)
W_{PSA}	Total energy consumption of the PSA system (MW)
W_{Pumping}	Work for pumping (MW)
W_{rebTEG}	Power loss due to TEG reboiler (MW)
$W_{\text{Refrigeration}}$	Refrigeration power (MW)
x_i	Mole fraction of component i on feed side
y_{fCO_2}	Mole fraction of CO_2 in the feed gas
y_i	Mole fraction of component i in permeate side at membrane surface
y_{SOx}	SOx concentration in the feed gas (ppm)

Greek symbols

$\alpha_{\text{CO}_2/i}$	Selectivity of CO ₂ over component <i>i</i>
δ	Membrane thickness (m)
$\Delta\phi_{\text{CO}_2}$	Solvent working capacity (mole CO ₂ /mole of solvent)
ϕ_{lean}	Lean solvent loading (mole CO ₂ /mole solvent)
ϕ_{rich}	Rich solvent loading (mole CO ₂ /mole solvent)
γ	Pressure ratio
$\eta_{\text{pump eff}}$	Pumping efficiency (85%)
η_{real}	Real process efficiency
μ_{solvent}	Solvent viscosity (centipoise)
θ	Stage cut
ρ_{bed}	Adsorber bed density (kg/m ³)

Publications

The following are research publications related to the work in this thesis:

Ho, M.T., G. Leamon, G. Allinson, and D.E. Wiley. The economics of CO₂ and mixed gas geo-sequestration from stationary greenhouse gas emitters. In: *Proceedings of the Seventh International Conference on Greenhouse Gas Technologies (GHGT-7)*. Vancouver, Canada, 2004.

Ho, M.T., G. Allinson, and D.E. Wiley. Economic evaluation of membrane systems for large-scale capture and storage of CO₂ mixtures. In: *Proceedings of the Separations Technology VI: New Perspectives on Very Large-Scale Operations*. Fraser Island, Australia, 2004.

Ho, M.T., G. Allinson, and D.E. Wiley, Comparison of CO₂ separation options for geo-sequestration: Are membranes competitive? *Desalination*. 2006, 192(1-3): 288-295.

Ho, M.T., G. Leamon, G. Allinson, and D.E. Wiley, Economics of CO₂ and mixed gas geo-sequestration of flue gas using gas separation membranes. *Industrial & Engineering Chemistry Research*. 2006, 45(8): 2546-2552.

Ho, M.T., D.E. Wiley, and G. Allinson. Reducing the cost of post-combustion CO₂ capture. In: *Proceedings of the Eighth International Conference on Greenhouse Gas Technologies (GHGT-8)*. Trondheim, Norway, 2006.

Allinson, G., M.T. Ho, P.N. Neal, and D.E. Wiley. The methodology used for estimating the costs of CCS. In: *Proceedings of the Eighth International Conference on Greenhouse Gas Technologies (GHGT-8)*. Trondheim, Norway, 2006.

Allinson, G., R. Dunsmore, P.N. Neal, and M.T. Ho. The cost of carbon capture and storage in the Perth Region. In: *Proceedings of the SPE Asia Pacific Conference*. Adelaide, Australia, 2006.

Chapter 1. INTRODUCTION: CO₂ CAPTURE AND STORAGE

1.1 Background

There is growing concern within the global community over the rising levels of the gas carbon dioxide (CO₂) being emitted into the atmosphere from industrial sources and motorised forms of transport. The Intergovernmental Panel on Climate Change's (IPCC) third assessment provides strong evidence that human activity has been the largest contributing factor to the climate change caused by global warming over the past 50 years, particularly through the burning of fossil fuels (IPCC, 2001). Since the start of the industrial era, atmospheric levels of CO₂ have risen from 280 ppm to 380 ppm today. The report on economic impact of climate change by Sir Nicholas Stern (Stern, 2006) argues that without stabilisation of CO₂ emission levels, extreme weather conditions caused by global warming could reduce global gross domestic product (GDP) by 5% to 10% and have adverse economic impact on both developed and developing countries. To be able to stabilise the atmospheric levels of CO₂ and control the rate of global warming, changes to the rate at which CO₂ is being emitted into the atmosphere is required.

The Kaya equation identifies possible approaches to stabilise levels of CO₂ emissions (Kaya, 1989). This equation expresses CO₂ emissions as follows:

$$Net(CO_2) = P \times \left(\frac{GDP}{P} \right) \times \left(\frac{E}{GDP} \right) \times \left(\frac{CO_2}{E} \right) - S \quad (1.1)$$

As illustrated in the above equation, as the global population (P) continues to grow and the expected standard of living (Gross Domestic Product per person - GDP/P) also increases with time, stabilisation of the net CO₂ emissions requires drastic changes to the concept of 'business as usual'. To control the quantity of CO₂ atmospheric emissions, changes in the economy would require:

1. A significant increase in the energy efficiency of electrical and fuel use (reducing the energy use per unit of GDP - E/GDP);
2. A decrease in the carbon intensity of energy sources (CO_2/E);
3. Greater use of renewable energy sources (CO_2/E); and
4. Greater use and maintenance of carbon sinks such as vegetation (S).

Furthermore, for the existing economy, which is largely dependent on fossil fuels, the challenge for government and industry is to seek a pathway for abating greenhouse gases that is compatible with the existing infrastructure. In recent years, the development of “transitional” technologies in the form of CO_2 sequestration, also referred to as CO_2 Capture and Storage (CCS), has come to the forefront as a viable and promising technology in addressing CO_2 emissions. Using these technologies, CO_2 is captured from an emission source and then transported to an alternate location for storage in a geological reservoir or utilised as a raw input material, as shown in Figure 1-1. CCS technologies aim to minimise the overall level of CO_2 that is emitted into the atmosphere by increasing the available sinks (S) in the Kaya equation.

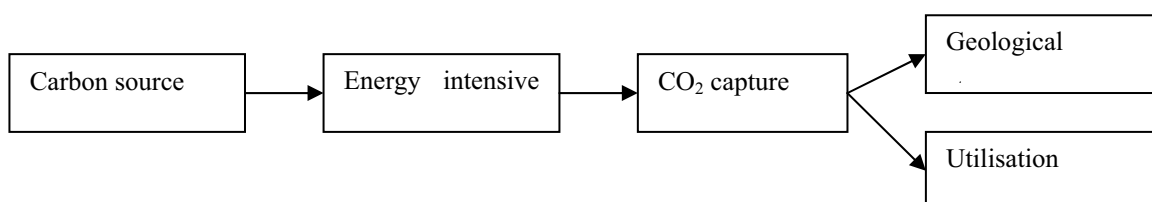


Figure 1-1 Capture and Storage/Utilisation of CO_2 emissions

CO_2 capture units can be employed directly at the site of the emissions source, in the case of large emission sources or they can be integrated into a central ‘hub’ that processes CO_2 from a number of emission sites.

1.2 Australian sources of CO_2 emissions

In 2004, Australia’s net greenhouse gas emissions totalled an equivalent of almost 550 million tonnes of CO_2 (AGO, 2006). Over half of these emissions are from stationary sources where there is the potential to apply CCS technologies. Figure 1-2 shows the breakdown of stationary emission sources in Australia for 2004.

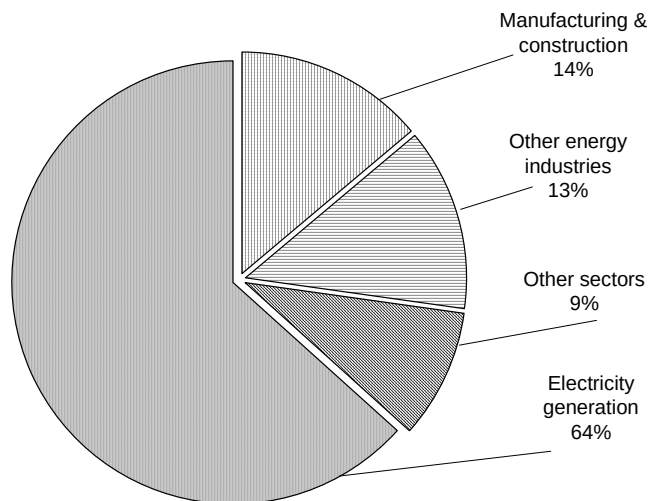


Figure 1-2 Stationary sources of CO₂ in Australia (Australian Greenhouse Office 2006 (AGO, 2006))

One of the major industries that would receive the greatest benefit from applying CCS technologies is the energy sector (electricity generation). Power stations account for 63% of stationary CO₂ emissions and 35% of total emissions, and are suitable candidates for separation and recovery of CO₂ (refer to Figure 1-2). According to the Electricity Supply Association of Australia (ESAA, 2003) and the Australian Bureau of Statistics (ABS, 2001), coal fired power plants account for over 75% of the total electricity generated in Australia. Because coal-fired power plants are likely to remain a key source of energy in Australia, the majority of the economic evaluations that are reported in this thesis investigate the cost of CO₂ capture from a black coal-fired pulverised power plant flue gas stream.

Natural gas production currently employs CO₂ separation technology to separate CO₂ from the methane product. According to Australian and US pipeline specifications, the natural gas delivered to the consumer must not contain more than 3% and 2% CO₂ respectively (1997). For businesses involved in removing CO₂ from raw natural gas, implementing CCS technologies for CO₂ mitigation purposes can easily be achieved without the need for excessive additional infrastructure.

In addition to power generation and natural gas processing, energy intensive industries such as petroleum refineries, petrochemicals, iron and steel manufacturing, and cement, lime, and soda ash production all depend on significant process heat and steam, which are typically derived from the combustion of fossil fuels. In principle, it is possible to capture CO₂ from the flue gases of these industries.

The opportunity for CO₂ capture will vary from industry to industry, and in some cases it may be straightforward to build or retrofit a manufacturing plant to accommodate CCS. In other cases, these changes may not be compatible with particular manufacturing processes and re-structuring of the plant layout and/or process may be required. The challenge in capturing CO₂ from industrial facilities is that the sources of CO₂ often originates from more than one stream (Simmonds et al., 2002).

1.3 CO₂ capture technologies

The objective of CO₂ capture is to isolate it from its many sources and produce a CO₂ stream suitable for transport and storage, or for later use as a raw material. The process of producing this stream of CO₂ (referred to as capture) incorporates all unit operations required to recover the CO₂. These operations may already be incorporated within the existing process scheme or be an additional process, and may include compression needed for transport.

CO₂ separation has been used in a variety of industrial applications, since the early 1920's. The technologies used are mature and technically well understood. However, the scale of industrial implementation has until recently only been small. The existing options for separation and capture of CO₂ from mixed gas streams can be categorised as:

1. Chemical and physical absorption;
2. Gas-solid based adsorption;
3. Membrane based gas separation; and
4. Low temperature separation.

The advantage of using these processes for recovering CO₂ is their high compatibility with existing plant design and infrastructure; they can simply be added in as a retrofit. However the main challenge with implementing CO₂ capture technologies is the large-scale at which the industrial CO₂ emitters operate. Currently the captured CO₂ generally has no commercial value and the recovery processes incurs both financial and energy penalties. A detailed review of these CO₂ capture technologies will be provided in Chapter 2.

1.4 Storage and utilisation

Following the effective capture of CO₂, there is a need to transport and store or otherwise utilise the CO₂ to reduce the net emissions into the atmosphere.

1.4.1 Utilisation: Direct usage and materials conversion

Direct usage of captured CO₂ has the least environmental impact. At present, the food and beverage industry is the largest user of CO₂, mainly in the development of carbonated drinks. However, this sector only has the capacity to consume less than 1% of the total CO₂ emissions. Another route for the direct utilisation of CO₂ as a commodity material is its application in closed loop refrigeration cycles (Brown et al., 2002). Captured CO₂ could also be used for direct synthesis of materials such as methanol, lower olefins or paraffins (Thambimuthu, 2002). However, research into large-scale utilisation of CO₂ in these applications is still at a preliminary stage.

1.4.2 Transport and storage

Once the CO₂ is captured, it can be transported to a selected storage site by pipeline or by a carrier such as an ocean-going tanker. Storage sites may include geological sinks and/or the deep ocean. Geological sinks for CO₂ storage includes deep saline formations (subterranean and sub-sea bed), depleted oil and gas reservoirs, enhanced oil recovery (EOR) operations, and enhanced coal bed methane (ECBM) operations. Table 1-1 shows the capacity of world wide geological and ocean storage sites. A detailed discussion of the issues related to geological storage is beyond the scope of this research project. General information can be found in a summary by Gough et al. (2002) and

specific information for Australian storage sites has been discussed by Cook et al. (2000).

Table 1-1 Order of magnitude estimates for worldwide capacity of CO₂ sinks (IPCC., 2005)

Storage Option	Order of Magnitude Estimate for Worldwide Capacity (Giga tonnes of carbon)
Active oil wells (EOR)	10
Enhanced Coal Bed Methane (ECBM)	5-10
Deep Saline Formations	100 – 10,000
Oil and Gas Reservoirs	100 – 1000
Ocean	1000 - >100,000

1.5 Research aims

In 2004, the Australian Federal Government released an energy white paper which establishes the policy framework for the development of the energy sector in Australia (ETF, 2004). In the report, CCS was highlighted as a key option for low emissions use of fossil fuels while enabling the expected growth to continue within the energy sector. However, previous research has indicated that the cost of capturing the CO₂ may be a major deterrent to wide-scale implementation of CCS. It has been estimated that the cost of CO₂ capture from power plant flue gas using commercially available technology can range from US\$30 to over US\$50 per tonne CO₂ avoided (Roberts et al., 2004, Rubin et al., 2004, Parsons, 2002, Gibbins and Crane, 2004a). Assuming a simple exchange rate conversion, and adding the costs for transport and storage, the total CCS cost could range from A\$50 to more than A\$100 per tonne CO₂ avoided depending on the characteristics and location of the storage facility (Allinson and Nguyen, 2003).

In 2005, the European Union began its Emissions Trading Scheme (ETS), with prices generally trading in the range of €20 to €27 per tonne CO₂ avoided in 2005, and from €25 to €30 per tonne CO₂ avoided in early 2006 (equivalent to approximately A\$30 to A\$45 per tonne CO₂ avoided) and subsequently falling to less than €10 by the end of the year (BBC_News, 2005, Capoor and Ambrosi, 2006). The IPCC Special Report on Carbon Dioxide Capture and Storage (IPCC, 2005) noted that, in the absence of such price signals or a mandated limit on emissions, it is unlikely CCS systems would be deployed on a large scale. If an emission trading scheme was established in Australia

with a cost of A\$30 to \$35 per tonne CO₂ avoided as proposed by the National Emissions Trading Task Force (NETT, 2006), it is unlikely that CCS using current technology would be competitive. Thus, for CCS technologies to be competitive, then either the emission trading prices need to increase or significant cost reductions in capture are needed or a combination of both. Technology and cost improvements for CO₂ capture may provide these reductions.

The objective of this thesis is to understand and evaluate the cost outcomes of implementing CO₂ capture for Australian CO₂ emission sources. This research project aims to:

1. Assess and compare the economic feasibility of CO₂ capture technologies (absorption, adsorption, membranes and low temperature separation) for Australian economic conditions.
2. Examine the key cost components of each CO₂ capture technology.
3. Explore areas of possible process and cost improvements for each capture technology.

The research examines CO₂ capture for different processes including post combustion power generation, pre-combustion power generation and major Australian industrial processes.

A techno-economic model incorporating process equations coupled with cost estimation algorithms has been developed specifically for this project. The outputs from the model assist in pre-feasibility analysis. The research project calculates the associated cost avoided for capture and compression of CO₂. A separate economic model for transport and storage of CO₂ for Australian offshore and geological conditions has been developed by the School of Petroleum Engineering (Allinson and Nguyen, 2003, Allinson and Nguyen, 2000). This research project is a collaboration between the University of New South Wales and the Australia Cooperative Research Centre for Greenhouse Gas Technologies (CO₂CRC).

1.6 Outline of thesis

This thesis consists of ten chapters. The structure of the thesis is as follows:

Chapter 2 provides a literature review related to of the technologies used for CO₂ capture. The reported costs of capture by previous studies are also described. Chapter 3 summarises all the processing and economic equations used in developing the techno-economic CO₂ capture model. Chapters 4 to 7 investigate the cost of capturing CO₂ from the flue gas of a supercritical black coal power plant. A sensitivity analysis is also undertaken in each chapter to determine the effect of processing parameters on the capture cost. In Chapter 4, the cost for CO₂ capture using chemical absorption technology is examined. The parameters investigated include solvent properties for regeneration, equipment cost and process waste heat integration. Chapter 5 investigates the capture cost using gas separation membranes. The processing parameters examined include membrane permeability and selectivity, pressure ratio and membrane costs. Chapter 6 discusses the effect on cost by improving adsorbent and processing conditions for pressure swing adsorption. In Chapter 7, “anti-sublimation” low temperature technology is investigated for CO₂ capture. Chapter 8 evaluates and compares the cost of capture for six major Australian industrial sources. The analysis also compares the suitability of different technology options for each of the sources. In Chapter 9, the uncertainties and impact of variability in the economic assumptions used is discussed. Chapter 10 summarises the conclusions of this thesis, and provides recommendations for future work. A full list of references is provided following Chapter 10. Appendix A lists the processing and economic assumptions of the literature studies reviewed in this thesis. Appendix B describes the equations used for modelling physical solvent systems. A summary of the solvent, membrane and adsorbent characteristics used in this study are outlined in Appendix C. Appendix D summarises the detail results of the analysis for Chapter 8.

Chapter 2. REVIEW OF CO₂ CAPTURE TECHNOLOGIES

2.1 Background

The idea of capturing CO₂ and storing it underground in a geological reservoir did not start with concern about global warming; rather it gained attention as a possible source of CO₂ for use in enhanced oil recovery (EOR) operations. In EOR, CO₂ is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. Several commercial CO₂ capture plants were constructed in the late 1970's and early 1980's in the US for this purpose (Arnold, 1982, Miller, 1986). However, when the price of oil dropped in the mid 1980's, the recovered CO₂ was too expensive for EOR operations and subsequently the CO₂ capture plants were shut down.

One of the first people to raise concerns over the rising levels of CO₂ in the atmosphere was Marchetti in 1977 (1977). He proposed the idea of separating CO₂ from power stations and storing the CO₂ in the depths of the ocean as a possible mitigation option (Marchetti, 1977). Later in 1979, Mustacchi et al. (1979) also reviewed various options for removing CO₂ from power plant exhaust gases followed by storage of the captured CO₂ in the deep ocean. Albanese and Steinberg (1980) also investigated the feasibility of capturing CO₂ for atmospheric control as part of the initial studies by the US Department of Energy's investigation into atmospheric emissions during the 1980's. In 1991, the concept of geo-sequestration was proposed by the International Energy Agency as an option for CO₂ abatement (Smith and Thambimuthu, 1991). Recently, a number of studies have been undertaken by the international community to assess the viability of current CO₂ capture technology for separating CO₂ from large industrial sources (Rubin et al., 2004, Singh et al., 2003, Herzog et al., 1997, Leci, 1996, Mimura et al., 2000a).

Although there are many CO₂ capture technologies, this research focuses on chemical and physical absorption, pressure swing adsorption (PSA), gas separation membranes

and low temperature separation. Previous studies on the economic feasibility for CO₂ capture, and the objectives of the Australia Cooperative Research Centre for Greenhouse Gas Technologies (CO₂CRC) highlight that these technologies have the most promise in delivering short and medium term CO₂ reduction goals. Table 2-1 lists the current salient features and advantages/disadvantages of these capture options.

Table 2-1 Summary of the advantages and disadvantages of CO₂ capture systems

Technology option	System requirements	Advantages	Disadvantages
Chemical Absorption	• Absorber and stripper sections • Solvent (eg. MEA)	• Technically mature • Uses common processing equipment • Suited to gas streams with low concentration	• High energy required for regenerating solvent • Large ratio of solvent to CO₂ for effective absorption • Large footprint • High capital cost
Physical Absorption	• Absorber and stripper sections • Solvent (eg. Selexol)	• Technically mature • Uses common processing equipment • Solvents are less susceptible to toxins in the feed gas streams	• Suitable only for high pressure gas streams • Large footprint • High capital cost
Adsorption	• Adsorber beds • Sorbents (eg. Zeolites)	• Suitable for low concentration streams	• High energy consumption • High capital cost • Low efficiency removal rate • Large footprint
Gas separation membranes	• Membrane housing • Membrane filters	• Compact • Suited to streams with high pressure, low concentrations • Can be operated off shore	• Can be energy intensive because of the high pressure differential required • High equipment cost (compressors) • Separation of CO₂ is not technically mature
Low temperature systems	• Refrigeration and distillation units	• Most suitable for binary gas streams • CO₂ product is ready for transport	• Energy intensive • Efficiency affected by other gas components in flue stream

2.2 Absorption

The most well known technology for recovery of CO₂ is solvent absorption. This technology was established over 80 years ago in the chemical and oil industries for the

removal of hydrogen sulphide and CO₂ from natural gas streams (Thambimuthu, 2002, GPSA, 2004). There are two kinds of solvents: chemical and physical. In physical absorption, the absorption rate and solvent loading is a function of the solubility of the gaseous solute (CO₂) in the solvent (Figure 2-1). In chemical absorption, there is a chemical reaction between the solute (CO₂) and the solvent. The specific nature of the feed gas stream and economic considerations determine which of the absorption processes would be optimal under different circumstances. However, as a general rule-of-thumb, chemical absorption is preferred when the CO₂ partial pressure is less than 3.5 bar (GPSA, 2004). For feed gas streams with high pressure, both chemical solvents and physical solvents are used, although physical solvents are usually preferred.

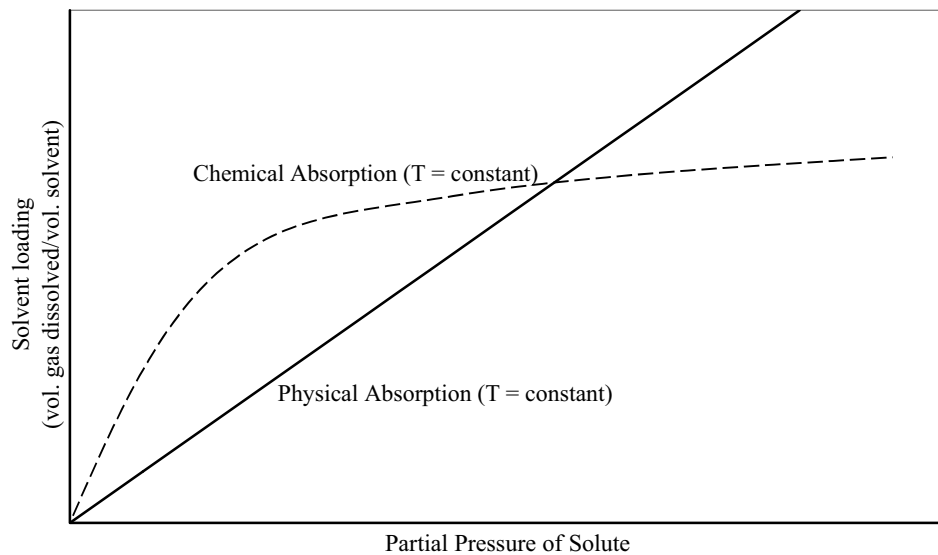


Figure 2-1 Characteristic solvent loading of chemical and physical solvents

2.2.1 Chemical absorption

In chemical absorption, weak chemical bonds are formed between the acid gas CO₂ and the alkaline solvent solution. Because of the formation of the chemical bond, the overall mass transfer of CO₂ from gas phase to liquid phase is enhanced, thus making chemical absorption kinetically faster than physical absorption.

Generally, alkaline solvents such as alkanolamines, hot potassium carbonate, and ammonia are used. This is because they react reversibly with the CO₂. Applying heat to the solvent-CO₂ complex, the solvent releases the CO₂, allowing the solvent to be

recycled and reused (regenerated). The chemistry can be represented in simplified form as (Desideri and Paolucci, 1999):



Contaminants found in the gas stream (SO_2 , NO_x , hydrocarbons and particulates) usually need to be removed before capture to prevent them from inhibiting the ability of the solvents to absorb CO_2 . Chemical solvents may react irreversibly with SO_x , NO_x , O_2 and CO present in the flue gas forming sulphites/sulphates, nitrate, oxidation products and formates, respectively. This leads to the loss of active solvent, and equipment corrosion. Therefore, for effective CO_2 removal, it is required that (Leci, 1996):

- The SO_x and NO_x content of the gas stream be below 10 ppm;
- Corrosion inhibitors are used with chemical solvents if O_2 and CO are present; and
- Particulate matter is less than 3 mg/Nm^3 .

Many commercial scale plants use chemical absorption for CO_2 recovery. In normal practice, CO_2 is considered a waste gas and is vented into the atmosphere. At present, there are ten industrial installations in which CO_2 is captured from an industrial source for CO_2 capture and storage or use (CCS) (IEA-GHG, 2006a). These include recovery of CO_2 from power plant flue gas based at Shady Point Power Plant (Oklahoma, USA), Warrior Run Power Plant (Maryland, USA), and Bellingham Cogeneration Facility (Massachusetts, USA). Other industrial facilities recovering CO_2 from on-site flue gases using chemical absorption include Petronas Fertilizer Co. (Malaysia), Sumito Chemicals Plant (Chiba, Japan), IMC Global Inc. (Trona, California, USA), Prosint Methanol Production Plant (Rio de Janeiro, Brazil) and The Indo Gulf Fertilizer Company Plant (Jagdishpur, Uttar Pradesh, India). The plants have been operational since the late 1980's and are reportedly operating well. The CO_2 recovered from these plants is used

for food processing, freezing, beverage production and chilling purposes, as well as in brine carbonation and in the manufacture of urea.

Chemical solvents for CO₂ capture

Alkanolamine (hereafter amine) solvents have been used extensively for commercial CO₂ recovery. Some of the most widely used amine solvents include monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA). Other alkaline solvents that are also commonly used include potassium carbonate, ammonia and propriety formulated solvents based on amine solvents.

For feed gases with low CO₂ concentration and low pressure such as post-combustion flue gas, MEA is considered the most suitable solvent because of its high affinity for CO₂. MEA is a primary amine with a high pH and has the lowest molecular weight of the available amines. It is completely soluble in water and is readily biodegradable (DOW, 2005). MEA has several advantages over other amine solvents. It has higher reactivity, lower solvent price, a low molecular weight (resulting in high absorption capacity on a weight basis), a reasonable thermal stability, and moderate thermal degradation rate. Due to the wide range of applications in which MEA is used compared to other alkaline solvents, it is often selected as the base case to compare the performance of newly developed solvents and remains the focus of most techno-economic studies for CCS. However, MEA has some drawbacks. The first is the considerable amount of energy that is required to break the CO₂-solvent complex bond. Secondly, the presence of O₂ in the feed gas can adversely affect the ability of the solvent to absorb CO₂. It can also cause corrosion in the processing equipment.

2.2.2 Advantages and disadvantages of chemical absorption

The main benefit of using chemical absorption for CO₂ capture is that the solvents used to absorb the CO₂ can be easily regenerated and re-used. The purity of the CO₂ stream obtained from the chemical absorption process is high, generally greater than 95%. In addition, the process has been used extensively for many decades, and thus the process is well studied and understood. This has resulted in the development and use of equipment that is considered conventional.³

According to Meisen and Shuai (1997) in their evaluation of CO₂ capture technologies, chemical absorption systems for CO₂ capture have some disadvantages. These include the limited absorption capacity of commercial solvents, the high energy requirements for regeneration, and the large size of equipment required. Researchers from Europe (Leci, 1997, Audus, 2000, Hendriks, 1994, Reiner et al., 1994, Gibbins and Crane, 2004b), North America (Singh et al., 2003, Rao and Rubin, 2002, Simmonds et al., 2002, Stork, 1999, Booras and Smelser, 1991, Rochelle and Jassim, 2005, Mariz, 1998, Desideri and Paolucci, 1999, Simbeck, 2001) and Asia-Pacific (Nsakala et al., 2001, Dave et al., 2000) who have investigated CO₂ capture from power plant flue gas using standard industrial MEA, have found that the economic feasibility of chemical solvent absorption is highly dependent on the energy required to regenerate the CO₂ in the stripper. This energy requirement can be up to 20% to 30% of the total energy output from a 500 MW power generator. Such a substantial level of energy consumption translates into very high operating costs and in the case of power plants, increased capital cost to pay for lost production capacity.

Solvent development

To address the inherent drawbacks of chemical absorption for CO₂ capture new solvents are being developed. Recent work has focused on the investigation and development of novel solvents that minimise steam consumption in the stripper. This has been achieved through the development of solvents that have a high chemical resistivity to CO₂ thus lowering the energy required for regeneration.

Mimura et al. (2000a) reports of a commercially available hindered-amine solvent called KS1. KS1 is a proprietary solvent developed by Mitsubishi Heavy Industries that has a much lower specific stripping heating requirement than MEA. Results have shown that, by using this solvent, the total energy consumption can be reduced by up to 20% compared to MEA (Mimura et al., 1997). The degradation rate of KS1 is much lower than MEA resulting in smaller solvent losses and therefore lower operating costs.

Fluor Daniel Inc. (Chapel et al., 1999) have also developed a commercially available solvent called Econoamine FG Plus. This solvent is a combination of improved solvent formulation coupled with an improved process layout to reduce the total energy consumption while maintaining effective absorption. Total energy reductions of up to 20% compared to MEA have been achieved in pilot studies.

Another propriety formulated solvent is the PSR solvent developed by Veawab et al. (2001). The PSR solvent requires less heating for regeneration while absorbing more CO₂ than MEA. The researchers maintain that the total solvent circulation rate with PSR is less than for MEA because of PSR's ability to maximise solvent loading. The result is that less energy is needed for CO₂ regeneration. This is coupled with benefits such as lower solvent degradation and corrosion rates. PSR is still being tested at the pilot-scale.

Other research into formulated solvents includes work by Yeh et al. (2001) comparing absorption and desorption properties of MEA and a hindered-amine called AMP. Their results show that although the absorption properties of AMP were not as effective as MEA, regeneration properties were superior. Further investigation into the economics and process integration is required before it can be assessed whether AMP is a better solvent.

New solvents developed by the research team at TNO called CORAL (CO₂ Removal Absorption Liquid) (Feron and Jansen, 1997) have shown absorption properties with mass transfer rates twice that of MEA while displaying similar regeneration properties. CORAL solvents also have much lower degradation rates and low corrosion rates, and can be used in carbon steel absorption towers. This results in lower capital costs.

Significant solvent development has also been claimed by Kim et al. (2004), and Ma'mun et al. (2004) into two solvents called M-H amine and AEEA respectively. These solvents are described as having lower regeneration requirements while maintaining or having slightly better absorption properties than MEA. These solvents however are still in the early stages of development.

In addition, Bonenfant et al. (2003) have also investigated new amine based solvents such as AEE (diamine) and AEPNH₂ (polyamine). Their study revealed that these solvents possess structural properties, which improve the CO₂ absorption loading and are much easier to regenerate compared to MEA solvent.

Chakma (1997), Aroonwilas et al. (2001), Sakwanttanapong et al. (2005), Chakravarti et al. (2001) and Xiao et al. (2000) examined the feasibility of CO₂ absorption using blended amines to utilise the fast reaction kinetics of MEA while exploiting the lower regeneration requirements of the other alkanolamines. For MEA-blends, the results show that the total regeneration energy requirement is a value between the heat duties of their parent alkanolamines, and depends on operating parameters and mixing ratios. Blended amine solvents have been used extensively since the 1980's as part of natural gas processing to recover CO₂ (Bullin et al., 1990, Chakravarty et al., 1985). There has, however, been no reported commercial demonstration of the ability of amine-blended solvents to recover CO₂ specifically from post-combustion power plant flue gas.

Research into non-alkanolamines such as potassium carbonate and carbonate blends is been undertaken by Rochelle et al. (Rochelle et al., 2005, Culliane et al., 2004). Their work, based on a pilot plant, found that the carbonate blends could be an attractive alternative to MEA at moderately high CO₂ partial pressures because of the lower regeneration energy required.

Other research work by Yeh and Bai (1999) has found that ammonia has significantly better absorption properties than MEA (solvent loading improvement of 100%) and exhibits lower degradation due to contaminants than MEA. However, their work did not investigate the regeneration/reboiler energy requirements and/or economic impacts.

Process development

Another way of improving the chemical absorption process is to ensure that there is maximum interaction between the solvent and the CO₂. Fei (2004, 2005) have developed highly efficient structured packing materials to reduce the absorber and

regenerator size which would result in lower capital and operating costs. However, no economic analysis has been published in the public domain that outline the cost benefits.

Other process configuration improvements such as an innovative design for the stripper have been proposed by Rochelle and Jassim (2005). The configurations include the use of multi-pressure strippers, vapour recompression and inter-cooling of the absorber. They found that the combination of all stripper improvements could generate energy savings of between 20% and 40% compared to simple stripping using MEA.

2.2.3 Physical absorption

For gas streams with high partial pressure of CO₂, the absorption of CO₂ in physical solvents can be modelled according to Henry's law. The solubility of CO₂ in physical solvents is linearly proportional to the partial pressure of the CO₂ in the feed gas stream. Popular commercial physical solvents include Selexol (dimethylether of polyethylene glycol) or Rectisol (cold methanol). In general, a physical solvent process should be considered when:

- The partial pressure of the acid gas in the feed is greater than 3.5 bar;
- The heavy hydrocarbon concentration in the feed gas is low;
- Bulk removal of the acid gas is desired; and/or
- Selective removal of H₂S is desired.

These processes are economically attractive because little energy is required for regeneration. The solvents are regenerated by:

- Multi-stage flashing to low pressures;
- Regeneration at low temperatures with an inert stripping gas; and/or
- Heating and stripping of solution with steam/solvent vapour.

The processes operate at ambient or sub-ambient temperature to enhance the solubility of the acid gases. The solvents are relatively non-corrosive so carbon steel can be used.

Chemical losses are low due to low solvent vapour pressure or refrigerated conditions. Physical solvents will absorb heavy hydrocarbons from the gas stream resulting in high hydrocarbon content in the acid gas stream as well as possibly significant hydrocarbon losses.

These solvents have been used in the natural gas industry since the 1950's, and thus have been extensively tested.

2.2.4 Advantages and disadvantages of physical absorption

The benefit of using physical solvents lies in the fact that the regeneration process is not as energy intensive as chemical absorption. For feed gas streams with high CO₂ partial pressure such as the synthesis gas in IGCC power plants, the energy consumption using physical solvents is 60% less energy intensive than for the chemical absorption process (David and Herzog, 2000).

Gases such as NO_x, O₂ and CO present in the flue generally pass through the system because of their poor solubility in the physical solvents. They therefore do not degrade the solvent. The main drawback of physical solvents is that they are more costly than chemical solvents such as amines.

Selexol and Rectisol are considered the leading and proven commercial options for physical absorption of CO₂ from high pressure feed gas streams. CO₂ capture using physical absorption from industrial streams such as IGCC power generation is still in the preliminary stages of technical economic investigation and thus there has been no reported solvent development work specifically for the purposes of CCS.

2.3 Membranes

Membranes have become an attractive alternative to traditional separation process in recent years since the development of ultra thin membranes by General Electric in the 1970's for O₂ enrichment, and later development by Permea in the 1980's of their hydrogen recovery membranes (Baker and Koros, 1991, Koros, 1991). Currently, a

wide variety of industrial applications, from air separation, natural gas processing, ammonia production, to petrochemical and power plants utilise membranes for gas separations.

Gas separation membranes rely on a difference in physical or chemical interaction between components of a gas mixture with the membrane material, causing one component to permeate faster through the membrane than the other. The membrane divides the feed gas stream into the permeate stream and the retentate stream as shown in Figure 2-2.

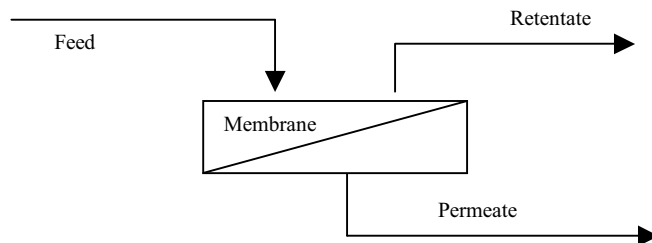


Figure 2-2 Schematic of a membrane module

Regardless of the exact mechanism for mass transfer across the membrane, the main driving force for the permeation through the membrane is the difference in partial pressure between the feed side and the permeate side, also referred to as the pressure ratio. The pressure ratio is the ratio of the permeate pressure to the feed stream pressure. In general, the higher the difference in pressures, the greater the driving force. As well as pressure, the selectivity of a membrane, the ability of a membrane to separate a gas mixture into its separate components also influences the quality of the separation.

Gas separation membranes can be prepared from a variety of materials, with the pore size and the material altered to improve the selectivity, and permeability (or flow through) of the membrane. Materials that can be used for CO₂ separation include polymeric membranes, facilitated transport membranes, molecular sieves membranes and palladium based alloy membranes used in the separation of H₂ from CO₂ rich gases (Feron, 1992). Generally polymer based membranes are the preferred option for separation as they allow a high degree of separation to be achieved and are able to

operate at the large economies of scale demanded by processes requiring CO₂ capture. Economically they are also the cheapest and easiest to manufacture and are the only membranes currently produced commercially at large scale.

In the 1980's Parro (1984) and Schendel (1984) demonstrated the use of membranes for large scale CO₂ recovery in enhanced oil recovery projects from natural gas fields. According to Baker (Baker, 2001), in 2001 there were several hundred installations in which membranes were used to recover CO₂ from natural gas. For the recovery of CO₂ from combustion flue gas streams using membranes, Chapel et al. (1999) claims that in 1999 there were no commercial applications in operation. No information in the public domain or research journals has pointed to the existence of a commercial membrane application since that date.

2.3.1 Advantages and disadvantages of polymeric membranes

A benefit of using gas separation membranes for CO₂ capture is that they are relatively easy to operate and have very small footprints compared to other traditional separation technologies. The following section summarises the advantages and disadvantages of polymeric membranes used for CO₂ separation.

The recovery and capture of CO₂ from natural gas streams has been described extensively in literature by Coady and Davis (1982), Mazur and Chan (1982), and Spillman (1989). They found that membranes were competitive against amine systems due to their flexibility in handling variations in gas feed compositions and flowrates, their operational simplicity and their lower up-front investment costs.

CO₂ capture for CCS using membrane technology has been investigated by Van der Sluis et al. (1992), Feron for the IEA GHG (1992) and Tokuda et al. (1997). These researchers focused on CO₂ recovery from low pressure post-combustion flue gases. The economic analysis undertaken by van der Sluis et al. (1992) and the IEA GHG (Feron et al., 1992) concluded that CO₂ capture by gas separation membranes is not as effective as other CO₂ recovery methods due to the low permeability and selectivity of commercially available membranes. Additionally, membranes suffer from degradation

of performance over time due to a variety of factors and operation is limited to near ambient temperature. However, Meisen and Shuai (1997) argue that further development of membranes with better selectivity, higher CO₂ permeability coupled with the ability for membranes to handle higher temperatures would make them more competitive.

Membrane development

Many researchers such as Fristsh and Peinemann (1995), Matsui et al. (Matsui et al., 1998), Al Masri et al. (2000), Dorkenoo et al. (1998) and Bondar et al. (2000) have explored the development of new polymeric membranes with higher selectivity for CO₂ and higher CO₂ permeability for separation of post-combustion flue gas. These researchers have reported moderate CO₂ permeability values ranging from 30 Barrer to 120 Barrer coupled with moderate CO₂/N₂ selectivity of 35 to 50. They also developed membranes with exceptionally high CO₂ permeability values in the range of 400 Barrer to 800 Barrer, although these were associated with reduced CO₂/N₂ selectivity values in the range of 2 to 14. These new membranes have been developed through new novel process or include new structures such as segmented block co-polymers (Bondar et al., 2000). In comparison, the current commercially available membranes such as the Polyphenylen-oxide membrane by Delair or the polyimide by UBE have CO₂ permeability values of 70 and 20 Barrer respectively and CO₂/N₂ selectivity of less than 20 (Feron 1992, Van der Sluis 1992).

Considerable progress has been made in developing new polymeric membranes for CO₂ recovery from natural gas processing. One of the most promising research has been undertaken by Costello and Koros (1994) who have developed a polycarbonate membrane with a CO₂/CH₄ selectivity of 60 coupled with a CO₂ permeability of 139 Barrer. Other significant research into CO₂ selective membranes for natural gas processing has been reported by Al-Masri et al. (2000), Fristch and Peineman (1995) and Tanaka et al. (1995). The reported values of CO₂/CH₄ selectivity and CO₂ permeability have been 32/190 Barrer, 35/110 Barrer and 36/91 Barrer respectively.

Hydrogen selective polymeric membranes have been developed by Tanaka et al. (1992), where H₂/CO₂ selectivity and permeability of 4 and 40 Barrer have been created. This value is still relatively low compared to the membrane performance for other component gases. CO₂ selective membranes using the block co-polymers by Bondar et al. (2000) have produced significantly better results with CO₂/H₂ selectivity of 10 and a CO₂ permeability of 120 Barrer.

The block co-polymer membranes as described by Bondar et al. (2000) have higher CO₂ selectivities and permeabilities compared to single layer membranes because of the composite segmentation of the membrane body. The different polymers used in the layers are able to selectively remove different component gases resulting in a selectivity value higher than for other polymers with similar CO₂ permeabilities.

The development of high-temperature membranes for CO₂ recovery has been explored for the past 10 to 15 years. The focus of most work has been the development of inorganic membranes, especially for hydrogen separation from synthesis gas. In Bresden et al.'s (2004) review of high temperature membranes, they reported the development of inorganic membranes with H₂/CO₂ selectivity of 11 to 1000 operating at temperatures of 200 to 600 °C, coupled with hydrogen permeabilities of 10 to 130 Barrer. The development of inorganic membranes for CO₂ recovery from high-temperature post-combustion flue gas continues but results have been unsatisfactory with reported low CO₂/N₂ selectivity (values range from 1 to 2) and low permeation rates (less than 10 Barrer) reported (Lagorsse et al., 2004, Kang and Hyun, 1999).

Process development

Hybrid configurations of membranes with other processes such as absorption have been proposed by McKee et al. (McKee et al., 1991) and Bhide et al. (1998). They investigated the idea of a hybrid configuration for natural gas processing where the membrane is placed at the front end of an existing absorption plant. The membrane removes the bulk of the CO₂ from the feed gas, and the amine unit removes the remaining low partial pressure CO₂. They have suggested that this significantly reduces the CO₂ capture costs. Hybrid configurations with adsorption have previously been

mentioned. Another hybrid configuration for natural gas process has been reported by Limb (1985). In this layout, the membrane enriches the CO₂ from 30% to 90% before further processing in a cryogenic distillation to obtain a purity of 99% for use in enhanced oil recovery.

The development of membranes processes such as gas absorption membranes has been widely explored for CO₂ capture. Gas absorption membranes are used as contacting devices between a gaseous feed stream and a liquid solvent stream. The removal of CO₂ is driven by the presence of the absorption solvent on one side of the membrane, which selectively removes the desired component. Commercially, the Kvaerner gas absorption membrane contactor has demonstrated in several natural gas field applications. In this application, the CO₂ is removed from natural gas using MEA solvent with a polymer membrane acting as the contacting device. Research has shown that gas absorption membranes have higher efficiencies and lower costs than gas separation membranes and chemical absorption processes (Feron et al., 1992, Chakma, 1995b). However they still suffer the same process drawbacks as chemical absorption process such as solvent degradation and high regeneration energy. Some additional problems include concerns about the stability of the membrane due to wetting and chemical attack by the solvent.

2.4 Adsorption

Adsorption is a process that occurs when a gas or liquid accumulates on the active surface sites of a solid adsorbent. The gas or liquid is adsorbed onto the porous site by physical attraction (van der Waal's forces or electrostatic forces) and/or chemical attraction until the adsorbent becomes saturated. The adsorption process can be used to separate gas mixtures of CO₂ by preferentially adsorbing one component gas over another. The ratio of adsorption of one component relative to another is referred to as the adsorbent selectivity.

Figure 2-3 shows the adsorption of CO₂ on a physical adsorbent to separate it from a gas mixture of CO₂/N₂.

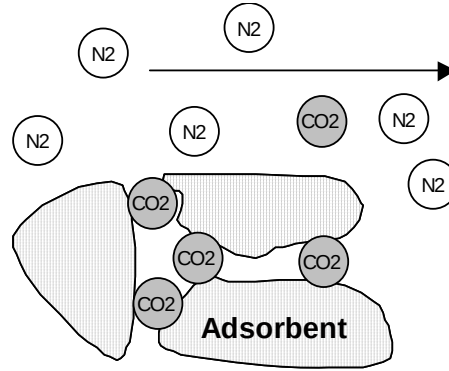


Figure 2-3 Adsorption of CO₂ onto a solid adsorbent

The extent of adsorption depends on physical parameters such as temperature, the difference in the adsorption and desorption pressure, concentration of the different component gases in the gas phase, and the surface area of the adsorbent. The amount of gas that is adsorbed is also influenced by chemical parameters such as the elemental nature of the adsorbent and the gas to be adsorbed. Low temperatures, high pressures, high surface areas, and highly reactive adsorbents generally favour rapid adsorption. The rate of adsorption can be described as the capacity or loading of the adsorbent.

The adsorption loading of an adsorbent is a function of pressure and temperature (as shown in Figure 2-4), and is usually described using isotherms. The simplest equilibrium isotherm expresses adsorbent loading as a function of partial pressure and results in Henry's law (Equation 2.1). Another commonly used isotherm for gas systems is the non-linear Langmuir isotherm (Equation 2.2). The format of this isotherm accounts for surface coverage. That is, when the fluid concentration is very high, a monolayer forms on the adsorbent surface, which is represented by a loading of A/B.

$$\text{Henry's law: } q_i = A_i \times P_i \quad (2.1)$$

$$\text{Langmuir isotherm: } q_i = \frac{A_i \times P_i}{1 + B_i \times P_i} \quad (2.2)$$

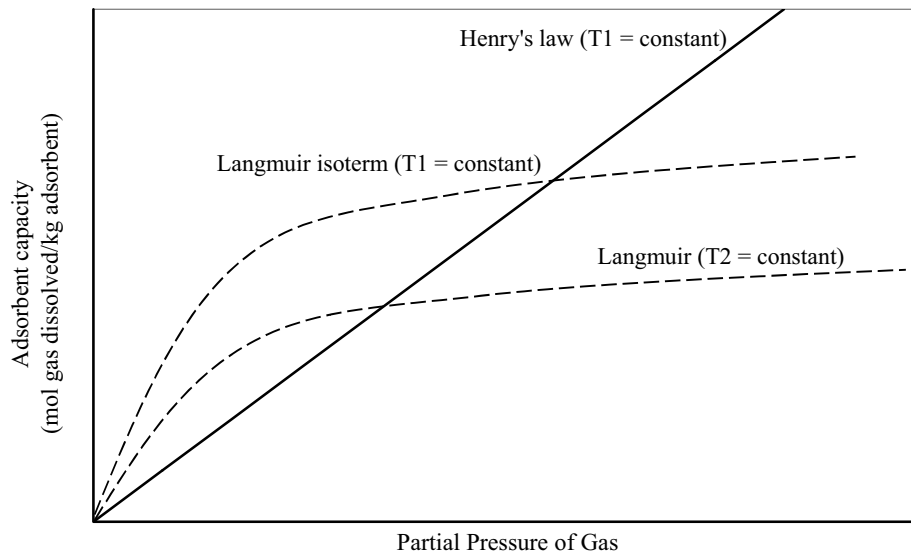


Figure 2-4 Adsorbent loading as modelled by Langmuir Equation and Henry's Law

To achieve continuous operation and to be able to re-use the adsorbent beds, regeneration of the adsorbed gas (referred to as desorption) is required. Since the extent of adsorption is dependent on temperature and pressure, methods of desorption can also be achieved by altering these same variables. There are four main ways to achieve desorption:

- Decreasing the internal pressure to reduce the partial pressure of the strongly adsorbed component (pressure swing adsorption: PSA);
- Increasing the temperature (temperature swing adsorption: TSA);
- Passing a stream of inert gas through the bed to reduce the partial pressure of the adsorbate (Inert-purge); or
- Passing a stream of gas over the adsorbent bed to “flush” out the trapped gas and reuse the regenerated bed (Displacement-purge).

Inert and displacement purges are not as effective for desorption and adsorber regeneration as PSA or TSA as they do not have a very strong driving force. However, they are often incorporated into PSA or TSA to enhance the overall desorption process.

Adsorption systems are suitable for flue gas streams with low concentrations of CO₂ and high pressure, as the solids have limited capacity to adsorb the gases (typically less than 20% by weight for CO₂ on a molecular sieve). The energy required for regeneration of the solids is also considered to be relatively high per unit of adsorbent due to the high affinity that the solid adsorbents have for CO₂.

Depending on the nature of the adsorbent, removal of contaminant gases such as SO_x, NO_x, particulate matter and water may be required prior to adsorption in order to avoid degenerating the solid adsorbent.

Adsorption systems were originally used as a process for oxygen (O₂) enrichment. Commercially, adsorption systems have been extended to recover CO₂ from natural gas streams and hydrogen processing streams (Mitariten et al., 2003). There are currently no commercial plants operating that recover CO₂ from flue gas.

Both PSA and TSA systems have been shown to be able to recovery CO₂, however PSA possesses several advantages over TSA. The regeneration cycles of the adsorber beds in TSA systems are quite long, measured in hours. In addition, the quantity of adsorbent in TSA is higher than in PSA systems (Ruthven, 1984). For the recovery of CO₂ from industrial streams such as power plant flue gases, this would lead to substantially large equipment sizes. As a consequence, most commercial applications use PSA. This research focuses on the development and evaluation of PSA systems rather than TSA.

2.4.1 Pressure swing adsorption (PSA)

Historically, the recovery of CO₂ using pressure swing adsorption (PSA) systems has been in industries such as natural gas processing and hydrogen production. In these industries the feed gas is at a high pressure and low temperature. Thus CO₂ can be recovered by using a readily available driving force such as the pressure difference between the high pressure feed for adsorption and a lower pressure for desorption. The driving force is generally referred to as the pressure ratio which is the ratio of the desorption pressure to the adsorption pressure.

Most adsorbents commonly used in PSA processes have a very strong affinity for CO₂, and require a very large pressure ratio to enable complete desorption of the CO₂. In the 1980's, vacuum swing adsorption (VSA) processes were being explored in place of the traditional PSA systems in order to increase the efficiency of regenerating the adsorbent bed (Yang, 1987, Ruthven, 1984, Ruthven et al., 1994). In VSA systems, the feed gas is delivered to the adsorber at atmospheric pressure or higher. However, the CO₂ is regenerated at a much lower pressure, typically 0.01-0.1 bar (Kikkinides and Yang, 1993, Chue et al., 1995, Doong and Yang, 1986, Kapoor and Yang, 1989). Using a vacuum desorption process, a sufficient pressure ratio is achieved without the need for large feed gas compressors. This reduces both the capital expenditure and the operating costs through reduced energy consumption.

2.4.2 Advantages and disadvantages of PSA

An inherent advantage of PSA systems is that they are simple to operate. Unlike absorption or cryogenic systems, PSA requires only a few vessels capable of withstanding pressure changes. In addition, like absorption, PSA systems have a regenerative adsorbent that can be re-used. The main weakness of PSA compared to other technologies, such as absorption, is the limited application of PSA for CO₂ recovery from industrial streams such as post-combustion flue gas.

Audus (1997), in his 1997 review of CO₂ capture technologies argues that the main inherent drawback of PSA systems is their inability to handle CO₂ gas concentrations above 1.5%. This makes them inappropriate for CO₂ capture from industrial streams where concentrations are generally greater than 8%. However, this conclusion could have been biased by the type of adsorbent used in the study (a molecular sieve). The particular details of the adsorbent were not reported. Adsorbent studies have shown that the different types of adsorbents such as carbon molecular sieve, zeolite molecular sieve or activated carbon have vastly different CO₂ adsorption properties.

One of the initial studies by the International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) in 1992 investigated adsorption technology for CO₂ capture from power plant flue gases using a PSA system (Reiner et al., 1994). The study found

that, using the Gemini ® process, the feed gas must to be compressed to at least 6.5 bar (655 kPa) and cooled to 40°C for effective removal. This process, which has been designed to recover and purify methane at high pressure, resulted in very high compression costs. Based on these results, the report concluded that “gas-solid adsorption, in its present state of commercial development, does not appear to be a suitable technology for the bulk capture of carbon dioxide from flue gas produced by fossil fuel power generating systems”. However, at the time of the analysis, there was little interest in CO₂ capture, and it was difficult to perform a thorough analysis. However, since then, the increase in interest in CCS technologies has resulted in many researchers investigating CO₂ recovery from flue gases using PSA systems. These studies using vacuum desorption conditions show that high and/or moderate rates of CO₂ recovery and purity can be achieved without the need for excessive compression of the feed gas stream.

Adsorbent development

In PSA systems, one of the most important parameters affecting the performance is the choice of adsorbent used. Ideal adsorbents should have high rates of adsorption and desorption for the desired gas (the working capacity). In addition both the amount of reversible adsorption of CO₂ and the difference in the amounts of adsorption between CO₂ and the other component gases (the selectivity) should be as large as possible.

Adsorbents with high surface areas, such as zeolite molecular sieves and activated carbon have been widely analysed for their CO₂ separation effectiveness. During the late 1980's Inui et al. (1988) investigated the characteristics of zeolites and their adsorption-desorption behaviour for CO₂ recovery. The more effective adsorbents were the highly crystallised zeolites with three-dimensional pore connection structures. Of the commercial samples tested, chabazite and 13X were found to be the most suitable.

Chue et al. (1995) compared the performance of zeolite 13X to activated carbon (AC) for post-combustion flue gas recovery. They concluded that zeolite 13X was a better adsorbent for CO₂ as it had a higher working capacity, lower purge requirement and higher equilibrium selectivity than activated carbon. However, according to Siriwardane

et al. (2001), zeolite 13X is a better adsorbent for low partial pressure CO₂, while activated carbon possesses better adsorption properties when the CO₂ is at higher partial pressures. Harlick and Tezel (2004) screened 13 different available adsorbents to evaluate their adsorption capacity for CO₂ recovery from post-combustion flue gas. They concluded that if the feed gas is available at a low pressure and a very low regeneration pressure is used, then zeolite 13X is the most suitable adsorbent. For higher feed and regeneration pressures, zeolite NaY is a better adsorbent.

Initial adsorbent development work by Takeguchi et al. (1992) proposed impregnating zeolite molecular sieves with metals to decrease the acidity of the adsorbent and enhance the adsorption performance of CO₂ in CO₂/N₂ mixtures. They determined that the presence of the metal crystals enhanced the adsorption rate for both CO₂ and N₂ but did not improve the selectivity between CO₂ and N₂.

Later in the mid-1990's, Burchell and Judkin (1996, 2001) proposed the development of carbon fibre composite molecular sieves. This work aimed at creating an adsorbent with a two tier structure; a strong macroporous shell allowing the free flow of gas through the adsorbent bed and a microporous inner where the CO₂ is selectively adsorbed. Thus far, their results indicate that the composite adsorbent may be an effective medium for CO₂ recovery in natural gas processing. However further investigations and process improvements are required. More recent work by Macario et al. (2005) involving the development for novel flue gas adsorbents produced adsorbents with high CO₂ working capacity (42 cm³/g) and good CO₂/N₂ selectivity (22). The development of these new adsorbents is still relatively immature with the best available adsorbents continuing to be commercially available products.

PSA processes development

Numerous modifications have been discussed in the literature to improve PSA processes. Specifically for CO₂ recovery, researchers have embarked upon discussions of improvements in process design. These consists of:

- 1) using three, four, or five beds;
- 2) including of a pressure equalisation step;

- 3) product purges;
- 4) pre-treating to remove strongly adsorbed components that might interfere with the separation; and/or
- 5) using extremely short cycle times to approach isothermal operation.

In 1993, Kikkinedes et al. (1993) was one of the first researchers who examined the feasibility of CO₂ recovery from flue gas, using activated carbon (AC) and carbon molecular sieves (CMS) as adsorbents. The results illustrated that a feed gas stream with a CO₂ concentration of 17% can produce an end product of 99% purity at a recovery rate of 68%. Later work by Korean researchers, Chue et al. (1995) found that for CO₂ flue gas recovery, 53% of the CO₂ could be recovered with a purity of 99% using zeolite 13X under vacuum conditions.

More recent PSA/VSA studies have focused on the optimisation and examination of non-traditional PSA processes. Using VSA configurations, Na et al. (2001, 2002) observed CO₂ recovery using activated carbon. The outcomes indicated that using a PSA process with 3-beds and 8-steps including pressure equalisation and product purge steps, a CO₂ recovery of 50% was obtained with a CO₂ purity of 90%. Choi et al. (2003) also investigated a similar PSA process using zeolite 13X, and found that CO₂ recovery and purity is enhanced to 78% and 85% respectively.

Chou and Chen (2003) reviewed the performance of VSA systems using a dual and three-bed process at various temperatures and pressure ratios. They showed that through using vacuum conditions for desorption, there was little performance benefit in increasing the feed pressure above 1.5 bar.

A two-stage process (cascade) was used by Cho et al. (2004) to recover CO₂ from flue gas using zeolite 13X. A recovery of 80% coupled with a purity of 99% was achieved. They also demonstrated that power requirements for pumping and compression was a strong function of CO₂ purity and the desorption pressure. Higher purity requirements and lower desorption pressure increased the total power consumption of the system. For

the two-stage process, power consumption ranged from 0.250 to 0.266 kWh/Nm³ of CO₂.

Another novel process referred to as fractionated vacuum swing adsorption (FVSA) was explored by Ko et al. (2004). In their research, they determined that FVSA could obtain higher CO₂ and N₂ purities than VSA systems but at lower CO₂ recovery rates. The energy requirement of FVSA systems is higher than that of the VSA system.

Further studies investigating hybrid configurations of PSA/VSA systems have been carried out. Pilot studies testing hybrid systems were undertaken by Xianshe et al. (1998) and Min and Moon (2000). They explored the use of a membrane to enrich the feed gas CO₂ followed by a PSA process. They observed that when the concentration of the CO₂ entering the adsorber is enriched due to the membrane step, the efficiency and purity of CO₂ is increased compared to traditional stand-alone systems.

Ishibashi et al. (1996) while exploring a combination of pressure swing and temperature swing adsorption (PTSA) found that they could achieve a CO₂ recovery of 90% and purity of 99%. However, the energy consumption of their configuration was high at 550-700 kWh per tonne of CO₂ recovered. Other Japanese researchers such as Uchida et al. (2002) have examined CO₂ recovery from flue gas by PSA followed by a super-cold separator. A CO₂ recovery of 90% with a purity of 99% was achieved compared to a purity of 50% for the PSA system alone.

To date, all of these studies have only been at the bench or pilot scale and no economic evaluations have been undertaken.

2.5 Low-temperature separation

Under certain temperature and pressure conditions, components of a gas mixture can exist in different phases. This phenomenon can be used to separate CO₂ from different source streams. Figure 2-5 shows the phase diagram of pure CO₂, where phase is a function of temperature and pressure.

In literature, two main methods have been proposed for CO₂ recovery under low temperature conditions. The first is cryogenic distillation of CO₂, where under the right temperature and pressure conditions, CO₂ can be separated as a liquefied product while other components in the feed stream remain in the gaseous phase. Cryogenic distillation systems are a low temperature physical approach in which CO₂ is separated directly by liquefaction or by using a solvent such as C₄-hydrocarbon (i.e. the Ryan-Holmes process). These systems are appropriate for gas streams with CO₂ levels above 40% by volume and high pressure, such as in the synthesis gas streams from IGCC power plants (Reiner et al., 1994). In addition, cryogenic distillation has been used extensively in several large scale enhanced oil recovery (EOR) operations to separate methane for sale and to purify the CO₂ for use in the EOR operations.

The second more novel method is refrigeration under pressure as proposed by Schussler and Kummel (1989). In this configuration, CO₂ is recovered at a lower temperature and pressure than in cryogenic distillation by using the reverse process of sublimation (changing from the gas phase directly to the solid phase).

From the phase diagram, it can be seen that both techniques will have their own appropriate applications. For feed gas streams with high partial pressure CO₂ (greater than 10 bar), cryogenic distillation would be most favourable, whereas for feed gas streams with lower CO₂ partial pressures (less than 10 bar), refrigeration under pressure would be better.

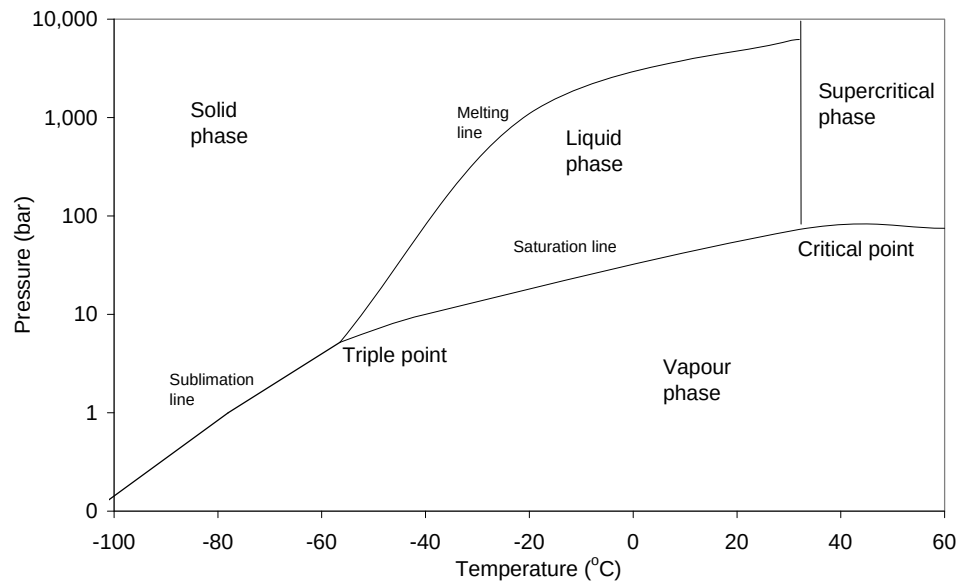


Figure 2-5 CO₂ phase diagram

2.5.1 Advantages and disadvantages of low temperature separation

The advantage of low temperature separation systems is that the CO₂ produced at the end of the separation step is a liquid. The CO₂ does not require any post-separation compression to make it ready for transport. The cost benefit is that the CO₂ stream can be pumped rather than compressed along the pipeline generating cost savings. In addition, the purity of the CO₂ stream is extremely high.

One of the main disadvantages of the cryogenic separation process is that traces of gases such as methane or water vapour have to be completely removed before separation. This is because methane has a high volatility relative to CO₂ and water solidifies at cryogenic temperatures or forms CO₂ hydrates. Most emissions of CO₂ considered for CCS are either from combustion processes (which produce water vapour) or is from natural gas processing (which contains methane). Therefore, it is necessary to pre-treat the feed gas streams before recovery. This may result in very high capital expenditure.

Schussler and Kummel (1989), and Hendriks (1994) examined the novel pressurised refrigeration system for CO₂ recovery from post-combustion flue gas. They respectively chose -100°C and -108°C as the temperature for their refrigeration systems. Such low temperatures were selected as the pressure of the system was set at a moderate value of

4.5 to 5 bar. The energy losses to the system were significant, with a typical power plant losing 32% of its original energy output.

An IEA GHG study (Intech, 1992) also investigated cryogenic distillation but only for streams with high CO₂ concentration such as in an IGCC or oxy-fuel combustion power plants. These studies concluded that implementing cryogenic systems in advanced power generation might be more beneficial than in pulverised coal power production.

The main drawback highlighted in these studies was that the energy requirement for low temperature systems is very high. As a consequence they are not competitive when compared to other CO₂ capture technologies. The energy requirements include:

- The power required to compress the inlet flue gas;
- The energy demand for the refrigeration plant; and
- Any energy required for drying the flue gases and for heating the flue gas before expansion.

Another disadvantage is that the equipment is much more elaborate as it is designed to withstand the extreme conditions necessary for proper function and is therefore expensive. Meisen and Shuai (1997) concluded that the phase behaviour of CO₂ is too complex and leads to the formation of solids which plug and limit the performance of the equipment. “In light of these limitations and the high cost of refrigeration, cryogenic processes can probably be used in special circumstances and as a adjunct to other processes”.

Process development

As a result of the reported intensive energy requirement, only a few researchers apart from those working in hybrid systems mentioned beforehand have pursued further development of low temperature CO₂ recovery systems for power generation flue gases. The majority of work has been instigated by Asian researchers such as Deng et al. (2004), Ogawa et al. (2004) and Zhang et al. (2003) who have looked at integrated evaporating liquefied natural gas (LNG) with new natural gas combined cycle (NGCC)

power plant designs. They have shown that by integrating the cooling energy of the LNG with the power plant, thermal efficiencies of 65% can be gained and CO₂ can easily be recovered in liquid form. In addition, there is a growing interest from commercial operators (Michel, 2005) engaged in research examining CO₂ recovery from natural gas streams using low temperature separation systems.

2.6 Novel CO₂ capture options

In addition to the four conventional CO₂ recovery processes discussed above, there are several novel technologies options that may bring about a step-change in CO₂ capture. These methods include CO₂-hydrate formation, electrochemical technology, chemical looping, novel membranes and solid sorbents impregnated with solvents. The biological fixation of CO₂ by algae has also been proposed (Stewart and Hessami, 2005).

Hydrate formation of CO₂ can be used to capture CO₂ from gas mixture by selectively trapping it in a cage of water molecules (Chatti et al., 2005, Kang et al., 2001). The US Department of Energy (DOE) is developing a high pressure process for carbon dioxide separation from IGCC processes (Tam et al., 2001). It focuses on the low temperature SIMTECHE process, where a shifted synthesis gas stream is combined with pre-cooled nucleated water in a CO₂ hydrate slurry reactor. The outlet mixture flows into a slurry separator where H₂ rich product gas is recovered, leaving behind a CO₂-hydrate slurry. Using heat, the CO₂-hydrates are melted and a CO₂ enriched stream is obtained for geological storage. One of the disadvantages of using hydrate formations for CO₂ capture is that it is limited to process streams with high pressures. Additionally, the temperature for formation is quite low (~0°C). If we consider using hydrate formation for CO₂ capture from sources such as pulverised coal power plant flue gases, a substantial amount of energy will be required for the feed gas compression and cooling.

Another novel method of CO₂ capture has been proposed by Walk et al. (1988) where a molten carbonate fuel cell is used to separate CO₂ from flue gases. In a closed electrical circuit, the molten carbonate fuel cell operates by reducing the CO₂ into carbonate ions. These carbonate ions can be transported across a membrane before oxidising the

carbonate ions back to CO₂. The advantage of electrochemical separation is that carbonate electrochemical cells are highly selective to CO₂ (close to 100%) and only a small amount of power is required to reduce and oxidise the CO₂. Unfortunately, there are some major disadvantages of these systems, namely that molten carbonate is highly corrosive and fabrication and handling of the system is complicated. Alternative solid sorbents have been proposed in place of molten carbonate membrane cells (Granite and O'Brien, 2005). In these systems, CO₂ is reduced under low pressure and oxidised under high pressure. Electrochemical separation of CO₂ is a relatively new process and shows promise.

Chemical looping has been described in detail by Ishida and Jin (1997) and Lyngfelt et al. (2001). The process uses a solid oxygen carrier (metal oxide) to bring O₂ from air to the fuel needed for combustion. The combustion process produces CO₂ and water, which can easily be separated. The key drivers of successful application of chemical-looping for CO₂ capture from fuel processing includes the capacity of metal oxide to transfer O₂ between reactors with realistic mass flow of solids and the robustness of the metal-oxide to be regenerated numerous times. Chemical looping is a promising and feasible option but further enhancement on metal oxides needs investigation.

Other novel CO₂ capture methods include enzyme-facilitated membranes, where an enzyme is used to selectively bind the CO₂ before transporting it across the membrane (Trachtenberg et al., 2004). Dry regenerable sorbents impregnated with amines have also been described by Gamborrata et al. (2001). This process is a hybrid of absorption and adsorption technology, where CO₂ is chemically absorbed onto a solid sorbent before is regenerated by increasing the temperature.

Novel CO₂ capture methods provide new opportunities to capture CO₂ without the need for excessive energy. However all of these technologies are still in the primary stages of development and cost data is not widely available or has yet to be determined.

2.7 Measuring the cost of CO₂ avoided

With the commencement of CO₂ emissions trading regimes in Europe in 2005, and proposed regimes for Australia and North America (Johnson and Heinen, 2004) to be established in the near future, a common economic indicator is required to translate and compare CO₂ emissions reduction schemes. One economic indicator that is widely used to characterise and compare alternative CO₂ mitigation options is the cost of CO₂ avoided (\$/tonne CO₂ avoided). The term \$/tonne CO₂ avoided provides CO₂ and greenhouse gas (GHG) emission point sources such as power plants, manufacturing plants and petrochemical facilities with a common accounting unit that can be applied and used for CO₂ trading at the international and national levels. It also provides a basis for assessing policy options.

For the purposes of CCS economics, the indicator of \$/tonne of CO₂ avoided or cost of CO₂ avoided is frequently used to describe the overall life cycle costs of CO₂ capture and storage options.

2.7.1 CO₂ avoided and CO₂ injected

The reduction of CO₂ emissions at any point source can be referred to as the amount of CO₂ avoided, which may in turn translate into carbon credits. The CO₂ avoided can be determined using the following equation:

$$\begin{aligned} \text{CO}_2 \text{ avoided} = & \text{net amount of CO}_2 \text{ emitted before applying mitigation option} \\ & - \text{net amount of CO}_2 \text{ emitted after applying mitigation option} \end{aligned} \quad (2.3)$$

For CCS technologies and sequestration schemes, the amount of CO₂ injected does not necessarily equate to the amount of CO₂ avoided. The CO₂ injected (or stored) represents the absolute quantity of CO₂ that is stored or injected into a geological reservoir ignoring any losses on injection or during subsequent storage over many thousands of years. The CO₂ avoided represents the net reduction of CO₂ emissions taking into account (Mollersten et al., 2003b):

- Total change in emissions from the stationary emission source;

- Any change in CO₂ emissions from an external power system corresponding to the change in net power exchange between the sources and the grid; and
- Changes in CO₂ emissions from external energy use corresponding to any fuel and/or heat generated from the CO₂ capture and storage process.

2.7.2 Energy penalty

The inclusion of a CO₂ capture and/or storage system into an existing process will consume energy. The additional energy required by CCS is defined as the energy penalty. The energy penalty as a percentage value can be defined as:

$$\text{energy penalty} = 1 - \frac{\eta_{CCS}}{\eta_{ref}} \quad (2.4)$$

Where

η = operating efficiency of the process or power plant

x = original output /consumption of energy of the reference process plant (MW)

y = output/consumption of energy of the same reference plant with CCS (MW)

The energy penalty can also commonly be described in the units MJ/tonne CO₂ captured:

$$\text{energy penalty (MJ/tonne)} = \frac{x - y}{n_{CO_2}} \quad (2.5)$$

where

n_{CO_2} = amount of CO₂ recovered in 1 second (tonne/s)

The percentage energy penalty is related to the amount of CO₂ avoided by:

$$\text{Energy penalty (\%)} = \frac{\text{CO}_2 \text{ captured (tonnes)} - \text{CO}_2 \text{ avoided (tonnes)}}{\text{Initial CO}_2 \text{ emissions (tonnes)}} \quad (2.6)$$

2.8 Reported costs of CO₂ capture

Many CCS economics studies have focused on electricity power generators, as they are one of the major sources of CO₂ emissions. Other studies have examined the economics

of CCS for industrial processes such as cement processing and steel production. The sections below review the reported cost of CO₂ capture for:

- Pulverised and advanced power plants; and
- Industrial processes.

In comparing the cost reported for CO₂ capture in the literature, it is important to note whether the reviewer had included any costs for transport and/or storage. David and Herzog (2000) included a value of \$US10/t CO₂ for transport and storage in their calculations in determining the overall mitigation cost, while others such as Audus (2000) have only examined the capture cost without accounting for any transport or storage. Dave et al. (2000) determined both the capture and storage costs for two storage options to give an overall mitigation cost. On the other hand, Simbeck (2001) included a revenue for CO₂ usage in EOR projects. To compare the cost of capture for the various studies, the cost for CO₂ storage needs to be omitted.

2.8.1 Capture costs for pulverised coal and advanced power plants

Table 2-2 summarises the values for CO₂ capture from various studies examining the cost to retrofit an existing coal-fired power plant as well as for the development of new plants with capture. The calculated cost is for pulverised coal-fired (PC) power plants fitted with post-combustion CO₂ capture. The technology options considered include chemical solvents (ABS), gas separation membranes (MEM), pressure swing adsorption (PSA) and low temperature separation (CRYO).

Table 2-2 CO₂ capture costs for power plants (not adjusted to a common year)

Study and cost year	Power plant	Capture technology	Energy penalty (%)	Δ CO ₂ emissions (kg/kWh)	Capture cost (US\$/t CO ₂ avoided)
Gibbins et al. (2004b) 2000	Existing PC	ABS (MEA)	21	0.625	30
Roberts et al. (2004) 2003	Existing PC	ABS (KS1)	20	0.655	31
Singh et al. (2003) 2001	Existing PC	ABS (MEA)	35	0.650	55
Dave et al. (2000) 2000	Existing PC	ABS (MEA)	28	0.750	42 (A\$62)*
Rao and Rubin (2002) 1999	Existing PC	ABS (MEA)	41	0.830	59 – 67
Simbeck (2001) 2000	Existing PC	ABS (MEA)	30	0.870	45
Leci (1996) --	Existing PC	ABS (MEA)	28	0.775	35
Booras and Smelser (1991) 1990	Existing PC	ABS (MEA)	35	0.765	35
Rubin et al. (2004) 2002	New PC	ABS (MEA)	27	0.680	47
Parsons (2002) --	New PC	ABS (MEA)	27-29	0.860	42 – 51
Stork (1999) 1999	New PC	ABS (MEA)	28	0.574	45
Hendriks (1994) 1990	New PC	ABS (MEA)	23	0.700	34
Audus (2000) --	New PC	ABS (MEA)	33	0.574	47
Herzog (1997) --	New PC	ABS (MEA)	32-37	-	39 – 45*
Hendriks (1994) 1990	New PC	MEM		0.700	54 – 68
Feron (1992) 1992	New PC	MEM	31	0.607	45
Van der Sluijs (1992) 1990	New PC	MEM			50 – 75
Monenco (1992) 1992	Existing PC	PSA	40	0.758	64**
Hendriks (1994) 1990	New PC	CRYO	27	0.700	34
Brockmeier (1994) --	New PC	CRYO			61
IEA GHG (Reiner et al., 1994)	IGCC	Selexol	14		23
Leci (1996) --	IGCC	ABS (MEA)	32	0.768	82
Stork (1999) 1999	IGCC	Selexol	17	0.576	37
Audus (2000) --	IGCC	Selexol	17	0.576	37
Dave et al. (2000) 2000	IGCC	ABS (MEA)	30	0.635	46 (A\$71)*
David and Herzog (2000) --	IGCC	Selexol	15	0.664	26
Simbeck (2001) 1999	IGCC	Selexol	16		25
Nsakala et al. (2001) --	IGCC	Selexol	--	--	23
Rubin et al. (2004)	IGCC	Selexol	14	0.720	22
IEA GHG (Reiner et al., 1994)	NGCC	ABS (MEA)	19		55
Stork (1999) 1999	NGCC	ABS (MEA)	16	0.309	35
Simbeck (2001) 2000	NGCC	ABS (MEA)	--	--	33
Freund & Thambimuthu (1999)	NGCC	ABS (MEA)	19		50 – 55***
Audus (2000) --	NGCC	ABS (MEA)	16	0.309	29
David & Herzog (2000) --	NGCC	ABS (MEA)	13	0.326	49
Rubin et al. (2004) 2002	NGCC	ABS (MEA)	17	0.324	50
CO ₂ Capture Project 2004	NGCC	ABS	--	--	62
CO ₂ Capture Project 2004	Gas fired power plant	ABS	--	--	88

*These reported costs include \$10-15/tonne CO₂ avoided for storage costs

**This number was re-calculated after examining the original IEA GHG report where calculation errors had produced the reported value of US \$97/tonne CO₂ avoided.

***CO₂ was recovered from post-combustion flue gas rather than synthesis gas

The studies show that for power plants using chemical absorption technologies (ABS), mostly with MEA solvent, the costs for capture range from US\$30 to US\$67 per tonne CO₂ avoided. The reported energy penalties also varied from 20% to 40% of the original power output. As discussed in section 2.2.2, the large energy penalty reflects the energy required for regeneration of the solvent. For adsorption (PSA) and membrane gas separation (MEM) systems, higher energy penalties of 30% to 40% have been reported compared to chemical absorption systems. The higher energy loss in the PSA and gas separation membrane systems is mainly because more power is needed to compress the inlet flue gas.

Numerous studies have evaluated the cost of capturing CO₂ from advanced power generation systems such as integrated coal-gasification combined cycle (IGCC) and natural gas-fired combined cycle (NGCC) power plants. These new power generation methods present an opportunity to develop power plants with increased efficiency, and lower emissions of CO₂ and toxic gases such as SO_x and NO_x. Implementation of CCS could also easily be incorporated in the process layout as new IGCC or NGCC power plants are being constructed.

For IGCC evaluations, capture of CO₂ from the post-combustion flue gas as well as recovery from synthesis gas has been studied. Because IGCC has not been widely used for power generation, most studies have been hypothetical and based on experience with gasification in petrochemical and petroleum refining (DOE, 2005).

Table 2-2 reports the capture cost for IGCC and NGCC power plants. It is assumed in all these studies that the reference was the same plant without CO₂ capture. For IGCC power plants, using physical absorption such as Selexol to capture the CO₂ from synthesis gas results in capture cost ranging from US\$22 to US\$37 per tonne CO₂ avoided. If the CO₂ is captured from a post-combustion flue gas using amine chemical absorption, the cost can be significantly higher at US\$80 (Leci, 1996) or US\$46 per tonne CO₂ avoided (Dave et al., 2000). The energy penalty for capturing CO₂ from flue gas is also higher than if the CO₂ is captured as part of the synthesis gas. The energy

penalty for flue gas recovery is approximately 30%, while synthesis gas recovery is in the mid-teens.

The reported cost for NGCC power plants using amine (MEA) chemical absorption range from US\$35 to US\$62 per tonne CO₂ avoided. The variable and higher capture cost for NGCC plants compared to IGCC or PC flue gas is a result of the assumption surrounding the higher the price of natural gas. The price of natural gas as a fuel source is typically much higher than the price of coal by at least three to five times. As a result, the operating cost and capture cost is significantly higher. However, one of the benefits of capturing CO₂ from a NGCC power plant is that the energy penalty for these systems is generally lower at 13% to 20% compared to other recovery systems such as those attached to pulverised coal power plants.

The wide range of costs reported for CO₂ capture in Table 2-2 reflects a range of factors. Different studies calculated costs in real terms at different points in time. There were varying assumptions in respect of storage cost, whether SO_x and NO_x separation units and post-separation compression of CO₂ were included. In addition, there were differences in processing and economic assumptions such as the plant operating capacity, the discount rate, fuel costs, flue gas compositions and the amount of CO₂ recovered from the flue gas. Further discussions on the impact of cost caused by variations in assumptions for the reference plant and uncertainties in costing will be presented in Chapter 9.

2.8.2 Capture costs for industrial sources

CO₂ can be captured from industrial processes. Those with the greatest potential to implement CCS are the large stationary emitters including oil and petrochemical refineries, iron and steel producers, ammonia producers, wood pulp/paper mills, cement manufacturers and natural gas processing plants. Table 2-3 shows the reported capture cost for petrochemical, iron and steel production, ammonia production and wood pulp/paper mills facilities.

Because the recovery and capture of CO₂ is an inherent part of natural gas processing plants, no economic studies have been published showing the economic feasibility and compatibility of incorporating CCS.

Cement plants are the largest industrial source of CO₂ other than power plants. The cement plant is a complex processing facility where sources of CO₂ emissions can come from multiple streams with different compositions. Hassan (2005) reports a cost of US\$49 to US\$54 per tonne of CO₂ captured for capturing CO₂ from a cement facility. In this evaluation, CO₂ is captured using amine chemical absorption from the cement kiln furnace flue gas. No cost of avoidance was reported.

Several economic evaluations for CO₂ capture from steel processing plants have been reported. The IEA GHG report into steel processing (IEA-GHG, 2000b) (based on the study by Farla et al. (1995), and Gielen (2003) investigate the cost of capturing CO₂ from blast furnace flue gas using amine chemical and physical absorption. The capture cost ranges from US\$19 to US\$35 per tonne CO₂ avoided. The lower cost is reported by Gielen (2003) who examines the possibility of retrofitting the steel process to incorporate a shift reactor following the blast furnace. Geilen (2003) also examines the cost of recovering CO₂ from advanced processes such as Corex or direct reduction iron (DRI). The capture cost of DRI can be as low as US\$10/tonne CO₂ avoided.

Based on Table 2-3, the capture cost for oil refineries and petrochemical plants range from US\$27 to US\$78 per tonne CO₂ avoided. The CO₂ is recovered from gas fired process heaters using amine chemical absorption. The highest cost has been reported by the recent CO₂ capture project capturing CO₂ from the boiler heats of the Grangemouth refinery, UK. This is the estimated cost for the baseline technology, however, it is expected with technology improvement, the capture cost can fall to US\$48 per tonne CO₂ avoided.

The capture cost for industrial processes, such as CO₂ recovery from ammonia production, is approximated at US\$8/tonne CO₂ avoided. This low cost, estimated by Farla et al. (1995), is a result of the fact that CO₂ is separated within the ammonia

production process. The cost for CCS included capital and operational expenditure for CO₂ treatment after separation and CO₂ compression, but did not include any costs for the separation facility.

Möllersten (2002) estimated that the cost of capturing CO₂ from black liquor produced in pulp and paper mills at US\$34/tonne CO₂ avoided using conventional amine chemical absorption. The use of a biomass gasifier enables further reductions in the cost to US\$25/tonne CO₂ avoided (Möllersten et al., 2004).

Table 2-3 CO₂ capture costs for industrial installations (not adjusted to a common year)

Study and cost year	Industrial plant	Capture technology	Capture cost for equivalent output (US\$/t CO ₂ avoided)
Farla (1995) 1990	Iron production	ABS (MDEA)	35
Gielen (2003) 2001	Iron production	Gasification (Selexol)	10-19
Farla et al. (1995) 1990	Ammonia synthesis	ABS (MEA)	8
Farla et al. (1995) 1990	Petrochemical	ABS (MEA)	46
Slater et al. (2002) 2001	Petrochemical	ABS (MEA)	33
IEA GHG (2000a) 1999	Petrochemical	ABS (MEA)	27
Möllersten (2002) --	Pulp/paper mill	ABS (MEA)	34
CO ₂ Capture Project 2004	Petrochemical	ABS	78 (reduced to 48)
Möllersten et al (2004) --	Pulp/paper mill	Gasification (Selexol)	25
Hassan (2005) 2005	Cement	ABS (MEA)	49-54 per tonne captured
CO ₂ Capture Project 2004	Coke gasification	ABS	15

2.9 Conclusion: Understanding the cost of CO₂ development

In this chapter, promising technologies for large scale CO₂ capture from industrial point sources have been reviewed. The key technologies for separation including absorption, membrane separation, physical adsorption and low temperature separation have been shown to possess both advantages and disadvantages. Development work has been undertaken by numerous researchers to address the disadvantages and improve the competitiveness of each technology.

A review of the costs for capturing CO₂ shows that the cost ranges from US\$8 to US\$75 per tonne CO₂ avoided, with an average of US\$40/tonne CO₂ avoided. The majority of the reported costs are for capturing CO₂ using commercial chemical or physical

absorption technology. Only six of the 46 reviewed studies considered adsorption (one), membrane separation (three) or low temperature separation (two) for CO₂ capture.

Given the rapid state and quantity of technology improvements such as VSA or the development of new adsorbents and membranes, the capture costs for these emerging technologies could be different to those reported in the literature. Additionally, much of the work in technology improvement has been in isolation. An evaluation of capture costs due to technology improvement is required. It is important that the suitability of each technology for different industrial applications also be assessed. By doing so, new opportunities for cost reductions could be highlighted, and insight into the areas that require further research and development work can be gained.

In addition, only one study by Dave et al. (2000) reported the capture costs for an Australia emission source. To understand the economic feasibility of implementing CCS technology for Australian industries, it is important to evaluate the costs based on Australian conditions.

Chapter 3. TECHNO-ECONOMIC MODEL DEVELOPMENT

3.1 Overview

This chapter outlines the equations and procedure used in developing the techno-economic model. It includes the equations for calculating mass and energy balances of the CO₂ capture process. The outputs from the process calculations are used in determining the total capital and operating costs of the system, and thus the total CO₂ capture cost. This chapter details the parameters that are important in calculating the performance of CO₂ capture process and the parameters used in estimating costs.

3.2 Defining the system boundary

In this study, the CO₂ capture system is defined as all the unit operations that make up the CO₂ capture facility, plus all the unit operations post-separation that are required for compression before transport and injection. The boundary for the capture system includes the CO₂ emission source, the CO₂ capture facility and any energy source that is required to power this capture system.

This definition is the same as that used in most of the literature on the economics of CO₂ capture.

3.3 Process model

The processing component of the techno-economic model incorporates models for the four CO₂ capture options of absorption (chemical and physical), pressure swing adsorption (PSA), gas separation membranes and low temperature separation.

The range of CO₂ sources incorporated into the model include post-combustion flue gas from pulverised coal and natural gas-fired combined cycle (NGCC) power plants, and

synthesis gas from integrated combined cycle (IGCC) power generation. Additionally, the model includes processing or waste gas from natural gas processing, hydrogen production, iron and steel production, cement manufacture and oil refineries.

In constructing the process model, the CO₂ separation and capture unit is treated as being separate from the rest of the CCS process. Mass and energy balances for the individual unit operations within the CO₂ separation module are established using general energy balances, mass equations, and “rule of thumb” equations. The model estimates key flowrates and energy requirements.

The outputs from the model are intended for pre-feasibility analysis and evaluation of CO₂ capture technologies, thus short-cut methods and correlations are used to approximate design and equipment sizing/costing. The model may be used as a basis for more detailed engineering studies.

The process model can be viewed as a series of unit operations including a pre-separation cooler, pre-separation compressor/blower, the CO₂ separation unit, and post-separation processing such as compression, expansion and cooling. Figure 3-1 highlights some of the key unit operations. The exact process layout varies for different CO₂ capture technologies, as well as for different CO₂ emissions sources.

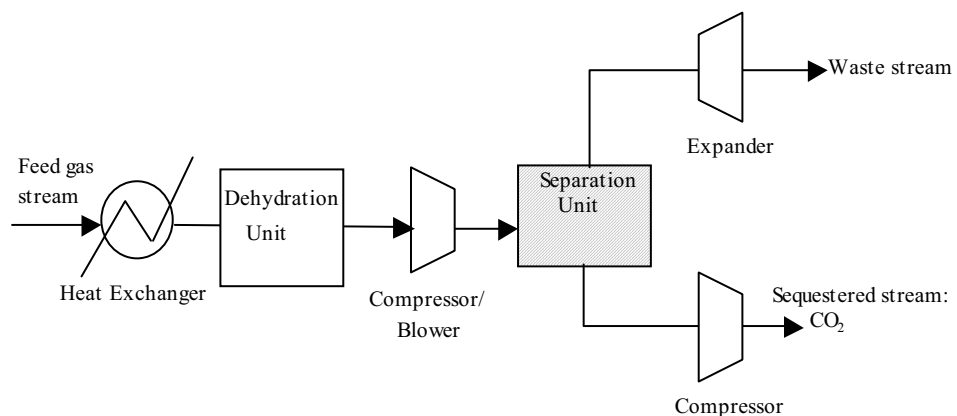


Figure 3-1 Typical layout of post-processing CO₂ capture

3.3.1 Configuring the process model

The process model is constructed to allow a user to configure the CO₂ capture system. Some of the key processing decisions that the user is required to make include:

Selection of CO₂ emission source: The process model includes default compositions and processing parameters such as operating pressure and temperature for common CO₂ emission sources. These default values are based on the reference conditions established for the CO₂CRC. The user can also define the feed gas composition and operating parameters for case specific studies.

Selection of the source of energy to power the CO₂ capture system: Energy is required to power the CO₂ capture system. The user can select the type of power and whether or not it is provided internally or externally from the industrial process. The power sources available in the model include pulverised coal power plants (black and brown), IGCC and NGCC.

The CO₂ capture technology option: The CO₂ capture technology options available include chemical and physical absorption, pressure swing adsorption (PSA), gas separation membranes and low temperature separation. For each capture option, specific decisions such as the operating pressure and temperature of the separation unit, process layout and choice of solvents/adsorbents/membranes can also be made.

CO₂ capture recovery efficiency: This is the fraction of CO₂ removed from the incoming feed gas. Most studies report the value of CO₂ capture or removal efficiency in the range 80% to 90%. The nominal value used in this thesis is 90% to be consistent with other studies, but the user can specify any value in operating the model.

3.3.2 Process equations

The process equations define the functional relationships. For each CO₂ capture technology option, the mathematical models employed are selected to enable process modelling of a wide range of different feed gases and processing parameters, and ease of computational processing. Equations for each of the capture technology options are discussed in detail in subsequent chapters.

Detailed below are the equations used in calculating mass and energy balances for the general process equipment common to all separation options. The exact processing conditions of the feed gas and the technology selected will determine which general ancillary equipment will be included.

Heat exchanger

The inlet feed gas is generally received at high temperatures, which is typical of post-combustion flue gases. This gas requires cooling before CO₂ is removed in the separation unit. This is especially true for absorption processes where solvents degrade at temperatures greater than 50°C (Dave et al., 2000). Feed gas cooling is also required for polymeric gas separation membranes where high temperatures may lead to plasticisation. For pressure swing adsorption (PSA) systems, low temperatures promote better adsorption onto the solid sorbent.

The heat exchanger sizes and mass and energy balances are determined by general heat transfer equations (Coulson and Richardson, 1954):

$$A_{\text{Heat exchanger}} = \frac{Q_{\text{Heat exchanger}}}{U \cdot \Delta T_{\text{lm}}} \quad (3.1)$$

In this model, it is assumed that cooling is achieved using cooling water. The condition for the cooling water is taken to be 25°C, with a maximum increase of 10°C (Coulson and Richardson, 1954).

Compressor: feed gas and enriched CO₂ product

For feed gases with low pressure (near or below atmospheric pressure), compression is generally required for separation processes such as gas separation membranes and pressure swing adsorption. For processes where the operating pressure is between 1.2 to 2 bars, this pressure increase can be achieved using gas blowers (Equation 3.2). For processes where the feed pressure needs to be elevated above 2 bar, compression of the feed gas is required (Equation 3.3).

Once the CO₂ is successfully separated from the feed gas, it then requires compression for transport and storage. The location of the storage facility and distance from the source will determine the pressure to which the CO₂ must be compressed. For this study, CO₂ is compressed to a minimum of 100 bar before being sent to the transport pipeline.

For processes where a stream of high purity CO₂ is not produced for transport, it is assumed that other component gases such as N₂ and O₂ can be separated from the CO₂ via vapour liquid separation. This is achieved using compression and cooling of the product gas to remove (or reject) the gaseous components and any CO₂ vapour. At 100 bar, the solubility of gases such as N₂ and O₂ is very low, and thus the purity CO₂ obtained for transport is high (Hendriks, 1994).

The power consumed for the feed gas blower can be estimated by the following equation as described in Chapel et al. (1999):

$$W_{\text{blower}} = \left(0.4 + \frac{16.4}{y_{\text{CO}_2 \text{ feed}}} \right) \times F_{\text{CO}_2} \quad (3.2)$$

The number of stages and power consumption for the compression process is calculated using general chemical engineering equations (Winnick, 1997). The power consumed by the compressors is calculated as:

$$W_{\text{compressor}} = P_{\text{In}} \times F_i \times \frac{r}{r-1} \times \left[\left(\frac{P_{\text{Out}}}{P_{\text{In}}} \right)^{\left(\frac{r-1}{r} \right)} - 1 \right] \quad (3.3)$$

In this model, the isentropic efficiency of the compressor is taken to be 75% to 85%. It is assumed that the compressor is adiabatic and the gas is ideal. Heat losses in the motor are neglected.

Depending on the pressure ratio between the feed gas and the outlet pressure, the number of compression stages is determined as:

$$\text{Number of compression stages} = \frac{\log\left(\frac{P_{\text{Out}}}{P_{\text{In}}}\right)}{\log(3)} \quad (3.4)$$

The inlet temperature (T_{in}) into each stage is assumed to be 30°C. The compressor calculations include the heat duty of the inter-coolers between each stage of compression. The outlet temperature (T_{out}) from the compressor at the i th stage is determined as:

$$T_{\text{out } i} = T_{\text{in}} \left(\frac{P(\text{out})_{i+1}}{P(\text{in})_i} \right)^{\frac{r-1}{r}} \quad (3.5)$$

The heat duty and cooling water flow-rate for inter-stage cooling heat exchangers is determined using equation 3.1.

Expansion of lean exiting gas

In separation processes that occur at high pressure, the lean exiting gas stream which is available at high pressure may be expanded prior to venting or the expanded gas may be used for cooling the feed gas stream or intercooling in the compressors.

The total energy from expansion is expressed as (Winnick, 1997):

$$W_{\text{Expansion}} = P_{\text{In}} \times F_i \times \frac{r}{r-1} \times \left[\left(\frac{P_{\text{Out}}}{P_{\text{In}}} \right)^{\left(\frac{r-1}{r} \right)} - 1 \right] \quad (3.6)$$

The number of stages and outlet temperature from each expansion stage is calculated based on simple Chemical Engineering equations and is the same as those for compression as represented in Equations 3.3 and 3.4.

In some analyses, such as those by Hendriks (1994) and van der Sluijs et al. (1992), the energy from gas expansion is used to produce electricity or used to drive the compressor turbines. Any power obtained by gas expansion offsets the power consumption of the feed gas compressor. However, discussions with an industrial compressor vendor (Siemens, 2004) indicate that joint expansion and compression units managing feed gas with flowrates typical of post-combustion flue gases are still in the research and development stage. For the purposes of this research, it is assumed that only a proportion of the energy from the expanders is transformed into usable electrical energy. The isentropic efficiency is assumed to be 85%, with an electric generator efficiency of 98%.

Dehydration systems

Separating gases using membranes, PSA or low temperature systems generally requires that the feed gas be dehydrated. In developing the process model, it is assumed that the majority of any water content in the feed gas is condensed in the first heat exchanger, and liquid water is removed using a knockout drum. The feed gas entering any pre-capture compressor or separation unit is treated in a glycol dehydration unit for feed gases with pressures above 5 bar. For feed gases at or near atmospheric pressure, the feed gas is dried in a molecular sieve before the entering the compressor or separation unit.

For feed gas at high pressure, based on calculations in the Engineering Data Handbook by the Gas Processors Suppliers Association (GPSA, 2004), the water vapour is assumed to be absorbed in an solvent absorption system using a physical solvent, which in this case is 99% weightt glycol dehydration (TEG). It is assumed that the solution has a circulation rate of 25 LTEG/kg of water absorbed. The dehydration duty for the glycol unit is estimated as:

$$Q_{\text{Dehydration}} = Q_{\text{reb_TEG}} = 400 \times F_f \quad (3.7)$$

For feed gas with low pressure, the feed gas is dehydrated by passing it through a tower filled with molecular sieves. When the molecular sieves are saturated with water, the

adsorbent is regenerated. This is achieved by passing hot air through the column. For the drying process, the energy required for this system corresponds to the energy needed for vaporisation of water. According to Hendriks (1994), during drying, approximately 26 g of water per m³ of flue gas is separated. The heat of desorption is negligible compared to the heat of vaporisation (Kohl and Riesenfeld, 1985), and thus will be neglected. Taking into account heat losses, which may be assumed to account for 20-40% of the total energy loss, the energy and corresponding power loss for dehydration can be calculated as follows (Hendriks, 1994):

$$Q_{\text{Dehydration}} = Q_{\text{Molecular sieves}} = \frac{0.026 \times F_f \times Q_{\text{vap_H2O}}}{0.7} \quad (3.8)$$

$$W_{\text{Dehydration}} = Q_{\text{Dehydration}} * \left(\frac{H_{\text{LP}} - H_{\text{Condenser}}}{H_{\text{LP}} - H_{\text{Reboiler}}} \right) \quad (3.9)$$

3.3.3 Model outputs

The outputs parameters from the model include:

1. The total energy required to operate the CO₂ capture system, as this describes the energy penalty incurred;
2. The size of the separation equipment, such as the membrane area required, number of absorbers and number of adsorbers; and
3. CO₂ purity.

Parameters such as the equipment size and energy requirement are used to determine the capital and operating costs of the CO₂ capture system. In addition, the output parameters are used to evaluate the overall effectiveness of the system in recovering and capturing CO₂ from stationary emission sources.

3.4 Cost model

The cost model is a scoping model developed to assist researchers and businesses in evaluating the economic feasibility of a CO₂ capture technologies. The outputs from

the process model are linked directly to the cost model. The economics can be used to evaluate the viability of the various CO₂ capture options, as well as evaluating the economics of CO₂ capture from different industrial emissions.

The cost model is designed to estimate the initial up front capital cost of a CO₂ capture system as well as its ongoing operating expenses including capital replacement.

3.4.1 Configuring the cost model

The cost model is constructed to allow the user to define key economic variables that would reflect the economic conditions of interest. It includes default conditions that reflect Australian conditions and are based on the reference values established for the Australian CO₂CRC. However, these economic parameters can be varied to suit specific case studies. The following summarises some of the variables that may be varied:

Cost year: This represents the year for which costs are estimated.

Currency: The two currencies that are available include Australian (A\$) and US (US\$). The choice of currency determines how the capital costing for the economic analysis is calculated.

Discount rate: The discount rate is used to determine the present value of future cash flows from a project. The reference value for the discount rate is 7% real based on 2005/2006 Australian economic conditions as typically used in the private sector.

Project life and number of years for construction: The project life represents the number of years that the CO₂ capture plant is expected to operate. By default, 25 years is assumed. The number of years for construction is the expected timeframe required for building the infrastructure. By default, 2 years is assumed.

Plant capacity factor or operating factor: The plant capacity factor represents the portion of a year that the CO₂ capture plant is expected to operate expressed as a percentage. It is less than 100% to account for the time lost to carry out required

maintenance (shut-down) and unforeseen stoppages. The nominal value is taken to be 85%.

Reference point and size: The reference point is selected to determine the incremental cost of CO₂ avoided. The reference point could be the same plant without CO₂ capture, or it could be another industrial facility.

Energy supply and cost: The energy used to power the capture plant can be provided in a number of ways. It may be parasitically extracted from the same process plant where the CO₂ is being captured or it could be from an external energy source. The user defines this option. If an external energy source used, then the cost for energy needs to be specified by the user. Defaults for the cost of electricity from PC, NGCC and IGCC plants are based on averages for the Australian National Electricity Market (NEMMCO, 2005).

3.4.2 Cost outputs and equations

The parameters used to evaluate the economic feasibility of the capture system include:

1. Amount of CO₂ avoided;
2. Cost of CO₂ avoided;
3. Total capital cost or expenditure; and
4. Total annual operating cost.

If the analysis is for a power generator such as a pulverised coal (PC), integrated combined cycle (IGCC) or natural gas-fired combined cycle (NGCC), then the incremental cost for electricity is also determined.

The methods for calculating each of these parameters are set out below.

Amount and cost of CO₂ avoided

The costs of CCS are the additional costs associated with adding a CO₂ capture facility to an industrial plant. The amount of CO₂ avoided represents the net CO₂ reduction taking into account energy consumption losses. This is described in detail in section 2.7.

The cost of CCS per tonne avoided is the carbon credit per tonne avoided that would be required as income to match the present value of the CCS project's capital and operating costs. These costs consist of:

- Capital expenditure (Capex);
- Operating expenditure spent each year during the life of the project (Opex); and
- Taxes payable during life of the project (Taxes).

The levelised cost per tonne avoided is defined as:

$$\$/\text{tonne CO}_2 = \frac{\sum_{i=1}^k \frac{\text{Capex}_i}{(1+d)^i} + \sum_{i=k}^n \frac{\text{Opex}_i + \text{Taxes}_i}{(1+d)^i}}{\sum_{i=k}^n \frac{(\text{CO}_2 \text{ avoided})_i}{(1+d)^i}} \quad (3.10)$$

As discussed by Allinson and Nguyen (Allinson and Nguyen, 2000), this formulation has many advantages in determining the cost per tonne avoided. These include the ability for capital expenditure to be incurred at any time throughout the project life. Similarly, operating costs and production do not have to be assumed to be constant throughout the project life and taxes can easily be incorporated. The amount of CO₂ avoided for the analysis can also vary throughout the project life. The formulation permits the analysis of projects with variable recovery rates of CO₂.

Total capital cost

The total capital cost is the sum of all direct equipment plus any indirect costs for facilities and processing. The total capital cost is:

$$\text{Total Capital Cost} = \text{Total Installed Cost} + \text{Set-up Cost} \quad (3.11)$$

The total installed cost (TIC) is the sum of all process area equipment and a general facilities cost accounting for unspecified equipment. The TIC also includes the costs of installation, piping and electrical wiring.

The Set up Cost includes contingencies, engineering fees, owner's fees or royalties and a start up cost. The breakdown of the capital cost is based on standard Chemical Engineering procedures as outlined in Peters and Timmerhaus (1980). Table 4.2 shows the capital cost model parameters and nominal values used in this research.

Table 3-1 Capital cost model parameter and nominal values

	Capital cost elements	
A	Process Equipment Cost (PEC)	Sum of all process equipment
B	General facilities	10-20% PEC
	Total Equipment Cost (TEC)	A+B
C	Instrumentation	10%TEC
D	Piping	10% TEC
E	Electrical	5 % TEC
F	Total Installed Cost (TIC)	A + B+ C+ D +E
G	Start-up costs	1% TIC
H	Engineering	5% TIC
I	Royalties/owners costs	Case by case scenario
J	Engineering, procurement, construction and owner's cost (EPCO)	F + G + H + I
K	Project Contingency	10% EPCO
L	Land costs	Case by case scenario
	TOTAL CAPITAL COST	= J + K + L

It is assumed in this thesis that capital cost is equity funded and therefore no interest payments have been incorporated. The opportunity cost of this equity is taken into account through the use of a 7% real discount rate.

Total Equipment Cost (TEC) and Total Installed Cost (TIC)

The equipment cost is estimated for each of the key component processes calculated in the performance model. The costs are estimated based on correlations reported in literature and through personal communications with industrial vendors.

The unit cost represents the bare cost of an equipment item without installation, piping or electrical components. The unit cost for different equipment items reported in

different literature sources will vary, firstly because of the differences in the size of the equipment estimated, and secondly because the equipment prices apply to different years. Scaling and multiplying factors are used to normalise the unit costs in the literature. To account the different equipment sizes, an equipment scaling factor with an exponent of 0.7 is used (Peters and Timmerhaus, 1980). To account for different equipment pricing years, the Chemical Engineering Plant Cost Index (CEPCI) located in the rear of the Journal of Chemical Engineering is used (CE, 2005).

The normalised cost for an item of equipment is:

$$C_i = C_{\text{ref}} \times \left(\frac{F_i}{F_{\text{ref}}} \right)^{0.7} \times \left(\frac{\text{CEPCI}_i}{\text{CEPCI}_{\text{ref}}} \right) \quad (3.12)$$

The normalised unit cost for key equipment items estimated in this thesis is shown in Table 3-2. The cost of ancillary equipment such as storage tanks, spare pumps, valves and the control system are estimated as part of “general equipment facilities” (B of Table 3-1). The calculated quantities such as number of trains and membrane area are described in the sections related to each specific capture processes.

Table 3-2 Equipment capital costing

Cost item	Equation and comments
Heat exchangers (PGE, 2005, Simbeck, 2001)	$C_{\text{Heat Exchanger}} = Q_{\text{Heat Exchanger}} \times k_{\text{Heat Exchanger}}$
Compressors (PGE, 2005, Simbeck, 2001)	$C_{\text{Compressors}} = W_{\text{Total compression}} \times k_{\text{Compressors}}$
Expanders (PGE, 2005, Simbeck, 2001)	$C_{\text{Expanders}} = W_{\text{Total Expansion}} \times k_{\text{Expanders}}$
De-sulphurisation unit (PGE, 2005, Simbeck, 2001)	$C_{\text{FGD}} = k_{\text{FGD}} \times F_f$
CO ₂ drying unit (PGE, 2005, Simbeck, 2001)	$C_{\text{CO}_2 \text{ Drying}} = k_{\text{Drying}} \times F_{\text{CO}_2}$
Absorber and regeneration system (PGE, 2005, Simbeck, 2001)	$C_{\text{Absorber}} = k_{\text{Absorber}} \times N_{\text{Absorber trains}}$ $C_{\text{Regenerator}} = k_{\text{Regen}} \times F_{\text{CO}_2}$ $C_{\text{ABS}} = C_{\text{Absorber}} + C_{\text{Regenerator}}$
PSA system (Smith and Westerberg, 1991)	$C_{\text{Adsorber Shell}} = P^{0.584} (4.93dl + 3.74d^2 + 739)$ $C_{\text{Adsorbent}} = k_{\text{Adsorbent}} \times W_{\text{Ads}} \times N_{\text{Adsorber Trains}}$ $C_{\text{Vacuum pump}} = k_{\text{Vacuum pump}} \times N_{\text{Adsorber Trains}}$

	$C_{PSA} = C_{Adsorbent} + C_{Adsorber\ Shell} + C_{Vacuum\ pump}$
Gas separation membrane system (van der Sluis et al., 1992)	$C_{Membrane\ material} = k_{Membrane} \times A_{Membrane}$ $C_{Membrane\ Housing} = \left(\frac{A_{Membrane}}{2000} \right)^{0.7} \times 250,000$ $C_{Membrane} = C_{Membrane\ Housing} + C_{Membrane\ Material}$
Low temperature separation (Hendriks, 1994)	$C_{Refrigeration} = P_{Refrigeration} \times k_{Refrigeration}$ $C_{Liquefaction} = k_{Liquefaction} \times F_{CO_2}$

Operational and maintenance cost

The operational and maintenance (O&M) cost of any processing system can be separated into two components:

1. Fixed operational and maintenance (FOM) cost
2. Variable operational and maintenance (VOM) cost

Table 3-3 Operating cost equations

Fixed operational and maintenance cost	
The fixed operational and maintenance (FOM) cost comprises of labour, non-income government taxes that may be payable and general insurance cost ($C_{Insurance}$).	
$FOM = 4\% \times \text{Total Capital Cost} + C_{Insurance}$ $C_{Insurance} = 2\% \times \text{Total Capital Cost}$	
Variable operational and maintenance cost	
The variable operational and maintenance (VOM) cost incorporates cost for energy, utilities, replacement cost of equipment, and chemicals and waste disposal.	
$VOM = C_{Cooling} + C_{Energy} + C_{Replacement} + C_{HPL}$	
Cooling	$C_{Cooling} = k_{Cooling} \times F_{Cooling\ water}$
Energy usage (purchased)	$C_{Energy} = k_{Energy} \times P_{Total} \times \text{operating hours}$
Chemicals replacement for chemical absorption system (Chapel et al., 1999)	$C_{Replacement} = C_{Solvent} + C_{Caustic} + C_{Activated\ Carbon} + C_{Waste}$ $C_{Solvent} = k_{Solvent} \times F_{Solvent\ consumed}$ $C_{Caustic} = k_{Caustic} \times F_{soda\ ash}$ $C_{Activated\ Carbon} = k_{Activated\ Carbon} \times F_{Activated\ Carbon}$ $C_{Waste} = 0.03 C_{Solvent}$
Membrane and PSA systems replacement	$C_{Replacement} = \frac{C_{Membrane}/C_{Adsorbent}}{\text{Number of years for replacement}}$

Low temperature system replacement cost (Intech, 1992)	$C_{\text{Cryo replacement}} = 4\% \times \text{Total Capital Cost}$
VOM for natural gas processing (Hao et al., 2002)	$C_{\text{LHP}} = F_{\text{LHP}} \times \text{Carbon intensity} \times k_{\text{Natural Gas}}$ If the analysis is for natural gas processing systems, the variable operational and maintenance includes the cost of loss hydrocarbon product (LHP)

Incremental cost of electricity

Specifically for power plants, a general method for calculating the cost of CO₂ avoided is to determine the difference in the cost of electricity (COE) generation for a power plant with and without CCS. The cost of CO₂ avoided is commonly calculated as (Rao and Rubin, 2002):

$$\$/\text{tonne CO}_2 \text{ avoided} = \frac{\text{COE}_0 - \text{COE}_{\text{CCS}}}{\text{CO}_{2,0}/\text{kWh} - \text{CO}_{2,\text{CCS}}/\text{kWh}} \quad (3.13)$$

The difference in the cost of electricity generation (the wholesale cost) is an important variable in accessing the economic feasibility of a mitigation option, because it represents the increase in costs that will be passed on to the consumers/purchasers of the electricity. However, it excludes the costs of electricity transmission and distribution. Therefore, the proportionate increase in the cost of electricity to final consumers is less than the proportionate increase in the wholesale cost.

To calculate the original cost of electricity generation (COE₀), the net present value (NPV) of the capital and operating costs of the power plant is divided by the number of operating hours in the *i*th year, and the reference power output:

$$\text{COE}_0 = \frac{\left(\sum_{i=1}^k \text{Capex}_i + \sum_{i=k}^n \text{Opex}_i \right)_{\text{Power Plant}}}{\sum_{i=k}^n \left(\text{Ref. power plant output} \times h_{\text{operating hours}} \right)_i} \quad (3.14)$$

In determining the revised cost of electricity generation for the power plant attributable to CCS (COE_{CCS}), the total NPV costs of the capital and operating includes the costs for both the power plant and the CCS facilities.

$$COE_{CCS} = \frac{\left(\sum_{i=1}^k Capex_i + \sum_{i=k}^n Opex_i \right)_{Power\ Plant} + \left(\sum_{i=1}^k Capex_i + \sum_{i=k}^n Opex_i \right)_{CCS}}{\sum_{i=k}^n \left(Net\ power\ output \times h_{operating\ hours} \right)_i} \quad (3.15)$$

The annual rate of CO_2 emissions from the power plant (tonne/MWh or kg/kWh) can be calculated as:

$$CO_2(kg / kWh) = \frac{CO_2\ emissions\ to\ the\ atmosphere}{Net\ power\ output \times h_{operating\ hours}} \quad (3.16)$$

The following table describes how the capital and operating costs for a power plant are estimated. The breakdown in cost is based on generalised methods used in studies carried out by IEA GHG.

Table 3-4 General capital and operating costing methods for power plants

Capital cost The total capital cost for the power plant is determined by scaling the unit cost of the reference plant to the size of the plant in the analysis	$Capex_{Power\ Plant} = k_{power\ plant} \times Size_{ref} (Size_i / Size_{ref})^{0.85}$
Operating cost The total operational and maintenance cost is the sum of the fixed costs and costs for fuel	$Opex_{Power\ Plant} = C_{O\&M} + C_{Fuel}$ $C_{O\&M} = 0.035 \times Capex_{Power\ Plant}$ $C_{Fuel} = \frac{k_{Fuel} \times Size_i \times h_{operating\ hours} \times 3600}{LHV_i}$

3.5 Evaluating CO_2 capture from Australian CO_2 emission sources

CO_2 capture can be achieved by post-combustion, pre-combustion and denitrification or oxyfuel combustion technologies.

- Post-combustion capture technology is where CO₂ is captured from the exhaust of a combustion process (Figure 3-2). It is applicable to the design of existing processes such as coal or NGCC power plants.
- Pre-combustion capture technology involves producing a hydrogen rich synthesis gas from which CO₂ is captured (Figure 3-3).
- Oxyfuel combustion capture involves burning a fuel source with pure oxygen (O₂) or oxygen enriched gas streams (with concentrations greater than found in air). Oxyfuel combustion produces CO₂ and water, which is relatively simple to separate. Currently oxyfuel combustion processes are limited by the materials of construction and also require a CO₂ recycle stream to moderate the combustion temperature. See Figure 3-4.

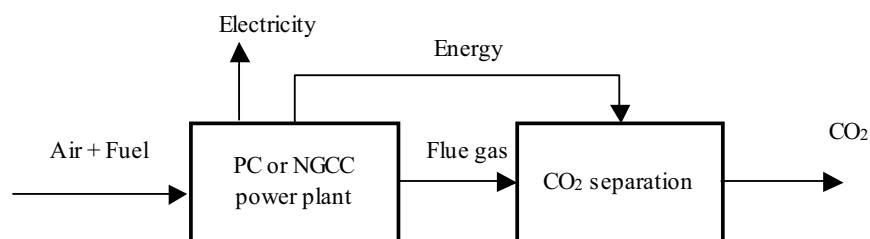


Figure 3-2 CO₂ capture using a post combustion system

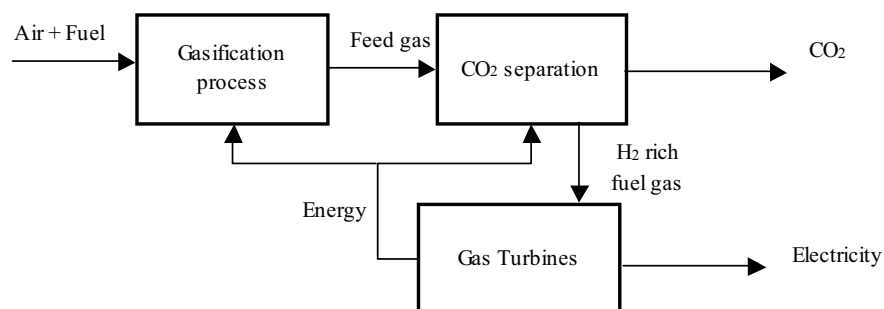


Figure 3-3 CO₂ capture using a pre combustion system in power plants

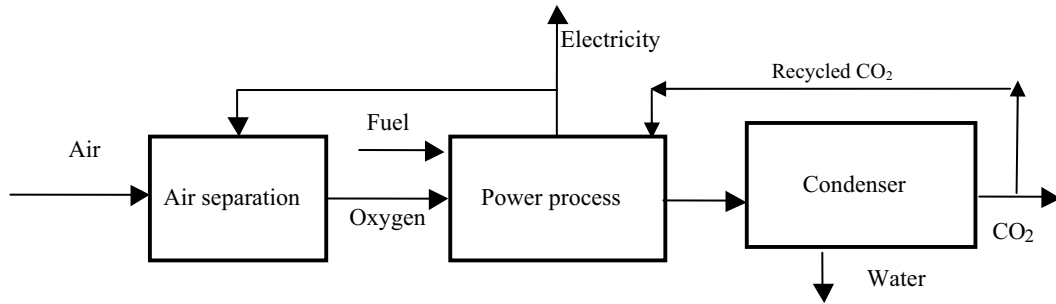


Figure 3-4 Oxyfuel combustion in power plants

For the purpose of this thesis, only post and pre-combustion technology are considered.

In Chapters 4 to 7, the cost of capturing CO₂ from a flue gas of a supercritical pulverised black coal power plant (SC-PC) is investigated. Capture is after combustion (post-combustion capture) and therefore does not simulate the power plant cycle.

A cost analysis for subcritical black coal and brown coal (lignite) power plants, and other advanced power generation facilities such as integrated combined cycles is discussed in Chapter 8. Chapter 8 also examines the cost of CO₂ capture from major industrial CO₂ emission sources such as natural gas processing, hydrogen production, petrochemical processing, metals production and cement manufacture. Both pre- and post-combustion capture options are considered, depending on the conditions of the CO₂ feed gas stream.

In this thesis, for all power generation capture options it is assumed that the CO₂ capture facility will be integrated into a newly built power plant, with a net power output set at 500 MW. CCS in Australia will most likely be introduced during the development of new coal-fired power plants because of the higher costs associated with retrofitting an existing plant (IPCC, 2005). However, retrofitting of power plants may also play an important role in the future, and the economic model has been configured to allow the user to estimate cost for retrofit options. For industrial non-power plant CO₂ emissions, the CO₂ capture facility is assumed to be a retrofit.

3.5.1 Economic assumptions

The key economic assumptions used in this thesis are listed in Table 3-5. The reference processing plant is assumed to be the same plant without an integrated CO₂ capture facility. The capital and operating costs have only been determined for CO₂ recovery, post-separation treatment and CO₂ compression. No allowance has been made for the cost of transport and storage, which is outside the scope of the research.

Table 3-5 Baseline economic assumptions

Parameter			
Cost year		2006	
Discount rate	%	7 real	
Project life	Years	25	
Construction period	Years	2 (40% Year 1, 60% Year 2)	
Operating capacity	%	85	
Currency		A\$	US\$
Exchange rate: \$US for A\$1		0.75	--
Cost of fuel (coal)	\$/GJ (LHV)	1.0 (ABARE, 2005)	1.5 (IEA-GHG, 2003b)
Cost of fuel (natural gas)	\$/GJ (LHV)	3.5 (ABARE, 2005)	3.0 (IEA-GHG, 2003b)
Unit cost for 500 MW power plant			
Sub-critical pulverised coal (S-PC)	\$/kW	1050 (Wibberley et al., 2006)	1050 (Simbeck, 2001)
Supercritical pulverised coal (SC-PC)	\$/kW	1150 (Wibberley et al., 2006)	1150 (Simbeck, 2001)
Integrated coal gasification combined cycle (IGCC)	\$/kW	2100 (Cottrell et al., 2003)	1700 (Herzog et al., 1997)
Natural gas combined cycle (NGCC)	\$/kW	800 (Cottrell et al., 2003)	450 (Herzog et al., 1997)
Purchased electricity cost from pulverised coal	\$/MWh	30 (ABARE, 2005)	32
Purchased electricity cost from NGCC	\$/MWh	35 (ABARE, 2005)	35

3.5.2 Processing assumptions for Chapters 5 to 7

The characteristics of the flue gas assumed for Chapters 4 to 7 are detailed in Table 3-6. The flowrate, composition and conditions are based on the flue gas of an East Coast Australian power plant examined in the study by Dave et al. (2000). These represent the conditions of a generic flue gas stream from an Australian black coal power plant.

In this thesis, it is assumed that at least 85% of the CO₂ contained in the flue gas is recovered in the separation unit to be consistent with previous studies. The separated CO₂ is compressed to 100 bar for transport. The SO_x content in the flue gas is treated in a Flue Gas Desulphurisation (FGD) unit, where the SO_x is removed to 10 ppm (Chapel et al., 1999).

Table 3-6 Flue gas composition of power generation facilities

Power plant type		Supercritical PC
Net power output	MW	500
Boiler type		Supercritical
Fuel type		Black coal
Thermal efficiency (LHV)	%	41
Temperature	°C	110
Pressure	Bar	0.95
Flowrate (volumetric, molar)	m ³ /s	670
	kmol/s	21.3
Mole fraction	CO ₂	0.13
	N ₂	0.75
	O ₂	0.05
	H ₂ O	0.07
	CO	--
	H ₂	--
	SO _x (ppm)	220
Initial CO ₂ emission	kg/kWh	0.83

3.5.3 Processing assumptions for Chapter 8

The flue gas compositions and characteristics for all the CO₂ emissions from industrial sources examined in Chapter 8 are set out in Table 3-7. The compositions of the flue gases for the subcritical power plant are based on the study by Dave et al. (2000) and communications with a power supplier (LoyYang, 2004). The composition of the flue gas from an IGCC power plant are taken from a study by Rubin et al. (Stork, 1999). For the IDGCC synthesis flue gas, the composition is the same as that used in the IEA GHG study for improvements in gasification technology (IEA-GHG, 2003a). For NGCC power plants, the advanced NGCC flue gas composition is estimated using the information provided through personal communications with a consultant (McKee, 2006), while the flue gas composition of the current commercial technology is from the IEA GHG study undertaken by Stork Engineering (Stork, 1999).

For the industrial emission sources, the following references are used:

- Hydrogen production: The synthesis gas is based on the study by Mak et al. (2004) for the gasification of coal for ammonia production.
- Natural gas processing: Variable CO₂ compositions of 5%, 10% and 15% as reported by Cook et al. (2000).
- Iron and steel manufacturing: The compositions for the blast furnace flue gas are defined in the study by Farla et al. (1995), while the composition of the synthesis gas is taken from Gielen (2003).
- Petrochemicals industry: The analysis is based on the generic flue gas of a gas-fired heater from the study by the IEA GHG (Zanganeh et al., 2004).
- Cement manufacture: The composition of the flue gas is based on the study by Hassan (2005), the concentration of CO₂ in the flue gas is representative of the combined CO₂ emissions from the calcination process and the combustion of fossil fuels.

Table 3-7 Flue gas compositions and characteristics of different CO₂ emission sources

	Power generation					Industrial sources							
	Brown coal (LoyYang, al., 2004)	Black coal (Dave et al., 2000)	NGCC (Stork, 1999)	NGCC (McKee, 2006)	IGCC (Rubin et al., 2004)	IDGCC (IEA-GHG, 2003a)	Hydrogen (Mak et al., 2004)	Natural gas (Cook et al., 2000)	Steel (Farla, 1995)	Steel (Gielen, 2003)	Steel (Wingrove et al., 1999)	Chemicals (Zanganeh et al., 2004)	Cement flue gas (Hassan, 2005)
Post or Pre combustion	Post	Post	Post	Post	Pre	Pre	Pre	Post	Post	Pre	Pre	Post	Post
Gross Power (MW)	535	535	508	508	594	816							
Net Power (MW)	500	500	500	500	535	767							
Comments	Sub-critical	Sub-critical	Current	Advanced	Texaco O ₂ blown		H ₂ production from coal	Variable CO ₂ content	Conventional blast	Synthesis gas	O ₂ blown flue gas - Corex		4.1 kg/kg cement
Thermal efficiency (% LHV)	31	37	56	56.2	39	43.9	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cost of electricity generated or purchased (A\$/MWh)	30 Produced	30 Produced	36 Produced	36 Produced	45 Produced	41 Produced	35 Purchased	35 Purchased	35 Purchased	35 Purchased	35 Purchased	35 Purchased	35 Purchased
Flue gas													
Flowrate	789 kg/s	630	812	438	150	351	69	Variable	393	442		177	70
	850 m ³ /s	705	850	450	6.55	26.87	1.43	5.5	12.9	15.6	57.5	207	81
	27.01 kmol/s	21.28	28	15.1	7.51	15.65	3.67	Variable	311	21.16	7.83	5.7	2.267
Pressure (bar)	1.01	1.01	1.01	1.01	29	25	60	45	1	19	3.5	1.00	1
Temperature (°C)	93	110	88	85	35	250	30	45	20	40	40	170	160
CO ₂	12	13	4	8	38	20	41	5/10/15	20	34	24	22	22
N ₂ + Ar + traces	60.5	75	75.5	83	1.3	31.5	1.5	1	50	46	12	70	68
O ₂	3	5	12.5	5								2	3
H ₂ O	24.5	7	8	4	7	18					1	6	7
H ₂					52	26	56		3	20	17		
CO					1.4	2.5	1.5		21		44		
CH ₄						2		87/82/77			2		
C ₂ H ₆								7					
SO _x ppm	200	220	2	2					2			200	
NO _x ppm	666												
CO ₂ emission (kg/kWh)	1.027	0.877	0.375	0.368	0.841	0.646							

Chapter 4. CHEMICAL ABSORPTION

4.1 Overview

This chapter examines the cost of capturing CO₂ from power plant flue gases using chemical absorption. The analysis initially examines the cost using commercially available chemical solvents. The analysis is based on Australian economic conditions using equipment prices in the year 2006. The latter sections of this chapter investigate opportunities for reducing the CO₂ capture cost. It examines the potential reductions that could be achieved from the developing new solvents with improved solvent working capacity, concentration and regeneration properties. Opportunities to reduce the capture cost through process developments such as waste heat integration, novel stripper design and lower initial capital costs are also analysed.

4.2 CO₂ capture using chemical absorption solvents

4.2.1 Introduction

Chemical absorption solvents are used extensively to recover CO₂ from industrial sources. An advantage of using chemical absorption for CO₂ capture is that the process involves well-established technology. Chemical absorption is the only commercially proven technology for recovering CO₂ from flue gas, and thus the technical feasibility is assured.

In this chapter, the cost of capturing CO₂ from flue gas using chemical absorption is determined. It is based on Australian costs and an Australian supercritical black coal power plant. Initially the cost of capture using commercially produced monoethanolamine (MEA), proprietary KS1 (Mimura et al., 2000b) and improved MEA solvent Econamine FG Plus solvents is evaluated. This chapter compares the capture cost of commercial solvents to the range of the European Union (EU) carbon trading prices, as described in Chapter 1. A sensitivity analysis is also carried out to investigate the opportunities for reducing the cost. The analysis examines the effect of using new

solvents with improved solvent working capacity, concentration and regeneration properties. It also examines the effect of waste heat integration, novel stripper designs and lower capital costs. The sensitivity analysis suggests the direction for future solvent development that may make CO₂ capture using chemical absorption economically viable at current carbon trading prices.

4.2.2 Chemical absorption process

Figure 4-1 show the process flow diagram of the CO₂ chemical absorption capture system.

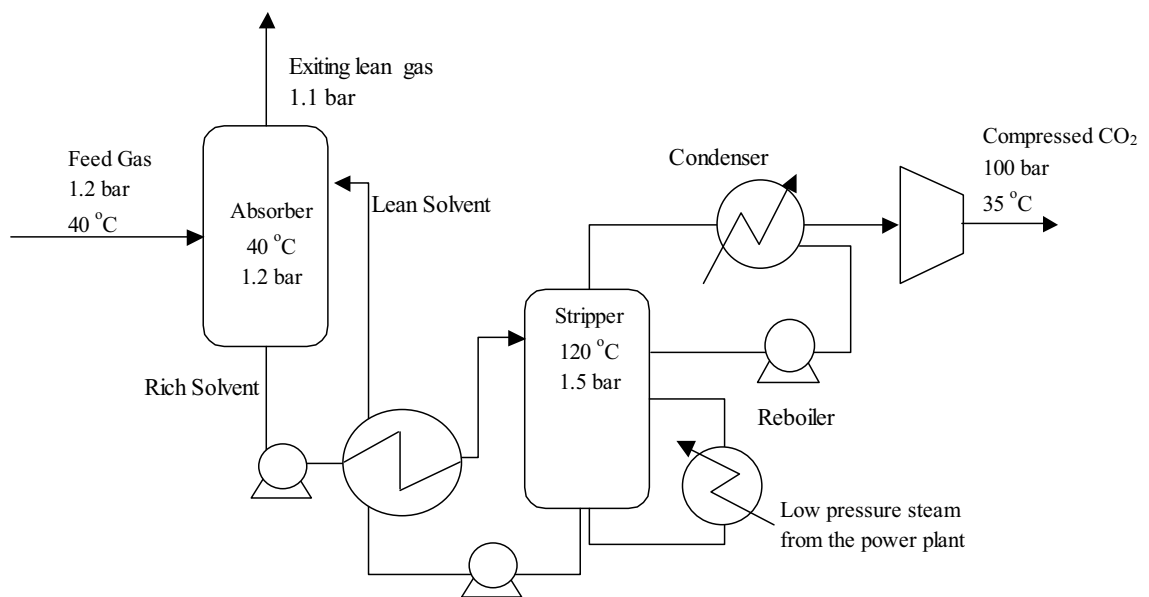


Figure 4-1 Process flow diagram for the chemical absorption process

Pre-treated feed gas containing CO₂ enters the bottom of the absorber and flows upwards. The absorption solvent enters from the top and counter-currently contacts with the gas flowing upward. CO₂ is absorbed into the solvent, and the lean treated flue gas leaves the top of the absorber. The rich solvent, now loaded with CO₂ leaves the bottom of the absorber and passes through a pre-heater before entering the top of the regenerator or stripper. The rich solvent is heated in the regenerator, releasing hot CO₂ gas through the top. Solvent and water vapour are cooled and condensed at the top of the stripper and recycled back to the system. The lean solvent, now free of CO₂, is reused in the absorber. The lean solvent loading (i.e. amount of CO₂ left in the lean solvent) is a critical factor in the operation of the absorption system; it sets the

minimum attainable CO₂ concentration in the scrubbed gas, and thus the maximum recovery rate.

4.2.3 Assumptions

The conditions of the flue gas and the economic assumptions used in this study are described in Chapter 3 (section 3.5).

The MEA solvent manufactured by Fluor Daniel (Econamine) is chosen as the baseline solvent as it has been commercially demonstrated for CO₂ recovery from power plant flue gas streams at three pilot plants. These are: a 4.5 tonne/day plant in Yokosuda Japan, a 2 tonne/day plant in Alberta Canada, and a 4 tonne/day plant at Boundary Dam, Canada (IEA-GHGRDP, 2002). KS1 has been commercially tested at the Petronas Fertilizer Company in Malaysia, while Econamine FG Plus has yet to be tested commercially but is a modification of the established Fluor Daniel process and solvent for Econamine MEA solvent.

The processing assumptions for the chemical absorption system and the properties of MEA are listed in Table 4-1. The parameters for KS1 and Econamine FG Plus, which are hindered amines, are proprietary. To complete the cost analysis, key parameters for these solvents had to be estimated. Through a process of trial and error, the solvent parameters were determined by matching the model outputs with the data given in the open literature (Mimura et al., 2000a, Mimura et al., 1995, Mimura et al., 1997, Reddy et al., 2003). It is assumed that the solvent price of KS1 is twice that for MEA and, for Econamine FG Plus, the price is equivalent to MEA.

For the KS1 solvent, 10% of the regeneration energy is assumed to be from using waste heat from the flue gas cooling with the power plant steam cycle. This is selected based on the reported findings by Mimura et al. (2000a). For Econamine FG Plus, low pressure steam generation for the power plant using the hot flue gas was incorporated into the model. This is consistent with the studies reported by Roberts et al. (2004) and Reddy et al. (2003).

Table 4-1 Processing conditions for CO₂ chemical absorption

Absorber temperature	°C	40		
Absorber pressure	Bar	1.2		
Reboiler temperature	°C	125		
Reboiler pressure	Bar	1.5		
Solvent		MEA (Chakma, 1997, Chapel et al., 1999)	KS1 (Mimura et al., 2000b)	FG Plus (Reddy et al., 2003)
Manufacturer		Fluor Daniel	MHI	Fluor Daniel
Cost	\$/kg	1.5	3.0	1.5
Solvent flowrate			<MEA	< MEA
Solvent concentration	%	30	--	--
Rich solvent loading	mol CO ₂ /mol solv	0.45	> MEA	> MEA
Lean solvent loading at reboiler temp. 125°C	mol CO ₂ /mol solv	0.23	--	--
Latent heat of vaporisation	kJ/kg	826	--	--
Heat of reaction	kJ/mol of CO ₂	85 (Jou et al., 1994)	< MEA	--
Reaction rate constant	mol/L.s	7600	--	> MEA
Solvent degradation rate	kg/tonne CO ₂	1.6	0.35	1.6

4.2.4 Chemical absorption model

Numerous rigorous models have been proposed to simulate the absorption of a gaseous solute at the gas-liquid film interface (Glasscock and Rochelle, 1989). These theories include film, penetration and surface renewal theories. Usually they require the solution of multiple ordinary or partial differential equations describing multi-component diffusion and reaction. The solution of these models requires significant physical-chemical property data such as the vapour liquid equilibrium data at various temperatures and pressure profiles. As this is a pre-feasibility analysis, short cut methods and correlations are used to determine the data. Short-cut methods of suitable accuracy have been developed through of the extensive experience of engineers with absorption processes in natural gas processing and chemical industries (Jones and Pearce, 1985, Brannan, 1994, Ludwig, 1997).

The key assumptions for the chemical absorption model include:

- The absorber and stripper operate under adiabatic conditions;
- The absorber sections are well-mixed in the liquid phase;
- The CO₂ stream for transport and storage has a purity of 98% (Kohl and Riesenfeld, 1960);
- Corrosion does not effect the performance of the solvent;

- Negligible pressure drop occurs in the absorber and stripper; and
- The regenerator is heated by low-pressure steam extracted from the power plant.

Performance equations

The processing parameters and mathematical equations used in the model are outlined in Table 4-2.

Table 4-2 Processing equations for the chemical absorption model

Parameter	Equation and nomenclature	
Solvent flow rate The solvent flowrate represents the total liquid flowrate of solvent plus dilution water that is being circulated in the absorption system. The solvent flowrate is dependent on both the lean and rich loadings of the solvent, and is generally 80% of the equilibrium value for the CO ₂ rich loading (Ludwig, 1997). According to Kohl and Resenfeld (1985), an approximate solvent flowrate can be estimated assuming a lean solution composition and using a correction factor.	The molar solvent circulation flowrate can be calculated using the equation as described in Ludwig (1983): $L = \frac{A1 \times n(\text{CO}_2)}{\Delta\phi_{\text{CO}_2} \times C_{\text{solvent}}} \quad (4.1)$ Specifically for MEA solvent, the flowrate can also be determined by the equation as described by Chapel et al.(Chapel et al., 1999): $L_{\text{MEA}} = 2700 \times n(\text{CO}_2) \quad (4.2)$	
Number of absorber trains The number of absorber trains is estimated from Chapel et al. (1999):	$N_{\text{ABS}} = \frac{A2}{4.5} \sqrt{\frac{n(\text{CO}_2)}{y_{\text{fCO}_2}}} \quad (4.3)$	
Absorber height The absorber height is determined using common engineering equations for packed columns.	$H_{\text{ABS}} = \frac{n(\text{CO}_2)}{K_{\text{Ga}} \times A_{\text{cross}} \times \Delta P_{\text{lm}} \times f_a} \quad (4.4)$	
Mass transfer coefficient For MEA solvent, the overall mass transfer coefficient can be estimated based on a correlation as described in Kohl and Resenfeld (1960).	$K_{\text{Ga}} = 0.15812 \mathcal{F} \left(\frac{L}{\mu_{\text{solvent}}} \right)^{2/3} \times \left(1 + 5.7(0.5 - \Phi_{\text{lean}}) \times C_{\text{solvent}} \times \exp(0.006 \mathcal{T}_{\text{abs}} - 3.4 p_{\text{CO}_2}) \right) \quad (4.5)$	
Cooling requirements The total area of heat exchangers and heat duty required for ancillary heat exchangers in the absorption capture system is calculated based on short cut methods of the Gas Processor's Suppliers Association (GPSA) (2004).	$A_i = b_i * L_1 \quad (4.6)$ $Q_i = C_i * L_1 \quad (4.7)$	
Heat Exchanger	b_i	C_i
Amine cooler	4.18	19.3
Rich-Lean Heat Exchanger	4.6	58
Reflux condenser	2.13	38.6
Reboiler	4.63	--

Chemicals consumption Solvent consumption (SC) For MEA solvent, the amount of solvent loss ranges between 1.6 – 2.0 kg of solvent per tonne of CO₂ recovered (Mariz, 1998). For streams with high SO_x content and no desulphurisation, the solvent loss is generally around 7.8 kg of solvent per tonne of CO₂, for flue gases with typical SO_x compositions of 250 ppm (Dave et al., 2000). Activated carbon (AC) Activated carbon is used with amine based chemical absorption for cleaning purposes. An activated carbon bed is used as a filter to remove solid particulates and other trace chemicals from the recirculating solvent (Chapel et al., 1999). Soda ash To avoid degradation of the amine by heat stable salts, the amine solvent is passed through an amine reclamation unit where a small quantity of soda ash is added to the spent amine solution (Chapel et al., 1999).	The chemical consumption for solvent (SC), activated carbon (AC) and soda ash has been estimated using the equations in Chapel et al. (1999): $SC(\text{kg/day}) = 1900 \left(\frac{y_{\text{SO}_x}}{y_{\text{rCO}_2}} \right) \times n(\text{CO}_2) \quad (4.8)$ $AC(\text{kg/day}) = 285 \times n(\text{CO}_2) \quad (4.9)$ $\text{Soda ash}(\text{kg/day}) = 510 \times n(\text{CO}_2) \quad (4.10)$
--	---

Energy consumption

The total power consumed by the capture unit reflects the efficiency of capture. The total power loss in the absorption capture system is the sum of the power for solvent regeneration, solvent pumping and the feed gas blower (GPSA, 2004, Hendriks, 1994). The equation for determining the work for the feed gas blower (W_{blower}) has been described in section 3.4.1.

$$W_{\text{ABS}} = W_{\text{Regenerator}} + W_{\text{Blower}} + W_{\text{Pumping}} \quad (4.11)$$

Power loss due to solvent regeneration (Oyenekan and Rochelle, 2004):

$$W_{\text{Regenerator}} = Q_{\text{Regeneration}} \frac{(T_{\text{condenser}} - 313)}{T_{\text{condenser}}} \quad (4.12)$$

where the thermal heat duty for regeneration is (Rao and Rubin, 2002):

$$Q_{\text{Regeneration}} = \exp \left(\frac{-2.4452 - 0.0037y_{\text{fCO}_2}}{-6.2743\phi_{\text{lean}} + 0.0254C_{\text{solvent}}} \right) \times L \quad (4.13)$$

Power loss due to solvent pumping (GPSA, 2004):

$$W_{\text{pumping}} = \frac{\left(\frac{W_{\text{amine soln}} + W_{\text{booster}} + W_{\text{reflux}} + W_{\text{coolers}}}{\eta_{\text{pump eff}}} \right)}{\eta_{\text{pump eff}}} \quad (4.14)$$

where

$$W_{\text{amine soln}} = 0.00031L_1P_{\text{abs}}$$

$$W_{\text{booster}} = 0.2L_1$$

$$W_{\text{coolers}} = 1.2L_1$$

$$W_{\text{reflux}} = 0.2L_1$$

The total energy penalty is the proportion of the net power plant output ($W_{\text{power plant}}$) that has been used for capture.

$$\text{Energy penalty}(\%) = \frac{W_{\text{Capture}}}{W_{\text{power plant}}} \times 100 \quad (4.15)$$

Model parameters and outputs

The chemical absorption model has been configured to allow the user to select the type of solvent and operating conditions for the absorber and stripper. This includes the pressure and temperature of the absorber and stripper. The outputs from the model used to assess the performance of chemical absorption as a CO₂ capture technology include:

1. The purity of the CO₂ product;
2. The recovery rate of the CO₂ from the feed flue gas;
3. The solvent flowrate for effective absorption affecting the energy for solvent pumping and regeneration;
4. Dimensions for the absorber and stripper for capital costing; and
5. The energy required for solvent regeneration (reboiler heat duty) contributing to the total energy consumption of the system.

The cost of CO₂ avoided (\$/tonne CO₂ avoided) and the energy penalty as described in section 2.7 will be used in throughout this thesis to as indicators of the performance of the capture system.

4.3 Baseline results for commercial solvents

The baseline techno-economic evaluation for chemical absorption is outlined in Table 4-3. The analysis examines the cost of capturing CO₂ using MEA, KS1 and Econamine FG Plus solvents.

Table 4-3 Economic results for CO₂ capture using chemical absorption

	This study			Rubin (2004)	Parsons (2002)	IEA GHG (Gibbins and Crane, 2004a, 2004b)		IEA GHG (Robert s et al., 2004)	Dave (2000)
Solvent	MEA	KS1*	FG Plus**	MEA	MEA	MEA	KS1	FG Plus**	MEA
Cost year	2006	2006	2006	2002	2000	2000	2000	2003	2000
CO ₂ recovery (%)	90	90	90						
CO ₂ purity in recovered stream (%)	>98	>98	>98						
Energy penalty (kJ/kg CO ₂ captured)	1650	1180	1235						
Energy penalty (%)	34	24	25	27	29	28	22.5	21	28
Capital investment for capture plant only A\$/kW, US\$/kW	1000 765	870 670	900 680	---	--	--	-- --	-- --	911 --
Total capital investment A\$/kW, US\$/kW	1440 1150	1210 960	1245 995	950	-- 938	-- 800	-- 700	-- 533	-- --
Capture cost A\$/tonne CO ₂ avoided US\$/tonne CO ₂ avoided	54 49	42 38	45 40	-- 47	-- 51	-- 45	-- 37	-- 30	60 --

*Includes partial heat integration from power generation

** Includes integrated steam generation using hot feed flue gas

Using current technology, the current cost (2006) of capturing CO₂ using MEA is A\$54/tonne CO₂ avoided. The cost using KS1 and Econamine FG Plus with partial heat integration is A\$41 and A\$45 per tonne CO₂ avoided respectively. The lower cost for the proprietary solvents arises firstly because of the partial heat integration and secondly because less energy is needed for regeneration (Figure 4-2). Even without the partial

heat integration, the costs and energy penalties for KS1 and Econamine FG Plus are less than for MEA. For KS1 the energy penalty is 29% and the cost is A\$42/tonne CO₂ avoided. For Econamine FG Plus the energy penalty is 31% and the cost is A\$48/tonne CO₂ avoided.

As shown in Table 4-3, the capital cost to set up a CO₂ capture facility ranges from A\$870/kW for Econamine FG Plus to A\$1000/kW for MEA solvent. The additional total capital investment costs for capture, that is the cost to set up both the capture processing facility and the additional power needed for capture ranges from A\$1210/kW for Econamine FG Plus to A\$1440/kW for MEA. For MEA, over A\$440/kW of capital is needed to cover the energy required by the system compared to A\$340/kW for Econamine FG Plus and A\$345/kW for KS1 solvents. Although both KS1 and Econamine FG Plus provide cost reductions compared to MEA, the costs remain higher than current carbon prices (section 1.5). This is a result of both high capital and operating expenses on the one hand and low CO₂ avoided on the other.

Figure 4-2 shows the total energy requirement for the baseline study with MEA, KS1 and Econamine FG Plus solvents. For MEA solvent, the regeneration energy accounts for over 60% of the total. The second largest amount of energy consumed is in compressing the CO₂ for transport. Although KS1 and Econamine FG Plus solvents significantly reduce the total energy requirement compared to MEA, solvent regeneration still consumes the greatest amount of energy (55%). As a result, the variable operating and maintenance (VOM) cost for the energy is the largest component of the operating cost for all three solvents, as illustrated in Figure 4-3.

In Figure 4-4, for all three solvents investigated the two largest capital equipment cost items are the absorption and regeneration units. Together, these two items account for approximately 50% of the total equipment cost, or 35% of the total capital expenditure. The breakdown of other equipment costs is relatively evenly distributed between the cost for equipment such as storage tanks, the desulphurisation unit, and the CO₂ dryers and compressors.

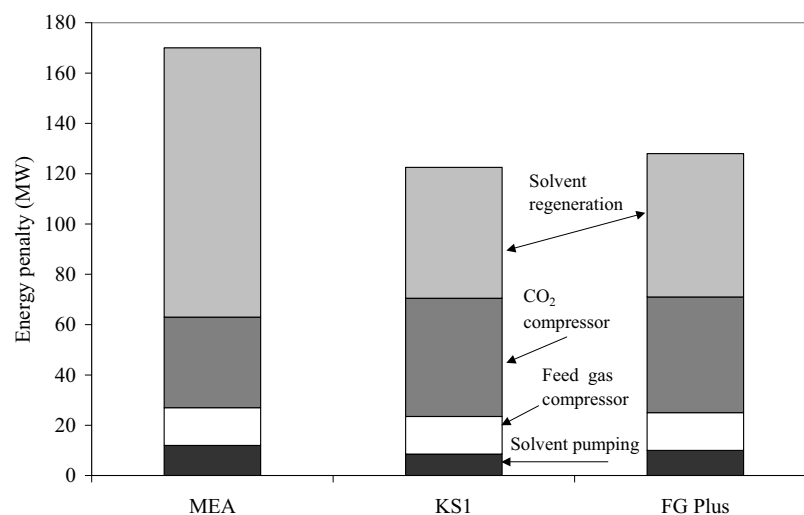


Figure 4-2 Total energy requirement for chemical absorption with MEA, KS1 and FG Plus solvents

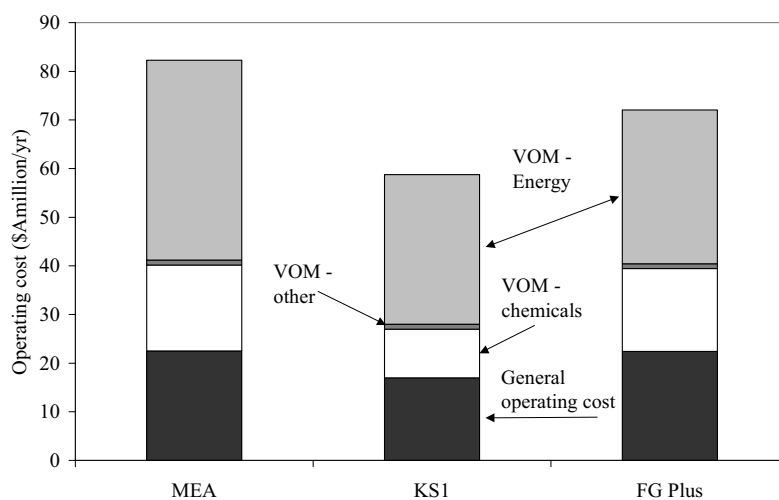


Figure 4-3 Breakdown of operating cost for MEA, KS1 and FG Plus solvents

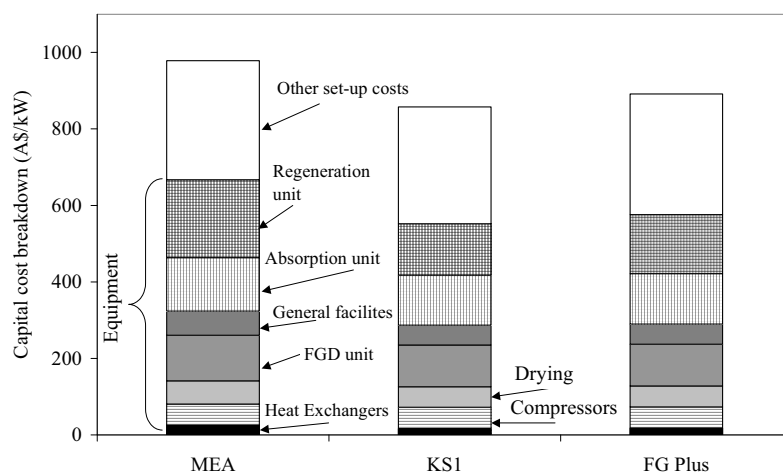


Figure 4-4 Breakdown of the capital investment for MEA, KS1 and FG Plus solvents

4.3.1 Comparison with other studies

For MEA chemical absorption, the cost for capture estimated in this study is A\$54 or US\$49 per tonne CO₂ avoided. Rubin et al. (2004) report a capture cost of US\$47/tonne CO₂ avoided using MEA solvent, while Parsons (2002) reports a cost of US\$42/tonne CO₂ avoided based on the same solvent. The only Australian study by Dave et al. (2000) reports a cost of A\$60/tonne CO₂ avoided. The IEA GHG (Roberts et al., 2004, Gibbins and Crane, 2004a) estimates the costs for MEA, KS1 and Econamine FG Plus solvents to be US\$45, US\$37 and US\$30 per tonne CO₂ avoided respectively. The capture cost estimated in this study is comparable to the other estimates, taking into account differences in both the economic and processing assumptions used. Details of the assumptions used in these studies are summarised in Appendix A.

One observable difference between this study and the IEA GHG study is the relative cost of KS1 compared to Econamine FG Plus solvent. In the IEA GHG analysis, the cost for Econamine FG Plus is lower than for KS1, while the reverse is observed in this study. The lower capture and capital costs in the IEA GHG study arise because the manufacturers of the Econamine FG Plus solvent undertook the analyses. Having access to proprietary cost data, they estimated much lower capital costs than that determined in this study, which used general equipment costs sourced from the open literature. If we assume a much lower capital cost is available for Econamine FG Plus solvent, say a 50% cost reduction in the absorber and regenerator cost compared to that for MEA, the capture cost is US\$35/tonne CO₂ avoided and the capital cost is US\$780/kW. Assuming a similar capital cost as the IEA GHG study (US\$533/kW), the capture cost is estimated to be US\$28/tonne CO₂ avoided.

The energy penalties for MEA, KS1 and Econamine FG Plus solvents in this study (24% to 34%) are higher than those reported in literature (21% to 27%). This discrepancy arises because in this study, the total energy requirement is calculated for the solvent regeneration, CO₂ compression, flue gas compression and solvent pumping. In contrast, the literature studies do not take into account the energy required for solvent pumping or the flue gas blower (feed gas compressor). If these values are neglected in

this study, the energy penalties are 29% for MEA, 20% for KS1 and 21% for Econamine FG Plus, which are similar to those reported in the literature. Under these conditions, the cost for capture would be US\$43, US\$31, US\$35 per tonne CO₂ avoided for MEA, KS1 and Econamine FG Plus respectively. Again, these are similar to those in the literature. By ignoring the additional energy for pumping and pre-separation compression, the capture cost decreases by approximately 10%. However, it is important that all energy requirements for the system be included otherwise the results may be underestimated.

4.4 Reducing the capture cost

Using current commercial solvent technology, the lowest cost of CO₂ capture has been estimated to be A\$42/tonne CO₂ avoided using KS1 solvent. However, considering the results of Figures 4-2 to 4-4, future cost reductions could be obtained by reducing the contribution of the largest items. That is costs could be reduced by:

- Reducing variable operating costs such as the costs for energy and solvent replacement; or
- Reducing the capital cost of the absorption and regeneration equipment; or
- A combination of the above.

Firstly, lower energy and solvent replacement costs can be realised by using cheaper solvents with low regeneration characteristics.

Secondly, waste heat from the absorption process could be integrated with the plant's low pressure steam cycle to minimise the energy requirements.

Thirdly, the capital cost for the separation equipment such as the absorption towers could be lowered through the use of innovative materials. Additionally more efficient packing materials can also be used to reduce the total capital expenditure.

These options are explored in the following sections.

4.5 Effect of solvent improvement

4.5.1 Regeneration energy requirements

The largest energy consumer in chemical solvent separation is the regeneration process as shown in Figure 4-2. The total energy required to regenerate a CO₂ loaded solvent can be expressed as:

$$\begin{aligned} \text{Total regeneration energy} = & \text{Sensible heat } (Q_{\text{sensible}}) + \text{Heat of reaction } (Q_{\text{reaction}}) + \\ (Q_{\text{Regeneration}}) & \text{Latent heat of vapourisation of water } (Q_{\text{H}_2\text{O}}) + \\ & \text{Latent heat of vapourisation of the solvent (partial) } (Q_{\text{solvent}}) \end{aligned} \quad (4.16)$$

The first step in the regeneration process is the sensible heat required to raise the solvent to the temperature of the stripper (Q_{sensible}). The amount of sensible heat required for this step is governed by the specific heat capacity of the solvent, which does not vary much among the different solvents available for CO₂ absorption (Chakma, 1995a). The next item is the energy needed to break the CO₂-solvent complex bond (Q_{reaction}). Another component of the regeneration process is the energy needed to vapourise the water in which the solvent is dissolved ($Q_{\text{H}_2\text{O}}$). The final component is the energy required for partial vaporisation of the solvent (Q_{solvent}).

Reducing the contributions of each of the components would lower the overall energy costs, and thus lower capture costs. As discussed in the studies by Freguia and Rochelle (2003) and Sakwattanapong et al. (2005), the two largest contributors to the total regeneration energy is the energy needed (a) to vaporise the water ($Q_{\text{H}_2\text{O}}$) and (b) to break the CO₂-solvent complex (Q_{reaction}). Together these two components account for more than 90% of the regeneration energy. Exploring opportunities to decrease these two energy requirements is discussed in detail in the following sections.

4.5.2 The impact of recent solvent developments

In recent years, many new solvents have been developed to improve the energy consumption of chemical absorption systems for CO₂ capture. As discussed in Chapter

2, some of these improvements can reduce the total energy consumption by as much 20% compared to MEA. Some of the new solvents for CO₂ capture include PSR (Veawab et al., 2001), AMP (Yeh et al., 2001) and CORAL solvents (Feron and Jansen, 1997). Unfortunately, all of these solvents are proprietary and there is insufficient information in the public domain that would enable the determination of solvent flowrates and mass transfer rates. Other non-proprietary solvents discussed in Chapter 2 have inherent disadvantages. For example AEEA (Ma'mun et al., 2004) has extreme corrosion properties and the ammonia-carbonate solids are difficult to regenerate (Huang et al., 2001, Hoffman and Pennline, 2001). In addition, there is limited information published to evaluate mass and energy balances. However, based on the information available in Cullinane et al. (2004, 2005) and Ciferno et al. (2005) it was possible to estimate the capture cost for potassium carbonate enhanced with piperazine (5 M K⁺/2.5 M PZ) and aqueous ammonia solvents respectively. The capture costs for these solvents are given in Table 4-4.

Table 4-4 Comparison of capture cost for MEA, 5MK⁺/2.5PZ and aqueous ammonia

Solvent	30% wt MEA BASELINE	5M K ⁺ /2.5M PZ	Aqueous ammonia
Thermal energy in the reboiler (kJ/kg CO ₂ captured)	4436	3072	1723
Total energy penalty (%)	34	29	19
Capture cost A\$/tonne CO ₂ avoided	54	40	38
US\$/tonne CO ₂ avoided	49	36	34

Potassium carbonate

The capture cost using the enhanced potassium carbonate (5M K⁺/2.5M PZ) solvent is A\$40 or US\$36 per tonne CO₂ avoided, which is approximately 30% lower than the baseline MEA solvent. According to Oyenekan and Rochelle (2004), the reboiler duty using potassium carbonate with piperazine is 30% less than for MEA. The results from this analysis show similar reductions in the energy penalty. The lower energy for regeneration is attributed to the lower heat of absorption, faster rate of absorption and increased absorption capacity for the enhanced potassium carbonate compared to MEA.

Aqueous ammonia

According to Ciferno et al. (2005), using aqueous ammonia as a solvent can reduce the reboiler duty to almost a third compared to MEA. Based on the physical data given by Ciferno et al. (2005), using the model developed for this thesis, the capture cost of aqueous ammonia is estimated at A\$38 or US\$34 per tonne CO₂ avoided, while the reboiler duty has been reduced to 40% of MEA. Costs are reduced primarily because of the lower energy penalty and smaller regenerators associated with the lower solvent flow rate.

Although aqueous ammonia shows considerable promise as an alternative solvent, one of its disadvantages is the need to dispose of the bicarbonate by-product. However, if the bicarbonate by-product could be sold as a fertilizer, this would be an advantage rather than a disadvantage.

Another disadvantage is the volatility of the solvent. Rochelle et al. (2005) identified that because of its high volatility, the use of ammonia solvent can result in residue concentrations of 3% ammonia in the flue gas. This is much higher than the environmentally acceptable levels of 10 ppm. Cooling equipment and processes would need to be included in the absorption system to address this, and would incur additional capital cost. If we assume that the total capital cost increases by 10% to account for the additional heat exchangers, the capture cost would increase by A\$1.5 and US\$1.5 per tonne CO₂ avoided. Furthermore, the reaction rate of ammonia is much slower than MEA, and may require absorbers with three times the height of a MEA absorber. The slower reaction rate has been taken into consideration in this analysis, and thus the capture cost is much higher than the US\$23/tonne CO₂ avoided reported by Ciferno et al. (2005).

4.5.3 Developing new low regeneration energy solvents

Although many of the new solvents currently being researched or marketed can result in reduced costs compared to MEA solvent, opportunities still exist to improve the solvent characteristics further and achieve a lower capture cost. The following sections of this chapter explore the impact on capture cost as solvent characteristics are hypothetically

improved. The hypothetical solvent is assumed to have similar baseline properties to that of MEA solvent (Table 4-1). In this analysis, many simplifications have been made including neglecting the kinetics, solvent stability, corrosion problems, and column design. Therefore the results are not accurate on an absolute basis but the trends in cost and energy consumption are indicative and will remain the same, irrespective of the simplifications.

Solvent working capacity

The solvent working capacity is the difference in the solvent loading between the lean and rich conditions. The lean solvent loading represents the residual amount of CO₂ in the solvent as it enters the absorber, while the rich loading is the amount of CO₂ in the saturated solvent leaving the absorber. Thus the solvent working capacity for CO₂ is the total amount of CO₂ that can be absorbed by the solvent. The units for solvent working capacity are mol of CO₂ absorbed per mol of solvent. The higher the solvent working capacity, the greater the affinity the solvent has for CO₂.

$$\text{Solvent working capacity} = \text{Rich loading} - \text{Lean loading}$$

$$\Delta\phi_{\text{CO}_2} \left(\frac{\text{mol CO}_2}{\text{mol solvent}} \right) = \phi_{\text{rich}} - \phi_{\text{lean}}$$

Figure 4-5 illustrates the change in capture cost when the solvent working capacity is increased. This can be achieved in two ways. The first option involves increasing the rich solvent loading (ϕ_{rich}) while keeping the lean loading (ϕ_{lean}) constant (at 0.23 mol CO₂/mol solvent). The second option is to decrease the lean solvent loading (ϕ_{lean}) while the rich loading (ϕ_{rich}) is held constant (at 0.45 mol CO₂/ mol solvent). The results also show the effect of varying the solvent working capacity on the thermal regeneration energy required. The units for the regenerator duty are MJ of thermal energy needed per kg of CO₂ captured.

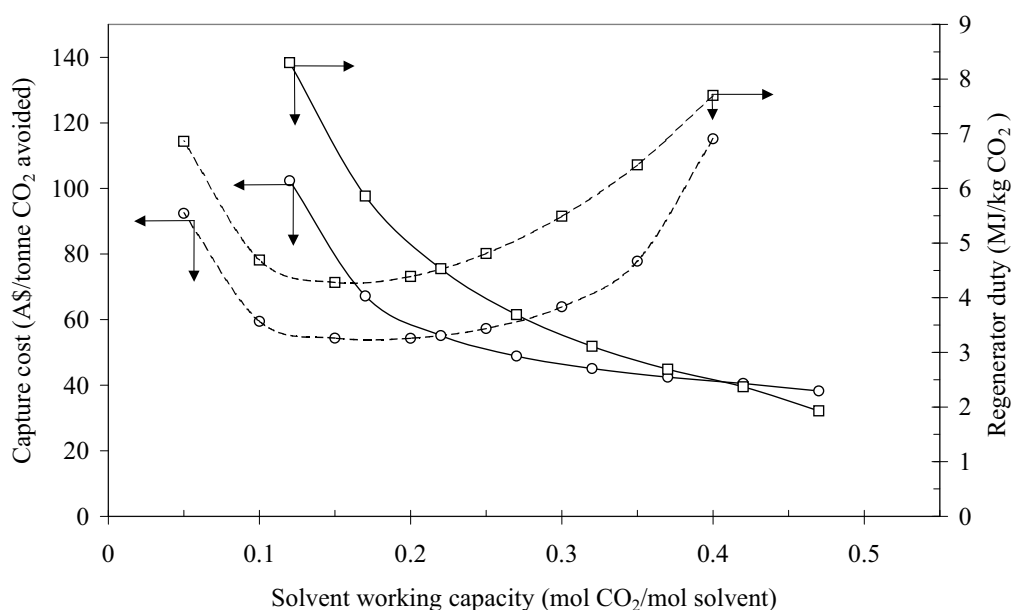


Figure 4-5 Capture cost ($\circ$) and thermal energy for regeneration ($\square$) as a function of solvent working capacity where 1) the rich solvent loading is varied (—) and 2) lean solvent loading is varied (---)

As shown in Figure 4-5, if the working capacity of the solvent is increased by increasing the rich solvent loading while keeping the lean solvent loading fixed, both the capture cost and energy demand decreases. This occurs because as the solvent working capacity increases, the amount of solvent needed to absorb the CO₂ decreases, as shown by Equation 4.1. By decreasing the solvent flowrate, the amount of energy required in the regeneration process to vapourise and liberate the CO₂ also decreases (Equation 4.13). Thus by decreasing the energy required for regeneration, both the total energy penalty and the capture cost decrease. At a working capacity of 0.5 mol CO₂/mol solvent, the capture cost decreases from the MEA baseline cost of A\$54 (where the working capacity is 0.25 mol CO₂/mol of solvent) to approximately A\$40 per tonne CO₂ avoided. Increasing the rich solvent loading can be achieved using either blended solvents such as the PSR solvents or additives to increase the reaction rates such as in KS1 and Econamine FG Plus. Large working capacities of up to 0.5 mol CO₂/mol of solvent have already been observed in the PSR solvents.

Alternatively, if the solvent working capacity for CO₂ is increased by decreasing the value of lean solvent loading rather than by increasing the value of the rich solvent

loading, the capture cost and thermal energy for regeneration appears to go through a minimum at a solvent working capacity of between 0.15 to 0.20 mol CO₂/mol solvent. When the solvent working capacity for CO₂ increases from 0.05 to 0.20 mol CO₂/ mol solvent, the capture cost decreases from over A\$90 to approximately A\$55 per tonne CO₂ avoided. This cost decrease is attributed to the decrease in the solvent flowrate with the increasing solvent working capacity. However, at solvent working capacity values above 0.2 mol CO₂/ mol solvent, the values for the capture cost and regeneration energy begin to increase rather than continue to decrease. Although the solvent flowrates at these higher solvent working capacities are low, to achieve this high solvent working capacities, the lean solvent loading must be very small, less than 0.25 mol CO₂/mol solvent. When the lean solvent loading is very low, the process requires more stripping for regeneration. Thus at these very low lean solvent loadings, the energy needed for additional stripping outweighs the energy benefits of having a smaller solvent flowrate through the regenerator.

The results of Figure 4-5 demonstrate that solvents with a large working capacity for CO₂ can lead to reductions in capture cost. However, this is best achieved by developing new solvents with higher rich solvent loading for CO₂ rather than by decreasing the lean solvent loading.

Solvent concentration

The solvent concentration reflects the amount of active ingredient dissolved in a solution such as water. Figure 4-6 illustrates the change in capture cost and regenerator energy (heat duty) as a function of the solvent concentration.

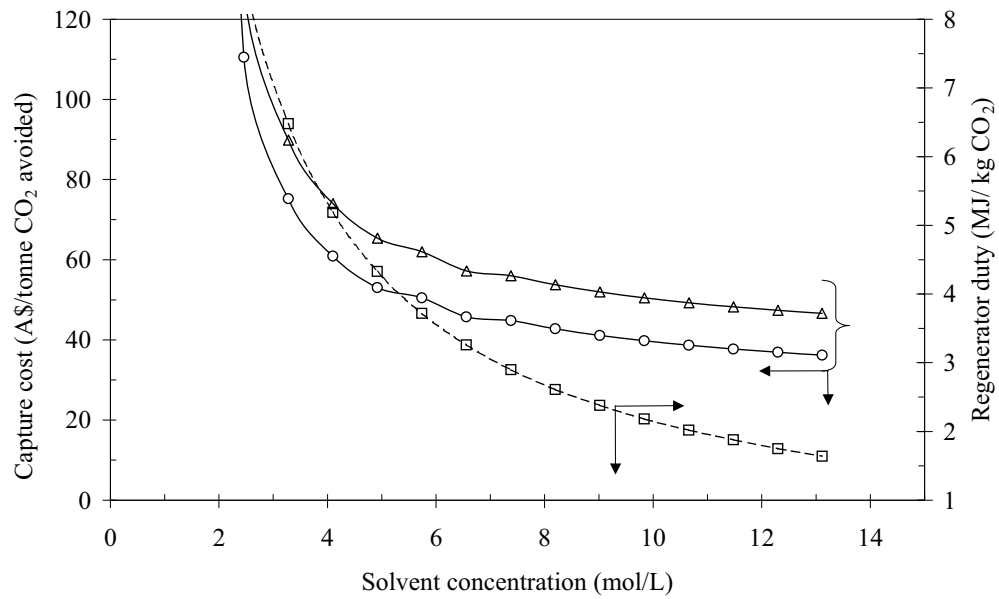


Figure 4-6 Thermal regeneration energy ($\square$) and capture cost at two different solvent prices; \$1.5/kg ($\circ$) and \$5/kg (Δ), as a function of solvent concentration

Increasing the solvent concentration decreases the capture cost and energy demand. As shown by Equation 4.1 by increasing the solvent concentration, the solvent flowrate will decrease because the solvent with a higher concentration can absorb more CO_2 per unit volume than one with a lower concentration. A lower solvent flowrate reduces the energy for solvent pumping. In addition, Equation 4.16 shows that by increasing the solvent concentration the amount of water that is vaporised in the regeneration process ($Q_{\text{H}_2\text{O}}$) decreases, reducing the energy required for regeneration. Therefore, with decreasing energy penalty through increased solvent concentration, the capture cost decreases substantially from over A\$120 to less than A\$40 per tonne CO_2 avoided.

As shown in Figure 4-6, the capture cost decreases most rapidly between concentrations of 2 and 4 mol/L, but only slightly decreases for concentrations above 6 mol/L. This arises because although the energy penalty decreases with increasing solvent concentration, by Equation 4.5 the mass transfer rate also decreases. Thus, with decreasing mass transfer rates a larger absorber is required increasing the total capital cost. For solvent concentrations up to 6 mol/L, the benefits of lower regeneration energy outweigh the increased cost for a larger absorber. However, for solvent concentrations beyond this, the benefits of the lower energy penalty are similar to the increased cost for

the absorber. This analysis may change if different unit costs are assumed for the absorber.

In this analysis it is assumed that the system is operating under ideal conditions and that increases in concentration do not adversely affect the corrosiveness of the system. In reality this is not the case and additives or inhibitors that prevent corrosion must be used such as those included in the Econamine FG Plus system, or the PSR solvents (Chakma, 1995a). It is likely that the addition of these inhibitors will increase the price of the solvent. In Figure 4-6, the effect of increasing the solvent concentration on capture cost is examined at two solvent prices, A\$1.5/kg and A\$5/kg. At a solvent concentration of 6 mol/L and a solvent price of A\$1.5/kg, the estimated capture cost is A\$45/tonne CO₂ avoided. If the solvent price is A\$5/kg, the capture cost is higher at A\$57/tonne CO₂ avoided. If new corrosion inhibitors can be developed that can be added to a solvent such as MEA without increasing its cost, increasing the concentration to 6 mol/L from the baseline assumption of 5 mol/L can result in cost reductions of up to 15%. If the cost of adding these inhibitors increases the MEA solvent price to more than A\$2/kg, increasing the solvent concentration in isolation without improving other solvent properties will not result in any observable capture cost reductions.

In addition, this analysis assumes that changes to the solvent concentration does not change the quality of the steam vapour required for stripping. In reality, higher solvent concentration may require higher quality heat from the power plant for regeneration and may adversely affect the power plant cycle.

CO₂ desorption energy

In addition to decreasing the solvent flowrate or increasing the solvent concentration, another option for reducing the amount of regeneration energy is to use solvents with a low value for the heat of reaction and heat of vaporisation. The heat of reaction represents the amount of energy needed to break the CO₂-solvent complex (Q_{reaction}). The heat of vaporisation is the amount of energy required for the solvent to be vaporised (Q_{solvent}). For amine based solvents, solvents with lower heat of reaction such as MDEA or TEA, also have lower heats of vaporisation (Chakma, 1997). Chakma (1997, 1999)

has shown that it is possible to formulate new solvents with a lower desorption energy than MEA by using either mixed-amine solvents or additives to increase the reaction rate of low heat of reaction solvents or a combination of both.

If the energy for desorption (heat of reaction) can be reduced without adversely affecting the overall rate of reaction, then costs can reduce. Figure 4-7 summarises the relative cost reductions that can be achieved by reducing the heat of reaction of a new solvent compared to the heat of reaction for MEA. As discussed earlier, the solvent latent heat of vaporisation only contributes a small component to the overall regeneration energy, and has been assumed to be constant in this analysis. Additionally, the reaction rate of the hypothetical solvent is taken to be constant assuming that the reaction mechanism has been altered (Draxler et al., 2004) and the impact of the solvent loading on the heat of reaction has been neglected (Jou et al., 1994).

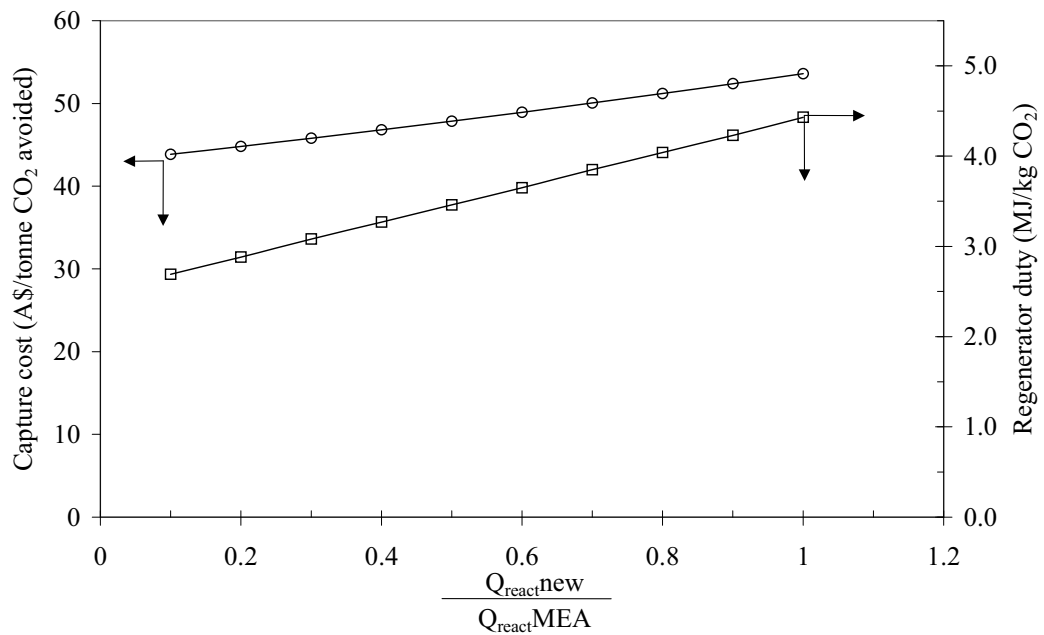


Figure 4-7 Capture cost (o) and thermal regenerator energy (□) as a function of solvent heat of reaction

The results of Figure 4-7 suggest that if the energy for CO₂ desorption is improved without improving other solvent properties such as solvent working capacity or concentration, only moderate cost reductions can be achieved. If the heat of reaction is halved compared to that of MEA, the capture cost decreases by 10%. If further

reductions can be obtained to create a desorption energy 10 times smaller than MEA's, the capture cost decreases by 20%.

4.5.4 Reducing solvent replacement costs

Solvent losses

The solvent losses in a chemical absorption process arise from vaporisation, solubility, damage from mechanical equipment, degradation and entrainment. The acidic components of the flue gas such as SO_x and NO_x react irreversibly with amine-based solvents such as MEA to form stable salts. This leads to solvent losses and limits the capacity of the solvent to absorb CO_2 . It is therefore necessary to control the amount of solvent loss in order to minimise operating costs and maximise the amount of CO_2 recovered. Reductions in solvent losses can be accomplished by designing new equipment that minimise entrainment and mechanical damage, as well as by designing new solvents that are less prone to degradation.

Figure 4-8 illustrates the rate of change in capture cost with decreasing amounts of solvent degradation (represented as solvent loss per tonne CO_2 captured) neglecting any improvements in equipment design. The analysis assumes three solvent prices of A\$1.5/kg, A\$5/kg and A\$10/kg.

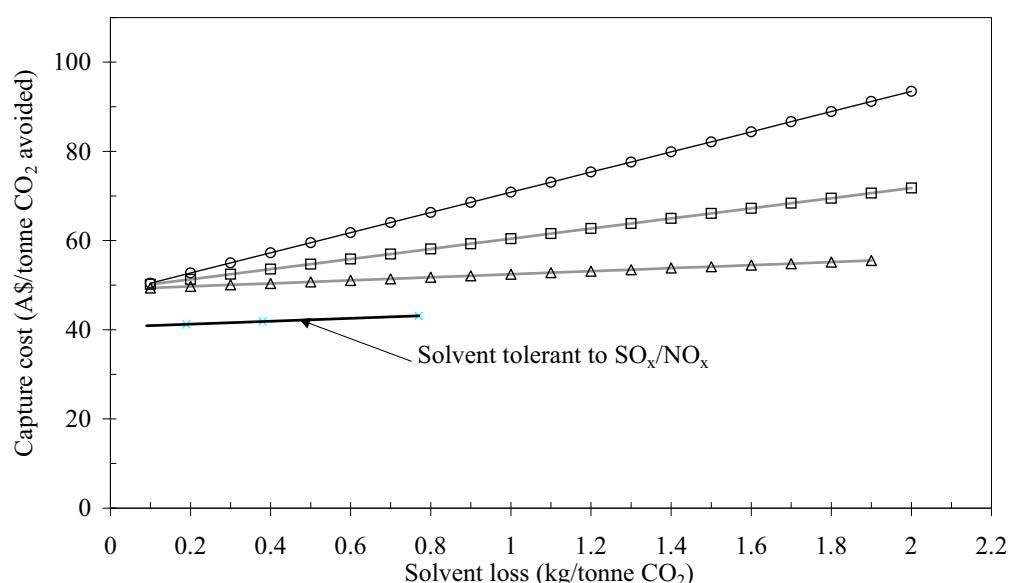


Figure 4-8 Capture cost as a function of solvent losses at solvent prices: A\$1.5/kg (Δ), A\$5/kg (□) and A\$10/kg (○)

If we can decrease the solvent losses using a solvent that has similar properties to MEA, the lowest capture cost obtained is A\$50/tonne CO₂ avoided. This is less than the baseline MEA cost because of the lower cost of chemical replacement. From Figure 4-8, it appears that at very low solvent losses (below 0.5 kg/tonne CO₂ captured), increases in the solvent price only have a marginal effect on the capture cost. This is because the cost of replacing these chemicals only makes up a small component of the operating cost, and the capture costs do not vary significantly between inexpensive and expensive solvents. However, at higher solvent losses (greater than 1 kg/tonne CO₂ captured), increasing the solvent price has a much more significant impact. The results also show that if the solvent is inexpensive (less than A\$1.5/kg), there is not much change in capture cost whether degradation is high or low.

Low solvent losses are already achievable using development solvents such as KS1 or PSR with reported losses at 0.35 kg and 0.5 kg per tonne of captured CO₂ respectively. These solvents have been designed with low degradation and vaporisation effects, which are much less than other amine solvents such as MEA, which has solvent losses of 1.6 to 2.0 kg per tonne of CO₂ captured (Chapel et al., 1999).

Alternatively, if a new solvent could be developed that is also SO_x and NO_x tolerant, the need for a flue gas desulphurisation and NO_x pre-treatment would be eliminated. This would have tremendous cost benefits. In Figure 4-8, the capture cost for 90% CO₂ capture using a solvent that has a high level of SO_x/NO_x tolerance is between A\$40 and A\$45 per tonne CO₂ avoided. This analysis assumes no need to pre-treat the flue gas and partial solvent losses (of up to 0.8 kg of solvent/tonne CO₂ captured).

4.5.5 Synopsis – “low cost solvent” for CO₂ capture

From the previous analysis, it can be concluded that, improving the regeneration properties of a solvent while maintaining good absorption characteristics will decrease the capture cost. This is because of the lower regeneration and pumping requirements and the use of a smaller absorber. This in turn is primarily because of a lower solvent flow rate and heat of reaction.

Figure 4-9 illustrates how capture cost changes in with increasing working capacity, and decreasing heat of reaction at a concentration of approximately 6 mol/L. The analysis assumes solvent losses of 1.6 kg/tonne CO₂ captured (MEA’s current level) and 0.5 kg/tonne CO₂ captured. From the results, a low cost solvent for CO₂ capture has the highest possible working capacity (without adversely affecting the reboiler temperature), the lowest possible heat of reaction and the lowest solvent losses.

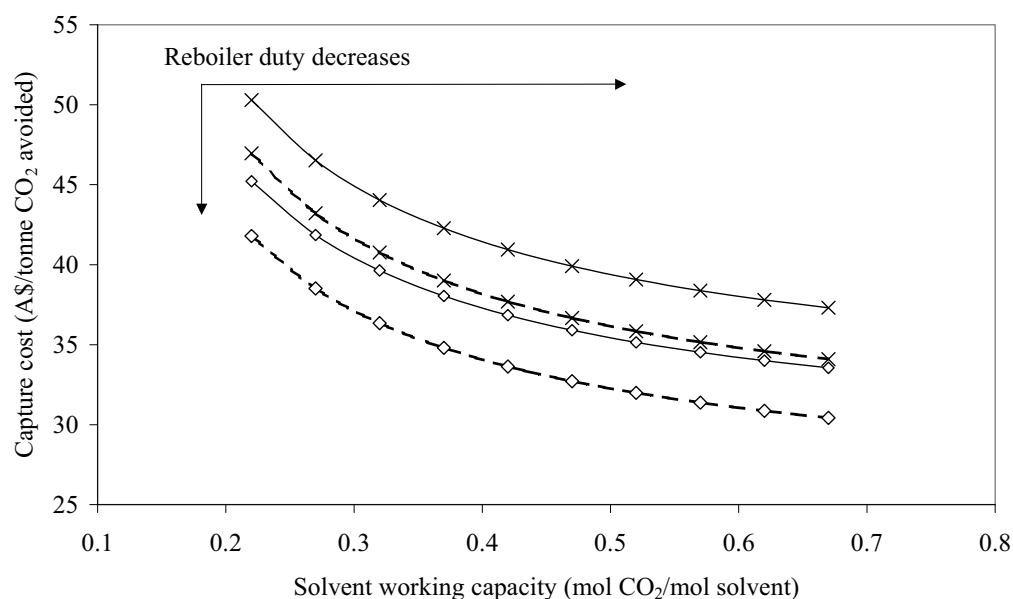


Figure 4-9 Variation in capture cost with increasing solvent working capacity at two solvent losses: 1.6 (—) and 0.5(---) kg/tonne CO₂ captured, and two heat of reactions: 45 kJ/mol (◇) and 85 kJ/mol (×)

In the following sections of this chapter, a low regeneration energy solvent is evaluated. Although many combinations of solvent properties are possible, the following properties were chosen:

- A concentration of 6 mol/L;
- A solvent working capacity of 0.52 mol CO₂/mol solvent;
- A heat of reaction of 65 kJ/kmol solvent; and
- A solvent loss of 0.5 kg/tonne CO₂ avoided.

These values were selected, as they are very similar to those of the PSR and KS solvents. The capture cost for this combination of properties is approximately A\$32/tonne CO₂ avoided. The thermal reboiler duty for this new low regeneration energy solvent is 1650 kJ/kg CO₂ captured. The absorption kinetics are assumed to be the same as for MEA.

4.6 Effect of process improvements

4.6.1 Steam and waste-heat utilisation

To regenerate the CO₂ enriched solvent, chemical absorption processes use low-pressure steam to heat the reboiler and vaporise or “strip” the CO₂ from the solvent. Gibbons and Crane (2004b) and Mimura et al. (1995) show that heat integration can also be used to reduce the energy penalty of the CO₂ capture system. This is achieved by utilising the waste heat from the absorption process back in the power plant cycle. Heat integration can include:

- (I) Low pressure steam generation using the waste heat from cooling the hot flue gas and inter-cooling in the CO₂ compressors;
- (II) Partial cooling of the regenerator overhead condenser to displace the need for low pressure steam from the power cycle; and
- (III) Using superheated steam from the power plant to heat part of the reboiler condensate to reduce the amount of low pressure steam sent to the reboiler.

Figure 4-10 illustrates these heat-integration options.

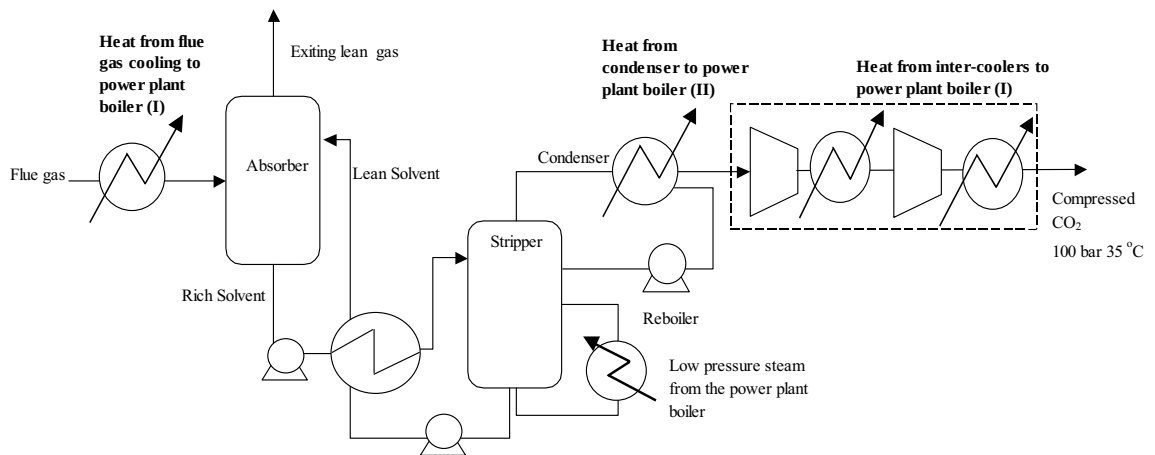


Figure 4-10 Integrating heat from the chemical absorption process with the boiler water for the power plant steam cycle

Table 4-5 shows how the capture costs for MEA, KS1 and Econamine FG Plus solvents can be improved using waste heat integration. The energy penalty and capture cost decrease by almost 10% for MEA, and approximately 5% for KS1 and Econamine FG Plus. The results agree with the analysis of heat integration by Gibbins and Crane

(2004b), where integration can generate 10% savings in the energy penalty and capture cost. No analysis was undertaken by Gibbins and Crane (2004b) for KS1 or Econamine FG Plus solvents. However their results for KS2 solvent also developed by Mitsubishi Heavy Industries shows similar results to this study for KS1 solvent.

If heat integration is used in addition to the new low regeneration energy solvent as defined in section 4.5.5, the capture cost can decrease to A\$30/tonne CO₂ avoided. By combining the improved solvent characteristics with improved process design, capture cost reductions of almost 45% can be achieved compared to the baseline scenario using MEA solvent.

Table 4-5 Capture costs for different solvents with process heat integration

	This study							IEA GHG (Gibbins and Crane, 2004b)			
Solvent	MEA	KS1	FG Plus	MEA	KS1	FG Plus	New solvent*	MEA	KS2	MEA	KS2
Heat integration	None	None	None	I+II+III	I+II+III	I+II+III	I+II+III	None	None	I+II+III	I+II+III
Energy penalty (%)	34	28	29	30	24	25	16	28	24	25	21
A\$/t CO ₂ avoided	54	42	48	51	39	43	30	--	--	--	--
US\$/t CO ₂ avoided	49	37	42	45	34	38	25	45	37	41	34

*New low regeneration energy solvent from section 4.5.5

4.6.2 Innovative stripper design

Rochelle and Jassim (2005) investigated the energy savings achievable by using an innovative design for the solvent stripper. The configurations examined included the use of multi-pressure strippers, vapour recompression and inter-cooling of the absorber as shown in Figure 4-11.

The solvent used in their study was MEA. The assumptions in their study included compression of the product CO₂ to 130 atm (128 bar) for transportation. This is achieved by using a multi-stage compressor with an isothermal efficiency of 75%. Table 4-6 summarises the capture cost that results from incorporating these conditions into the absorption model. The results shows that better stripper designs give cost reductions of up to 10%.

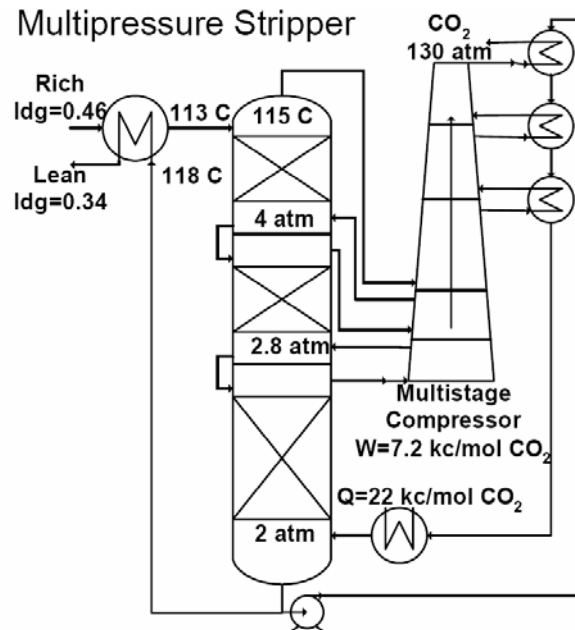


Figure 4-11 Multipressure stripper with 5°C temperature approach and vapour recompression (Rochelle and Jassim, 2005)

Of all the cases examined, the option of vapour compression where the CO₂ compressor is inter-cooled by the stripper bottoms results in an increase in the capture cost even though the energy penalty is decreased. By using the stripper bottoms to cool the compressor rather than cooling water, the temperature of the CO₂ entering each stage of the compressor is higher. This in turn increases the total compressor duty and a larger compressor is required, and thus the higher capital and capture costs. However, if further energy savings are incorporated into the design such as multi-pressure stripper operation, both the capture cost and energy penalty reduces.

Rochelle and Jassim (2005) also examined the effect of using a hypothetical solvent that is significantly more reactive than MEA. Based on the results of their study, the thermal duty for the reboiler is 2090 kJ/kg CO₂ captured. By coupling the new solvent with the innovative stripper design, the capture cost can decrease by 10% compared to the base case.

Table 4-6 Capture costs for the different stripper scenarios examined in Rochelle and Jassim (2005).

	Capital cost for capture facility (A\$/kW)	Capture cost (\$/tonne CO ₂ avoided)	
		A\$	US\$
Base Case MEA solvent	1050	55	50
Optimised L/G MEA solvent	1033	54	49
+ 5 C approach MEA solvent	1025	53	48
+ vapour recompression MEA solvent	1175	56	50
+ multi-pressure stripper MEA solvent	1100	52	47
+ intercooling MEA solvent	1095	51	45
+ new solvent + multi-pressure	1100	52	46
+ new solvent + multi-pressure + intercooling	1075	50	44

Combining the results of the above sections, the use of waste-heat integration between the power plant steam cycle and the absorption plant coupled with an innovative stripper design can reduce capture costs by up to 13% and energy penalties by up to 45% compared to the baseline cost using MEA solvent.

4.7 Effect of reducing the unit cost for capital

4.7.1 Efficient packing material

The development of better packing material with higher mass transfer efficiencies provides the opportunity to reduce the capital cost of absorbers and regenerators. New packing materials developed by Fei (2004, 2005) and structured packing such as Mellapak 500Y provide mass transfer rates of one and half to two times that of standard Mellapak 250Y or Rashig rings. In the baseline analysis, it was assumed that Mellapak 250Y packing is used in the absorber.

Figure 4-12 illustrates the capture cost benefits that can result if new efficient packing material is utilised. This analysis assumes that the cost for the new packing material is similar to Mellapak 250Y. By doubling the packing efficiency and mass transfer coefficient, the absorber height decreases by approximately half. This translates into lower capital cost, and reduces the CO₂ capture cost by 10%. Also shown in Figure 4-12, improving the packing efficiency has a larger impact on the cost for MEA solvent than for the hypothetical low regeneration energy solvent (section 4.5.5). This is

because the amount of CO₂ avoided for this solvent is considerably higher than for MEA, and thus small cost reductions in capital do not significantly reduce the capture costs.

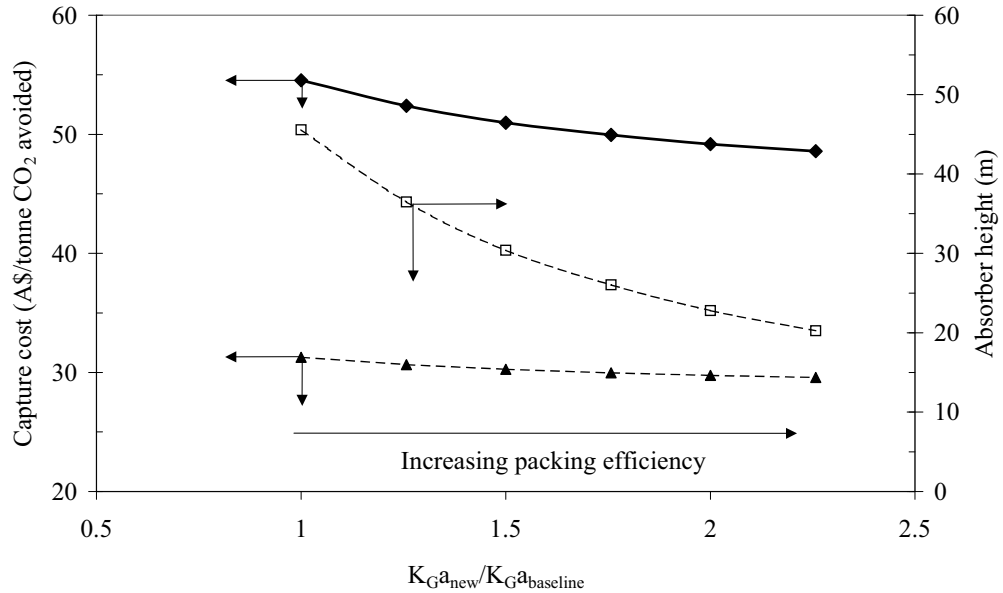


Figure 4-12 Capture cost for MEA (◆) and the new solvent (▲), and the absorber height (□) as a function of increasing mass transfer rates and packing efficiency

4.7.2 “Fit for purpose” equipment

Figure 4-4 shows that the capital costs for the absorption and regeneration systems represent almost half of the total equipment cost. In this analysis, the capital costs are estimated for 4 trains of absorbers and regenerators (strippers), with cylindrical diameters of 5 m. These designs and costs are based on established equipment used in high pressure natural gas processing systems. For large scale low pressure flue gas CO₂ recovery, there is the opportunity to use “fit-for-purpose” equipment without the design constraints of those imposed in high pressure systems (such as the need for small cylindrical absorbers made of steel). Mitsubishi Heavy Industries (Mimura et al., 2000a) has investigated using very large square absorbers in a single train to recover 6000 tonne/day of CO₂ from flue gas. If a single absorption train rather than multiple trains is used in the baseline analysis, the absorber diameter and height would be 20 m and 35 m, rather than 5 m and 45 m respectively.

Assuming that the costs for the absorbers and regenerators are lower and a single absorption train is used with a new solvent with low regeneration properties, Figure 4-13 illustrates the extent of capture cost reductions that can be achieved. Lower costs for the absorbers/regenerators are assumed because the equipment is operating at low pressure and thus there is the opportunity to use less costly materials for the vessel walls. Additionally, lower unit costs could arise if a large number of installations are constructed around the world.

The transition from a multiple to a single train results in a cost reduction of 10% for MEA. This is because economies of scale can be exploited by building one single large absorption tower compared to multiple towers. If the unit cost for the absorbers and regenerators equipment is halved, the capture cost for MEA solvents can fall to almost A\$45/tonne CO₂ avoided. Figure 4-13 shows that the effects of combining lower equipment cost, higher efficiency packing materials, a low regeneration energy solvent and waste heat utilisation, can reduce the capture cost to A\$26/tonne CO₂ avoided. This is more than half of the base line cost estimated for MEA solvent.

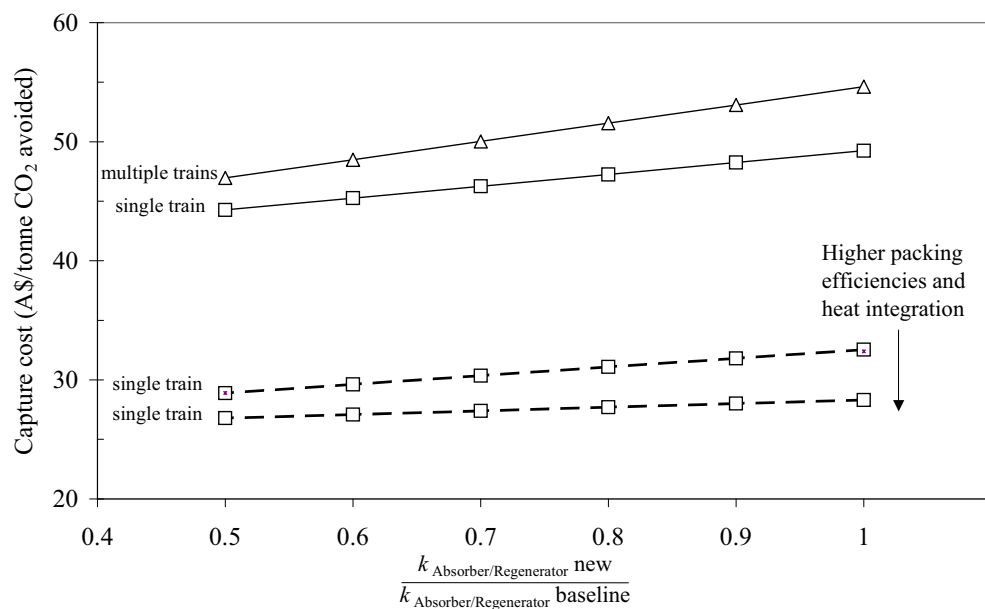


Figure 4-13 Effect of reducing unit production cost of absorbers/regenerators for MEA (—) or a new solvent (---), costed as multiple (Δ) or single (□) absorption train

The results of Figure 4-13 are only indicative of the possible general cost reductions that may be achievable due to lower equipment costs. Each site is unique and has specific costs depending on geographical locations, proximity to existing transport infrastructure and local labour costs. These factors will influence the exact cost reductions that may be achievable for specific case studies.

4.8 Conclusion

The cost of capturing CO₂ using commercially available solvents ranges from A\$42 to A\$54 per tonne CO₂ avoided. This cost reflects the high capital needed for large equipment and the high operating cost of regenerating the chemical solvent.

The sensitivity analysis in this chapter showed that the capture cost can be lowered to A\$25 to A\$30 per tonne CO₂ avoided by using in concert:

1. New solvents with a low heat of reaction, a large solvent working capacity, low degradation rates and losses, good absorption properties and is inexpensive;
2. High efficiency packing material which reduce the absorber and stripper size;
3. Lower equipment cost using low cost materials in a single absorption train; and
4. Integration of waste heat energy from the absorption process with the power plant to generate low-pressure steam for the stripper reboiler.

The results shows that by applying technology improvements, the reduced cost of capture using chemical absorption may make CCS a competitive greenhouse mitigation option based on the current carbon trading prices. However, the results of the analysis in this chapter are only indicative, and the modelling does not examine complex design configurations. Further process modelling, simulation and optimisation is required to confirm where reductions are achievable.

The results in this chapter are applicable to the cost of CO₂ capture using solvent chemical absorption. The following chapters investigate other capture technologies before a comparison of all technologies is presented in Chapter 8.

Chapter 5. GAS SEPARATION MEMBRANES

5.1 Overview

This chapter investigates the feasibility and cost-effectiveness of polymeric gas separation membranes technology for recovering CO₂ from post-combustion power plant flue gas. Initially the analysis examines the cost of CO₂ avoided using commercially available membranes. The later part of this chapter highlights the direction of future membrane development required to achieve capture cost reductions. To our knowledge, this is the first analysis of membrane technology for CO₂ capture under Australian conditions.

5.2 CO₂ capture using polymeric membrane technology

5.2.1 Introduction

Polymeric membranes have been used for many years for the separation of CO₂ from hydrocarbon mixtures in the natural gas and chemical industries. The application of membranes for CO₂ recovery from power plant flue gases could be of tremendous economic value. Their small footprint, lower upfront capital cost and ease of operation are features that make membranes an attractive processing option, especially for adding to the backend of the power plant cycle.

This aim of this chapter is to evaluate the economic cost of capturing CO₂ from a supercritical black coal pulverised power plant using commercially available membranes. Similar to the analysis for chemical absorption in Chapter 4, this chapter contains an evaluation of the limitations of current technology. In addition, a sensitivity analysis examining the effect of improvements in permeability and selectivity under new operating conditions is carried out. The purpose of the analysis is to highlight the direction of future membrane development in order to achieve deep cuts in the capture cost.

5.2.2 Membrane process

The process layout for membranes can involve a single stage membrane layout or a multi-stage membrane system. A single stage membrane layout (SMS) as shown in Figure 5-1 is the simplest arrangement. It comprises of only the flue (feed) gas, compressor and the membrane, which incorporates both the membrane housing pipe work and the membrane fibres. The permeate stream from this layout is the mixed gas stream that is compressed and N_2/O_2 off gas is separated from the product gas prior to pipeline transport and geological storage (Hendriks, 1994). SMS layouts have been shown by Feron (1992) to have the lowest compression costs, membrane area requirement, and operating costs of different membrane layouts. In practice, SMS layouts consist of many physical membrane modules operating in parallel. Conceptually, however, these modules operate as a single unit or stage and can be modelled and costed as a single unit.

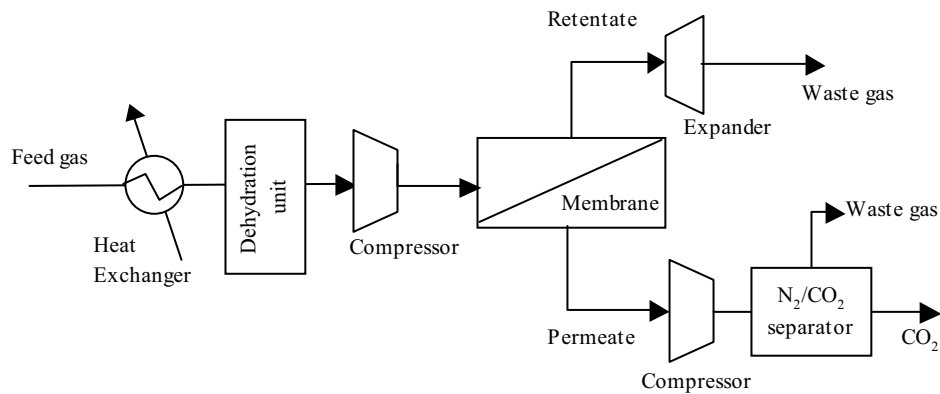


Figure 5-1 Single-stage membrane system (SMS)

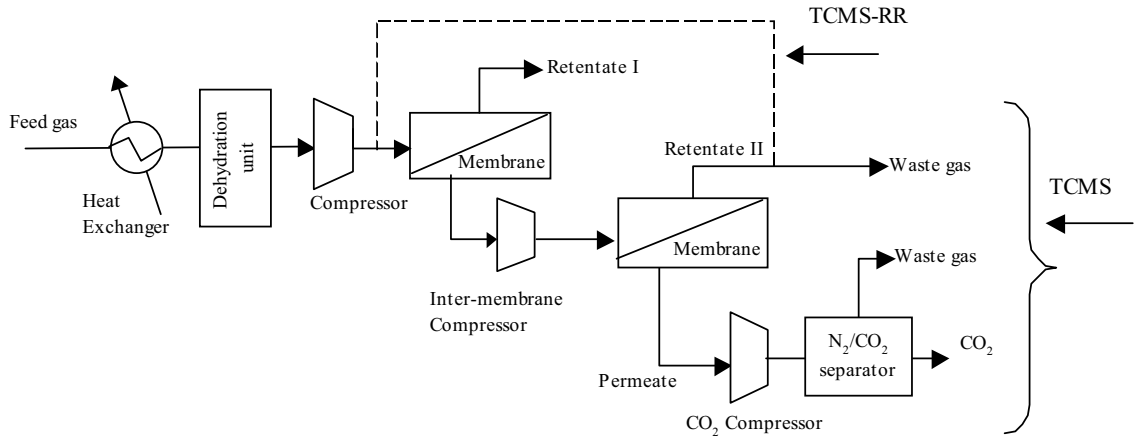


Figure 5-2 Two-stage cascade membrane systems (TCMS), the dotted line represents the retentate recycle for the TCMS-RR process

One of the consequences of using gas separation membranes is that the permeate or retentate stream contains other component gases as well as the desired CO_2 . To increase the concentration of CO_2 in the transport compressor, the stream from the first membrane that is enriched with CO_2 can be recompressed and then passed through a second membrane. This layout is referred to as a two-stage cascade membrane system (TCMS), shown in Figure 5-2. The TCMS layout incorporates a feed gas compressor, an intermediate compressor and two membrane stages. Recycle streams can also be included. Figure 5-2 also shows the configuration of a TCMS where the retentate from the second membrane is recycled with the feed gas stream into the first membrane (TCMS-RR). This configuration has the advantage of increasing the total amount of CO_2 recovered while still obtaining a high level of CO_2 purity (van der Sluis et al., 1992).

As outlined in section 3.3.2, if the CO_2 enriched gas stream has other component gases such as N_2 and O_2 , these can be separated from the CO_2 via vapour liquid separation. This is achieved using compression and cooling of the CO_2 enriched product gas to remove (or reject) the gaseous components and any CO_2 vapour. The cost and power consumption for this step is included as part of post-capture compression.

In this chapter, SMS and two-stage membrane systems (TCMS and TCMS-RR) process layouts are investigated.

5.2.3 Assumptions

Details of the economic assumptions and processing conditions of the flue gas used in this analysis are in Chapter 3 (section 3.5).

Table 5-1 outlines the processing and membrane characteristics for the baseline gas separation membrane system. A feed pressure of 15 bar with a permeate pressure of 1 bar was adopted to ensure sufficient driving force across the membrane is achieved. Properties of the Poly phenylene oxide (PPO) membrane manufactured by Delair (now Aquilo Gas Separation BV) were chosen, as it is a commercially available membrane with a moderate CO₂ permeability and reasonably good CO₂/N₂ selectivity value (Feron, 1992). It is assumed that the flue gas is dehydrated prior to entering the membrane module, as the baseline membrane selected for this analysis is sensitive to liquid water.

Table 5-1 Physical properties of commercially available membranes

Gas system		Multi-component
Feed pressure	Bar	15
Permeate pressure	Bar	1
Temperature	°C	35
Membrane		Poly (phenylene oxide) (PPO) (Feron, 1992)
Manufacturer		Delair
Cost	A\$/kg	65 (Feron 1992)
CO ₂ Permeability	Barrer	72
CO ₂ /N ₂ selectivity		19
CO ₂ /O ₂ selectivity		4

5.2.4 Membrane models

To mathematically model a single stage membrane, the flow models that can be used to describe the flow pattern within the membrane include the perfect mixing, one-sided mixing, cross flow and counter/co-current flow models.

The cross-flow model was selected for this study as it adequately describes polymeric gas separation membranes, regardless of the exact flow pattern generated in the membrane module (hollow fibre or flat sheet) (Pan, 1986). Numerous studies have been conducted to evaluate the different flow models. The majority of researchers have concluded that for a range of stage cut values (Shindo et al., 1985, Li et al., 1990,

Thundiyil and Koros, 1997, Hao et al., 2002, Marriott and Sorensen, 2003, Qi and Henson, 1997, Saltonstall, 1987), the results from the models for cross-flow and counter-current flow patterns are more efficient at removing the more permeable gas than either the co-current, one-sided mixing or perfect mixing models. In certain cases the cross-flow pattern can give greater separation because of better feed distribution.

The cross-flow model described by Shindo et al. (1985) was adopted in this study due to the ability of the model to be expanded for any number of gas components. As a result this model is advantageous over other cross flow models such as Pan and Habgood (1978), Li et al. (1990) and Hao et al. (2002). For the purposes of a pre-feasibility analysis, the model by Shindo et al. (1985) is also preferred due to the lower number of numerical calculations required, the ability to run both binary and multicomponent calculations, and the ability to obtain a direct solution by numerical calculations rather than through a trial-and-error procedure.

The key assumptions incorporated into the mathematical membrane model include the following:

- The rate of permeation of each component obey Fick's Law;
- The effective membrane thickness is constant along the length of the membrane where permeation occurs;
- All components in the feed gas stream are permeable;
- The permeability of a gas in a multi-component mixture is the same as for the pure gas and is independent of pressure;
- Negligible pressure loss of the feed and permeate gas streams occur along the membrane.

Cross flow membrane model

For a single stage membrane with a single type of membrane, Equations 5.1 and 5.2 can be solved for all unknown mole fractions on the high pressure side (x_i), the membrane area (A_{membrane}) and the mole fractions on the low pressure side (y_i) with changes in the value of the stage cut (θ) from 0 to 1.

$$\frac{ds}{d\theta} = \frac{1}{\sum_{k=1}^n a_k (x_k - \gamma y_k)} \quad (5.1)$$

$$\frac{dx_i}{d\theta} = \frac{a_i (x_i - \gamma y_i) - x_i \sum_{k=1}^n a_k (x_k - \gamma y_k)}{(1 - \theta) \sum_{k=1}^n a_k (x_k - \gamma y_k)} \quad (5.2)$$

where:

$$s = A_{\text{Membrane}} \left(\frac{P_m^*}{\delta} \right) \frac{P_f}{F_f} \quad \gamma = \frac{P_p}{P_f}$$

$$\theta = \frac{F_p}{F_f}, F_r = F_f - F_p \quad a_i = \frac{1}{\alpha_{\text{CO}_2/i}} = \frac{P_i^*}{P_{\text{CO}_2}}$$

For a specified CO₂ recovery rate (n_{CO_2}), the stage cut can be determined (θ), and thus the flowrates of the retentate (F_r) and permeate (F_p) streams, and mole fractions of the gas components in both the retentate (x_i) and permeate (y_i) streams can also be calculated.

$$\theta = \frac{n_{\text{CO}_2}}{y_{\text{CO}_2} F_f} \quad (5.3)$$

In modelling two or more membrane stages, the mass balance for the whole system consists of the sum of balances calculated separately for each individual membrane unit.

Energy consumption

The total energy consumption for the membrane system (W_{Membrane}) can be approximated by combining the total power consumed by the feed gas compressor, product CO₂ compressor and any work required for dehydration. If exiting lean gas is expanded, the energy gained from the expansion is used to offset some of the energy consumed by the system. This is represented as:

$$W_{\text{Membrane}} = W_{\text{compressor}} + W_{\text{Dehydration}} - W_{\text{Expansion}} \quad (5.4)$$

The equations for determining the work for compression, expansion and dehydration have been described in section 3.4.1.

5.2.5 Model parameters and outputs

In the CO₂ membrane model, the user configures and selects the pressure for the feed, retentate and permeate streams. They can also select the process layout, choosing a SMS, TCMS or TCMS-RR. The membrane material based on characteristics such as CO₂ permeability and selectivity values can also be specified.

As discussed in section 3.3.3, the model outputs used to assess the performance of membrane technology for CO₂ capture include:

1. The purity of the CO₂ in the product gas (either in the retentate or permeate streams depending on the membrane properties);
2. The recovery rate of the CO₂ from the feed gas;
3. The total flowrates of the permeate and retentate streams;
4. The total membrane area; and
5. The total energy penalty.

5.3 Baseline results for commercial membranes

The baseline economic cost for recovering CO₂ from a coal fired power plant flue gas using commercial PPO gas separation membranes is shown in Table 5-2.

Table 5-2 CO₂ capture costs of single and two-stage membrane systems

	This study			Hendriks (1994)	Feron (1992) (IEA GHG)
	SMS	TCMS	TCMS-RR	SMS	SMS
Cost year	2006	2006	2006	1990	1992
Overall CO ₂ recovery (%)	90	90	88	90	80
CO ₂ purity in recovered stream (%)	43	72	76	< 53	50
Energy penalty (kJ/kg CO ₂ captured)	2374	2587	2550	--	--
Energy penalty (%)	49	54	53	--	31
Capital investment for capture plant only A\$/kW, US\$/kW	1850 1325	1833 1315	1785 1275		
Total capital investment A\$/kW, US\$/KW	2650 2030	2755 2130	2680 2070		-- 1470
Capture Cost A\$/tonne CO ₂ avoided US\$/tonne CO ₂ avoided	93 80	103 90	102 89	-- 68	-- 45

The capture cost of CO₂ avoided for a single stage membrane system (SMS) is A\$93/tonne CO₂ avoided, and for the two-stage systems are A\$102 and A\$103 per tonne CO₂ avoided. The cost using a SMS is lower than for two-stage membrane systems, even though the concentration of the CO₂ in the permeate stream is much higher in the two-stage systems. This cost is approximately 10% lower because of the lower energy penalty of the SMS. The two-stage system requires more energy because an intermediate compressor is needed to re-compress the permeate stream from the first membrane in order to provide a driving force across the second membrane. The total capital investment for the capture plant is similar for all three systems.

The very large energy penalties associated with CO₂ capture using membrane technology is a result of the substantial amount of energy needed for compression. From Figure 5-3, it can be seen that the energy required by all three membrane systems to compress the flue gas from atmospheric pressure to a membrane of 15 bar accounts for the majority of the energy penalty. The high energy required reflects the need to compress the exceptionally large feed gas flowrate. In addition, the need to compress the CO₂ permeate stream to the transport pressure is also relatively large, accounting for 22% to 31% of the total energy. The energy for CO₂ product compression is considerable because of the large flowrate of the stream, which contains other component gases such as N₂ and O₂. The presence of these gases increases the flow-

rate. Thus a much larger post-capture compressor, consuming a greater amount of energy, is required. A part of the total energy requirement is provided through the expansion of the retentate and off-gas waste streams.

For all three membrane systems, the large pre- and post- separation compressors account for approximately 60% of the total equipment cost as illustrated in Figure 5-4. The other major equipment costs include general costs for non-specified equipment such as storage tanks and pumps, and for the FGD system. The membrane unit comprises only a small component of the cost at approximately 5% of the total costs.

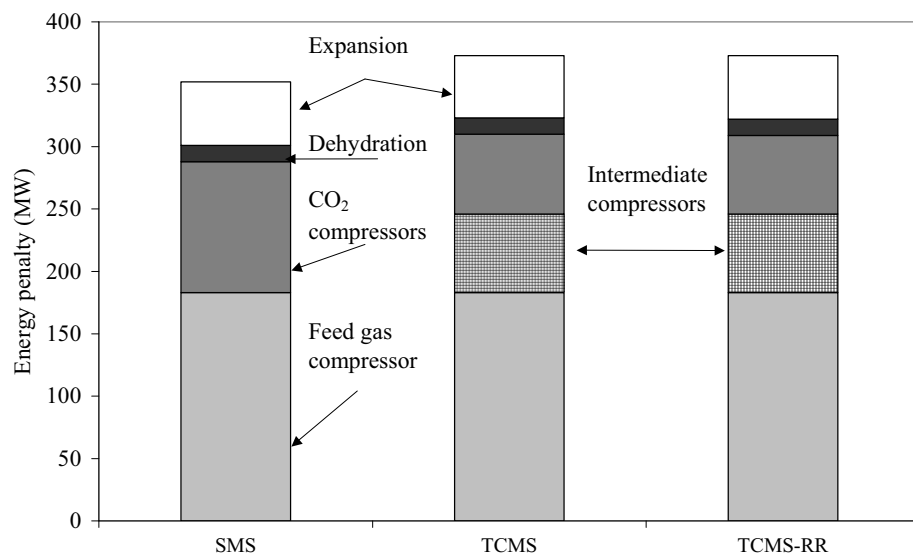


Figure 5-3 Total energy requirement for SMS, TCMS and TCMS-RR layouts

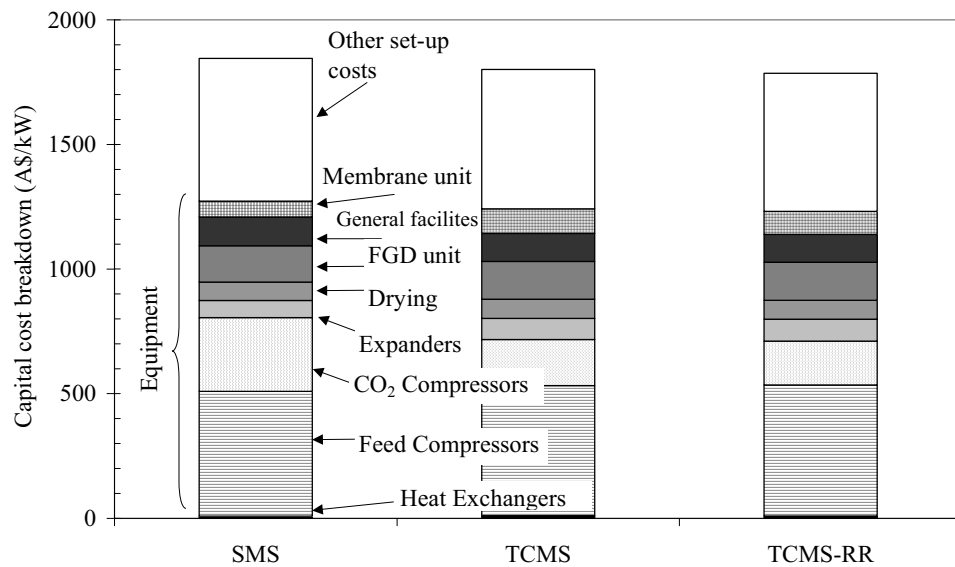


Figure 5-4 Breakdown of the capital investment for SMS, TCMS and TCMS-RR layouts

5.3.1 Comparison with other studies

Table 5-2 also compares the capture cost for this study with the most recent gas separation membrane techno-economic assessments. The comparison is for the SMS process layout, as this was the process layout used in the published literature. For CO₂ capture using gas separation membranes, the capture cost reported in this study is US\$80/tonne CO₂ avoided. In previous literature, Feron (1992) undertaking a study for the IEA GHG reported a capture cost of US\$45/tonne CO₂ avoided, while Hendriks (1994) reported costs of US\$68/tonne of CO₂ avoided. The lower cost reported by Feron (1992) is a result of the fact that the study only considered the change in CO₂ emissions at the power plant and neglected to include the costs and energy penalty for post-separation CO₂ compression. Thus his total capital investment and energy penalty is significantly less than for this study. If compression power losses and costs were taken into account for the Feron (1992) study, the capture cost would increase to US\$65/tonne CO₂ avoided. In comparison, the capture cost for the membrane system studied by Hendriks (1994) is closer in value to this study because that study also includes the costs for CO₂ transport compression to 80 bar.

The main cost differences in the three studies arise primarily because a different feed pressure was adopted and a different membrane was used (as in the study by Hendriks

(1994)). The literature studies were also carried out approximately 13 to 15 years prior to this study, with different economic assumptions, which is also likely to have an impact on the reported costs. For all three studies, the purity of the CO₂ in the permeate is similar, with values generally less than 50%.

5.3.2 Changes in capture cost with increasing CO₂ recovery

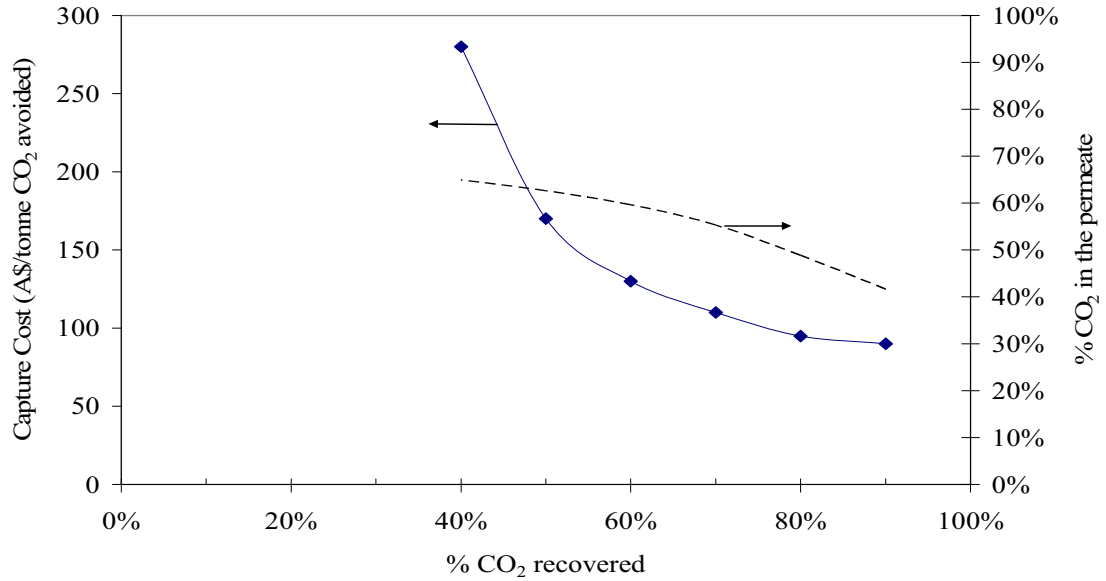


Figure 5-5 Change in capture cost (♦) and permeate CO₂ purity with changes to the percentage of CO₂ recovered

Figure 5-5 shows for the baseline membrane, the changes in capture cost and CO₂ purity in the permeate stream as the CO₂ recovery increases from 50% to 90%. With increasing CO₂ recovery, both the purity of the CO₂ in the permeate stream and the cost of capture decreases. From equation 3.10, by increasing the amount of CO₂ recovered, the amount of CO₂ avoided increases. Similarly, from Fick's Law

$$J_i = \frac{P_i^*}{\delta} A_{mem} (x_i P_f - y_i P_p) \quad (5.5)$$

increasing the amount of CO₂ recovered will increase the membrane area and decrease the CO₂ purity in the permeate, which has the effect of increasing the total capital cost. However, because the change in the amount of CO₂ avoided exceeds the increase in the capital cost, the overall capture cost decreases.

5.4 Recent membrane development

Previous research undertaken by van der Sluis et al. (1992) and Feron et al. (1992) concluded that the main drawbacks of CO₂ capture using gas separation membranes was because of the low permeability and selectivity of commercially available membranes. The baseline cost of CO₂ capture using the PPO polymeric membrane was based on the original investigation by Feron in 1992. Since that time, significant research and development has been undertaken. As discussed in Chapter 2, many new membranes have been developed with higher CO₂ permeability and selectivity values. The following section of this chapter will investigate the effect on capture cost of changes in membrane characteristics. The analysis is for the SMS process layout as it is the most simplified process configuration and it has the lowest capture cost.

Selecting the development membranes

Using a polymer membrane database developed by the A.V. Topchiev Institute of Petrochemical Synthesis (TIPS), a selection of development membranes was compiled for an economic analysis. The TIPS database contains an up-to-date collection of details about research-based membranes. The membrane selection criterion for the cost analysis was that the new membrane must exceed the traditional restrictions of the Robeson diagram. In 1991, Robeson (1991) showed that for polymer membranes, a correlation exists between the permeability of a membrane and the selectivity of gas pairs. Thus, as the permeability of a component gas in a membrane increases, then the selectivity of that gas compared to the other gas decreases. The membranes selected for cost analysis from the TIPS database were all above the traditional Robeson upper limit for the CO₂/N₂ gas pair. Table 5-3 outlines the type and characteristics of the membranes extracted from the database and the associated capture cost and purity of CO₂ in the permeate stream.

Table 5-3 Properties of the development membranes extracted from TIPS database

Study	Membrane type	CO ₂ Perm. (Barrer)	Selectivity		% CO ₂ in permeate	Mem-brane area x10 ³ (m ²)	Capture cost (A\$/t CO ₂ avoided)
			CO ₂ /N ₂	CO ₂ /O ₂			
This study	PPO	72	20	6	43	200	93
Fritsch and Peinemann (1995)	PAI	40	41	6.5	56	439	85
	PAI	32	39	6	55	541	89
	PAI	55	36	7	54	312	84
	PAI	74	33	7	53	228	83
	PAI	111	36	7	54	155	80
Al-Masri et al. (2000)	PI	200	23	6	47	73	85
Matsui et al. (1998)	PI	854	2.3	6	19	9	643
Tanaka et al. (1992)	PI	431	14	4	39	33	100
Dorkenoo et al. (1998)	PDCN	111	13	4	38	119	106
Bondar et al. (2000)	Co-polymer	120	51	--	60	156	75
	Co-polymer	66	56	--	62	290	78
Yampolskii (2006)	PI	210	42	9.5	57	86	76

The cost of capturing CO₂ from post-combustion flue gas using the selected development gas separation membranes range from A\$75/tonne CO₂ avoided to over A\$650/tonne CO₂ avoided. The majority of the capture costs fall below the baseline cost of A\$93/tonne CO₂ avoided, however the three cases that do not include the polyimides developed by Matsui et al. (1998) and Tanaka et al. (1992), and the poly(n-decylnorbornene) chain membrane developed by Dorkenoo et al. (1998). These three development membranes all have exceptionally high CO₂ permeabilities of 110 (Dorkenoo), 400 (Tanaka) or 800 (Matsui) Barrer, but the CO₂/N₂ selectivity is very low with the highest at a value of 14. As a result, the purity of CO₂ in the permeate stream is very low, with values of 39%, 38% and 19% respectively. The increased permeability reduces the amount of required membrane area significantly compared to the baseline PPO membrane, thus reducing the membrane price. However as noted in Figure 5-4 membranes account for less than 5% of the total capital investment. The lower purity permeate requires a much larger CO₂ compressor and, thus increases the total compressor costs and energy consumption (the greatest proportion of both capital and operating costs). As a result the capture cost for these membranes is higher than for the commercial PPO membrane.

The development membrane that results in the most significant cost reduction is the 55PEO/PA7 co-polymer block membrane developed by Bondar et al. (2000). Co-polymer membranes utilise the benefits of different polymer structures to enable improved permeability coupled with improved CO₂/N₂ selectivity. Compared to the baseline PPO membrane, the membrane area of the co-polymer is reduced from approximately 200x10³ m² to 160x10³ m². The CO₂ purity in the permeate stream is also improved from 43% to 60%. The smaller membrane and enriched permeate result in a lower capital and capture costs.

5.5 Reducing the capture cost

The development of new membranes with better CO₂ permeability and higher CO₂/N₂ selectivity has generated possible cost savings of up to 20% compared to the cost of using commercially available PPO membranes. Although the cost reductions are beneficial, the total cost of using gas separation membranes is still higher than the cost compared to other CO₂ capture technologies such as chemical absorption (Chapter 4) or current carbon prices (Chapter 1). Improving membrane characteristics in isolation without improving other parameters such as the operating conditions does not result in achieving significantly large cost reductions.

As detailed in section 5.3, the major capital and operating costs arise due to the requirement to compress the large flowrate for the feed flue gas, coupled with the need to compress a low purity CO₂ product stream. It is reasonable to assume that by minimising these two costs, significant reductions in the capture costs could be achieved. The following section of this chapter examines the effect on capture cost by changing the operating conditions and characteristics of the membrane system. It determines what changes are required to achieve significant cost reductions and the extent of the savings.

The economic assumptions of the above baseline economic evaluation are used as the basis for the sensitivity analysis, the membrane price is assumed to be A\$65/m² (Table

5.1) and remains constant. In this analysis it is assumed that improvements in either the CO₂ permeability or the CO₂/N₂ selectivity does not affect the other.

5.5.1 Pressure differential

As shown previously, the largest contributing factor in the capital and operating costs is the energy required to compress the inlet feed gas to a suitable pressure. The following analysis examines whether or not cost reductions could be achieved by decreasing the pressure of the membrane feed, and if so by how much.

Figure 5-66 illustrates the changes in capture cost for a SMS where the pressure ratio across the membrane is increased by reducing the feed gas pressure while the permeate pressure remains constant at 1 bar. The results show that by decreasing the feed gas pressure from 15 bar to 8 bar, the capture cost decreases from A\$93/tonne CO₂ avoided to A\$90/tonne CO₂ avoided, or a cost reduction of less than 5%. This is not a very significant cost reduction. In addition, if the feed pressure is reduced to below 6 bar, the capture cost increases to over A\$100/tonne CO₂ avoided.

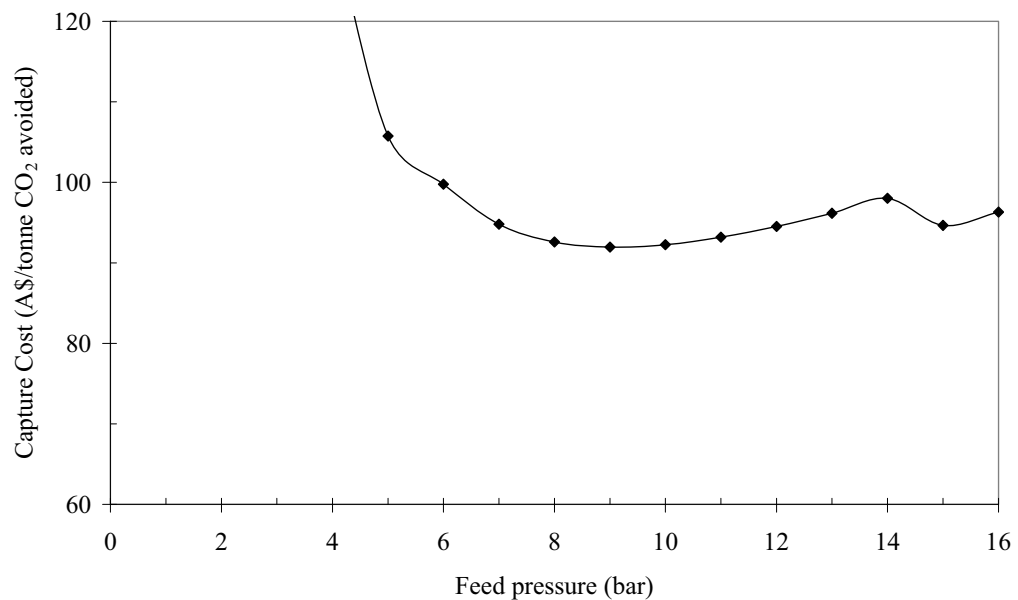


Figure 5-6 Capture cost as a function of feed pressure for SMS layout

From Fick's law, as the feed pressure decreases (P_f), the driving force across the membrane also decreases. Therefore, to obtain the same CO₂ recovery from the feed gas, the membrane area must increase. Furthermore, by increasing the pressure ratio (permeate pressure over feed pressure), the CO₂ concentration in the permeate stream also decreases, and thus a larger post-separation CO₂ compressor is required. As the feed pressure decreases, the cost of the feed compressor also decreases. However, the cost reductions gained are only marginally better than the increased costs for the larger membrane area and the larger CO₂ compressor. Therefore, only a small decrease in capture cost is obtained, as shown in Figure 5-6.

For feed gas pressures lower than 8 bar, the costs for the large membrane area and the large CO₂ compressor required exceed any costs benefits gained from reducing the size of the feed gas compressor. As a result, the overall capital, operating and capture costs increases with decreasing feed pressure.

Figure 5-7 also shows that although the contribution of the feed compressor may decrease with decreasing feed pressure, the overall cost contribution of compressors (above 40%) is still high because of the increase in the CO₂ compressor. The CO₂ capture cost using gas separation membrane technology will remain high as long as the compressors continue to dominate the overall cost.

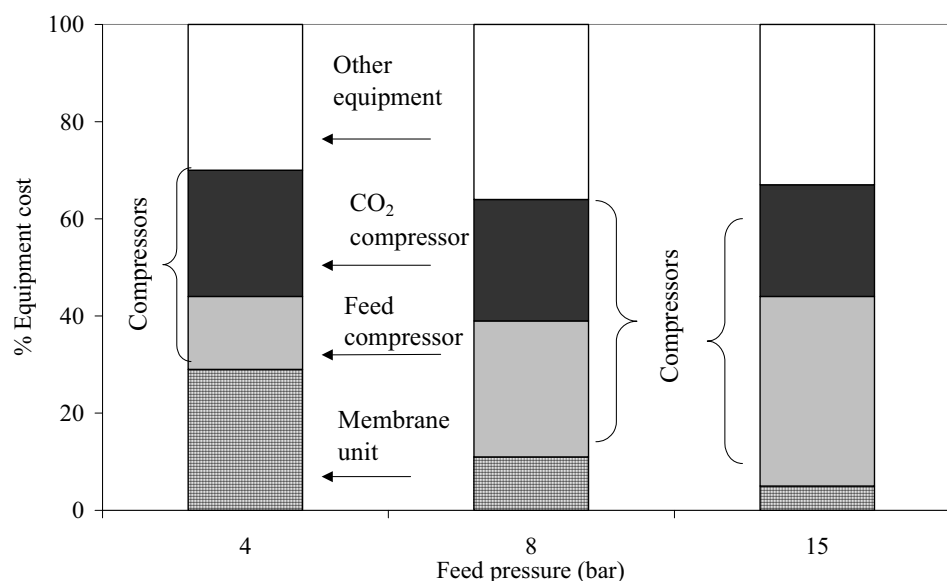


Figure 5-7 Breakdown of the major equipment costs for the SMS layout at three feed pressures: 4, 8 and 15 bar

5.5.2 Vacuum membrane systems

In the previous analysis, it was assumed that the permeate pressure is set at atmospheric conditions, and the feed gas has to be compressed to achieve a driving force. Thus P_p is fixed, while P_f is manipulated to provide the necessary flux.

As discussed in Chapter 2, in pressure swing adsorption (PSA) systems, the driving force is also the pressure differential between the adsorption (feed) and evacuation/desorption steps. Initial investigations into the economic feasibility of PSA systems for CO₂ capture also examined process configurations where the feed gas is compressed to a high pressure for adsorption, while the desorption stage is set at atmospheric conditions (Monenco, 1992). Later research work has investigated the use of vacuum conditions for the desorption stage to optimise the process. Similarly, a vacuum process could also potentially be applied to gas separation membranes.

For gas separation membrane systems, the pressure in the permeate stream would be set below atmospheric, while the feed gas pressure would be set at a value close to atmospheric. In this configuration, to obtain the necessary flux of CO₂ across the membrane, P_p rather than P_f is manipulated.

Configurations of polymeric gas separation membranes where the permeate stream is under vacuum conditions has been investigated by researchers such as Bhide and Stern (1991) in the early 1990's. The research into vacuum permeate pumping investigated methods to enhance O₂ recovery from air. Bhide and Stern found that the optimum configuration for O₂ recovery was a single membrane with vacuum pumping of the permeate stream. The feed gas was set at 1.1 bar, with a permeate pressure of 0.25. The commercial viability of this configuration has been demonstrated by Kimura and Browall (1986). In 1986 a demonstration plant recovering 28,300 L/min of O₂ under vacuum conditions was successfully operated for a six-month period.

Vacuum membrane distillation has also been successfully implemented for the extraction of dissolved gases and the selective removal of volatile solutes from aqueous streams (Bandini et al., 1997). In this process, the distillate operates under vacuum conditions to enhance the recovery of volatile gases.

Two key literature sources have been cited where CO₂ has been recovered under vacuum conditions.

Work undertaken by Ge et al. (2001) investigated CO₂ capture using an enzyme-based facilitated transport membrane to recover CO₂ from a respiratory gas stream in Advance Life Support applications. This research work was tested experimentally to inspect the performance of the membrane under vacuum conditions. They found that permeate vacuum conditions enhanced the overall recovery of low concentration CO₂.

In addition, Hagg and Lindbrathen (2005) have investigated CO₂ capture from a natural gas fired power plant flue gas. This study also used a facilitated transport membrane, although the analysis was simulated rather than tested experimentally. The results from the work undertaken by Hagg and Linbrathen (2005) showed that due to the low concentrations of CO₂ in the flue gas (typically less than 4%), successful recovery of CO₂ required both a high pressure feed of 4 bar in addition to the vacuum pumping of the permeate stream (0.1 bar).

No economic evaluations have yet investigated the cost of CO₂ recovery under vacuum conditions.

The successful application of vacuum permeate pumping using polymeric gas membranes for O₂ recovery, the successful experimental work by Ge et al. (2001) for CO₂ recovery and experimental work in vacuum membrane distillation suggests that permeate vacuum pumping could potentially be a viable option for CO₂ recovery.

5.5.3 Baseline results for vacuum permeate conditions

Table 5-4 outlines the capture cost for the baseline PPO membrane with vacuum permeate conditions. The analysis is for a single stage and two-stage membrane system with and without retentate recycle.

Figure 5-8 shows the process flow diagram of a SMS with vacuum permeate pumping. The figure shows that in this process layout, the membrane feed pressure of 1.5 bar is obtained using a gas blower rather than a compressor. It is assumed in the modelling that membrane feed pressures of 1.5 bar is can be obtained via gas blowers, but higher pressures are obtained using a compressor (Chapter 3). Vacuum conditions are assumed to be obtained through positive displacement pumps, which have operating pressures down to 0.04 bar (Everest, 2005). Taking into account leaks in the system, the minimum operating pressure possible is assumed to be 0.05 bar. However, a permeate pressure of 0.08 bar is selected to account for any further leaks in the systems and to obtain a pressure ratio of 0.05.

Table 5-4 Comparison of capture cost for membrane technology under vacuum conditions

	High pressure (HP) feed SMS	SMS Vacuum	TCMS Vacuum	TCMS-RR Vacuum
CO ₂ purity in permeate (%)	43	45	74	77
Energy penalty (%)	49	27	32	31
Capital investment for capture plant only (A\$/kW) (US\$/kW)	1850 1325	1260 983	1490 1163	1380 1080
Capture Cost (A\$/tonne CO ₂ avoided) (US\$/tonne CO ₂ avoided)	93 80	65 54	87 72	82 68

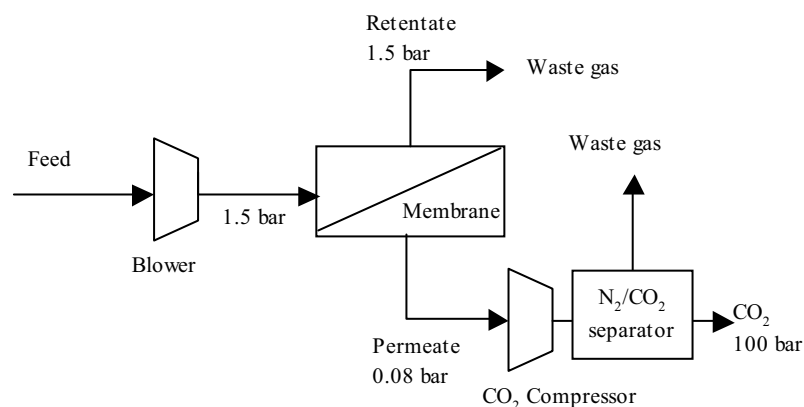


Figure 5-8 Simplified diagram of SMS with permeate vacuum conditions

Using vacuum permeate conditions, the cost for capturing CO₂ using gas separation membranes reduces significantly (Table 5-4). For the SMS, the cost reduces from A\$93 to A\$65 per tonne CO₂ avoided, or by 35%. For both two-stage membrane systems (with and without retentate recycle), the capture cost is also lower than the high pressure feed by approximately 15%. This cost reduction is the result of removing the feed gas compressor.

Figures 5-9 and 5-10 shows the breakdown of the equipment and operating costs for the three membrane systems with vacuum permeate conditions.

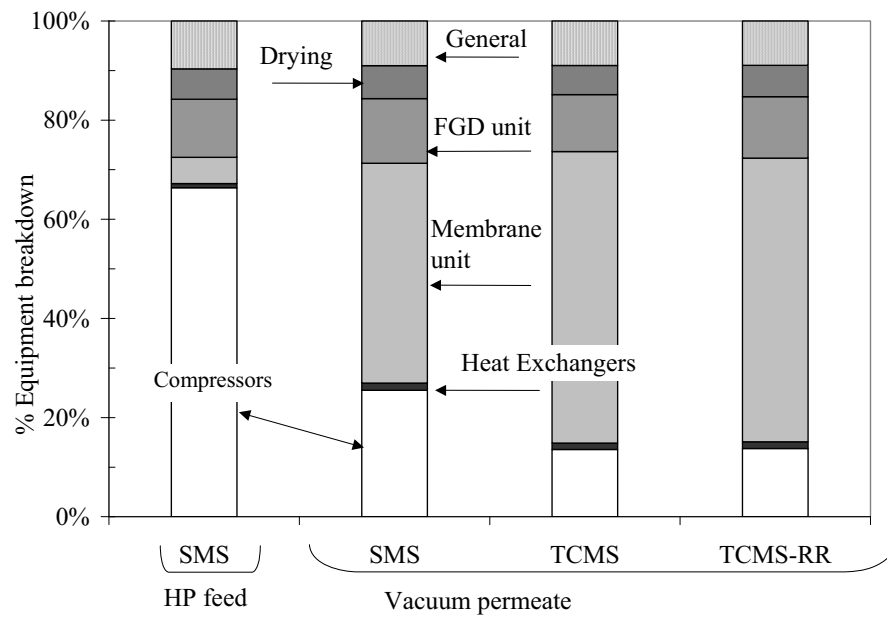


Figure 5-9 Breakdown of equipment costs for a high pressure feed and vacuum membrane systems

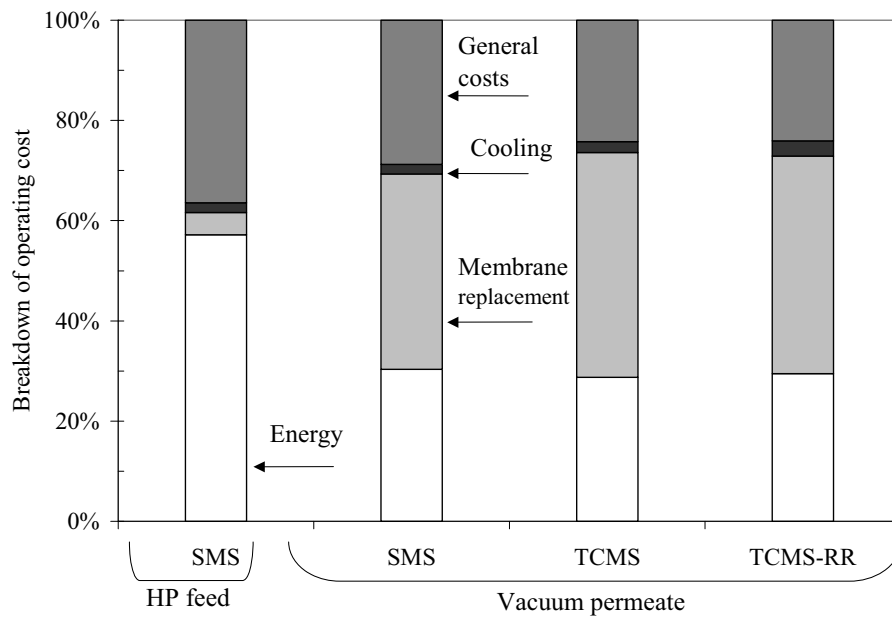


Figure 5-10 Breakdown of operating costs for a high pressure feed and vacuum membrane systems

Transitioning from a process that uses a high pressure feed to one that utilises vacuum permeate conditions reduces the cost of capture using membrane technology. However, the costs are still high. The lowest estimate is A\$65/tonne CO₂ avoided, this is much higher than the cost of capture using alternative technologies such as MEA solvent

absorption (Chapter 4). To make membrane technology a competitive CO₂ capture option, further cost reductions are necessary.

Examining the results of Figures 5-8 and 5-9, the costs for the membrane unit and for replacing the membranes emerges as the largest cost item. The CO₂ compressor is the second largest. Together, these two items account for approximately 70% of the total equipment and operating costs, and would likely influence the cost effectiveness of the capture system. Therefore the cost capture could be lowered by:

1. Reducing the cost of the membrane and/or decreasing the required membrane area; and
2. Reducing the cost of the CO₂ compressor by increasing the purity and decreasing the flowrate of the permeate.

These opportunities are explored in greater detail in the following sections

5.5.4 Reducing the costs of membrane units

Effect of membrane prices

Figure 5-11 illustrates the impact of membrane prices on the capture cost for a SMS operating with a high pressure feed and for membrane systems operating under vacuum permeate conditions. The analysis is for the baseline PPO membrane.

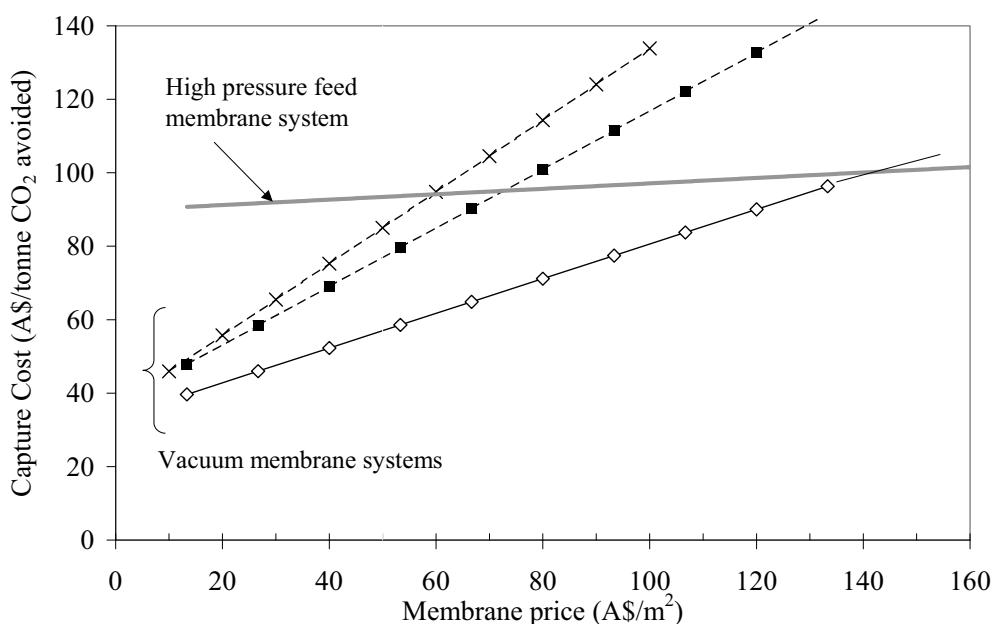


Figure 5-5 Capture cost as a function of membrane price for the high pressure feed SMS (—), and vacuum membrane systems: SMS ($\diamond$), TCMS ($\blacksquare$) and TCMS-RR ($\times$)

For the membrane with the high pressure feed, because the membranes account for such a small component of the overall capital cost (Figure 5-4), reductions in the price of the membrane do not have a significant effect. In comparison, for the membranes with vacuum permeate conditions, reducing the price from the baseline of \$A67/m² to \$A15/m², the capture cost decreases to almost A\$40/tonne CO₂ avoided. However, for these systems if the membrane price is very high (at values above A\$150/m²) the results in Figure 5-5 indicate that it would be more economical to operate with a high pressure feed than under vacuum permeate conditions.

Effect of membrane permeability

The CO₂ permeability influences the rate at which the membrane removes the CO₂ from the feed gas. For a fixed flux of CO₂ across the membrane, increasing the membrane CO₂ permeability will decrease the required membrane area and thus reduce the capital cost. Figure 5-62 shows the changes in capture cost for the vacuum membrane systems as the CO₂ permeability value increases from 10 to 1000 Barrer, assuming the membrane cost is constant. The CO₂/N₂ selectivity of the membrane is assumed to be constant at 20 and is not affected by the improvements in the permeability.

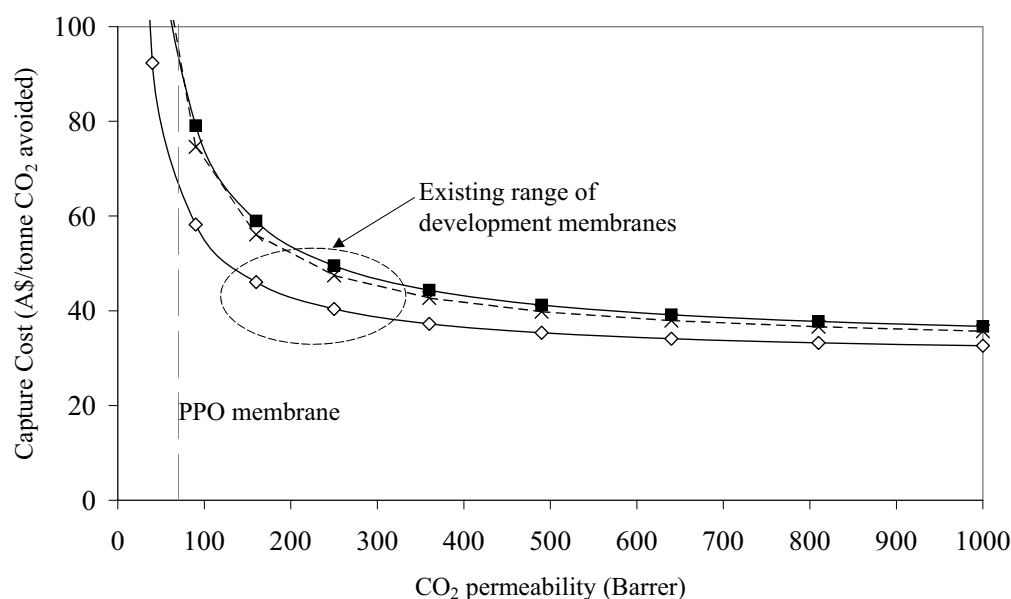


Figure 5-6 Capture cost as a function of CO₂ permeability for the vacuum membrane systems: SMS (◇), TCMS (■) and TCMS-RR (×)

As shown in Figure 5-62, increasing the membrane CO₂ permeability from 70 Barrer to 350 Barrer reduces the capture cost from A\$60 to A\$35 per tonne CO₂ avoided. This is because the membrane area is almost five times smaller and the capital cost is 50% lower. However, for CO₂ permeability values greater than 500 Barrer, the capture cost does not decrease significantly because the observed change in membrane area is not very large beyond this point.

The results also show that by using the characteristics of the development membranes outlined in Table 5-3, coupled with vacuum conditions, a capture cost of A\$40/tonne CO₂ avoided or less could be obtained.

5.5.5 Reducing the CO₂ compressor costs

Understanding the parameters that effect CO₂ purity

Changing the configuration of the membrane system into one which utilises vacuum permeate conditions significantly reduces the capture cost, especially for the SMS configuration. However, one remaining disadvantage is that the purity of the CO₂ in the permeate stream is still low (less than 50%). For gas separation membranes to be

competitive against other CO₂ capture technology options such as chemical absorption and cryogenic distillation where the CO₂ purity is high (greater than 98%), the ideal membrane system would also produce a CO₂ product stream with high purity.

Using Fick's law, if we compare the flux of one component gas (say CO₂) to another gas (N₂) then the ratio of the fluxes for the two gases is:

$$\begin{aligned} \frac{n(\text{CO}_2)}{n(\text{N}_2)} &= \frac{P_{\text{CO}_2}^* \left(x_{\text{CO}_2} - \frac{P_p}{P_f} y_{\text{CO}_2} \right)}{P_{\text{N}_2}^* \left(x_{\text{N}_2} - \frac{P_p}{P_f} y_{\text{N}_2} \right)} \\ &= \alpha_{\text{CO}_2/\text{N}_2} \frac{(x_{\text{CO}_2} - \gamma y_{\text{CO}_2})}{(x_{\text{N}_2} - \gamma y_{\text{N}_2})} \end{aligned} \quad (5.6)$$

Equation 5.6, shows that the ratio of the flux of CO₂ to N₂ (or the purity of CO₂ in the permeate stream), can be increased by 1) increasing the CO₂/N₂ selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) and/or 2) decreasing the pressure ratio (γ).

Figure 5-13 summarises the effect on the permeate CO₂ purity with changes in the CO₂/N₂ selectivity at different pressure ratios for the SMS process layout. At a high pressure ratio of 0.1, a selectivity value of 1000 is required to obtain 90% CO₂ in the permeate stream. At lower pressure ratios, where there is a greater difference between the pressure in permeate and feed streams, a CO₂ purity of 90% in the permeate stream can be obtained with selectivity values and pressure ratio combinations of 200/0.01, 250/0.03 and 350/0.05 respectively.

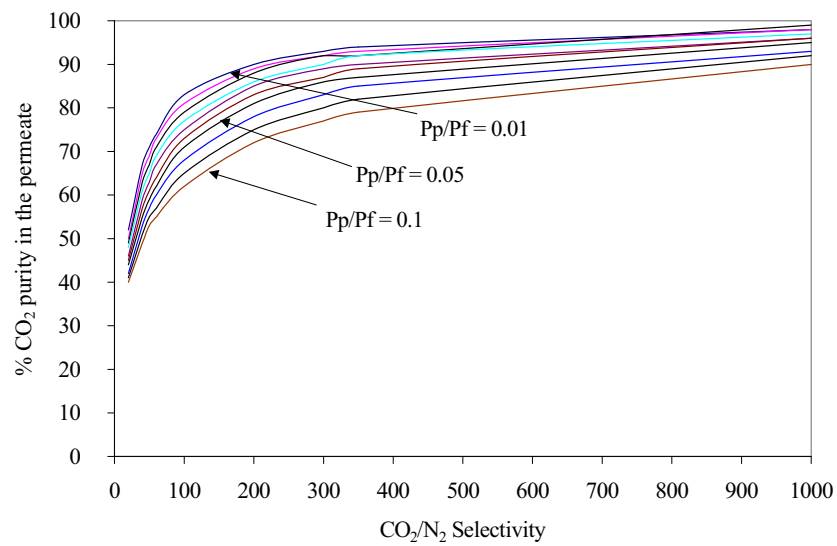


Figure 5-7 Effect on permeate CO₂ purity with changes in the CO₂/N₂ selectivity at pressure ratios of 0.01 to 0.1 (in 0.01 increments)

For the two-stage membrane systems, Figure 5-14 shows the relationship between the CO₂ purity in the permeate stream and pressure ratio/selectivity combinations. At a pressure ratio of 0.05, 0.07 or 0.1, 90% CO₂ purity can be achieved with a selectivity of approximately 40 for both of the two-stage process layouts. Increasing the membrane selectivity value beyond 40 does not significantly improve the CO₂ purity. This is because the two-stage configurations have been designed to obtain a high CO₂ purity product. Thus, improvements in selectivity values do not produce noticeable changes in the concentration of CO₂ in the permeate stream.

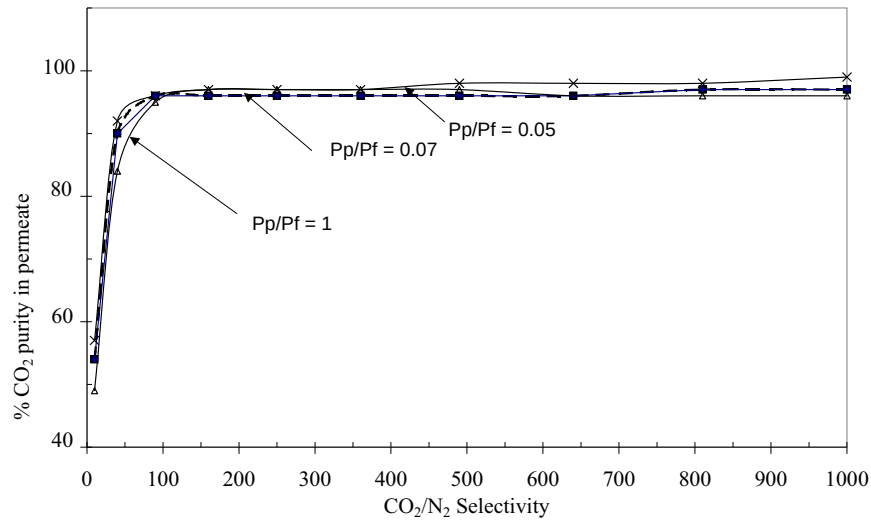


Figure 5-8 Effect on permeate CO₂ purity with increasing CO₂/N₂ selectivity for the two-stage membrane layouts

Effect of CO₂ selectivity

Figure 5-15 illustrates the changes in capture cost with increasing CO₂/N₂ selectivity for the high pressure feed single stage membrane system, and both the vacuum permeate based TCMS and SMS. It is assumed in this analysis that as the selectivity of CO₂ compared to N₂ is improved, the selectivity of CO₂ compared to O₂ also improved. The new CO₂/O₂ selectivity is obtained by dividing the CO₂/N₂ selectivity by a factor of five. This value is selected following the work of Alentiev and Yampolskii (2000), which shows that the relative permeability coefficients of N₂ compared to O₂ is five in the majority of glassy polymer membranes. The pressure ratio for all systems is approximately 0.05 and the CO₂ permeability is assumed constant at 70 Barrer.

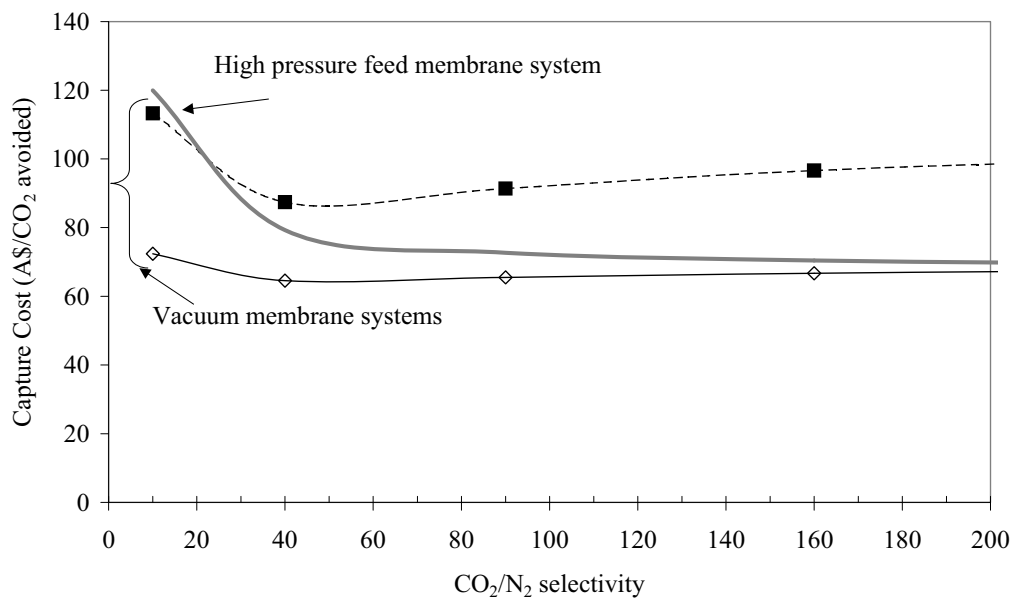


Figure 5-9 Capture cost as a function of CO₂/N₂ selectivity for the high pressure feed SMS (—) and vacuum membrane systems: SMS (◇) and TCMS (■)

The results show that as the CO₂/N₂ selectivity increases, the capture cost decreases for all systems from a value of 10 to 40. For the high feed pressure system, the cost continues to decrease. However, for the vacuum permeate membrane systems the cost begins to increase for selectivity values beyond 40.

From Fick's law, as shown in Equation 5.5, increasing the selectivity increases the mol fraction of CO₂ in the permeate (y_{CO_2}) and decreases the mol fraction of CO₂ in the retentate (x_{CO_2}). Consequently the driving force across the membrane is also reduced. To obtain the same amount of CO₂ recovered; that is the same number of mols of CO₂ removed, the membrane area and thus membrane cost increases. On the other hand, as the CO₂ purity of permeate stream increases, the flowrate of the permeate decreases resulting in a smaller CO₂ compressor. It is the balance between the cost savings generated by the CO₂ compressor and the increase in membrane costs that influence the cost trends.

For the high pressure feed membrane system, increasing CO₂/N₂ selectivity decreases the costs of CO₂ compressor, although the cost of the membranes increases. However, as shown in Figure 5-4, because membranes account for only a small component of the

capital cost and the CO₂ compressor accounts for a much larger proportion, the cost benefits of the smaller compressor outweigh the increasing membrane cost. For the vacuum based membrane systems, this trend is also true for CO₂/N₂ selectivity values up to 40. But for selectivity values above 40, the larger costs of the very large membrane area exceed the cost reductions gained by having a smaller CO₂ compressor.

From the Figure 5-15, the lowest cost for the vacuum membrane systems occur at a CO₂/N₂ selectivity of 40. Some of the new membranes that have CO₂/N₂ selectivities close to or above this include those by Fritsch and Peinemann (1995), Bondar et al. (2000) and Yampolskii (2006). Advantageously this corresponds to a permeate CO₂ purity of 90% for the TCMS processes. However, the CO₂ purity of the permeate for the SMS at this selectivity is still low at approximately 60%.

Effect of pressure ratio

In addition to selectivity, the pressure ratio can also be manipulated to increase the CO₂ concentration in the permeate stream. As shown in Figure 5-7, decreasing the pressure ratio will increase the CO₂ purity. The pressure ratio can be decreased by either increasing the feed pressure or decreasing the permeate pressure, or both. For the baseline evaluation of the vacuum membrane systems, the feed pressure was set at 1.5 bar and the permeate pressure was set at 0.08 bar. Figure 5-10 illustrates the changes in cost as a function of the pressure ratio for the SMS process. The analysis explores results for the commercial PPO membrane and a development membrane with CO₂ permeability of 200 Barrer and CO₂/N₂ selectivity of 40.

From Figure 5-10, if the permeate pressure is varied and the feed pressure is constant at 1.5 bar, the minimum cost occurs at a pressure ratio of 0.015. This corresponds to a permeate pressure of 0.03 bar. As the permeate pressure decreases, the driving force across the membrane increases resulting in both an increase in the CO₂ purity (and thus smaller CO₂ compressor) and a decrease in the membrane area (less membrane costs). Hence there is a decrease in capture cost. However, because current large scale commercial vacuum pumps do not operate much lower than 0.05 bar, 0.05 bar would be considered the optimum operating permeate pressure.

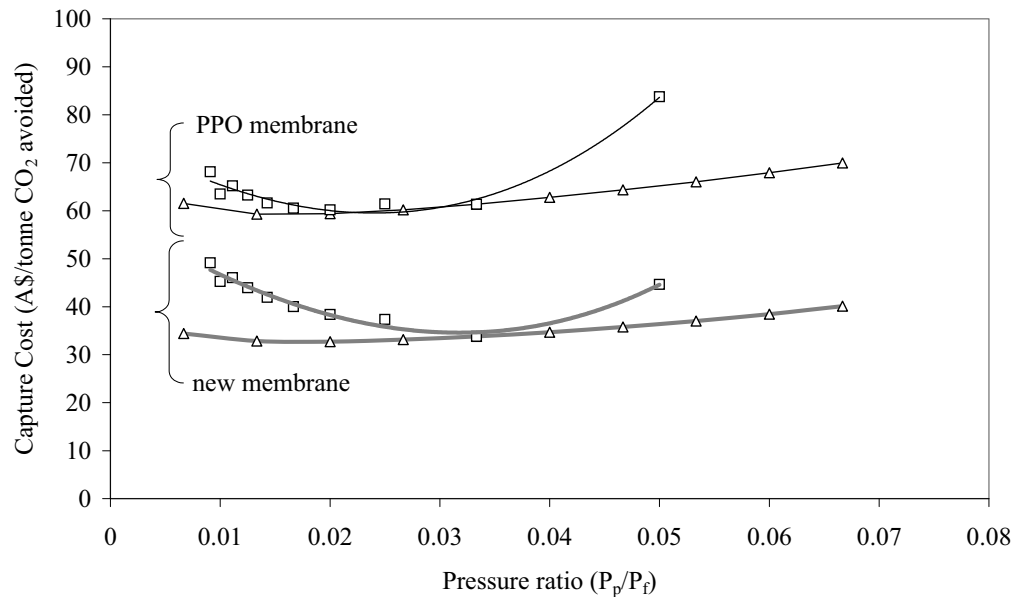


Figure 5-10 Capture cost as a function of pressure ratio for the PPO membrane (—) and the new development membrane (—) when 1) P_p is constant at held constant at 0.05 bar (□) and 2) P_f is constant at 1.5 bar (Δ)

In contrast if the pressure ratio is varied by changing the feed pressure while fixing the permeate pressure at 0.05 bar, the lowest capture cost occurs at a pressure ratio of 0.03. This corresponds to a feed pressure of 1.5 bar. For very low pressure ratios, say less than 0.02, the corresponding feed pressure must be greater than 2 bar. Based on the assumptions in section 3.4, to achieve this pressure, expensive compressors are used rather than lower cost gas blowers. Hence there is an increase in capture cost. At the higher pressure ratio value of 0.05, the feed pressure is 1 bar. In this scenario, the cost of capture is higher than at a feed pressure of 1.5 bar because the cost of the larger membrane area offsets the cost savings of the feed gas blower.

It can be concluded that for membrane systems, the lowest cost operating conditions are a feed pressure of 1.5 bar and a permeate pressure of 0.05 bar.

5.5.6 Synopsis – “low-cost membrane systems”

The results from the sensitivity analysis above demonstrate that gas separation membrane technology can be a viable and feasible CO_2 capture option if:

1. new novel operating conditions such as vacuum permeate pumping is employed;
2. CO₂ permeability increases;
3. CO₂/N₂ selectivity is improved; and
4. membrane prices decreases.

If these improvements are utilised in concert rather than individually, the cost of capture using membrane technology could be significantly reduced from the current cost of over A\$90/tonne CO₂ avoided.

Figure 5-17 illustrates the relationship between CO₂ permeability, CO₂/N₂ selectivity and membrane prices for the vacuum permeate SMS process. In this analysis, the changes in capture costs are examined for two prices (A\$/m² 67 and 13) and two selectivity values (40 and 250). Similarly, Figure 5-18 shows the capture cost reductions achievable for the two-stage membrane systems. However, in the two-stage systems, increasing the CO₂/N₂ selectivity above 40 does not enhance the performance of the membrane and is not included in the displayed results. Figures 5-17 and 5-18 show that with improvements in technology can reduce the capture cost to less than A\$30/tonne CO₂ avoided.

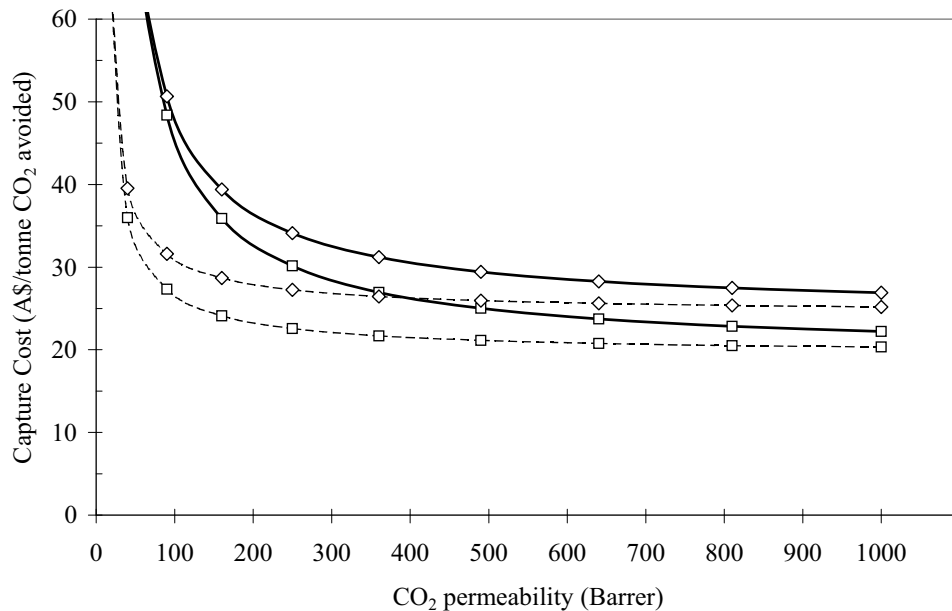


Figure 5-11 Capture cost as function of improved membrane characteristics at two membrane prices: A\$13/m² (---) and A\$66/m² (—), and two CO₂/N₂ selectivities: 40(◆) and 250 (□)

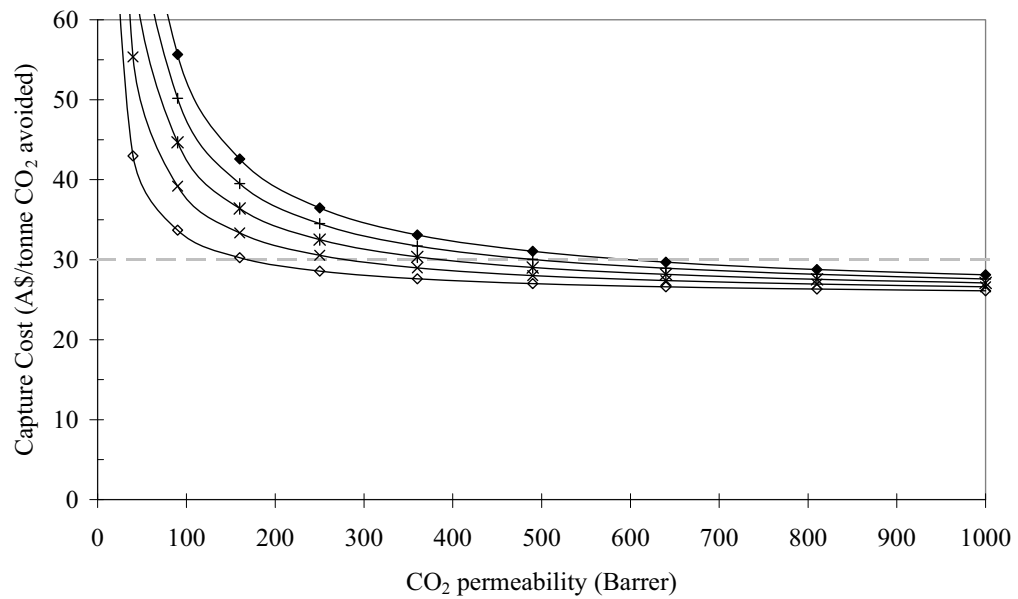


Figure 5-12 Capture cost with changes in CO₂ permeability for the TCMS-RR configuration at CO₂/N₂ selectivity of 40 and different membrane prices: A\$13/m² (◇), A\$27/m² (×), A\$40/m² (*), A\$53/m² (+), A\$66/m² (◆)

From Figure 5-11, the results also show that reductions in membrane price have a more significant effect at low permeability values than at high values. For CO₂ permeability values up to 500 Barrer, reducing the membrane costs will have a greater impact on reducing the overall capture cost rather than increasing the CO₂/N₂ selectivity at a fixed CO₂ permeability. However, for CO₂ permeability values above 500 Barrer, the combined effect of large CO₂ permeabilities and improved CO₂/N₂ selectivity will have a greater impact. This is because for permeabilities above 500 Barrer, the total membrane area is a small contributor to the total capital costs. Thus, reductions in membrane prices are not as beneficial. From this analysis, it can be concluded that if a manufacturer or researcher had developed a membrane with a CO₂ permeability of, say, 200 Barrer, reducing the production cost of the membrane will yield lower capture costs than efforts at improving the CO₂ selectivity. Conversely, if the newly developed membrane had an exceptionally high CO₂ permeability (greater than 800 Barrer), the capture system would be made more cost-effective by improving the CO₂/N₂ selectivity than lowering the membrane price.

At the time of writing, the range of European Union Emissions Trading Scheme (EU ETS) traded carbon prices range from A\$30 to \$45 per tonne CO₂ avoided equivalent* (Capoor and Ambrosi, 2006) and the carbon price recommended by the Australian National Emissions Trading Taskforce (NETT) for CCS participation is A\$30 to A\$35 per tonne CO₂ avoided (NETT, 2006). To enable CCS to be an economically feasible mitigation option, the combined cost of CCS must fall within these ranges. Other studies show that storage costs can be significantly less than A\$10 per tonne avoided (Allinson and Nguyen, 2003). Assuming a notional cost of A\$30/tonne CO₂ avoided for capture, and using the results of Figures 5-17 and 5-18, Figure 5-199 summarises the different combinations of membrane permeabilities and membrane prices needed to achieve this value. The CO₂/N₂ selectivity for the SMS is 250 and TCMS (-RR) is 40, and correspond to a CO₂ purity in the enriched permeate of 90%. The results shows that if membranes could be produced at relatively low cost - less than A\$20/m² - then using the development membranes such as those developed by Bondar et al. (2000) or Yampolskii (2006), CO₂ capture using membrane technology would be a cost competitive option based on current carbon prices.

* These prices fell sharply to below A\$16 per tonne CO₂ avoided in 2006

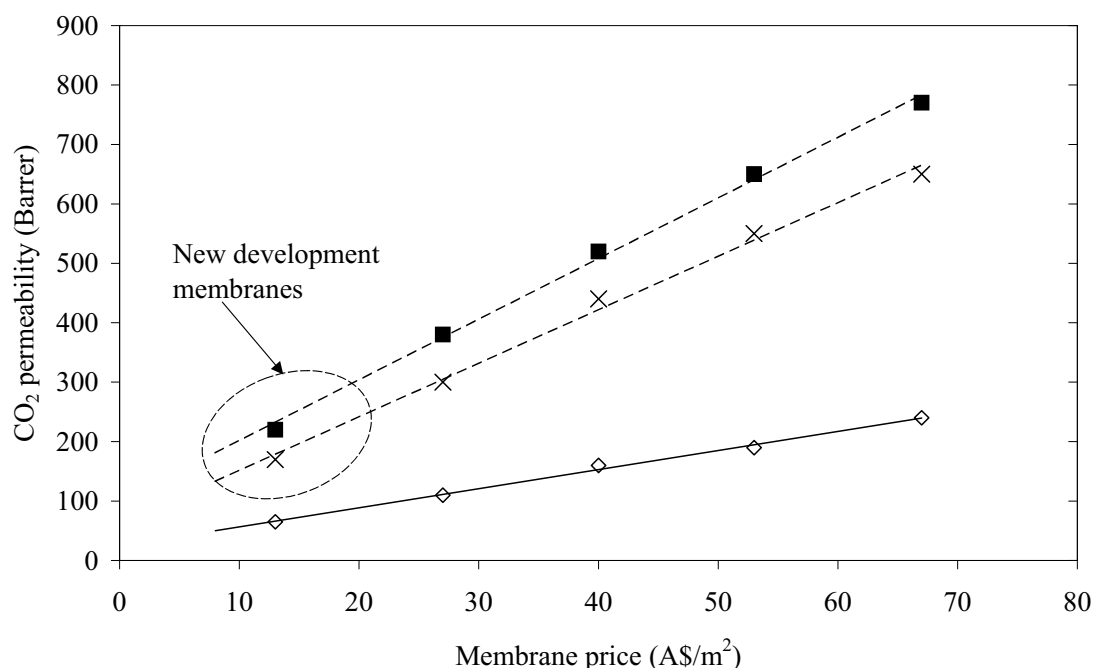


Figure 5-19 Membrane characteristics and price combinations to achieve a cost of A\$30/tonne CO₂ avoided for the SMS (◇), TCMS (■) and TCMS-RR (×) process layouts

Although achieving a specific capture cost can entail many different combinations of processing conditions, membrane characteristics and prices, this analysis illustrates the potential cost reductions achievable due to membrane development.

5.6 Conclusion

The recovery of CO₂ from post-combustion flue gas using commercial polymeric gas separation membranes with a high pressure feed results in very high capture costs - over A\$90/tonne CO₂ avoided. This is dominated by the capital and operating expenses of the flue gas and post-capture compressors. However, the capture cost can be significantly reduced by utilising a membrane system, where the permeate is under vacuum, coupled with improvements in membrane CO₂ permeabilities, CO₂/N₂ selectivities and reductions in the membrane price. Thus, improvements in technology would enable the application of membranes to capture CO₂ from power plant flue gases at a cost that is competitive based on current carbon prices.

The results show that for vacuum permeate membrane systems; if the membrane price is moderate or high (53 to 66 A\$/m² or 40 to 50 US\$/m²) then the focus should be on creating membranes with very high permeability (300 to 550 Barrer) and moderate CO₂/N₂ selectivity (40 to 60). However, if the membrane price is low (13 to 40 A\$/m² or 10 to 30 US\$/m²) then the aim should be to use current membranes with permeability of 200 Barrer with CO₂/N₂ selectivity in the range 40 to 60 and to reduce the production cost of the membrane.

The economic analyses of vacuum permeate membrane systems in this chapter assumes that the operational learning of vacuum permeate membrane systems for O₂ recovery is also applicable for CO₂ capture. It is recommended that experimental work be undertaken to validate the potential of CO₂ capture using vacuum permeate membrane systems. Additionally, further modelling of alternative process configurations and optimisations would also be beneficial.

Chapter 6. PRESSURE SWING ADSORPTION

6.1 Overview

This chapter investigates the cost of using pressure swing adsorption to recover CO₂ from post-combustion power plant flue gas. The analysis considers both high pressure feed and vacuum desorption. Considerations of the improvements in adsorbents characteristics and process cycle that would reduce the capture cost are presented in the later part of this chapter. Based on the current literature, we believe this is the first CO₂ capture economic assessment of PSA and VSA for Australian conditions.

6.2 CO₂ capture using pressure swing adsorption

6.2.1 Introduction

Pressure swing adsorption (PSA) processes have been used extensively for gas separation, especially in the separation of hydrogen from CO₂, and in air separation. An early study by the IEA GHG (Monenco, 1992) examining CO₂ capture by PSA concluded that the high cost of feed gas compression limited the cost competitiveness of PSA systems. However, in recent years the use of vacuum swing adsorption (VSA) for CO₂ capture has been investigated. As discussed in Chapter 2 (section 2.3), VSA consumes less energy than PSA and could be a viable alternative for CO₂ capture.

The aim of this chapter is to assess the cost of capturing CO₂ from post-combustion power plant flue gas using pressure swing adsorption technology, both with a high pressure feed (PSA) and with vacuum desorption (VSA). The initial analysis assesses the cost of capture using commercial adsorbent zeolite 13X. A sensitivity analysis is also undertaken to examine the effect of improving adsorbent properties on the capital cost, energy penalty and overall capture cost. The parameters examined include adsorbent working capacity and adsorbent CO₂/N₂ selectivity. Improvements to the process cycle cost will also be evaluated.

6.2.2 The PSA cycle

The separation of gas mixtures using pressure swing adsorption (PSA) is carried out in cycle batch processes where the adsorber bed is saturated and then regenerated. Each step in the cycle is a transient process, however over a long period of operation, the whole cycle can be considered to achieve a cycle steady state. PSA in its simplest configuration consists of with two fixed beds operating in parallel, where as one bed is adsorbing, the other bed is desorbing at a lower pressure, as shown in Figure 6-1.

As discussed in Chapter 5 for the membrane separation process, if the CO₂ enriched gas stream from the adsorption process has other component gases such as N₂ and O₂, these can be separated from the CO₂ via vapour liquid separation. This is achieved using compression and cooling of the CO₂ enriched product gas to remove (or reject) the gaseous components and any CO₂ vapour. The cost and power consumption for this step is included as part of post-capture compression.

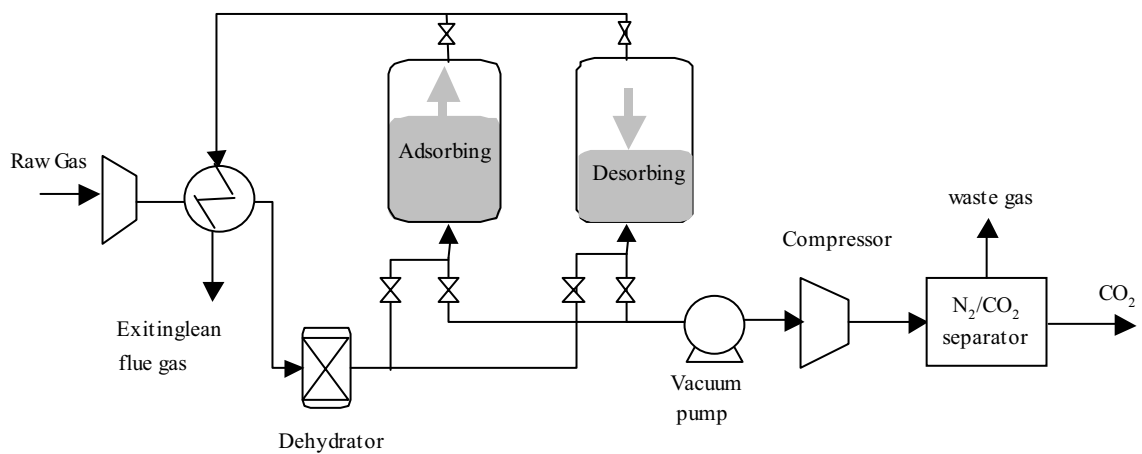


Figure 6-1 Simplified flow diagram of a pressure swing adsorption (PSA) process

The most basic sequence of steps for a PSA process is the four-step cycle developed by Skarstrom (Skarstrom cycle) in 1960 (Skarstrom, 1960). The Skarstrom cycle is illustrated in Figure 6-2.

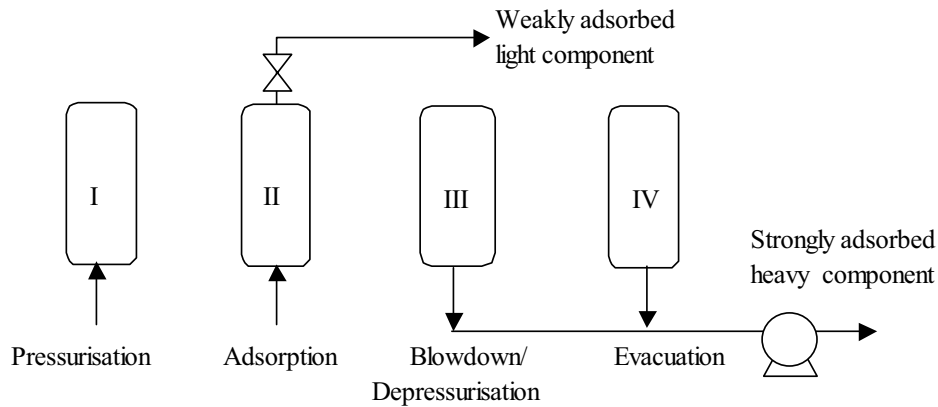


Figure 6-2 Four-step Skarstrom cycle

The Skarstrom cycle consists of the following steps:

- (I) **Feed pressurisation** - High pressure feed gas is fed at one end of the adsorber to increase the pressure inside the vessel, while the other end of the bed is closed. During this step, the gas with a higher affinity for the absorbent (often called the heavy component) is adsorbed while the gas with the lower affinity (referred to as the light component) passes preferentially through the bed and is enriched at the closed end of the adsorber.
- (II) **Adsorption** - When the bed reaches a set pressure, the adsorber outlet valve is opened and the light component that is not adsorbed is withdrawn. Adsorption continues until the bed is saturated with the heavy component.
- (III) **Countercurrent blowdown/depressurisation** - The pressure in the adsorber bed is lowered to atmospheric or sub-atmospheric pressure to release the adsorbed gases (mostly the heavy component) from the adsorbent surface.
- (IV) **Evacuation** - The final step is evacuation of the strongly adsorbed gas (the heavy component) from the adsorber by pumping. Often the evacuation step includes a purge of the adsorber bed with the light component to remove the heavy component from the void spaces. This minimises the amount of the heavy component within the bed at the beginning of the next cycle.

The concentration profile of the light component along the adsorber bed during each step of the cycle is shown in Figure 6-3.

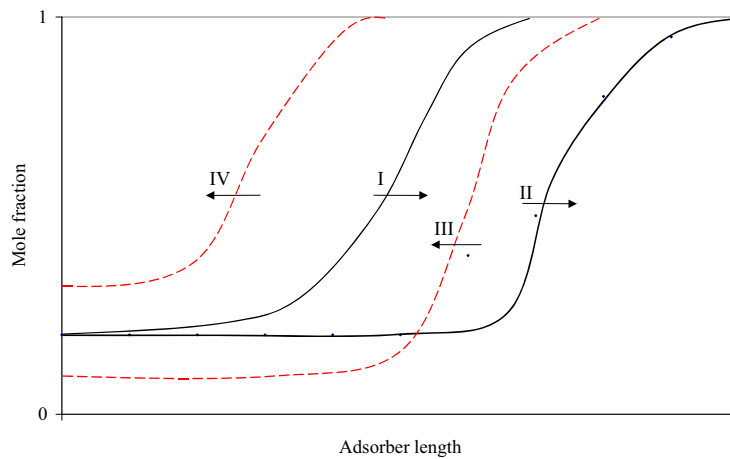


Figure 6-3 A typical concentration profile of the light component and direction of travel along the adsorber bed for a PSA process

6.2.3 Assumptions

The economic and processing assumptions for the flue gas used in this analysis are described in section 3.5.

The cost for adsorbent zeolite 13X is assumed to be A\$5/kg (Webley, 2005) and US\$5/kg (Smith and Westerberg, 1991). The processing conditions and adsorbent properties for the PSA process are described in Table 6-1. The Skarstrom 4-step cycle is selected for the baseline analysis because of the simplicity of the process. The adsorbent zeolite 13X is chosen as it has been shown experimentally to have better adsorption properties for CO₂/N₂ systems than other commercially available adsorbents and the adsorption isotherms are widely available in the literature (Chue et al., 1995).

Table 6-1 Physical and processing conditions for PSA process

Gas system		Binary (CO ₂ /N ₂)	
PSA cycle		Skarstrom 4-step cycle	
		Pressure swing adsorption (PSA)	Vacuum swing adsorption (VSA)
Adsorption pressure	bar	6	1.5
Desorption pressure	bar	1	0.05
Temperature	°C	35	
Time step	S	90	
Adsorbent		Zeolite 13X (Chue et al., 1995)	
Bulk bed density	kg/m ³	750	
Bed porosity		0.348	
Parameters for Langmuir isotherm (Chue et al., 1995)			
Absorbent capacity for CO ₂ q _m (CO ₂) = A/B	mol/kg	4.65	
Henry's constant A(CO ₂)	mol/kg	40.78	
Langmuir constant B(CO ₂)	1/bar	8.76	
Absorbent capacity for N ₂ q _m (N ₂) = A/B	mol/kg	0.95	
Henry's constant A(N ₂)	mol/kg	0.76	
Langmuir constant B(N ₂)	1/bar	0.8	

6.2.4 PSA model

PSA processes are typically described by two types of rigorous mathematical models: the equilibrium approach and the dynamic approach. The equilibrium approach assumes instantaneous equilibrium is achieved between the component gases and the adsorbent. In the dynamic approach, it is assumed that equilibrium is never achieved and the kinetics of adsorption is based on the diffusion rate of the gas phase on the adsorbent surface. For both these models, the resulting equations are sets of partial differential equations that describe the changes in gas composition along the inside of the adsorber bed (Raghavan et al., 1985).

Various parameters such as the adsorption isotherms, heat and mass transfer coefficients, heat capacity, heat of adsorption, physical properties of the adsorbent, and other variables are required to fully describe the system.

However, for broad-brush scoping economics, it is impractical to measure and estimate all of these variables. A less complicated method than either the rigorous equilibrium or dynamic approach is required. In developing the PSA model for this thesis, the short cut method described by Chung et al. (1998) is adopted. This short-cut model is able to easily describe characteristics of the PSA process including the effect of different

operating pressures and changes on the adsorption isotherm, step time and composition of the feed gas. It enables quick evaluation of the economic viability of the PSA process for CO₂ capture. The limitation of the short cut method is that it does not accurately describe the behaviour of the gas phases within the adsorber, and neglects the kinetics of adsorption and column design.

The short-cut PSA model described by Chung et al. (1998) categorises the four steps of the Skarstrom cycle into two groups. Pressurisation (step I) and adsorption (step II) are merged into one group called “adsorption”. While depressurisation/blow-down (step III) and evacuation (step IV) is grouped into “desorption”. By condensing the four steps into two groups, the short-cut model simplifies the process and reduces the number of numerical calculations. Figure 6-4 shows an illustration of the model.

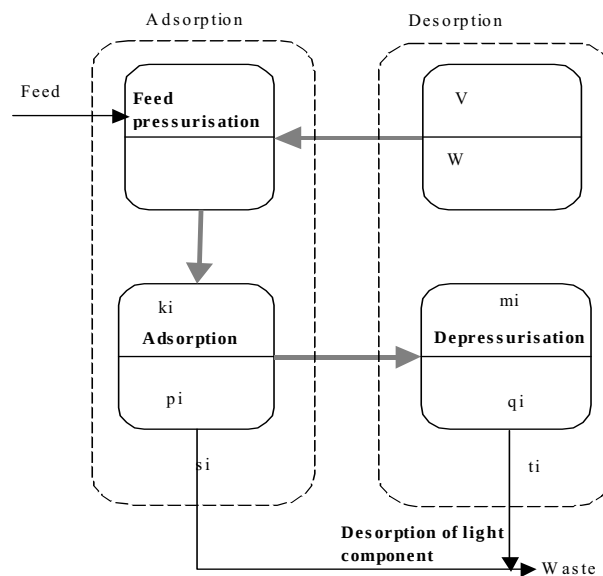


Figure 6-4 Short-cut PSA model

The following is a list of the key assumptions relevant to the short-cut PSA model used in this thesis:

1. All steps are assumed to operate in batch mode;
2. A batch system consists of a vessel with a fixed volume;
3. Equilibrium exists between two homogeneous phases: the bulk-gas in the adsorbent voids; and, the adsorbed gas on the surface of the adsorbent;

4. The desorbed bed does not contain residual component gases; and
5. Adiabatic adsorption.

Short-cut PSA batch equilibrium model

For the short-cut PSA model, the extended Langmuir equation (Equation 6.1) has been used to describe the rate of adsorption, however any isotherm with relationships between pressure (P) and partial pressure (p_i) can be used. The extended Langmuir isotherm is preferred in this research because it models accurately most commercial adsorbents for CO₂ recovery such as zeolite 13X, zeolite CaX and activated carbon (Chue et al., 1995).

In the PSA model, Equations 6.1 to 6.6 which describe the material balance of a gas mixture under equilibrium, are solved simultaneously to obtain a solution for the unknowns k_i , s_i and p_i given the adsorber temperature (T), the bed density (ρ_{bed}), the weight of adsorbent (W), and the adsorption pressure (P_{ads}) and desorption pressure (P_{des}).

Adsorbent isotherm

$$p_i = \frac{A_i P_i W_{ads}}{1 + \sum_i^n B_i P_i}, \quad A_i = q_{m,i} B_i \quad (6.1)$$

Mass balance

$$f_i = k_i + p_i + s_i \quad (6.2)$$

$$P_i = \frac{k_i}{\sum k_i} P_{system} \quad (6.3)$$

$$W_{ads} = \rho_{bed} V_{void} \quad (6.4)$$

$$P_{system} V_{void} = \sum k_i RT \quad (6.5)$$

$$\frac{k_i}{\sum k_i} = \frac{s_i}{\sum s_i} \quad (6.6)$$

Energy consumption

It is assumed that there is no separate heating or cooling component specific to the adsorber. The total energy consumption for the PSA process is the sum of any work required for compression, pumping, and dehydration. The equations for the work of compression, expansion and dehydration have been described in section 3.4.1.

$$W_{\text{PSA}} = W_{\text{compressor}} + W_{\text{pump}} + W_{\text{Dehydration}} - W_{\text{Expansion}} \quad (6.7)$$

where

$$W_{\text{pump}} = \frac{n \times R \times T \times \log\left(\frac{P_{\text{ads}}}{P_{\text{des}}}\right)}{\eta_{\text{pump eff}}} \quad (6.8)$$

6.2.5 Outputs from the PSA model

The outputs from the PSA model used to assess the performance of the technology for CO₂ capture include:

1. The CO₂ concentration in the product gas stream (desorbed stream);
2. The rate of CO₂ recovery;
3. The total energy requirement;
4. The total weight of adsorbent; and
5. The size of the absorber.

The PSA model allows the user to select and define the type of adsorbent, operating conditions (temperature and pressure), adsorption cycle time-step and adsorber volume.

6.3 Baseline results for commercial adsorbents

The baseline techno-economic results for recovering CO₂ from flue gas using physical adsorption are outlined in Table 5-2. Two operating conditions have been analysed; one with a high pressure feed and atmospheric desorption (PSA), and the second with a low feed pressure and vacuum desorption (VSA).

Table 6-2 Economic results for CO₂ capture using pressure swing adsorption

	This study		IEA GHG (Monenco, 1992)
	VSA	PSA	PSA
Cost year	2006	2006	1992
CO ₂ recovery rate (%)	85	85	95
CO ₂ purity in recovered stream (%)	46	48	--
Absorber volume (m ³)	650	380	--
Number of adsorber trains	16	1	--
Energy penalty (%)	31	37	40
Capture Cost			
A\$/tonne CO ₂ avoided	53	62	--
US\$/tonne CO ₂ avoided	48	53	64
Capital investment for capture facility	950	1335	--
A\$/kW, US\$/kW	800	890	--
Total capital investment	1350	1750	--
A\$/kW, US\$/kW	1150	1330	1500

The capture cost for PSA using standard commercial zeolite 13X adsorbent is A\$62/tonne CO₂ avoided, which is higher than other CO₂ capture technology options such as MEA solvent absorption as described in Chapter 4. Additionally, the CO₂ purity from this process is low, being less than 50% compared to over 95% using chemical absorption. The capital investment for the capture facility is also very high at over A\$1,335/kW (Figure 6-6). The majority of the cost is for the compressors, which accounts for over 50% of the total equipment cost. The large number of compressors in the system are needed, firstly, to compress the feed gas to a high pressure of 6 bar and, secondly, to compress the low purity CO₂ product for transport.

In comparison, when VSA is used, the cost for capture is A\$53/tonne CO₂ avoided. This is a cost reduction of 25%. The lower cost reflects the lower energy penalty (31% compared to 37%) because there is no need to compress the feed gas (Figure 6-5). However, the concentration of the CO₂ obtained from the desorbed stream in VSA process is similar to that from the PSA process, at less than 50%. As a result, the energy required for CO₂ compression accounts for a large proportion of the energy penalty (Figure 6-5) and capital costs (Figure 6-6). In the VSA system, the adsorbent costs also contribute to a larger proportion of the equipment cost (30%) compared to the PSA system (less than 5%).

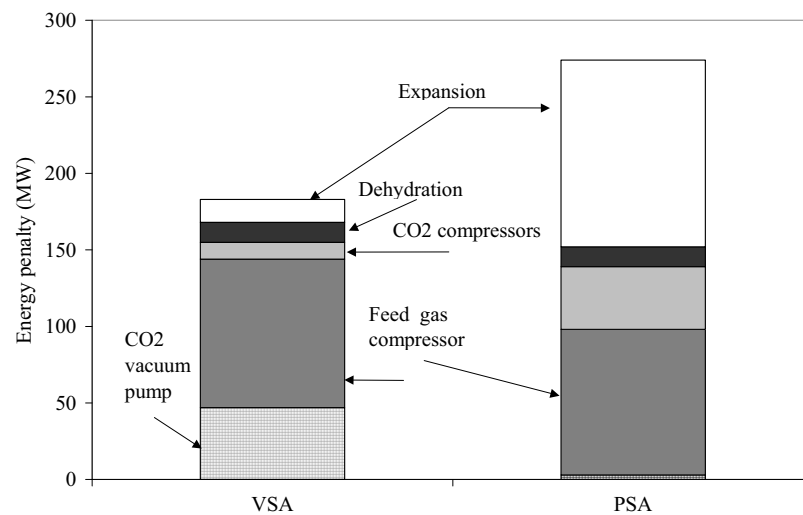


Figure 6-5 Total energy requirement for the VSA and PSA processes

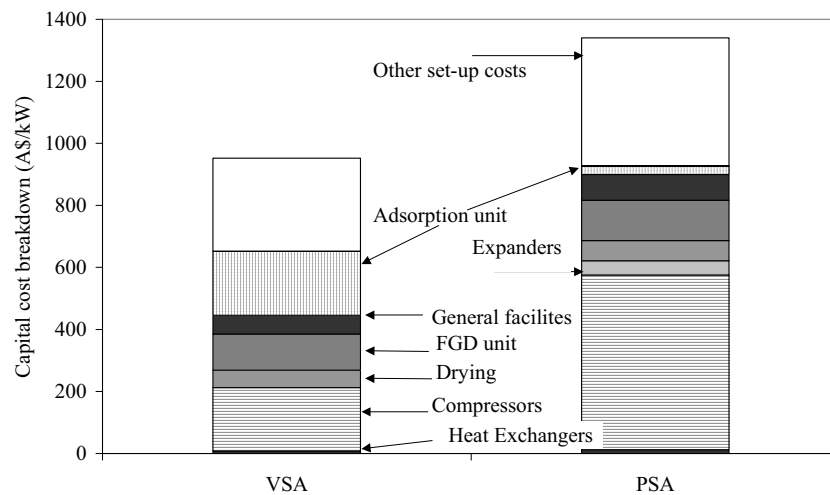


Figure 6-6 Breakdown of the capital investment for the VSA and PSA processes

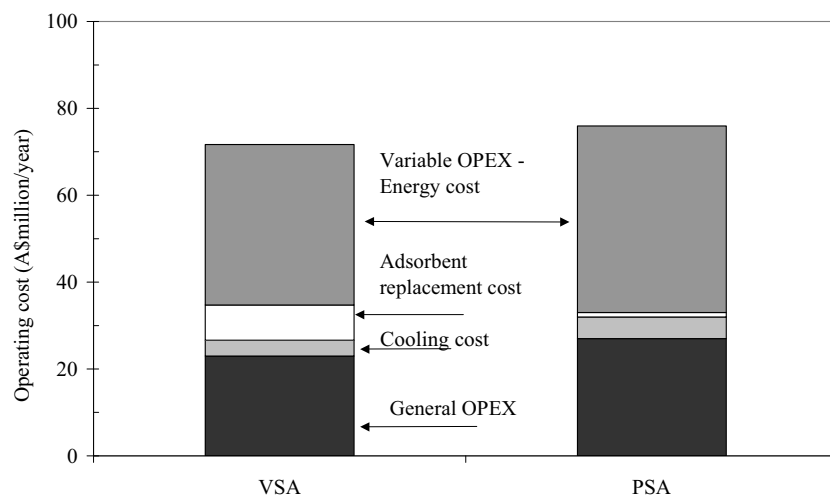


Figure 6-7 Breakdown of annual operating cost for the VSA and PSA processes

6.3.1 Comparison with other studies

The most recent techno-economic analysis of CO₂ capture using PSA was carried out in 1992 by Monenco for the International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) (Monenco, 1992). The study found that with the desorption set at atmospheric pressure, the feed gas must be compressed to at least 6.5 bara. The study estimates a CO₂ capture cost of US\$64/tonne CO₂ avoided. The high capture cost is due to the high capital and operating costs associated with compressing the feed gas. The total investment cost is estimated to be US\$1500/kW, with an energy penalty of 40%. In comparison a capture cost of US\$53/tonne CO₂ avoided is obtained in this study. The differences in the reported cost arise due to the different economic assumptions, PSA cycle and adsorbent used in the two studies. Unfortunately, the details of the PSA cycle and adsorbent used in the IEA GHG study are proprietary and no public information is available to enable a comparison with the results of this study.

No techno-economic studies have been published examining the cost of CO₂ capture under vacuum conditions.

6.4 Reducing the capture cost

6.4.1 Effect of adsorbent characteristics

The current cost of CO₂ capture using VSA technology with commercial zeolite 13X is A\$53/tonne CO₂ avoided. Although this cost is currently competitive with other CO₂ capture technologies such as solvent and membrane separation (Chapters 4 and 5), it is still higher than current carbon prices (section 1.5). Thus lower costs for capture are required. If we examine the capital and operating costs breakdown (Figures 6-6 and 6-7), the largest contributor to both the capital and operating costs is the CO₂ compressors and the associated energy usage. If it is possible to increase the CO₂ purity in the evacuated stream, this could reduce the size and cost of CO₂ compressors. The second largest component of costs is for the adsorbent unit and adsorbent replacement. For the VSA system evaluated above, the size of the adsorbers is very large. At least 10 to 20 adsorber beds with volumes in excess of 600 m³ are required. Investigating ways in

which the size of the adsorbers can be reduced, coupled with lower cost for the adsorbents will have both cost and operating benefits.

6.4.2 Adsorbent working capacity and selectivity

The following section of this chapter contains a sensitivity analysis of adsorbent characteristics and examines the parameters that may lead to significant capture cost reductions. For this analysis, vacuum desorption conditions have been assumed with the operating and economic conditions as outlined in Table 6-1. However, to remain consistent with literature studies, the label PSA is used for both PSA and VSA. In developing better adsorbents for PSA processes, two key characteristics that influence the performance of the PSA process are the adsorbent working capacity, and the adsorbent selectivity.

Adsorbent working capacity

The extent of adsorption depends on physical parameters such as temperature, the difference in the adsorption and desorption pressure, the concentration of the different component gases in the gas phase, and the surface area of the adsorbent. The rate of adsorption can be described as the capacity or loading of the adsorbent. The adsorption capacity for a component gas can be described mathematically by an isotherm such as the extended Langmuir equation. For a binary mixture of CO₂ and N₂, the extended Langmuir equation for CO₂ is represented as:

$$q_{CO_2} = \frac{A_{CO_2} y_{CO_2} P_{System}}{1 + B_{CO_2} y_{CO_2} P_{System} + B_{N_2} y_{N_2} P_{System}}$$

where

$$A_{CO_2} / B_{CO_2} / B_{N_2} = f(T, P) \tag{6.9}$$

An important characteristic of a good adsorbent is that the adsorbent has a high adsorption capacity for the heavily adsorbed component. The working capacity is defined as the difference between the amount of the heavy component (CO₂) adsorbed at the adsorption pressure and the amount adsorbed at the desorption/evacuation pressure (Equation 6.10).

$$\Delta q_{CO_2} = q_{CO_2 \text{ Adsorption}} - q_{CO_2 \text{ Desorption}} \quad (6.10)$$

The higher the working capacity of an adsorbent for CO₂, the greater the CO₂ recovery rate from the capture process. Adsorbents with high working capacity between the adsorption and desorption steps typically have a linear isotherm. Graphically this is illustrated in Figure 6-8. In this example, the working capacity for the adsorbent with a linear isotherm is almost one and a half times that of the non-linear isotherm of pure CO₂ on zeolite 13X given the operating conditions chosen in this study. However, very few commercially available adsorbents display linear properties.

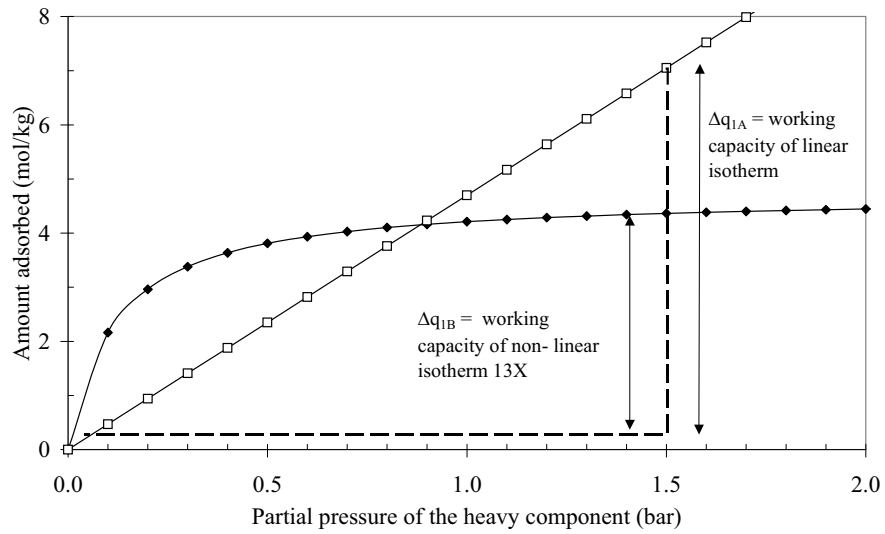


Figure 6-8 Comparison of an adsorbent's working capacity for CO₂ with a linear (□) and non-linear (◆) isotherm

In addition to having a high working capacity for the preferred component, a good adsorbent would also display a low working capacity for the lighter component or N₂. The ratio of the working capacities for CO₂ relative to N₂ is also an important parameter. The higher the ratio, the greater the adsorbent's preference for CO₂. The working capacity selectivity ratio (R) can be defined as:

$$\text{Working capacity selectivity ratio (R)} = \frac{\Delta q_{CO_2}}{\Delta q_{N_2}} \quad (6.11)$$

Adsorbent selectivity

In a binary system, as assumed in this study, the adsorbent selectivity is defined as follows:

$$\alpha_{1,2} = \frac{x_1 y_2}{x_2 y_1} \quad (6.12)$$

where x_1, x_2 are the mole fractions of the two components on the adsorbed surface and y_1, y_2 are the corresponding mole fractions in the gas phase. We assume that the components on the adsorbed surface are the more strongly adsorbed species.

Using the extended Langmuir equation, the adsorbent selectivity for CO₂ compared to N₂ can be defined as:

$$\alpha_{\text{CO}_2/\text{N}_2} = \frac{q_{m\text{CO}_2} b_{\text{CO}_2}}{q_{m\text{N}_2} b_{\text{N}_2}} \quad (6.13)$$

The product $q_{m\text{CO}_2} b_{\text{CO}_2}$ corresponds to the initial slope of the isotherm, or Henry's constant (A_{CO_2}), for component CO₂. Due to the nature of the extended Langmuir model, the selectivity of CO₂ compared to N₂ can be represented as a singular value. However, if a different model such as the Langmuir-Freundlich model was used to represent the isotherm, the selectivity would also be dependent on other parameters such as the operating pressure of a PSA cycle (Ruthven et al., 1994).

Adsorbent selection parameter

According to Rege and Yang (2001), the product of the two parameters adsorbent selectivity (α) and working capacity selectivity ratio (R) is the adsorbent selection parameter (S). The parameter S can be used to compare the performance of two adsorbents, the higher the S value, the better performing the adsorbent.

6.4.3 The effect of recent adsorbent development for PSA CO₂ capture

As discussed in Chapter 2, many new adsorbents have been developed specifically for the recovery of CO₂ from power plant flue gas. The literature on these new adsorbents indicates that they have relatively high adsorption capacities and selectivity for CO₂.

Unfortunately, many of these new adsorbents are proprietary, and no information on the adsorption isotherms and physical properties has been published in the public domain.

The only source of information on adsorbent properties suitable for a techno-economic analysis is the paper by Macario et al. (2005). While Langmuir parameters are not specified, it is possible to make estimates based on the graphical data given in the paper. Two adsorbents from the study have been selected for an economic analysis:

1. The adsorbent containing iron (Fe-M), as it has the highest working capacity; and
2. The pure silica adsorbent (Si-6), which possesses a high CO₂/N₂ selectivity.

Table 6-3 gives the operating conditions, estimated Langmuir parameters and physical properties of the development adsorbents and the economic results.

Table 6-3 Processing and physical properties of new adsorbents

Gas system		Binary (CO ₂ /N ₂)	
Volume of single adsorber	m ³	650	650
Time step	s	90	90
Adsorbent		Fe-M	Si-6
Bulk bed density	kg/m ³	1393	1020
Bed porosity		0.31	0.37
Parameters for Langmuir isotherm			
Absorbent capacity for CO ₂	Mol/kg	1.75	0.92
A(CO ₂)	Mol/kg	21.5	0.92
B(CO ₂)	1/bar	12.3	0
Absorbent capacity for N ₂	Mol/kg	0.73	0.04
A(N ₂)	Mol/kg	8.95	0.04
B(N ₂)	1/bar	12.2	0
CO ₂ /N ₂ selectivity		2.4	22.5
S parameter		6.3	97
Results		Fe-M	Si-6
CO ₂ recovery rate	%	60	35
CO ₂ purity in recovered stream	%	20	65
Energy penalty	%	47	13
Capture Cost			
	A\$/tonne CO ₂ avoided	350	63
	US\$/tonne CO ₂ avoided	336	56

The cost of capturing CO₂ using the two development adsorbents as developed by Macario et al. (2005) is A\$63 and \$A350 per tonne CO₂ avoided. Of the two adsorbents investigated, the pure silicate adsorbent Si-6 has a lower cost than the metal

impregnated adsorbent Fe-M. However, the capture cost using these development adsorbents is still higher than the capture cost using commercial zeolite 13X adsorbent (as shown in Table 5-2). If we compare the S parameter for pure CO₂, the values for these new adsorbents are significantly lower at 6.3 and 97 than for zeolite 13X, which has a value for 340. This suggests that the performance of these new adsorbents is inferior to zeolite 13X.

The capture cost using Fe-M adsorbent is exceptionally high. The adsorbent has a good working capacity and a moderate CO₂ recovery rate of 60%. However the selectivity of the adsorbent for CO₂ to N₂ is very low (~2.4), and thus the concentration of the CO₂ in the product stream is also very low (at 20%). As a result, the size of the post-separation compressor is very large, which increases the total energy consumption and capital cost.

For the silicate adsorbent, Si-6, the capture cost is lower than for Fe-M. This adsorbent has a higher CO₂/N₂ selectivity (22.5), and the resulting CO₂ purity in the product steam is 65%. A higher CO₂ purity in the product stream requires a smaller post-separation compressor, and hence a lower capture cost. However, in comparison to the adsorbent zeolite 13X, Si-6 has a lower working capacity. The working capacity of Si-6 is 0.9 mol/kg of adsorbent compared to a working capacity of 4.5 mol/kg for zeolite 13X. This lower working capacity gives a lower CO₂ recovery rate for the same adsorber bed volume. Thus, the capture cost is also higher for Si-6 than for zeolite 13X. To improve the CO₂ recovery using Si-6, either the feed pressure or the adsorber volume must increase. Even when these process changes are implemented, the capture cost for Si-6 is still higher than for zeolite 13X.

It can be concluded that commercial zeolite 13X adsorbent remains a better adsorbent for CO₂ capture than either Si-6 or Fe-M. To achieve the criteria set for low cost capture, new adsorbents with superior working capacity and selectivities are needed.

The following sections of this chapter will explore the effect on capture cost and the performance of the PSA process by improving the adsorbent working capacity for CO₂, and the adsorbent CO₂/N₂ selectivity. The adsorbent isotherm is assumed to be

modelled by the extended Langmuir equation. This was selected because although linear isotherms have higher working capacities (Harlick and Tezel, 2004), most commercial adsorbents display non-linear adsorption characteristics. Therefore it is likely that any new adsorbents that will be developed for CO₂ capture will also be described by a non-linear isotherm. The baseline properties are assumed to be similar to those of zeolite 13X.

6.4.4 Reducing the cost of the CO₂ compressor

As shown in section 5.5.5 for membrane technology, increasing the concentration of the CO₂ in the enriched product stream will reduce the cost for the CO₂ compressor, and thus reduce the overall capture cost. As is the case with membrane technology, the CO₂ concentration in the enriched stream of the PSA process is less than 50%. It is reasonable to assume that if the CO₂ concentration from the PSA process is increased, cost can be reduced.

The following sections of this chapter investigate how:

1. The pressure ratio; and
2. The adsorbent CO₂/N₂ selectivity,

affect the concentration or purity of the CO₂ in the enriched product stream and thus the cost.

Pressure ratio

The pressure ratio is a critical design parameter of the PSA process. Kayser and Knaebel (1986), and Ritter and Yang (1991) have shown that a high pressure ratio increases the purity of the lightly adsorbed product and increases the concentration of the heavy product in the desorbed stream. Both Kikkenedes and Yang (1993) and Chou and Chen (2003) have investigated the effects of changing pressure ratio for CO₂ recovery, however no economic assessment was undertaken.

Adsorption pressure

Increasing the pressure ratio by increasing the feed/adsorption pressure will improve the CO₂ purity in the product stream, providing the amount of CO₂ recovered and adsorber

volume are fixed. This is illustrated in Figure 6-9 where the adsorption pressure is increased from 1 bar to 5 bar, while the evacuation desorption pressure is constant at 0.05 bar. The CO₂ recovery is set at 85%.

At an adsorption feed pressure of 1 bar, the CO₂ purity in the enriched product stream is 47%, and the capture cost is approximately A\$60/tonne CO₂ avoided. At a higher feed pressure of 5 bar, the CO₂ purity increases to 52%, but the capture cost also increases to over A\$70/tonne CO₂ avoided. Figure 6-9 shows that the minimum capture cost occurs at a feed pressure of 1.5 bar. The cost decreases from 0.5 to 1.5 bar because the CO₂ product concentration increases, thus a smaller post-separation compressor is required. Additionally, when the feed pressure increases, a smaller adsorber volume is needed for a set CO₂ recovery rate. This is because at higher feed pressures, the partial pressure of CO₂ increases and the zeolite has a higher adsorption capacity (as illustrated in Figure 6-8 and Equation 6.1). However, when the feed pressure exceeds 2 bar, the capture cost increases. This is because any cost savings generated by a higher CO₂ concentration in the product stream and a smaller adsorber volume are offset by the cost of the larger feed gas compressor. Similar trends are observed by both Chou and Chen (2003) and Liu and Ritter (1996) in their analysis of PSA processes for recovering strongly adsorbed gases.

Thus it can be concluded that for PSA processes operating under vacuum desorption conditions, feed pressures above 2 bar do not necessarily enhance the performance of the process. Similar trends occur with desorption/evacuation pressures set at 0.1 bar.

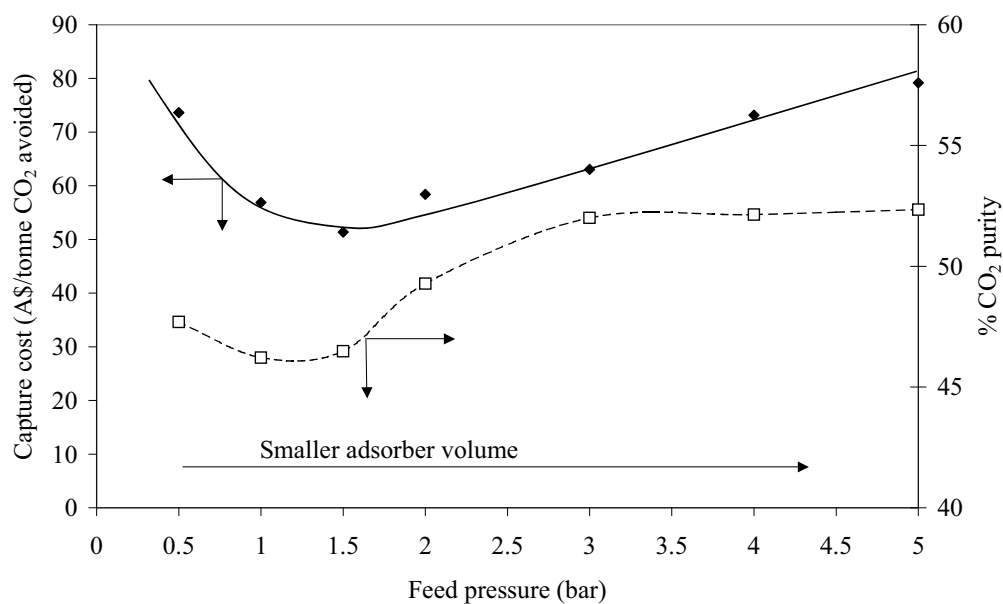


Figure 6-9 Effect of feed pressure on CO₂ product purity (□) and capture cost (◆)

Desorption pressure

Increasing the pressure ratio by decreasing the evacuation or desorption pressure improves both the CO₂ recovery and purity (Kikkinides and Yang, 1993, Yoshida et al., 2003, Diagne et al., 1995, Liu and Ritter, 1996). At a lower evacuation pressure, more CO₂ is liberated from the adsorbed bed, thereby increasing the overall recovery rate and the purity of the evacuated stream. This is shown in Figure 6-10. The feed pressure is constant at 1.5 bar.

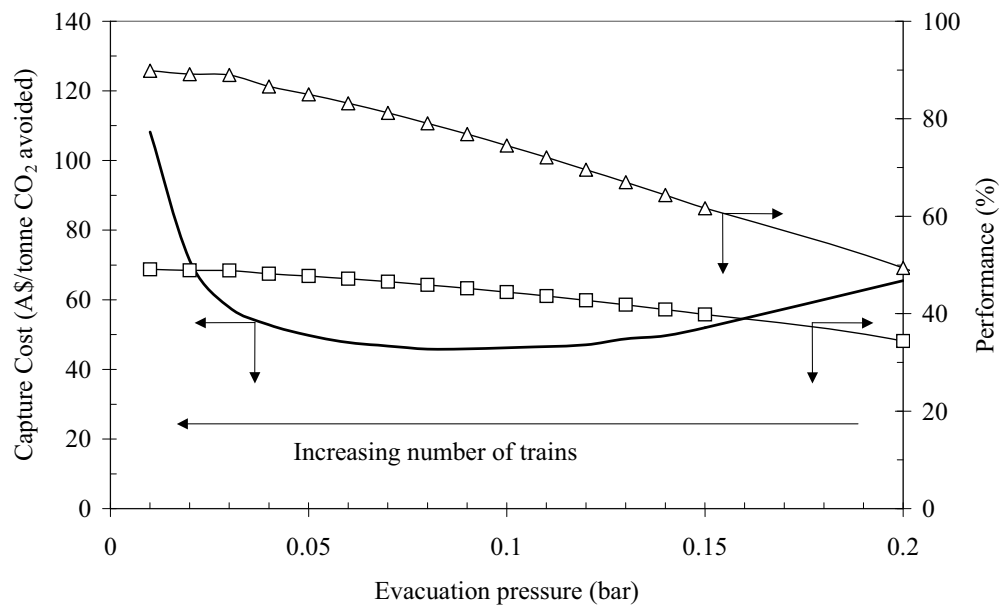


Figure 6-10 Effect of desorption/evacuation pressure on CO₂ recovery (Δ), purity (□) and capture cost (—)

For the Skarstrom PSA cycle, the CO₂ recovery rate decreases from approximately 90% at an evacuation pressure of 0.01 bar to less than 50% recovery at 0.2 bar. When the evacuation pressure is low (less than 0.1 bar), there is a large driving force for the liberation of the CO₂. At higher evacuation pressures, the driving force decreases as the pressure differential decreases and thus less CO₂ is recovered.

The results show that the optimal capture cost occurs at evacuation pressures between 0.05 to 0.1 bar. At very low evacuation pressures (less than 0.03 bar), the number of adsorption trains is high resulting in a large expenditure on capital. The total number of trains is determined by the vacuum blower requirement, the lower the vacuum pressure the larger the volumetric requirements and the larger is the number of trains required (Webley, 2005). At higher evacuation pressures (greater than 0.15 bar), the recovery rate of CO₂ and purity of CO₂ in the product stream is low. This results in a low amount of CO₂ avoided and a higher CO₂ capture cost.

Taking into account leaks in the process, we can conclude that the optimal operating desorption/evacuation pressure is 0.07 bar. Therefore, the optimal pressure ratio is 0.07/1.5 (0.05).

Adsorbent selectivity

As shown by Equation 6.12, increasing the adsorbent CO_2/N_2 selectivity also increases the purity of the CO_2 in the enriched product stream. Figure 6-11 shows the relationship between the CO_2 purity and the adsorbent CO_2/N_2 selectivity. The results show that to obtain a concentration of 90% CO_2 in the enriched stream, an adsorbent selectivity of at least 500 at pressure ratio of 0.05 is required.

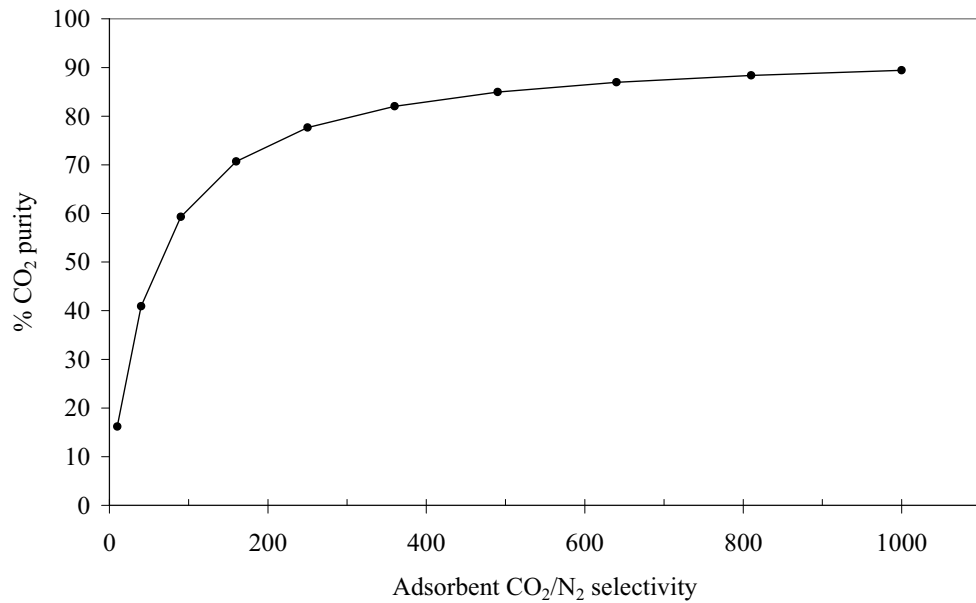


Figure 6-11 Effect on CO_2 purity with changes in the adsorbent CO_2/N_2 selectivity at a pressure ratio of 0.05(●)

6.4.5 Reducing the cost of the adsorption units

The effect of changing CO_2 and N_2 adsorbent properties

As shown in Figures 6-6 and 6-7, one of the largest contributors to the capital and operating costs of the PSA process are the costs for the adsorbent unit and for replacing the adsorbent. This arises because of the large amount of adsorbent required and the large size of the adsorbers. New adsorbents with increased working capacity could reduce the costs. From the extended Langmuir equation describing the isotherm for CO_2 (Equation 6.1), for a fixed CO_2 recovery, increases in the adsorption capacity (q_{CO_2}) would decrease the adsorber weight (W_{ads}) and adsorber volume (V).

In the following analysis, the simulations of the PSA process were controlled to ensure at least 85% of the feed gas CO₂ was recovered. Figure 6-12 shows the decrease in adsorbent volume required as the adsorption capacity for CO₂ increases (based an adsorption pressure of 1.5 bar and a desorption pressure of 0.05 bar). The analysis is for three CO₂/N₂ selectivity values, of 50, 100 and 500.

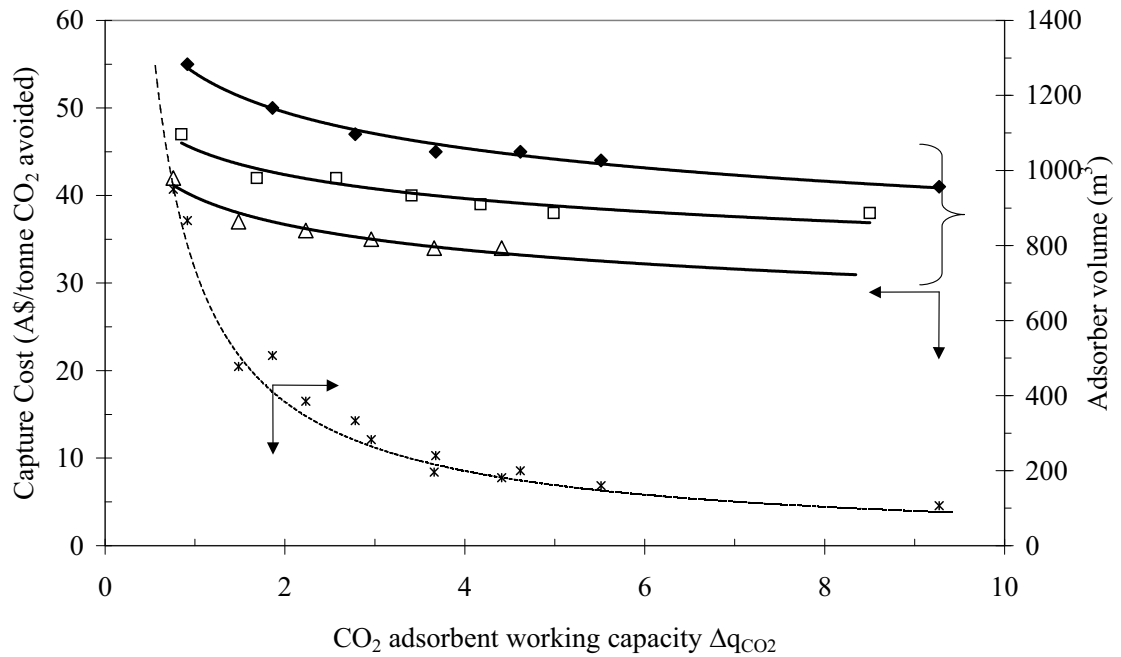


Figure 6-12 Changes in CO₂ capture cost (—) and adsorber volume (---) with increasing CO₂ adsorbent working capacity at three CO₂/N₂ selectivities: 50 (◆), 100 (□) and 500 (Δ)

By increasing the CO₂ adsorbent working capacity, a smaller adsorber volume is required. Therefore the capital and capture cost decrease. If we improve the CO₂ adsorbent working capacity from 1 to 4 mol CO₂ per kg of adsorbent (but not the CO₂/N₂ selectivity), the capture cost can decrease from over A\$50 to A\$45 per tonne CO₂ avoided. Increasing the adsorbent working capacity beyond this generates further possible cost savings of up to A\$5/tonne CO₂ avoided. This is not a very large saving because for adsorbent working capacities larger than 4 mol CO₂/ kg of adsorbent, the adsorber volume does not decrease by much. We can drive down costs further if we couple increases in adsorbent working capacity with increases in the CO₂/N₂ selectivity. For instance, increasing the selectivity from 50 to 500 reduces the capture cost to almost A\$35/tonne CO₂ avoided. This is a reduction of 35% compared to the baseline cost.

6.4.6 Effect of process improvements

In addition to the traditional Skarstrom cycle, the PSA cycle can be improved with steps such as adsorber bed pressure equalisation, depressurisation and product purges. Many different combinations and process steps have been proposed in literature (Na et al., 2001, Na et al., 2002, Chou and Chen, 2003, Chue et al., 1995, Rajasree and Moharir, 2000, Park et al., 1998). One of the most commonly suggested PSA processes is the seven-step cycle, shown in Figure 6-13. This consists of:

- (I) Feed pressurisation;
- (II) Adsorption (AD) of the heavy component;
- (III) Depressurisation (DP) of the adsorber bed to enhance the withdrawal of the light component;
- (IV) Pressure equalisation (PE) where the adsorber bed A at the end of the adsorption step is connected to adsorber bed B at the end of the evacuation step through the outlets;
- (V) The fifth step is purging the adsorber bed with enriched (CO_2) product;
- (VI) The adsorber bed is then reduced to the desorption pressure; and
- (VII) The final step is the evacuation of the heavy component at low pressure.

These steps are discussed in detail by Na et al. (Na et al., 2001). By removing steps III, IV and V, the cycle reverts back to the simple four-step Skarstrom cycle.

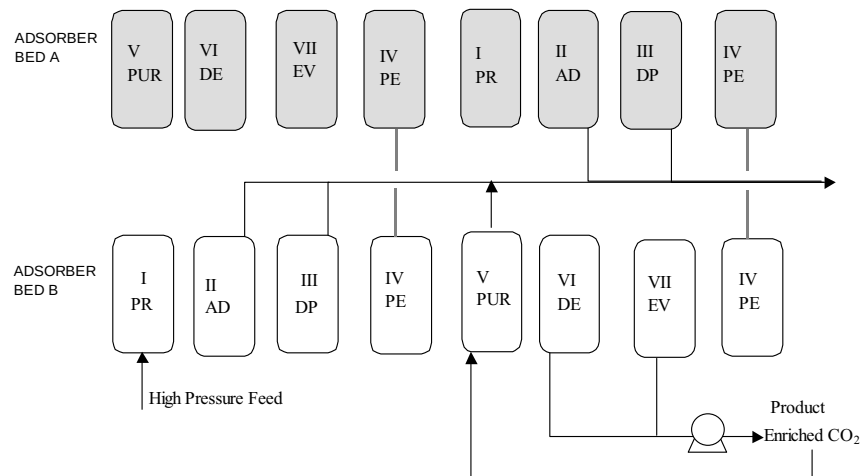


Figure 6-13 Seven-step PSA cycle

This chapter has so far examined the capture cost for the simple four-step Skarstrom cycle. The following sections of this chapter will evaluate the economics of modifying this cycle. Other aspects, namely the cycle conditions and the adsorbent characteristics, are the same as for the baseline case study (Table 6-1).

The effect of depressurisation and pressure equalisation

One of the first process improvements to the Skarstrom cycle was the introduction of a pressure equalisation (PE) step (Ruthven et al., 1994, Yang, 1987). The principal objective of which is to conserve energy. It does this by using the compressed gas from the high-pressure bed to partially pressurise the low-pressure column, instead of venting it. The pressure achieved at the end of the PE step ($P_{\text{equalisation}}$) can be determined by the equation given in Warmuzinski and Tanczyk (2003).

$$P_{\text{equalisation}} = \sqrt{P_{\text{des}} \times P_{\text{ads}}} \quad (6.14)$$

Figure 6-14 shows the performance of the PSA process as the simple Skarstrom cycle, a five-step cycle with the depressurisation (DP) set at 1 bar, and a six-step cycle with DP and PE. The corresponding CO₂ capture costs are also shown. The capital cost and operating cost components are set out in Figures 6-15 and 6-16 respectively.

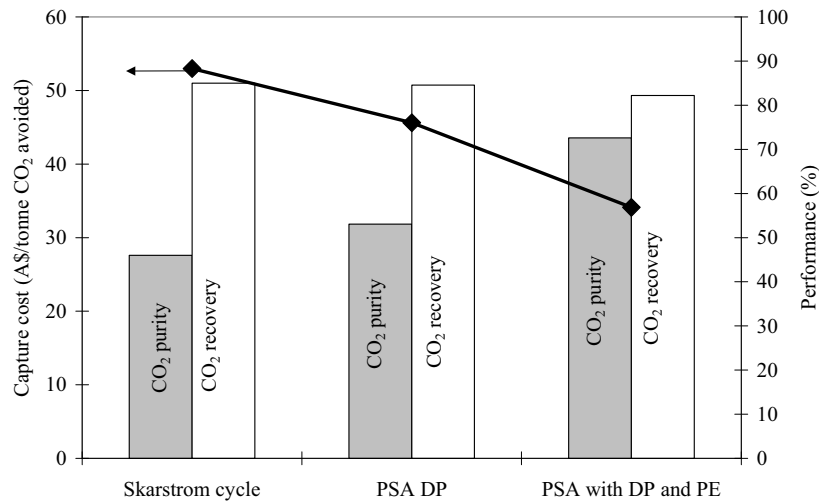


Figure 6-14 CO₂ purity (■), CO₂ recovery (□), and CO₂ capture cost (◆) for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE

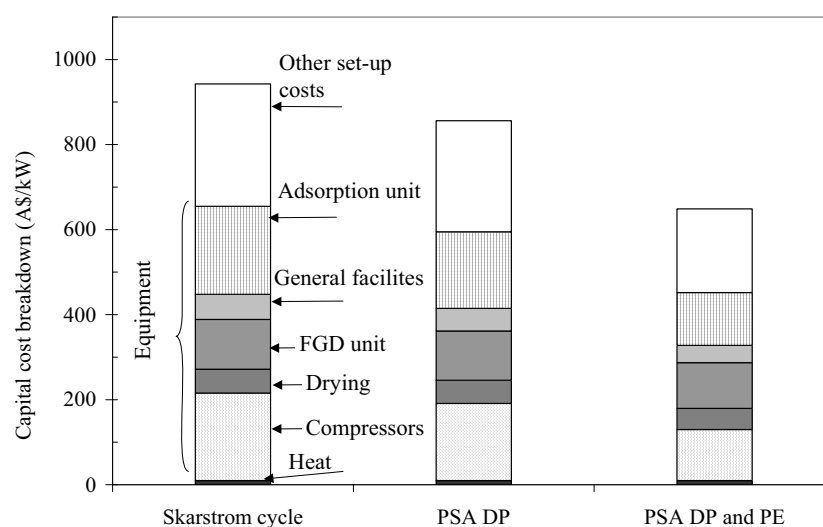


Figure 6-15 Breakdown in equipment item cost for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE

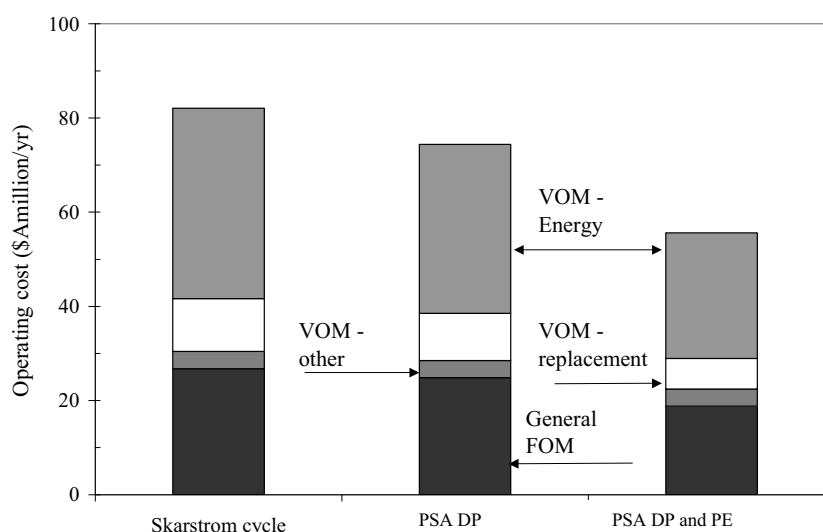


Figure 6-16 Breakdown of operating cost for the Skarstrom cycle, a PSA cycle with DP, and a PSA cycle with DP and PE

When the process is the Skarstrom cycle, the CO₂ purity and recovery rate are 46% and 85% respectively. Figure 6-14 shows that if the cycle includes a DP step, the CO₂ purity increases to 50%. If both DP and PE are included the CO₂ purity increases to 70% without adversely affecting the recovery rate. As a consequence of the higher CO₂ purity in the product stream, a smaller post-separation compressor is required (Figure 6-15), thus reducing the capture cost per tonne CO₂ avoided.

The amount of CO₂ recovered is dependent on the adsorption pressure of the PSA cycle, adsorbent type and weight. For all three cycles, the adsorption pressure and adsorbent properties are the same, and thus the amount of CO₂ recovered is similar. The differences in purity between the processes reflect the differences in the effect of N₂ adsorption. For the Skarstrom cycle, the amount of N₂ adsorbed in the adsorption step is the amount of N₂ that is evacuated with the CO₂ in the enriched product stream. Thus the CO₂ purity is the lowest. When DP is included a small amount of N₂ was desorbed at 1 bar and the CO₂ purity increases, although the increase is not very significant (less than 10%). However, if a PE step is also incorporated with the DP step, a higher CO₂ purity stream is obtained. During the PE step, the pressure of the bed is decreased to 0.3 bar from 1 bar and a greater quantity of N₂ is desorbed. Na et al. (Na et al., 2001) have also report a similar observation in their study which investigated CO₂ recovery and purity when the PSA process includes the DP and PE cycle steps.

In the six-step cycle with DP and PE, the amount of CO₂ recovered is marginally less than for the Skarstorm cycle or the five-step cycle with DP. This is because, a portion of CO₂ is also desorbed during PE, thus reducing the overall quantity of CO₂ liberated during evacuation.

The effect of product purge

For the PSA process where the strongly adsorbed component (CO₂) is the desired product, purging with the enriched CO₂ further enhances the purity of the CO₂ obtained from the evacuated stream. The Skarstrom cycle can be modified to include a product purge step by including it in the cycle between the adsorption and evacuation steps. This is graphically illustrated as step V in Figure 6-13.

Figure 6-17 shows the CO₂ product purity, CO₂ recovery rate and capture cost due to product purging. It is assumed in this analysis that 30% of the CO₂ enriched product stream is used for purging the adsorber bed.

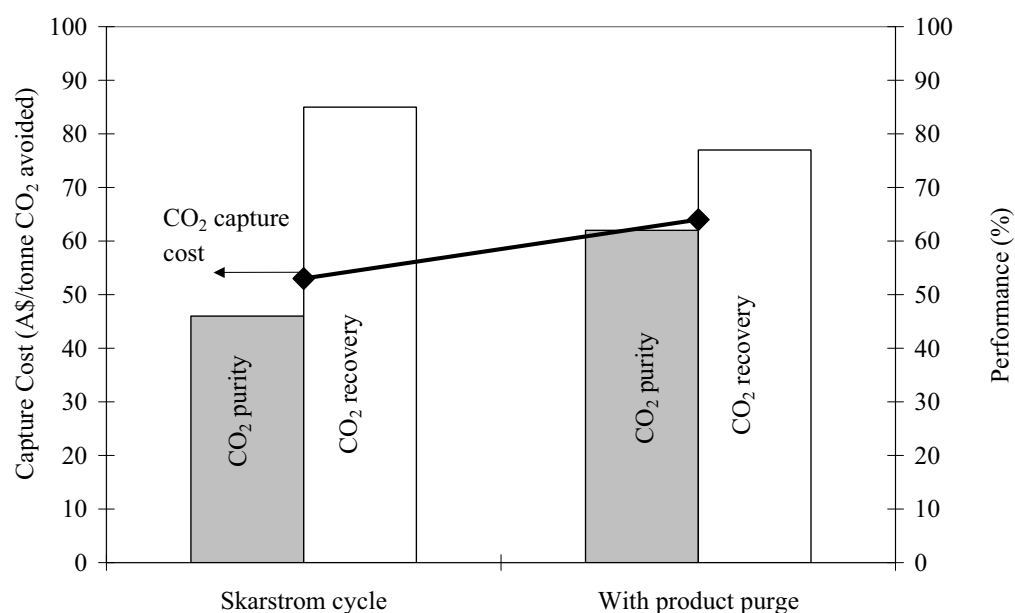


Figure 6-17 The performance of the PSA process shown as CO₂ purity (■) and CO₂ recovery (□), and CO₂ capture cost (◆) for the Skarstrom cycle and a PSA cycle with product purge

Including a purge stream increases the CO₂ purity from 46% to 60%. This is because the main function of the product purge is to displace any N₂ gas remaining in the void volume and adsorbent surface with high purity CO₂. However, because a proportion of the product gas is used for the purge or sweep, the overall recovery is lower. Purging increases the capture cost to A\$65/tonne CO₂ avoided because the total amount of CO₂ avoided is lower than the baseline case.

Increasing the percentage of product used to purge the adsorber bed increases the purity of the CO₂ but decreases the overall amount of CO₂ recovered. Figure 6-18 shows that minimising the product purge also minimises the capture cost. Although increasing product purge results in a higher concentration of CO₂ in the product stream and a smaller post-separation compressor is used, the increased power needed to pump the purge and the decrease in the amount of CO₂ recovered increases the capture cost. If adsorbents with exceptionally high working capacities for CO₂ can be developed to achieve very high recovery rates, including a product purge will have less of an effect on the CO₂ capture cost than for zeolite 13X.

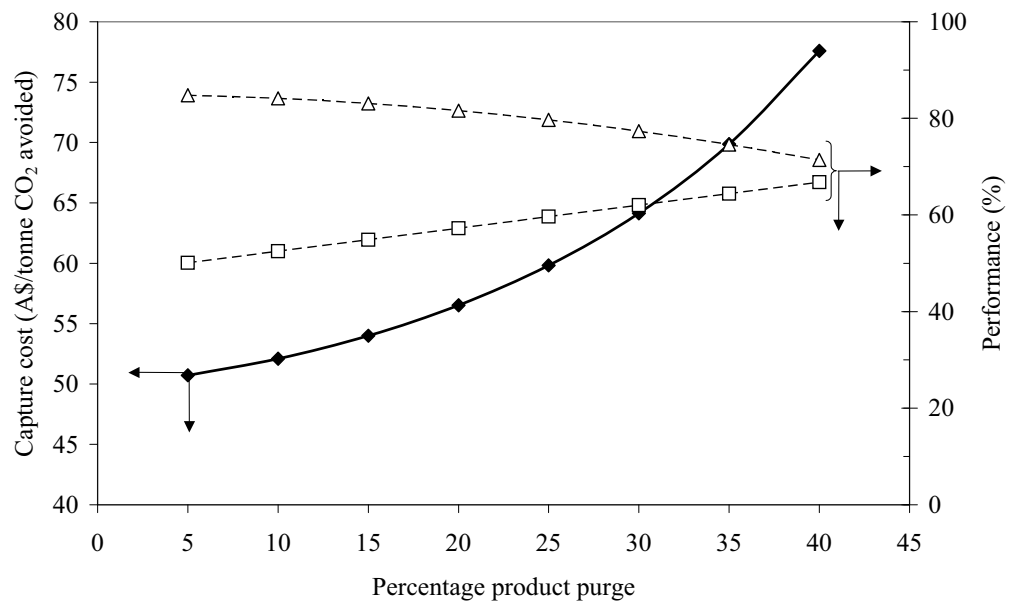


Figure 6-18 Capture cost ($\blacklozenge$), CO₂ purity ($\square$) and recovery (Δ) as a function of the percentage of CO₂ product purged

6.4.7 Effect of adsorption step time

The adsorption step time for a PSA process is another important variable. The adsorption time affects the cycle time of the process: a short process time results in a quick turnover time for each adsorber bed and reduces the number of adsorber beds required. However this is achieved at the expense of recovering more CO₂. Figure 6-19 shows the effect of adsorption step time on the PSA performance.

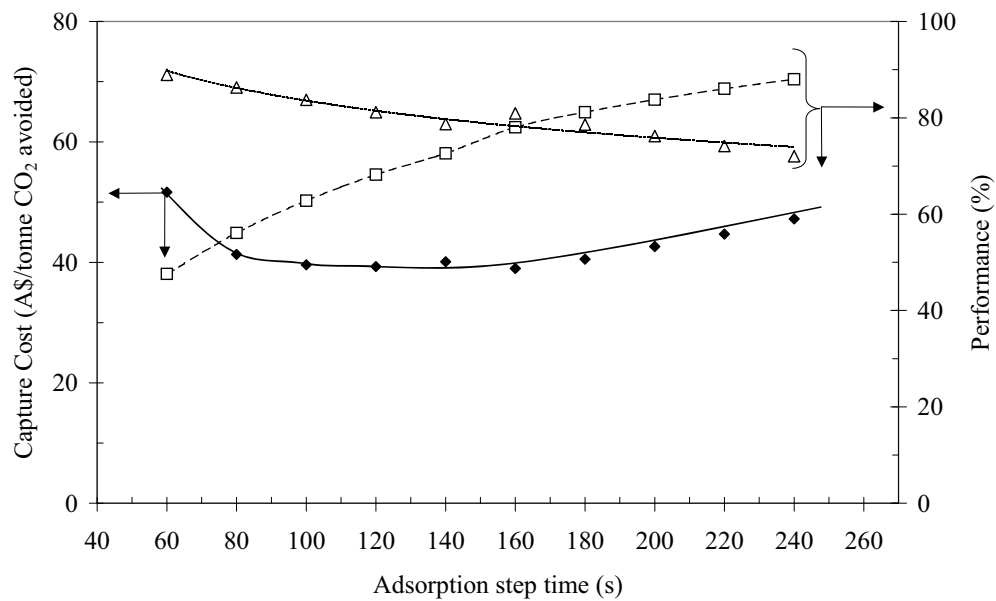


Figure 6-19 Effect of the adsorption step time on the CO₂ purity (□), CO₂ recovery (Δ), and capture cost (◆)

From Figure 6-19, the CO₂ recovery decreases but the CO₂ purity in the enriched product increases with adsorption step time. By increasing the adsorption step time, more CO₂ enters the system and is more likely to breakthrough into the light product (waste gas), which decreases the overall CO₂ recovery. However, as more CO₂ enters the system, more N₂ also enters the system and is also likely to breakthrough into the light product (waste gas). Because the adsorption properties of N₂ on 13X are much lower than for CO₂, a greater proportion of adsorbed N₂ is more likely to break through into the light product (waste gas). Therefore, during evacuation, the amount of CO₂ adsorbed is higher than the amount of N₂ adsorbed and thus the CO₂ purity increases.

Figure 6-19 also illustrates the effect of adsorption step time on the capture cost. The capture cost decreases with increasing adsorption time until approximately 200 seconds, and then slowly increases. For adsorption time steps of up to 200 seconds, the gain in CO₂ purity reduces the size and cost of the post-separation CO₂ compressors. This saving outweighs any losses due to lower CO₂ recovery rates. However, as the time increases and the proportion of CO₂ recovery decreases, the benefits of having a smaller CO₂ compressor become diminished by the decreasing amount of CO₂ avoided. Coupled with the need for more adsorbers due to the longer cycle times, the capture cost

steadily increases. The results show that the lowest cost occurs at an adsorption step time of approximately 100 seconds.

6.4.8 Synopsis – “low cost PSA systems”

Based on the sensitivity analysis above, we can conclude that the lowest capture cost occurs for vacuum desorption PSA with a feed pressure at 1.5 bar, an evacuation pressure at 0.07 bar, and an adsorption step time of 100 seconds. The process should also include a DP or waste gas blowdown followed by PE.

Figure 6-20 illustrates the relationship between the capture cost using these processing conditions and increasing adsorbent working capacity.

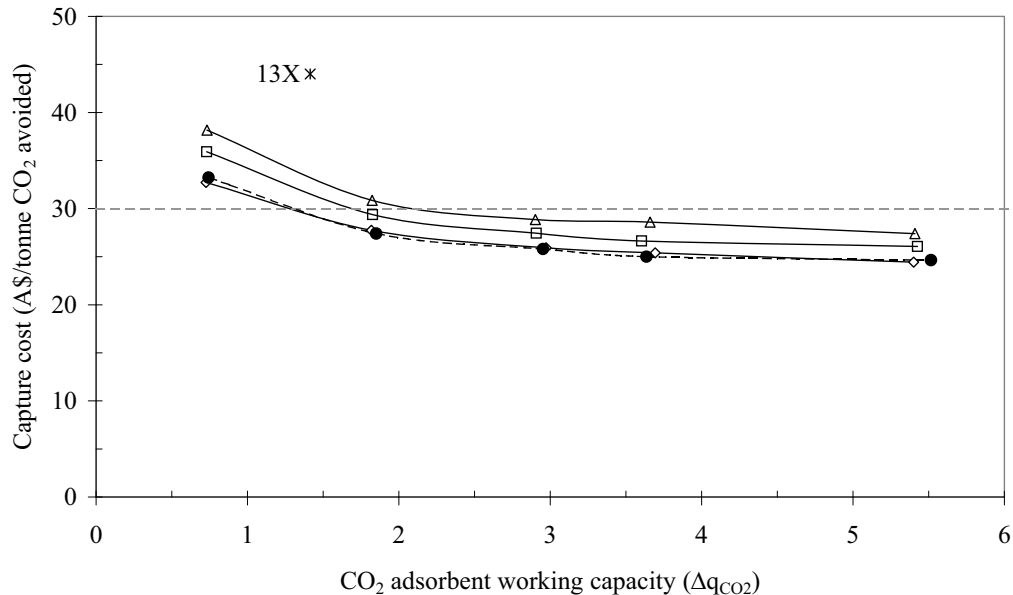


Figure 6-20 Capture cost with changes in CO₂ adsorbent working capacity at CO₂/N₂ selectivity and purge combinations of 200/0% (●), 140/5% (◇), 100/10% (□) and 80/15% (Δ)

The analysis is for three combinations of selectivity and purge ratios. The selectivity and purge combinations for Figure 6-20 were selected so that the concentration of CO₂ in the enriched product stream is at least 90%. The CO₂ recovery is set at 85%. These output parameters were chosen to enable a fair comparison of PSA technology with other CO₂ capture options such as chemical absorption where high recovery rates and high CO₂ purity product are obtained. The adsorbent cost is A\$5/kg.

In Figure 6-20, if the seven-step PSA cycle using adsorbent 13X is considered, to recover 85% CO₂, the capture cost is approximately A\$44/tonne CO₂ avoided and the CO₂ product purity is 75%. This is achieved using a product purge of 30% and the adsorbent selectivity is 54. In comparison, if a new adsorbent with the same adsorbent working capacity but higher selectivity is used, the capture costs decreases to A\$35 to A\$30 per tonne CO₂ avoided. Further improvements in the adsorbent working capacity reduce the capture cost to less A\$25/tonne CO₂ avoided. Figure 6-20 also shows that for the PSA process, similar performance and capture costs can be obtained using an adsorbent with a CO₂/N₂ selectivity of 200 and no product purge, or a lower selectivity of 80 and a product purge rate of 15%.

Examining the results of Figure 6-20 in detail, Figure 6-21 summarises the adsorbent characteristics, purge ratios and adsorbent price combinations that correspond to a notional capture cost of A\$30/tonne CO₂ avoided.

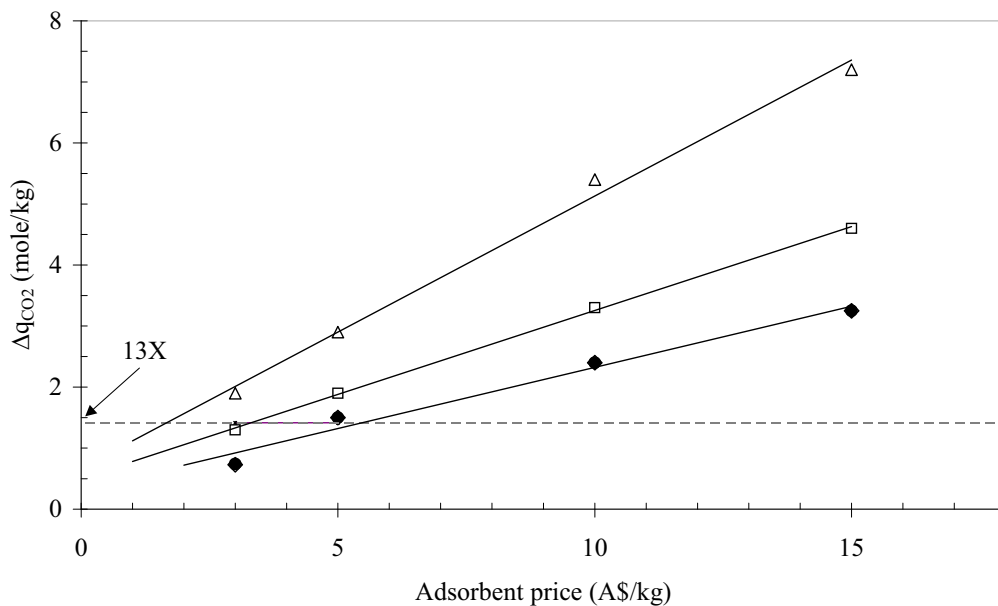


Figure 6-21 Adsorbent characteristics and price combinations to achieve a cost of A\$30/tonne CO₂ avoided at CO₂/N₂ selectivity and purge combinations of 200/0% (●), 140/5% (◇), 100/10% (□) and 80/15% (Δ)

The results in Figure 6-21 show that if new adsorbents could be produced at low cost – less than A\$5/kg – than improving the adsorbent selectivity compared to that of adsorbent zeolite 13X while maintaining the same adsorbent working capacity for CO₂

will yield a lower capture cost. However, if adsorbent prices are high – greater than A\$5/kg – improvements in both the working capacity and selectivity is required to achieve capture cost reductions.

The results of Figures 6-20 and 6-21 are based on a simple analysis including a simple seven-step PSA cycle, a single adsorbent type and neglects absorption kinetics. However, many different combinations of processing conditions, cycles and adsorbent characteristics are possible. In addition, adsorption kinetics will influence the performance of the PSA process. Therefore the results of the analysis may not be accurate on an absolute basis; however, they are indicative of the potential cost reductions and highlight the direction of future adsorbent development to achieve these cost reductions.

6.5 Conclusion

This chapter analyses pressure swing adsorption for CO₂ capture from flue gas. It is the first analysis under Australian conditions.

The results show that using commercially available zeolite 13X and the Skarstrom cycle with vacuum desorption, a CO₂ recovery of 85% and a product enriched with 46% CO₂ is achievable. The corresponding capture cost is A\$53/tonne CO₂ avoided. To reduce this cost, new adsorbents with higher working capacity for CO₂ and a high CO₂/N₂ selectivity is required. This will reduce the capital cost for the adsorption system and the CO₂ compressor. If the new adsorbent is coupled with improved processing cycles such as depressurisation, adsorber bed equalisation and product purge, a capture cost of less than A\$30/tonne CO₂ avoided is achievable. Therefore, as illustrated in this chapter, improvements in adsorption technology could help reduce the cost of CCS and improve economic viability.

The results of this analysis show that CO₂ recovery from flue gas using physical adsorption technology can be competitive with other separation technologies such as chemical absorption (Chapter 4) or membrane separation (Chapter 5). The results from

this chapter have been based on a short-cut simulation method, and therefore the results are only indicative. A more complete evaluation would require experimental data coupled with economic modelling.

Chapter 7. LOW TEMPERATURE CO₂ CAPTURE

7.1 Overview

This chapter analyses the feasibility and cost-effectiveness of low temperature separation technology for recovering CO₂ from post-combustion power plant flue gas. Initially the analysis examines the cost of CO₂ avoided using a novel CO₂ separation technique - subliming the CO₂ under pressure. The analysis then focuses on how costs can be reduced through changing the sublimation pressure and through heat integration. Similar to adsorption and membrane technology, to our knowledge, this is the first Australian analysis of CO₂ capture economics for low temperature separation.

7.2 Low temperature CO₂ anti-sublimation process

7.2.1 Introduction

The low temperature separation configuration for CO₂ capture, described by Schussler and Kummel (1989) is selected as a basis for the analysis. As discussed in section 2.5, this configuration is chosen as it is a more suitable and effective option than cryogenic distillation for recovering low partial pressure CO₂. In addition, the scheme consists of classical process technologies such as heat exchangers and refrigeration units that are widely available and used in chemical industries.

In contrast to other traditional separation processes such as membrane, PSA or absorption, CO₂ separation sublimation is still at the primary research stages and has not yet been demonstrated commercially. Thus the analysis in this chapter examines a novel technique, and costs estimates are more uncertain than in previous chapters.

Under certain conditions with respect to temperature and pressure, different components of a mixture can exist in different phases. Thus, Schussler and Kummel proposed that CO₂ could be recovered from flue gas streams using the reverse process of sublimation. In this method, CO₂ is recovered by cooling the gaseous CO₂ in the flue gas directly

into a solid product, while the other gases in the feed stream remain in a gaseous form. The solid CO₂ is then melted to form a liquid ready for transport and storage. This is represented in Figure 7-1

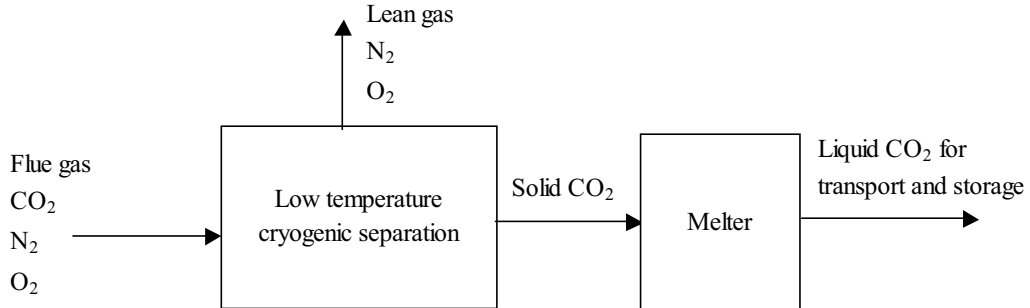


Figure 7-1 Schematic of CO₂ recovery by anti-sublimation

Sublimation is the phase change from solid to gas, whereas the reverse process has no designated terminology. Some researchers such as Schussler and Kummel also describes the process as sublimation, while others refer to it as anti-sublimation (Clodic and Younnes, 2004). In this study, the phase change from gas to solid will be referred to as “anti-sublimation” and from solid to gas as “sublimation”.

For pure CO₂, the point of sublimation occurs below the triple point (5.26 bar and 216.6 K or -56.4°C). At atmospheric pressure, gaseous CO₂ can be completely solidified (or solid CO₂ can be completely gasified) at -56.6°C (216 K). However, complete solidification or gasification is not possible for gas mixtures such as power plant flue gases. A proportion of the CO₂ will always remain in the gas phase due to the equilibrium imposed at the sublimation pressure. Because a thermodynamic equilibrium exists between the solid and gaseous CO₂, the CO₂ sublimation pressure can be equated with the partial pressure of the gaseous CO₂. This means that as the gas mixture is compressed and cooled to the sublimation pressure, the partial pressure of CO₂ rises until it reaches a pressure where it will solidify or “anti-sublime” to keep its partial pressure in the gas mixture on the sublimation curve. At the beginning of the separation process before cooling, the partial pressure of CO₂ (p_{CO_2}) depends only on its mole fraction (y_{CO_2}) and the total pressure of the feed gas (P_f), as shown in Equation 7.1.

$$p_{CO_2} = y_{CO_2} P_f \quad (7.1)$$

However, at the point where solid CO₂ is recovered by anti-sublimation, the CO₂ partial pressure for sublimation (p_{subCO_2}) depends on the pressure of the refrigeration unit ($P_{\text{refrigeration}}$), the mole fraction of CO₂ in the feed (y_{CO_2}), the feed gas flowrate (F_f) and the amount of CO₂ that is recovered (n_{CO_2}). This relationship is shown as Equation 7.2.

$$p_{\text{subCO}_2} = \frac{A1 \times P_{\text{Refrigeration}}}{1 + A1} \quad (7.2)$$

$$A1 = (1 - n_{\text{CO}_2}) \frac{y_{\text{CO}_2} F_f}{(1 - y_{\text{CO}_2}) F_f}$$

Assuming that the sublimation pressure of CO₂ is equivalent to the CO₂ vapour pressure, the temperature at which CO₂ anti-sublimes ($T_{\text{sublimation}}$) can be calculated by Antoine's equation and constants for CO₂.

$$T_{\text{Sublimation}} = \frac{B}{A - \log_{10} p_{\text{subCO}_2}} - C \quad (7.3)$$

7.2.2 Processing and economic assumptions

CO₂ capture using low temperature separation is schematically represented in Figure 7-2. The path of CO₂ in the process from the flue gas (point A) to the specified stream for sequestration (point H) is shown in the phase diagram for CO₂ (Figure 7-3).

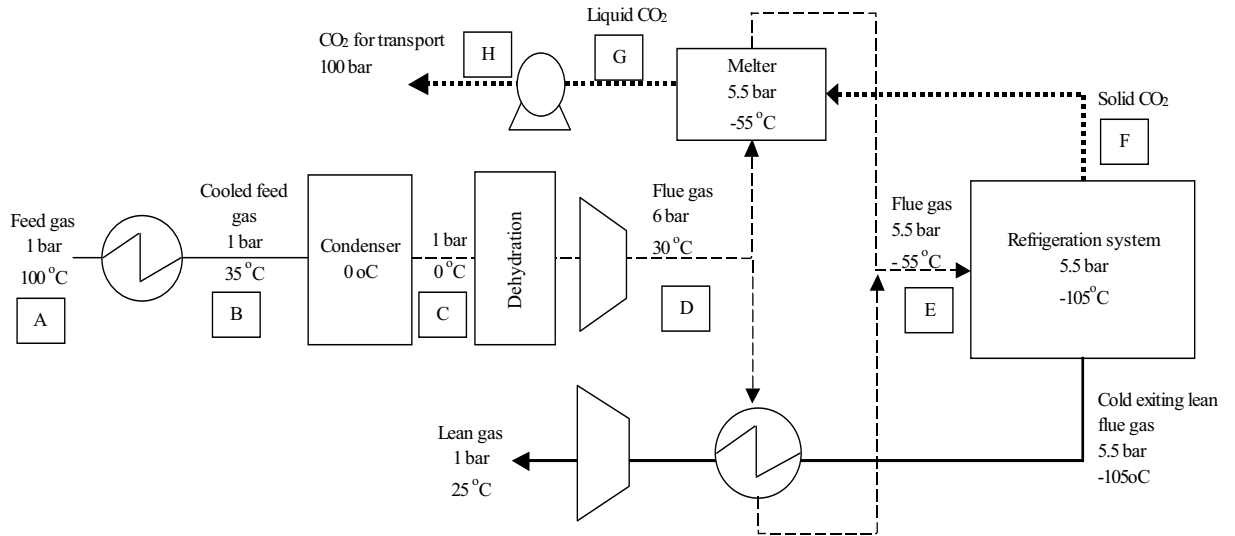


Figure 7-2 Simplified diagram of the baseline conditions for the low temperature separation

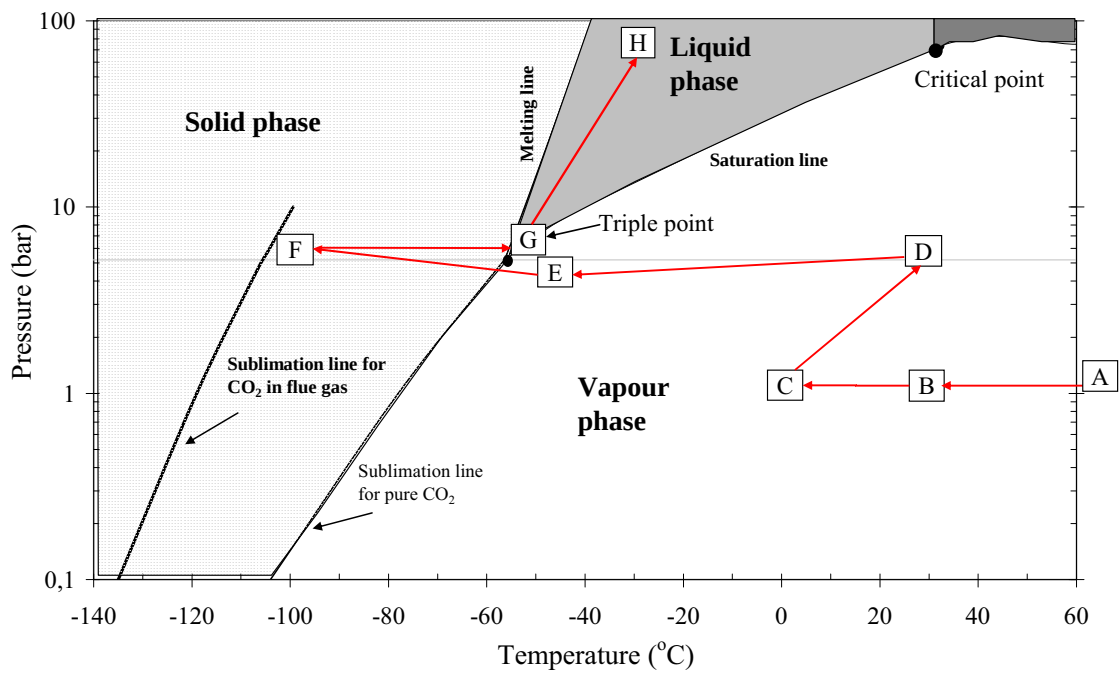


Figure 7-3 Temperature-pressure diagram for CO₂

The process steps are as follows:

- The feed flue gas (A) enters at 95°C and 1 bar and is cooled at constant pressure to 35°C (B);
- The flue gas then enters a refrigeration unit where it is cooled to 0°C to condense and remove any water from the stream (C);

- Any remaining moisture is removed in a molecular sieve dehydration unit;
- The flue gas is then compressed to a pressure 10% above the refrigeration pressure to allow for pressure losses along the heat exchangers (D);
- The flue gas is further cooled before entering the refrigeration (anti-sublimation) unit. This is achieved by splitting the flue gas into two streams. One stream passes through the CO₂ melter where it is cooled by the production of liquid CO₂, while the other stream passes through a heat exchanger where it is cooled by the lean waste gas. The two streams are recombined (E) before being sent to the anti sublimation refrigeration unit.
- The flue gas enters to the refrigeration (anti-sublimation) unit where solid CO₂ is formed and recovered (F). The lean waste gas is expelled from the unit and used to partially cool the incoming flue gas stream.
- The solid CO₂ is recovered from the refrigeration unit using a scraper. It is then melted (G), and pumped to 100 bar for transport and storage (H).

The processing assumptions for the flue gas and the economic conditions used in this analysis are described in section 3.5.

For the baseline analysis, it is assumed that the flue gas is cooled to a temperature of -55°C before entering the refrigeration unit. The pressure of the refrigeration unit is set to 5.5 bar with a corresponding sublimation temperature of -105 °C (168 K). After the CO₂ is solidified in the refrigeration unit, it enters a melter where it is liquefied at 5.5 bar to a temperature of -55°C (218K). The exiting lean flue gas is heated and expanded back to ambient temperature and pressure.

As shown in the phase diagram (Figure 7-3), for CO₂ to melt from a solid into a liquid, a minimum pressure of 5.2 bar is required. At a pressure lower than this, the CO₂ will sublime back into its vapour phase. In the baseline analysis, it is assumed that the CO₂ solid is melted into a liquid to minimise transport compression. Thus both the refrigeration unit and the CO₂ melter have a design pressure of 5.5 bar. The melter and refrigeration unit must be physically partitioned by a separator and rotary valve. This

prevents any backflow and loss of liquid CO₂ into the refrigerator and maintains the pressure of the melter.

7.2.3 Low temperature separation model

Performance equations

A low temperature separation model has been constructed to follow the process shown in Figure 7-2. In this process, the key unit operations include the refrigeration unit for condensation and CO₂ anti-sublimation; heat exchangers to cool the flue gas, melt the solid CO₂ and condense water vapour; compressors; expanders and dehydration. The model calculates the size of the equipment and determines total energy required for separation. Each of the process equations used to determine the mass and energy balances of the key unit operations are discussed below. The assumptions used in the model include:

- In the refrigeration unit, the partial pressure of the CO₂ is equal to the sublimation pressure;
- There is a 10% pressure drop across the heat exchangers (Schussler and Kummel, 1989);
- The gas behaviour is ideal (Schussler and Kummel, 1989);
- There is a minimum 10°C temperature difference across the heat exchangers (Hendriks, 1994);
- The condensation of trace contaminants has a negligible effect on the recovery rate of CO₂ in the refrigeration unit;
- The coefficient of deviation (COD) for the refrigerator is taken to be 0.45 (Schussler and Kummel, 1989);
- In recovering solid CO₂, the purity of the melted CO₂ for transport is at least 99% (Schussler and Kummel, 1989, Brockmeier et al., 1994, Hendriks, 1994, Intech, 1992); and
- The CO₂ recovery rate is 90% for all cases.

Heat exchangers: The material and energy balances for heat exchangers used within the model are determined using Equation 3.1 described in Chapter 3 (section 3.4.1).

Refrigeration (anti-sublimation) unit: As for the other capture technologies in this thesis; the exact refrigeration process has not been simulated precisely. In practice, multiple vapour compression cycles are used in low temperature processes such as the liquefaction of natural gas (Haywood, 1975). In that case, the natural gas is cooled from ambient temperature down to -157°C . For CO_2 capture, the sublimation temperature of CO_2 is above this value. It is assumed that multi-vapour compression cycles could adequately be used to “anti-sublime” the CO_2 (Hendriks, 1994, Clodic and Younnes, 2004).

To determine the energy needed in the refrigeration unit, the equivalent electrical work is calculated using the equation given by Schussler and Kummel (1989).

$$W_{\text{Refrigeration}} = -C_{p_{\text{CO}_2}} T_o \ln \frac{T_{\text{Refrigeration}}}{T_{\text{In}}} - C_{p_{\text{CO}_2}} (T_{\text{In}} - T_{\text{Refrigeration}}) / \eta_{\text{real}} \quad (7.4)$$

and

$$\eta_{\text{real}} = \left(1 - \frac{T_o}{T_{\text{Refrigeration}}} \right) \text{COD}$$

It is assumed that the temperature of the environmental heat sink (T_o) for the refrigeration cycle is ambient air temperature of 25°C (298 K).

Compressors, expanders and dehydration: The equations for the number of stages and work of compression, expansion and dehydration have been described in Chapter 3 (section 3.4.1).

Energy consumption

The total energy consumption of the system includes:

- The energy to compress the feed gas to the set pressure;
- The energy to pump/compress the CO_2 product to the transport pressure;
- The energy to maintain the system at the lowest refrigeration temperature;
- The energy required for dehydration;
- The energy to condense the water vapour; and

- Any energy gained from gas expansion.

The total energy requirements is:

$$W_{\text{Low temp}} = W_{\text{Feed compressor}} + W_{\text{CO}_2 \text{ compressor/pump}} + W_{\text{Refrigeration}} + W_{\text{Dehydration}} + W_{\text{Condensation}} - W_{\text{Expansion}} \quad (7.5)$$

The equations for the compressors, expanders, dehydration and refrigeration work are described above.

7.2.4 Model parameters and outputs

The low temperature separation model allows the user to select the pressure for the refrigeration unit. The performance criteria for CO₂ capture include:

1. The rate of CO₂ recovery;
2. The CO₂ purity for transport;
3. The total energy requirement (penalty); and
4. The economic cost due to equipment sizing.

7.3 Baseline results and comparison with literature

The baseline cost for recovering CO₂ from a power plant flue gas using low temperature technology is shown in Table 7-2. The results indicate that the capture cost is approximately A\$70/tonne CO₂ avoided, with an energy penalty of 42%. In US dollars, the capture cost is estimated to be US\$60/tonne CO₂ avoided. The capital investment cost for the capture plant is estimated to be A\$1305/kW (US\$940/kW). Figure 7-4 outlines the breakdown of capital and operating costs, and the energy penalty.

The key equipment used in estimating the capital cost includes pre-treatment processes such as flue gas desulphurisation unit, heat exchangers, the feed gas compressor and the feed gas drier. For the "cryogenic" component of the process, the equipment costed includes the anti sublimation refrigeration unit, CO₂ melter/liquefier, pumps and the

lean waste gas expander. In addition 10% of the total equipment cost is assumed to account for general unspecified equipment. In this analysis, because anti-sublimation technology is more novel than other capture processes such as absorption or adsorption, the unit cost for the equipment such as heat exchangers is assumed to be higher than for heat exchangers used in other processes.

Table 7-1 Economic results for CO₂ capture using anti-sublimation technology

	This study	Hendriks (1994)	Brockmeier et al. (1994)
Cost year	2006	1990	--
Total energy penalty (%)	42	27	52
Capture cost			
A\$/tonne CO ₂ avoided	70	--	
US\$/tonne CO ₂ avoided	60	34	58 - 61
Capital investment for capture plant only A\$/kW, US\$/kW	1305 940		--
Total capital investment A\$/kW, US\$/kW	1900 1465	-- 1020	--

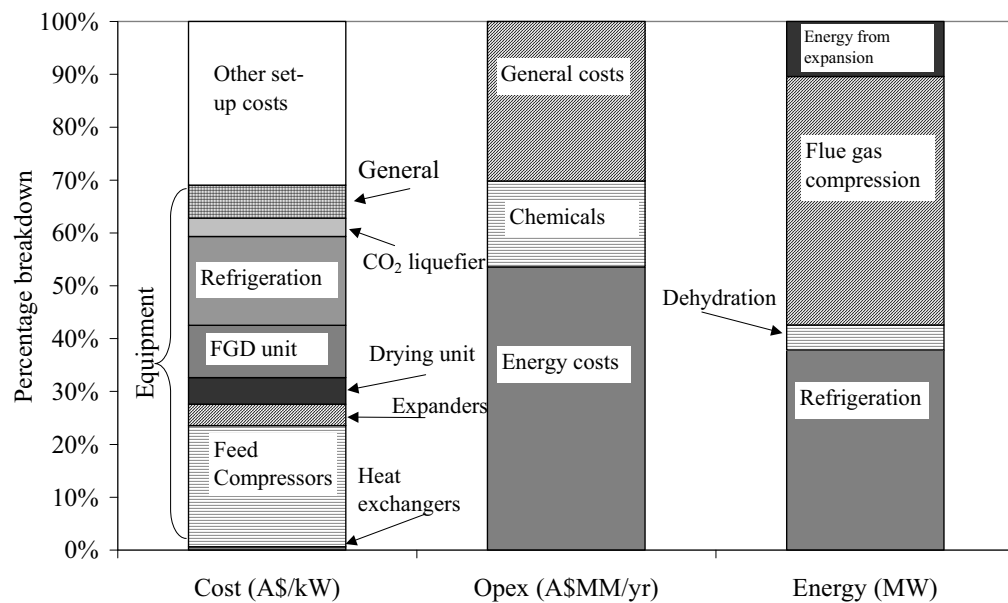


Figure 7-4 Percentage breakdown of capital cost, operating cost and energy consumption for the low temperature separation

The cost for capture using “cryogenic” low temperature systems (US\$60/tonne) is consistent with that reported by Brockmeier et al. (1994) (US\$58-61/tonne CO₂ avoided). However, Hendriks (1994) reported a much lower cost of US\$35/tonne CO₂ avoided. The discrepancy in the reported cost between this study, that of Brockmeier et

al. (1994) and that of Hendriks (1994) arise primarily due to the difference in cost year the discount rate, and the items of equipment included in the costing. If this study evaluated the capture cost for a cost year of 1990 with a discount rate of 5% as in the Hendriks' study, a capture cost of US\$40/tonne CO₂ avoided and total capital expenditure of US\$1100/kW is determined. The higher estimate for this study also arises because equipment such as the flue gas desulphurisation unit is included in the costing, while in the Hendriks study it was not. Unfortunately, insufficient detail was given in the study by Brockmeier et al. (1994) to allow a comparative analysis.

As illustrated in Figure 7-4, the two largest capital cost items and energy consumers in the low temperature process are the feed gas compressor and the refrigeration unit. The feed gas compressor accounts for almost 30% of the capital cost, and over half of the total energy requirement. The refrigeration cycle accounts for 25% of the equipment cost and 40% of the total energy requirement. As a result, the operating costs are dominated by the energy costs for the flue gas compression and refrigeration. It would appear that for capture cost reductions to be achieved; this would be accomplished by reducing either or both the capital cost and energy consumption of the feed gas compressor and the refrigeration unit. The following section of this chapter reports the effect of changing the operating conditions of the system – in particular the refrigeration pressure and temperature and the ways in which waste heat is used.

7.4 The effect of processing parameters on the capture cost

7.4.1 Refrigeration pressure

The largest contributor to both the capital and operating cost for the low temperature separation of flue gas is the feed gas compressor. One possibility of reducing this cost is to operate the anti-sublimation refrigeration unit at a lower pressure and thereby reduce the need for feed gas compression. However, as discussed in section 7.2, operating at a pressure below 5.2 bar, the recovered solid CO₂ does not melt into a liquid but sublimates back into a gas. This requires additional post separation compression for transport.

According to Hendriks (1994), a gas-lock or similar device could be used in the CO₂ melter to create a back pressure of up to six bar above that of the pressure in the refrigeration unit. In our initial analysis, we assumed that a minimum pressure of 5.5 bar was maintained in both the refrigeration unit and the CO₂ melter to ensure that the solid CO₂ forms into a liquid. However, if a gas-lock delivers a pressure of 6 bar higher in the CO₂ melter than in the refrigeration unit, then liquid CO₂ is still formed and there is no need for a post-separation compressor.

Figure 7-5 shows the change in capture cost and energy consumption if the refrigeration pressures range from 1 to 10 bar. Two options are considered. In the first, a gas-lock is used in the CO₂ melter and liquid CO₂ is formed. In the second, gaseous CO₂ sublimates from the solid and post-separation compression is required. Figure 7-6 shows the energy consumption for both cases. The energy components include the total energy, energy for compression, refrigeration and the energy gained from the expansion of the exiting lean flue gas.

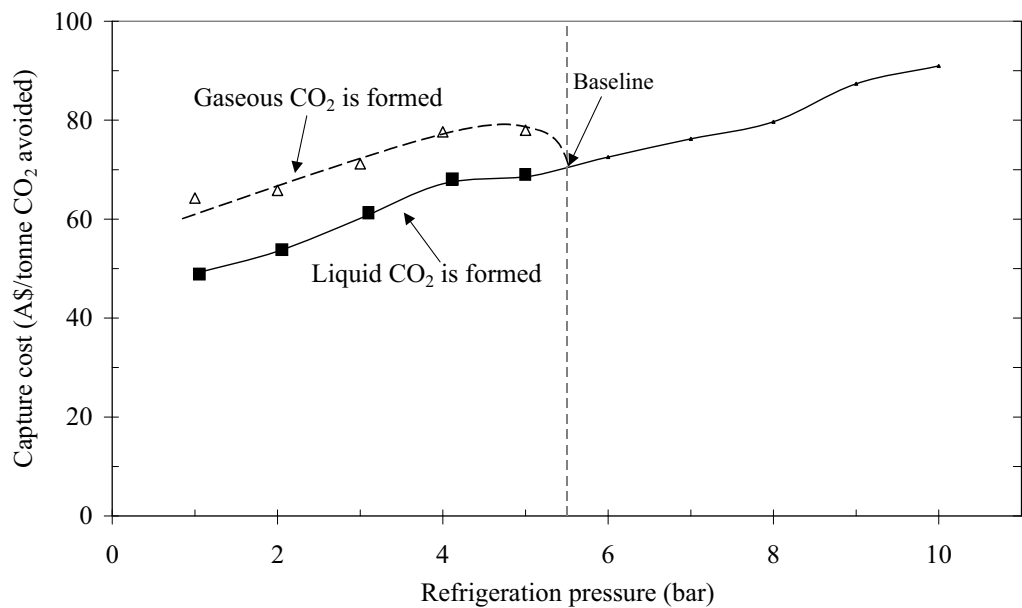


Figure 7-5 Changes in the capture cost with increasing refrigeration pressure when a gas-lock is used (■) and when no gas-lock is used (Δ)

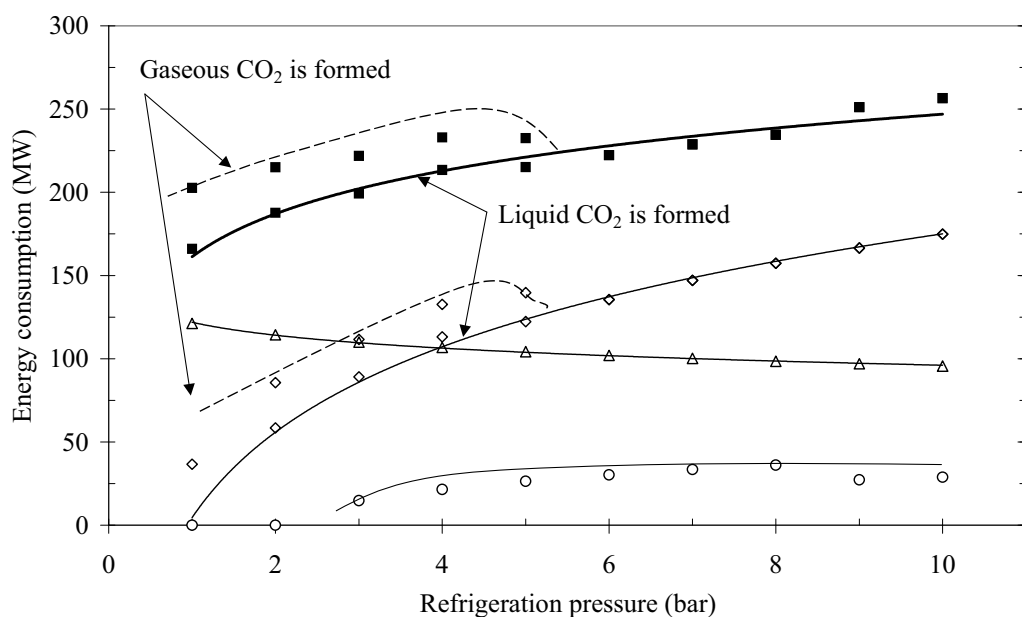


Figure 7-6 Energy consumption [total (■), compression (◇), refrigeration (Δ) and expansion (○)] for low temperature separation at different refrigeration pressures

From Figure 7-6, increasing the pressure in the refrigeration unit increases the compression energy, but decrease the energy needed in the refrigeration unit to solidify the CO₂. This occurs because the temperature required for anti-sublimation is higher at higher pressures, and hence less energy is needed to cool and solidify the gaseous CO₂. However, the energy needed to compress the feed gas to higher pressures exceeds any energy gained from the reduced work in the refrigeration unit, thus increasing the total pressure will increase the total energy requirement and the capture cost.

As shown in Figure 7-5, when a gas-lock is used and CO₂ liquid is formed, the capture cost decreases from A\$90 to A\$50 per tonne CO₂ avoided as the refrigeration pressure decreases from 10 bar to 1 bar. With no gas-lock, the capture cost decreases with decreasing refrigeration pressure to a value of 5.2 bar. After this point, a slight increase in cost is observed before the cost again begins to decrease. This is because without the gas-lock, additional post-separation compression is needed for CO₂ transport. This added compression increases the total energy and capital cost, thus the capture cost is higher at a refrigeration pressure of 5 bar than at 6 bar. Nevertheless, the capture cost continues to decrease with decreasing refrigeration pressure and, at a refrigeration

pressure of less than 3 bar, the capture cost for this system is less than for the baseline case.

When a gas-lock is used, the lowest capture cost is A\$50/tonne CO₂ avoided and this is obtained with a refrigeration pressure of 1 bar. If no gas-lock is used, the capture cost at atmospheric pressure is A\$65/tonne CO₂ avoided. The results of Figure 7-5 suggest that the lowest capture cost occurs when the refrigeration unit is at atmospheric pressure, especially if a gas-lock or similar device is used.

7.4.2 Maximising the heat transfer of the lean waste gas

In the baseline analysis, the temperature of the flue gas entering the refrigeration unit is assumed to be –55°C. The flue gas is cooled to this temperature by the energy gained through warming the exiting lean gas and melting the solid CO₂ into a liquid. In the baseline analysis, the amount of heat extracted from the lean exiting flue gas was not optimised. However, if the heat recovery from the lean exiting flue gas could be optimised, a greater proportion of the cooling energy would be extracted. Thus, the temperature of incoming flue gas could be cooled to a temperature lower than –55°C, and the energy needed in the refrigeration unit would be lower.

Figure 7-7 shows the how the capture cost change as the temperature of the flue gas entering the refrigeration unit changes. The variation in the flue gas temperature is obtained by varying the proportion of flue gas that is cooled by the lean flue gas and the proportion that is cooled by the melting CO₂. As shown in Figure 7-7, it is feasible to cool the flue gas down to a temperature of –105°C if the refrigeration pressure is 1 bar, or –95°C if the refrigeration is 5.5 bar. This is achieved using only the latent energy of the heated lean flue gas and the melted CO₂. With the refrigeration unit at atmospheric pressure, the capture cost can be reduced to \$28 from \$50 per tonne CO₂ avoided if a gas-lock device is used. It can be reduced from A\$65 to A\$35 per tonne CO₂ avoided if no device is used. Similar cost reductions can be obtained when the refrigeration pressure and temperature is 5.5 bar and – 105°C respectively. The capture cost reduction arises because the refrigeration unit requires less energy resulting in a lower total energy penalty and less capital investment.

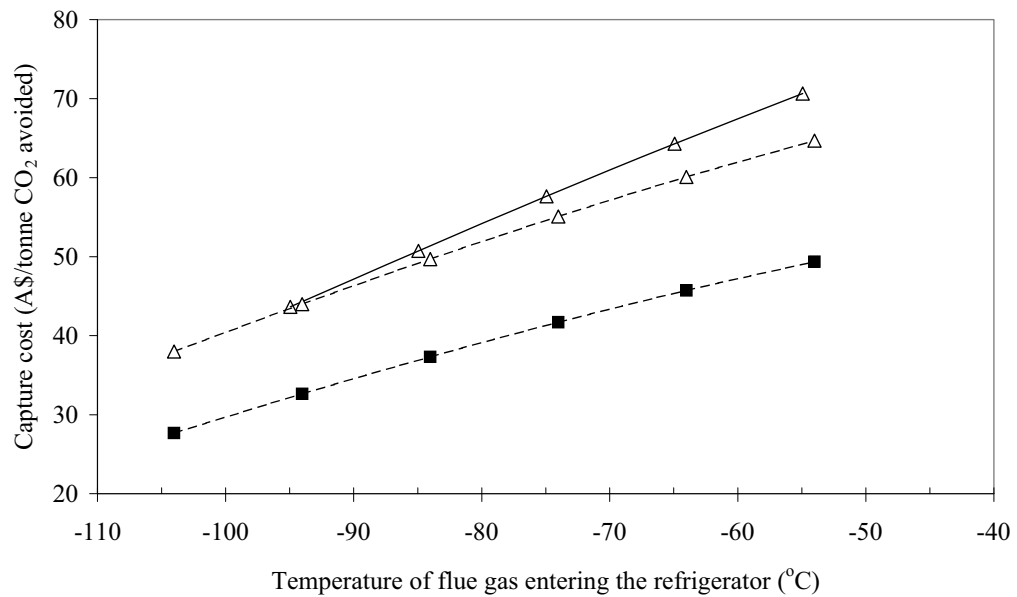


Figure 7-7 Effect of flue gas inlet temperature on capture cost at refrigeration pressures of 5.5 bar (—) and 1 bar (---), when a gas-lock is used (■) and when no gas-lock is used (Δ)

Let us consider the situation where the incoming flue gas is cooled to -105°C and a gas-lock is used in the melter. We refer to it as “Case A”. The schematic of the process is shown in Figure 7-8. The pressure of the refrigeration unit is 1 bar, and the temperature for anti-sublimation is -120°C .

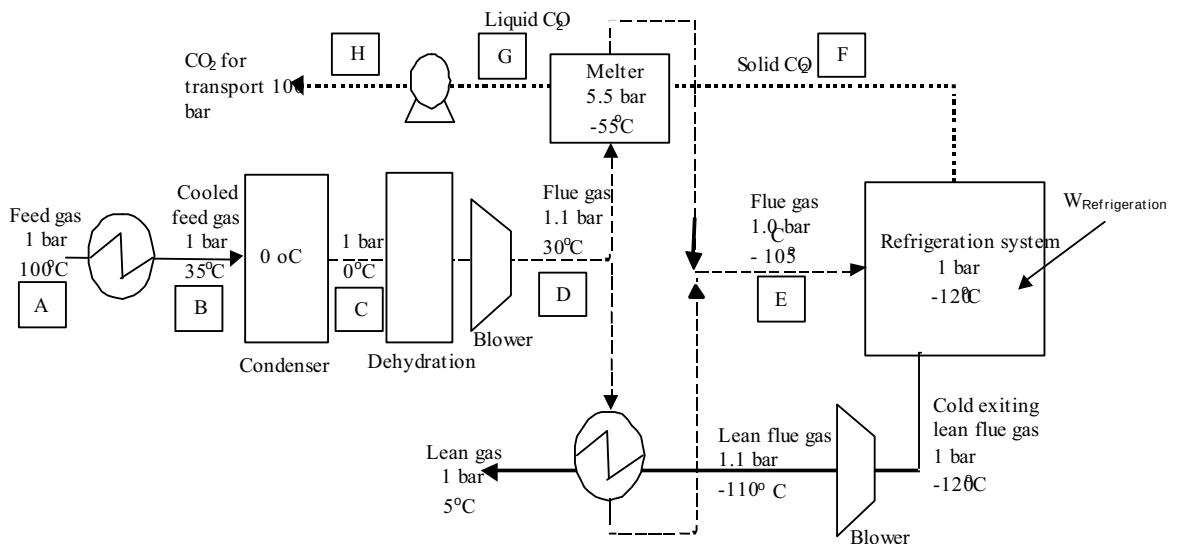


Figure 7-8 Schematic of “Case A”

The capture cost corresponding to “Case A” is A\$28/tonne CO₂ avoided. This is a reduction of approximately 60% compared to the baseline cost of A\$71/tonne CO₂ avoided. Figure 7-9 shows a comparison between the capital cost for the baseline scenario and Case A.

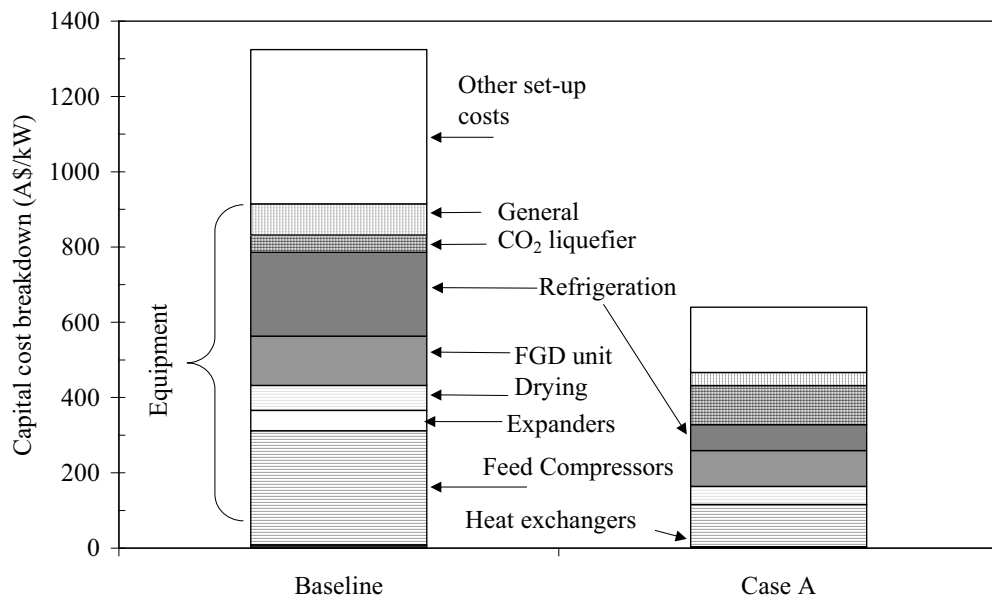


Figure 7-9 Comparison of the capital cost breakdown for the baseline case and Case A

For “Case A”, the capital cost of the system is reduced to A\$650/kW from A\$1325/kW in the baseline scenario. Additionally, the compressor/gas blowers and the refrigeration unit combined account for less than 35% of the total equipment cost compared to 55% in the original analysis. By operating at a lower pressure (1 bar compared to 5.5 bar) and reducing the energy needed in the refrigeration unit through maximising the heat transfer from the exiting lean flue gas, the energy penalty and cost capital costs decreases significantly for Case A. Therefore the overall capture cost is lower.

In this analysis, the impact of additional costs for materials of construction that might be required to operate under lower temperatures or higher pressures was not considered. However, if the capital cost for equipment was expected to increase by 20% to 50% to account for this, the capture cost for Case A would be expected to increase from A\$28 per tonne CO₂ avoided to between A\$30 and A\$33 per tonne CO₂ avoided respectively.

7.4.3 Utilising the waste energy of an external source

Work undertaken by Deng et al. (2004) and Ogawa et al. (2004) shows that the energy from heating liquid natural gas (LNG) to ambient temperature can be used to provide supplementary energy for processes such as energy power generation, air separation, production of liquefied carbonic acid and cold storage . Normally, LNG is gasified using seawater and the latent heat is wasted. However, the latent heat of LNG gasification could be used by the proposed CO₂ separation system. Thus, instead of using a refrigerant, the energy from the vapourising LNG could cool the flue gas for the anti-sublimation. Schematically this is shown in Figure 7-10.

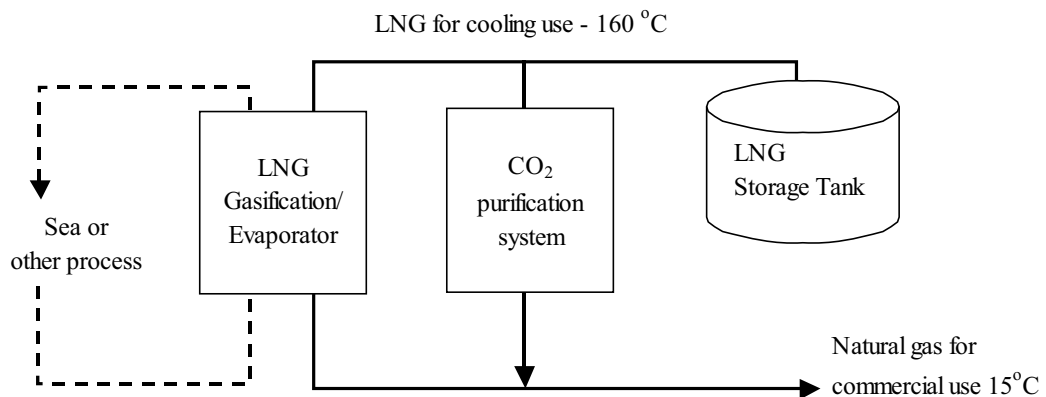


Figure 7-10 Utilisation of the LNG gasification for low temperature CO₂ capture

For the low temperature separation process, the amount of energy needed in the refrigeration unit is approximately 500kJ/kg CO₂ captured. If the latent heat of LNG could be used in the refrigeration unit, then 0.55 kg of LNG would be needed for every kg of CO₂ captured. This is based on the assumption that 919 kJ of heat is released for every kg of LNG evaporated (Amin et al., 2004). Table 7-2 shows the capture cost that could be obtained if the low temperature CO₂ capture system is integrated with a gasifying LNG facility. For Case A, where a gas-lock device is used and the refrigeration unit has been set at atmospheric pressure, if all of the energy needed for anti-sublimation comes from the LNG facility, the capture cost is A\$21/tonne CO₂ avoided. Similarly for the scenario where no gas-lock is used and the refrigeration pressure is 5.5 bar, heat integration reduces the capture cost from A\$38 to A\$30 per tonne CO₂ avoided.

Table 7-2 Effect on capture cost for Case A by integrating the refrigeration unit with gasifying LNG

Gas-lock used	No	No	No	Yes	Yes	Yes
Temperature flue gas into refrigerator (°C)	-105	-105	-105	-105	-105	-105
Pressure of refrigeration unit (bar)	1	1	1	1	1	1
Percent of heat integration (%)	0	50	100	0	50	100
LNG (kg/s)	--	30	60	--	30	60
Capture cost	38	34	30	28	24	21
A\$/tonne CO ₂ avoided	33	30	25	24	20	17
US\$/tonne CO ₂ avoided						

Although there are economic and energy benefits in integrating the refrigeration unit with an external process, one of the key considerations would be the relative location of the CO₂ emission source and the external energy source. They should be in near physical proximity to each other, otherwise the costs for establishing pipelines and compressors between the process units will add extra costs that may negate any savings achieved from the heat integration. Another consideration is the rate at which the energy is being provided. To be useful to the CO₂ capture system, the availability of that energy as kJ/s must match the energy needs of the CO₂ production cycle.

7.5 Conclusion

Refrigeration is a mature technology in which energy efficiency constraints have driven the development of highly efficient equipment. The recovery of CO₂ from post combustion flue gas using low temperature separation can be achieved using anti-sublimation technology at a current cost of A\$71/tonne CO₂ avoided. Using low pressures in the refrigeration unit and maximising the utilisation of heat from exiting gas streams, can reduce the capture cost to A\$38/tonne CO₂ avoided. If a device such as a gas-lock could be used in the CO₂ melter to obtain liquid CO₂, the cost is A\$28/tonne CO₂ avoided. Integrating the refrigeration unit with an external energy source to provide the cooling energy can further reduce the capture cost to A\$21/tonne CO₂ avoided. The results of this chapter demonstrate that low temperature separation technology could be an alternative low cost option for capturing CO₂.

This study examines the capture cost of low temperature separation using a simplified process model, and the results are indicative only. It is suggested that detailed modelling

including the thermodynamic data for refrigeration process and process optimisation be evaluated, especially for multi-component gas mixtures. Additionally, there is technical uncertainty in the applicability of the technology for large scale handling of solid CO₂. At present, this technology has only been demonstrated at a small laboratory scale. Exploring the feasibility of this option would be valuable.

Chapter 8. CO₂ CAPTURE FROM INDUSTRIAL SOURCES

8.1 Overview

This chapter investigates the cost of capture for six major stationary CO₂ emissions sources in Australian conditions. The analysis compares the cost of capture using absorption, adsorption, membrane and low temperature technology. It also assesses the feasibility and suitability of each technology option for the different emission sources.

8.2 Introduction

Chapters 4 to 7 of this thesis investigated the cost of capturing CO₂ from a supercritical black pulverised coal power plant using different CO₂ capture technologies. However as discussed in Chapter 1, many different industrial applications also have the potential for CO₂ capture and storage (CSS). To date, only a few studies have examined the economic feasibility of CO₂ capture from these large industrial processes (IEA-GHG, 2000a, IEA-GHG, 2000b, Hassan, 2005, Farla et al., 1995) and all of the studies assume overseas economic conditions. The objective of this chapter is to make an initial assessment of CO₂ capture from industrial processes based on Australian economic conditions, and to compare the feasibility of different CO₂ capture technologies for each process.

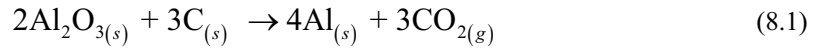
This chapter compares the cost of CO₂ capture for the following industrial applications:

1. Power generation using black and brown coal in pulverised and advanced combined-cycle technologies;
2. Hydrogen production (including ammonia manufacture);
3. Natural gas processing;
4. Iron and steel processing;
5. Petrochemicals processing; and

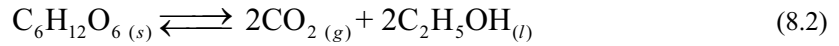
6. Cement manufacture.

The above industrial facilities are selected because they represent approximately 60% of the total 2004 CO₂ emissions in Australia, and account for over 90% of the total stationary emission sources (AGO, 2006).

Although aluminium smelting constitutes 15% of Australian's industrial CO₂ emissions, the direct production of CO₂ is from the reduction of alumina to aluminium. This is represented by the equation:



In this reaction, pure CO₂ is produced in this reaction. For the purpose of CCS, it would be straightforward to recover the gaseous CO₂ from the reduction process and compress it for transport.



Similarly by Equation 8.2, the capture of CO₂ from the fermentation of biomass into ethanol would require only transport compression and storage because a stream of pure CO₂ is produced. Most fermentation facilities emit their CO₂ to the atmosphere, with some collecting it for use in carbonate beverages. For the fermentation vessels that do not collect CO₂, the vessels can easily be adapted by adding a pipe to the fermenters' vent for the purpose of CCS. According to Khesghi and Prince (2005), and Mollersten et al. (2003a), the fermentation process could be carried out at a pressure above atmospheric to reduce the energy needed to compress the CO₂ ready for transport. This would reduce the compression energy by 830 J/kg CO₂ captured for every increase in one bar of pressure.

For aluminium smelting and fermentation of biomass, there is no cost associated with the capture process other than compression, and therefore these processes have not been considered in this chapter.

8.3 Method

8.3.1 Processing assumptions

The characteristics of the industrial sources considered in this study are set out in section 3.5.3 (Chapter 3). The schematic diagrams for post and pre-combustion capture technologies are shown in Figures 3.2 and 3.3.

The CO₂ capture technologies evaluated for each industrial process are:

- Absorption (chemical and physical);
- Gas separation membranes;
- Pressure swing adsorption (PSA); and
- Low temperature separation.

These technology options were selected to be consistent with the analysis adopted in the previous chapters and is based on known technologies. Although novel or hybrid technologies have not been considered, they could be evaluated from an economic standpoint using the tool developed for this study. It is reasonable also to assume that if CCS were to be deployed in the near future, use of the above processes would be more probable than the use of novel technology options (Chapter 2).

Absorption:

- For streams with a high partial pressure of CO₂, physical absorption has been selected, and for streams with low CO₂ partial pressure chemical absorption will be used to recover CO₂. The attractiveness of each process has been discussed in section 2.2 of Chapter 2.

Membrane and adsorption systems:

- For low-pressure flue gas streams, the results of Chapters 5 and 6 show that vacuum based permeate/desorption will result in a lower energy penalty. High pressure feed will be used for CO₂ rich effluent streams already available at high pressure.

Low temperature separation:

- For high pressure processing streams, liquefaction of CO₂ will be examined, and for low CO₂ partial pressure streams, “anti-sublimation” technology will

be considered. The benefits of these two processes are outlined in section 2.5 of Chapter 2.

For post-combustion CO₂ capture sources, current technologies are compared with state-of-the-art commercial technologies as well as hypothetical improved technologies.

For pre-combustion CO₂ capture from synthesis gas, only a few studies have reported the use of novel hybrid systems such as hydrogen membrane reactors or hydrogen membrane reformers. Due to the complex nature of these designs and the limited cost data available, this chapter focuses on current commercial technology. Where sufficient data is available, for emerging absorption, membrane or adsorption technologies, these will be included. There are no publications on low temperature pre-combustion technology.

8.3.2 Process modelling

The mathematical equations used to determine the performance of each of the CO₂ capture technologies are described in detail in Chapters 4 to 7. The process equations used for physical absorption are described in Appendix B.

The parameters and costs of the different solvents, membranes and adsorbents used in the process modelling are tabulated in Appendix C.

8.3.3 Economic assumptions

The economic conditions used in this chapter are summarised in Section 3.5.1.

This chapter analyses the cost of building a new power plant with and without CO₂ capture for power generation options - PC, NGCC, IGCC or IDGCC. For industrial CO₂ emission - natural gas processing, hydrogen production, petrochemical processing, metals production and cement manufacture, the capital and operating cost of the CO₂ capture facility are estimated assuming a retrofit. The power for the CO₂ capture facility is assumed to be supplied externally at a cost of A\$35 and US\$35 per MWh from a NGCC power plant with a CO₂ emission of 0.4 tonne/MWh.

The results presented in this chapter for each of the industrial sources include only the CO₂ capture cost, the unit capital cost for the capture facility and the energy penalty. The detailed results including CO₂ recovery rates, CO₂ purity in the product stream and operating expenses are provided in Appendix D.

8.4 Power generation

In Australia 75% of the total electricity generated in 2004/2005 was provided by 24 existing pulverised coal power plants, with black coal accounting for 54% and brown coal 21% of the total. The remaining power is supplied by eight natural gas turbine power plants that provide 15% of the electricity, oil 1.5% and renewables 8% (NEMMCO, 2005). In addition to the existing facilities, a new demonstration plant for integrated coal gasification combined cycle (IGCC) plant has been proposed by Stanwell Corporation (Stanwell, 2006).

The following section of this chapter examines the feasibility of CO₂ capture for:

- Existing subcritical pulverised brown coal (Brown PC) and black coal (Black PC);
- Natural gas combined cycle (NGCC);
- Integrated coal gasification combined cycle (IGCC); and
- Integrated brown coal drying gasification combined cycle (IDGCC).

The capture cost for supercritical black pulverised coal power plants has already been investigated in Chapters 4 to 7. For pulverised brown coal and NGCC power plants, the CO₂ capture facility is considered as a post-combustion option where CO₂ is recovered from the flue gas. For IGCC and IDGCC, the CO₂ capture facility is a pre-combustion option where CO₂ is recovered from the synthesis gas.

8.4.1 Economic results for post-combustion capture

Brown and black subcritical pulverised coal power plants

The CO₂ capture cost in Australian dollars for brown and black coal subcritical and supercritical power plant flue gas is shown in Figure 8-1. Table 8-1 contains details of the capital cost for the capture facility, the energy penalty and the cost in US dollars.

The capture cost is examined for different stages of development of each technology and is compared to the cost for capture from a supercritical black coal power plant.

Table 8-1 Capture costs for pulverised coal power plants

	Absorption			Membranes		Adsorption		Low temperature
	Current	SOA	New	Current	New	Current	New	New
Brown PC – subcritical								
Energy penalty (%)	45	27	20	48	36	28	28	24
Capital cost A\$/kW	1530	1000	875	1135	930	925	930	860
A\$/t CO ₂ avoided	66	37	33	56	38	38	34	28
US\$/t CO ₂ avoided	62	33	29	54	35	35	31	23
Black PC – subcritical								
Energy penalty (%)	36	20	17	42	30	24	24	22
Capital cost A\$/kW	1100	750	680	930	640	700	680	700
A\$/t CO ₂ avoided	57	35	31	52	36	36	32	28
US\$/t CO ₂ avoided	52	32	28	49	32	33	29	24
Black PC – supercritical (Based on results of Chapters 4 –7)								
Energy penalty (%)	34	20	16	41	29	22	22	19
Capital cost A\$/kW	1000	750	640	840	640	660	660	680
A\$/t CO ₂ avoided	54	34	30	50	34	35	31	28
US\$/t CO ₂ avoided	49	31	27	48	31	32	28	24

* SOA is “state of the art”

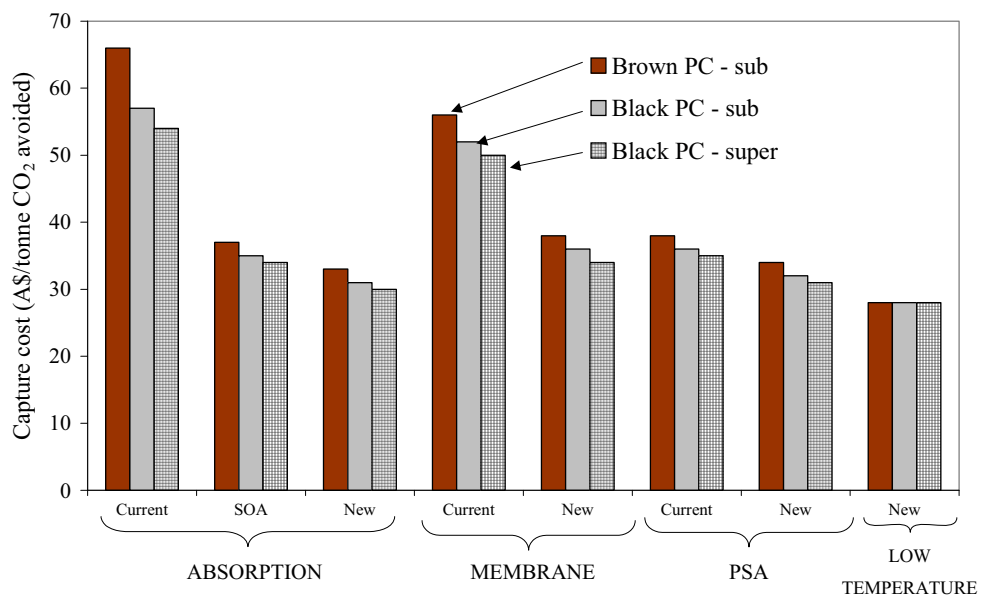


Figure 8-1 Comparison of capture costs for Australian pulverised coal power plants

The cost of CO₂ capture from a subcritical brown coal power plant based on current MEA solvent technology is A\$66/tonne CO₂ avoided. This cost decreases to A\$37/tonne CO₂ avoided if KS1 solvent is used, coupled with waste heat integration and a single absorption train. If we examine the cost trends based on technology improvement, the cost of capture using CO₂ anti-sublimation (low temperature) is the lowest. Low costs are also achieved using a new ideal chemical absorption solvent and vacuum swing adsorption with an ideal adsorbent. Similar trends are observed for capture of subcritical black coal power plant flue gases. The capture cost for black coal ranges from A\$24 to A\$52 per tonne CO₂ avoided.

If the cost of capture for the two subcritical coal power plants is compared, the cost for the brown coal is approximately 5% to 10% higher than for the black coal. This is a result of the higher flowrate associated with the flue gas from the brown coal combustion process. Additionally, the flue gas has a higher water content (24% compared to 7% for black coal), which increases the energy penalty and the cost for dehydration in capture technologies such as membranes or adsorption.

As shown in Chapters 4 to 7, the capture cost for a supercritical black coal power plant is approximately 5% less than for the subcritical plant. This is because the efficiency of

the supercritical plant is much higher. The assumed value for the thermal efficiency in the supercritical plant is 41% compared to 37% for the subcritical plant. This higher efficiency coupled with the lower energy penalty for the supercritical flue gas reduces the incremental cost of energy required for capture. This suggests that implementing CO₂ capture technologies at newer higher efficiency power plants may be more economical than for existing power plant technology.

From Table 8-1 and Figure 8-1, chemical absorption technology with heat integration has the lowest energy penalty for both brown and black pulverised coal power plant flue gases. It has also one of the lowest unit capital costs (as \$/kW) if “fit for purpose” equipment is considered. Membrane, adsorption and especially low temperature anti-sublimation technologies also show considerable promise, with capture costs less than A\$35/tonne CO₂ avoided. However, using low energy intensive solvents coupled with low cost equipment are likely to be the first likely steps in reducing CO₂ capture costs. Future cost reductions and the development of new power plant facilities may see other technologies or hybrids being adapted. According to Aaron and Tsouris (Aaron and Tsouris, 2005), it is expected that once low cost highly selective membranes are developed that can tolerate high temperatures, membrane separation may be the most economical approach.

NGCC power plants

Natural gas combined cycle (NGCC) power plants are an advanced power generation option where natural gas is combusted to generate energy and electricity. One of the main advantages of using natural gas over coal or petroleum for power generation is the efficiency of the combustion process. A higher amount of energy is obtained per unit of natural gas than either coal or petroleum. Additionally, the flue gas emissions from natural gas contain fewer pollutants (such as SO_x) than traditional pulverised coal power.

Figure 8-2 compares the capture cost of different CO₂ capture technologies for both current and advanced NGCC power plants. Table 8-2 also includes results for the capital costs and energy penalty of both power plant cycles. The advanced NGCC power plant

is modelled using the IEA GHG approach involving recycling flue gas into the gas turbine (IEA-GHG, 2004). This has the effect of doubling the CO₂ concentration and reducing the volume of flue gas for CO₂ recovery. The cost for recycling the flue gas is considered as part of the cost for the power plant.

Table 8-2 Capture costs for NGCC power plants

	IEA GHG (2004)	Absorption			Membrane		VSA		Low temp.
	MEA	Current	SOA	New	Current	New	Current	New	New
Current NGCC power plants									
Energy penalty (%)	16	17.5	13	8	58	34	16	15	28
Capital cost A\$/kW	--	568	360	296	1183	640	250	228	430
A\$/t CO ₂ avoided	--	57	37	31	240	110	58	41	73
US\$/t CO ₂ avoided	41	45	29	24	186	85	46	33	55
Advanced NGCC power plants									
Energy penalty (%)	15	16	12	8	25	16	14	13	14
Capital cost A\$/kW	--	345	280	240	286	211	248	240	240
A\$/t CO ₂ avoided	--	41	30	24	60	38	42	34	35
US\$/t CO ₂ avoided	30	32	23	19	46	30	34	28	26

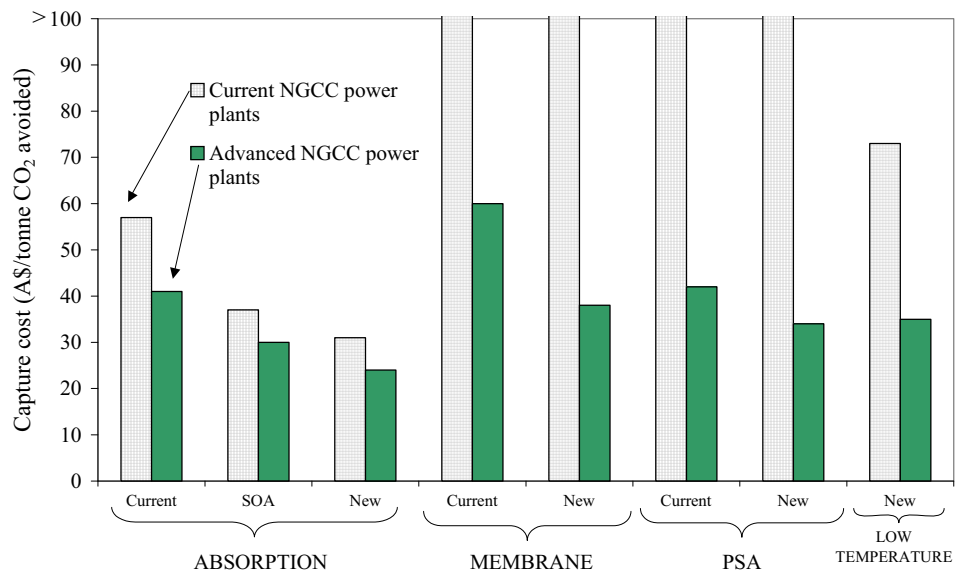


Figure 8-2 Comparison of capture costs for current and advanced NGCC power plants

The cost of capture using absorption technology for a current NGCC flue gas is A\$57/tonne CO₂ avoided with MEA solvent and an energy penalty of 16%. This decreases to A\$31/tonne CO₂ avoided for a new solvent with lower regeneration properties, waste heat integration and a single absorption train. However, the costs using membrane, adsorption or low temperature technology are significantly higher because the CO₂ concentration in the flue gas is very low, multiple stages are needed in the separation process.

By comparison, if CO₂ is captured from the flue gas of an advanced NGCC power plant, the capture cost reduces by at least 30% across all the capture technologies. By concentrating the CO₂ and decreasing the volume of the flue gas, smaller equipment and less energy is required. Thus advanced NGCC power plants give greater cost reductions than current NGCC power plants.

As with CO₂ capture from pulverised coal power plant flue gases, chemical absorption yields the lowest energy penalty for capture from both current and advanced NGCC flue gases. The lowest capture cost is based on the use of new solvents coupled with lower equipment cost and heat-integration. Although emerging technologies such as membrane, adsorption and low temperature separation can reduce the cost to less than A\$30/tonne CO₂ avoided for advanced NGCC power plants, the capture cost for absorption systems at least 30% lower. This suggests that future research aimed at CO₂ capture for NGCC power plants should focus on developing and integrating absorption systems with the power plant cycle.

As shown in Tables 8.1 and 8.2, current commercial technology is more costly for existing pulverised coal and NGCC power plants than advanced NGCC power plants. This is because advanced NGCC power plants are cleaner, more efficient and less capital-intensive. The results suggest that early implementation of CO₂ capture would be more advantageous in advanced NGCC power plants than for existing pulverised coal or NGCC facilities. However, the cost of capturing CO₂ from power plants is highly sensitive to the fuel cost. In this analysis, the cost of natural gas is assumed to be A\$3.5/GJ. If the price is A\$7/GJ, the capture cost from the advanced NGCC flue gas

using MEA solvent increases from an estimate of A\$41 to A\$55 per tonne CO₂ avoided. If the gas price is higher than A\$7/GJ, the cost of capture for advanced NGCC flue gas capture is higher than for black pulverised coal. Internationally the market price for natural gas has fluctuated from a spot price of approximately US\$2.5/GJ to over US\$9/GJ from 2000 to 2005. If the price of gas rises above the A\$7/GJ while coal prices remain less than A\$1.5/GJ, it may be cheaper to build a new super-critical coal power plant with capture than an advanced NGCC power with capture.

8.4.2 Economic results for pre-combustion capture

This section focuses on the CO₂ capture costs from advanced integrated coal-gasification combined cycle (IGCC) and integrated coal-drying gasification (IDGCC) power plants. The simplified flowsheet for pre-combustion process is has been shown in Figure 3-3. IDGCC power plants are designed for the gasification of high moisture content coals such as Australian brown coal or American North Dakota Lignite. IGCC and IDGCC power plants operate under the principle of gasifying the fuel source (coal) with O₂ or air to form synthesis gas. Steam generated by waste heat boilers in the gasification process is used to power steam turbines and the hydrogen rich fuel remaining after CO₂ capture is burned in a turbo electric expander to produce power.

The current costs of capture technology are summarised in Table 8-3 and Figure 8-3. The results are based on the synthesis gas of a Texaco-quench oxygen blown gasifier using commercially available capture technology (Rubin et al., 2004). The only new technology considered in this analysis is a new membrane. Although low temperature process such as SIMTECHE is being evaluated (Tam et al., 2001), there is limited data available which did not allow an analysis to be carried out. No new technologies have been reported for absorption or adsorption for this capture option. The capture cost ranges from A\$26 to A\$44 per tonne CO₂ avoided for IGCC power plants, and A\$40 to A\$59 per tonne CO₂ avoided for IDGCC power plants.

Table 8-3 CO₂ capture costs for new IGCC and IDGCC power plants

	Rubin (2004)	IEA GHG (2003a)	Absorption	Membrane		Adsorption	Low temp.
	Current	Current	Current	Current	New	Current	Current
IGCC power plants							
Energy penalty (%)	14	12	11	17	20	21	25
Capital cost A\$/kW	--	--	970	1022	1057	1154	1396
A\$/t CO ₂ avoided	--	--	26	28	28	31	44
US\$/t CO ₂ avoided	20	16	20	23	23	27	37
IDGCC power plants							
Energy penalty (%)	--	--	8	18	18	28	22
Capital cost A\$/kW	--	--	1611	2150	1800	2212	2042
A\$/t CO ₂ avoided	--	--	40	54	42	59	59
US\$/t CO ₂ avoided	--	--	31	44	35	51	49

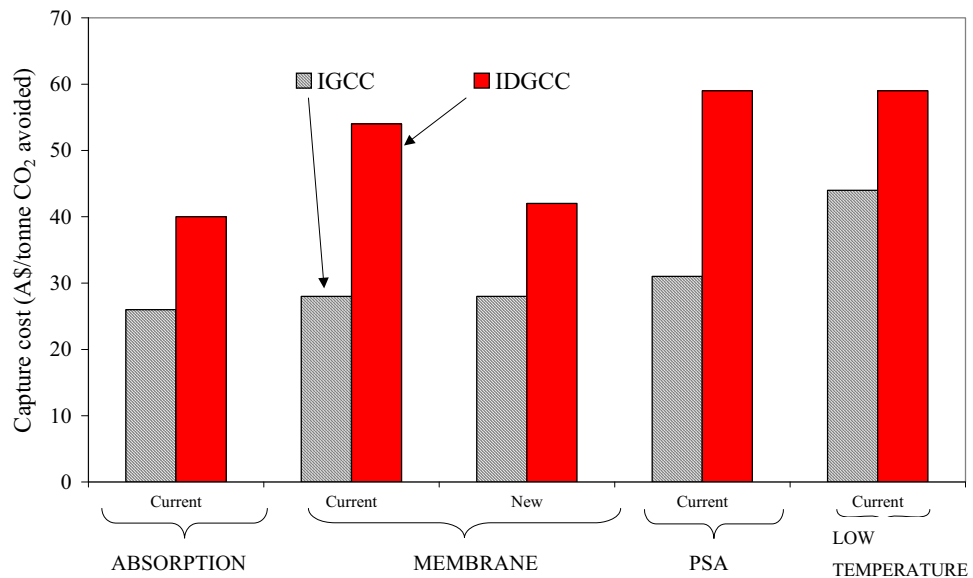


Figure 8-3 Comparison of capture costs for IGCC and IDGCC power plants

IGCC power plants

For IGCC power plants, the lowest capture cost is A\$26/tonne CO₂ avoided using Selexol solvent. The cost of capture using physical adsorption with zeolite 5A or polymeric gas separation membranes is marginally higher by 5% to 10%. However, for the PSA and membrane systems the purity of the CO₂ for transport is low at 81% and 65% respectively. The capture cost using liquefaction technology is high at A\$44/tonne CO₂ avoided.

According to Stielgel and Ramezan (2006) and Bresden et al. (2004), membrane technologies are being explored for hydrogen production from fossil fuels using processes such as in IGCC power plants. If a sol-gel membrane with a high CO₂/H₂ permeability is used (Diniz da Costa et al., 2002), the purity of the CO₂ stream increases from 65% to 82%. New membranes that function as both the synthesis gas reactor and the CO₂ recovery unit will provide further cost reductions. By functioning as both the water-shift reactor and the separation process, the total capital cost decreases (Dijkstra et al., 2003, Damle and Dorchak, 2001, Alderliesten and Bracht, 1997). Assuming that the membrane-shift-reactor cost US\$500/m², the capture cost using membrane reactors is estimated at less than A\$20/tonne CO₂ avoided. However, because published capital cost estimates for membrane synthesis gas reactors is limited, this cost estimation is only indicative.

The possibility of using the adsorption system to act as both a water-shift reactor as well as a CO₂ separator has also been examined. Air Products and Chemicals (Hufton et al., 1999, Carvill et al., 1996) have developed a technique referred to as a sorption-enhanced reaction process (SERP) where a CO₂ selective adsorbent separates the CO₂ and produces a medium purity hydrogen (~95%) stream. A commercial process called Gemini® described by Sircar and Kratz (1988) is able to simultaneously recover both high purity hydrogen and CO₂ purity streams. Unfortunately, the conditions and cycle steps of the Gemini and SERP processes are very complicated and they use a proprietary adsorbent. This did not allow an economic evaluation of either process to be conducted in this analysis.

Comparing the results for pre-combustion (Table 8-3) with post-combustion capture (Tables 8-1 and 8-2), using conventional technology, the current cost of recovering CO₂ from IGCC synthesis gas is approximately half the cost of recovering CO₂ from pulverised coal and NGCC power plant flue gases. This reflects the high partial pressure of the CO₂ in the synthesis stream and the higher efficiency of the IGCC power plants. However, as noted earlier in Section 2.8.1, the reference cost of electricity for IGCC power plants is different to that for pulverised coal and NGCC power plants, and thus the basis for comparison of the capture cost is different. Depending on the objective of

the comparison of the capture costs of different power generation options; a reference cost of electricity should also be considered. An examination of the effect of the reference plant and the capture cost for different power plant options is discussed in Chapter 9.

Many literature studies have suggested that early implementation of CO₂ capture in these facilities would be more cost effective than implementation in pulverised coal power plants (IPCC, 2005, Reiner et al., 1994, Herzog et al., 1997, Simbeck and McDonald, 2000). This may be an effective solution for many countries such as the US and Europe where the cost of electricity generation is lower for IGCC power plants with capture (US\$60/MWh) than for pulverised coal power plants with capture (US\$70 to US\$85 per MWh). However, in Australia, the cost of electricity generation without capture is much lower for pulverised coal (A\$35/MWh) than for IGCC power plants (A\$45/MWh) (Wibberley et al., 2006). Thus, although the incremental cost for capture may be less for IGCC power plants, the final cost of electricity due to capture is similar for either option (A\$65/MWh for coal and A\$70/MWh for IGCC).

IDGCC power plants

For IDGCC synthesis gas, the lowest capture cost is for Selexol solvent at A\$37/tonne CO₂ avoided. For the membrane, adsorption and low temperature technologies, this analysis assumes that all the water vapour is removed prior to separation, and thus the high water content in the IDGCC synthesis gas adds a considerable cost for dehydration. This results in higher capital costs, energy penalty and capture costs. The results suggest that the most promising capture technology for IDGCC synthesis gas would be absorption technology.

In Table 8-3, the results show that the cost for all capture technologies is higher for IDGCC synthesis gas than for IGCC. The IDGCC synthesis gas has higher water content, a lower CO₂ concentration and larger flowrate than the synthesis gas of the IGCC plant. These increases the size of the equipment needed, therefore the total capital investment and capture costs are also higher. Similarly the results in Table 8-1 show that the capture cost from power plants using brown coal (lignite) is higher than for

black coal due to the additional cost of dehydrating the coal. The innovative nature of IDGCC and the way it uses water indicate the need to search for more novel capture approaches.

8.5 Hydrogen production

Hydrogen (H_2) is produced world wide for use in a variety of industries including ammonia fertiliser and for oil refinery hydrotreating. Large-scale CO_2 separation systems already exist in the ammonia and hydrogen plants in order to produce a pure stream of hydrogen. Hydrogen is being touted as an alternative CO_2 -free energy carrier for the future. Hydrogen can be used for transport and for electricity production. If the “hydrogen economy” does emerge, worldwide production of hydrogen will grow substantially.

The majority of hydrogen is currently produced by steam methane reforming (SMR) of natural gas. The hydrogen can also be produced by gasification of coal using the same process that produces the hydrogen enriched fuel from IGCC power plants. The key difference between hydrogen production and IGCC is that the hydrogen gas produced for power generation does not need to be of very high purity. In hydrogen production facilities, further processing after CO_2 removal is required to produce a high purity hydrogen stream, as shown in Figure 8-4.

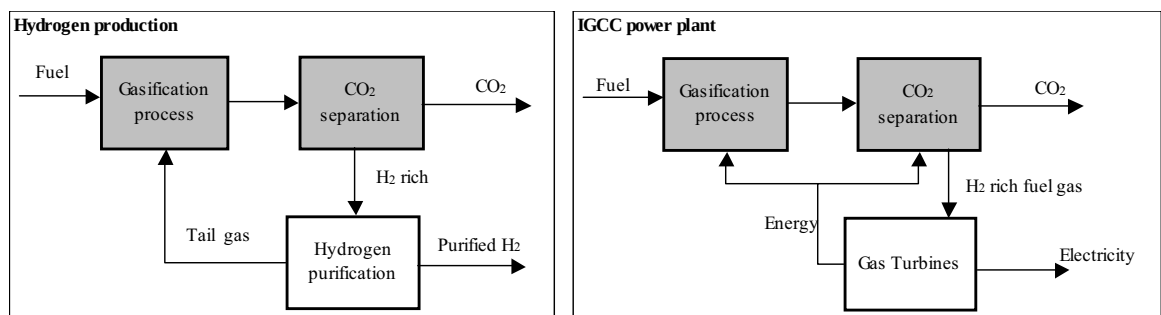


Figure 8-4 Schematic of the hydrogen production process compared to an IGCC power plant

The following section of this chapter focuses on the cost of CO_2 capture from the synthesis gas of a hydrogen production facility with a high purity H_2 stream as well as a high purity CO_2 stream for storage. In this analysis, the cost estimates reported are for a

part of the normal process that is used to manufacture H₂. This is different from the cost estimates for post combustion flue gas capture from pulverised coal or NGCC power plants where the CO₂ flue gas is normally vented to the atmosphere. Additionally, only the process-generated CO₂ from the water shift reaction is considered for capture. For simplicity, alternative hydrogen production processes where further CO₂ is removed using PSA purification has not been evaluated.

Table 8-4 summarises the capture cost for hydrogen production. The capture cost ranges from A\$14 to A\$30 per tonne CO₂ avoided.

Table 8-4 Capture costs for hydrogen production

	NRC (2004)	Farla (1995)	Absorption	Membrane		Adsorption	Low temperature
Status	Unknown	Current	Current	Current	New	Current	Current
Capital cost (\$/tonne CO ₂ captured/year)	--- US\$4.10	--	A\$70 US\$51	A\$51 US\$39	A\$43 US\$33	A\$66 US\$52	A\$69 US\$51
CCS energy penalty (kJ/kg CO ₂ captured/year)	785	322	681	510	640	795	1090
A\$/t CO ₂ avoided	--	--	19	14	14	20	30
US\$/t CO ₂ avoided	4.4	8	16	12	12	17	26

The lowest cost is for the gas separation membrane (A\$14/tonne CO₂ avoided), but this technology produces a low purity CO₂ stream for transport with a CO₂ concentration of 60%. This implies that a substantial amount of hydrogen is lost. This could be improved if new membranes with a higher H₂/CO₂ selectivity became available. For example, if a sol-gel membrane with a H₂/CO₂ selectivity of 40 (Diniz da Costa et al., 2002) is used, the CO₂ purity increases and the cost for post-separation compression decreases. The highest capture cost is for the low temperature liquefaction system, estimated to be greater than A\$30/tonne CO₂ avoided. Cost estimates using absorption and adsorption are approximately A\$16 and A\$17 per tonne CO₂ avoided.

The North American National Research Council (NRC, 2004) also examined the cost of hydrogen production from coal. The reported cost is US\$4.40 per tonne of CO₂ avoided for a futuristic hydrogen facility. This is significantly lower than cost estimates in this study. Unfortunately, the NRC study examines a futuristic low cost scenario and limited

information about the capture facility was published for a comparison. The study by Farla et al. (1995) examines only the cost of compressing the CO₂ from an ammonia plant, and did not include the separation cost, and thus their reported cost is also much lower than in this study.

The results show that CO₂ capture from hydrogen production facilities can cost less than A\$20/tonne CO₂ avoided. By developing advanced technologies, the cost of CO₂ capture (and producing hydrogen) would be even lower than the current estimates. According to Stiegel and Ramezan (2006), the cost could reduce by 25% to 50%. As with CO₂ capture from IGCC power plants, incorporating the water-shift reactor with the CO₂ separation and hydrogen purification step in either a membrane reactor or an adsorption reaction process will further reduce the cost. It has been estimated that by using a membrane water-shift reactor, the capture cost can decrease to approximately A\$10/tonne CO₂ avoided.

8.6 Natural gas processing

Removing CO₂ to meet pipeline specifications is an essential part of natural gas production. In Australia, pipeline specifications require the CO₂ concentration in the natural gas delivered to the customer to be less than 3% (1997). Typically most of the natural gas fields in Australia contain CO₂ levels above 5% and in some cases this is as high as 27% (Cook et al., 2000). Currently the CO₂ removed from the natural gas is flared onsite.

However the recovered CO₂ could be stored. CCS has been undertaken at the Sleipner Field in the North Sea Norway (IEA-GHG, 2006a, Torp and Gale, 2004), and is proposed at the Snohvit gas field in the Barents Sea Norway (Statoil, 2003) and at Barrow Island off the west coast of Australia (Gorgon Project) (Cherrvon_Texaco, 2004).

The following analysis examines the cost of capturing CO₂ from natural gas production facilities. The cost of CO₂ avoided includes the total cost of equipment and the

operating expenses related to the recovery and compression of CO₂. Although the CO₂ separation is an integral part of the existing process, the objective of this study is to compare different CO₂ capture technologies. Thus it is necessary to include all the equipment and processing costs. In processing the natural gas, part of the hydrocarbon product (methane) is lost as vapour or as part of the permeate/desorbed streams. The value of the methane losses is included in the total operating cost (Bhide et al., 1998) (Table 3-3 shows the cost penalty function). The separation cost is the total annual cost divided by the amount of natural gas delivered to the consumer. The analysis examines the cost for low, medium and high feed gas CO₂ contents, 5%, 10% and 15%.

The results in Figure 8-5 show that with increasing CO₂ concentration, the capture cost decreases. Table 8-5 includes results of the separation cost, capital costs and energy penalty. The lowest capture cost is achieved using chemical absorption or membrane technology for a CO₂ concentration of 15% in the feed gas with an estimate of A\$26 to A\$30 per tonne CO₂ avoided. The capture cost using low temperature separation is marginally higher at A\$38/tonne CO₂ avoided. PSA technology is the most costly. This is because although the total capital cost using adsorption technology is low, the amount of CO₂ recovered is also low and the energy penalty of the system is high. Based on the assumption that zeolite NaY is used as the adsorbent, multiple process steps were required to increase the CO₂ purity ready for transport. This increased the energy penalty and reduced the overall amount of CO₂ avoided and raises the capture cost. If the CO₂ is not captured for storage but only removed and vented, then for 10% of CO₂ in the feed gas, the amount of methane recovered increases to 95% and the separation cost falls to A\$0.15/MMSCF. PSA technology is thus a low cost option for CO₂ removal from natural gas processing streams if high purity CO₂ is not required.

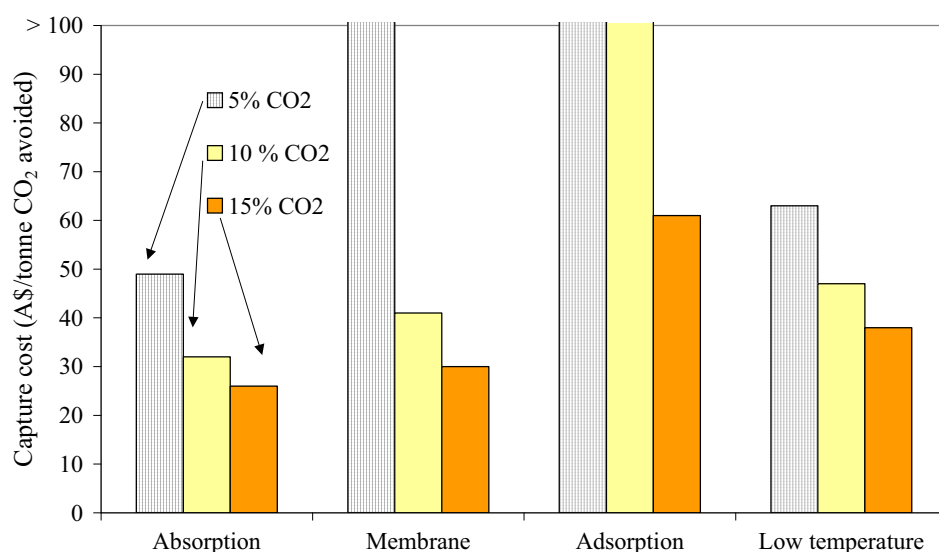


Figure 8-5 Comparison of capture costs for different CO₂ feed concentrations

Table 8-5 Capture costs for natural gas processing for low, medium and high CO₂ concentration feed gases

	Absorption	Membrane	Adsorption	Low temperature
Process status	Current	Current	Current	Current
CO₂ concentration in feed (%)	5			
Separation cost (A\$/MMSCF)	A\$0.11	A\$0.25	A\$0.38	A\$0.15
Capital cost (\$/tonne CO ₂ captured/year)	A\$102 A\$81	A\$140 US\$114	A\$115 US\$98	A\$100 US\$70
CCS energy penalty (kJe/kg CO ₂ captured)	1330	1716	3690	1611
A\$/t CO ₂ avoided	49	107	270	63
US\$/t CO ₂ avoided	43	92	240	53
CO₂ concentration in feed (%)	10			
Separation cost (A\$/MMSCF)	A\$0.16	A\$0.20	A\$0.36	A\$0.18
Capital cost (\$/tonne CO ₂ captured/year)	A\$105 US\$85	A\$81 US\$64	A\$100 US\$65	A\$90 US\$65
CCS energy penalty (kJe/kg CO ₂ captured)	740	1103	1852	1389
A\$/t CO ₂ avoided	32	41	105	47
US\$/t CO ₂ avoided	27	35	95	40
CO₂ concentration in feed (%)	15			
Separation cost (A\$/MMSCF)	A\$0.19	A\$0.23	A\$0.33	A\$0.27
Capital cost (\$/tonne CO ₂ captured/year)	A\$85 US\$68	A\$66 US\$50	A\$70 US\$56	A\$79 US\$60
CCS energy penalty (kJe/kg CO ₂ captured)	738	945	1378	117
A\$/t CO ₂ avoided	26	30	61	38
US\$/t CO ₂ avoided	23	26	53	32

The capture cost for natural processing is generally lower than the cost for post-combustion CO₂ capture from black coal pulverised power plants. For approximately the same concentration of the CO₂ in both feed gas stream, the higher pressure of the natural gas stream increases the partial pressure of CO₂. This allows a process such as physical absorption to be used which has a lower energy penalty than chemical absorption. In addition, for membrane and adsorption processes, the stream is already at a high pressure and there is no need for vacuum suction or compression to achieve a high separation factor. By eliminating the need for a vacuum pump or a feed gas compressor, the compression duty for the recovered CO₂ decreases and the overall energy penalty is less. However, the capture cost for low temperature separation is higher for natural gas processing than for the capture of pulverised coal flue gas. This is because liquefaction rather than “anti-sublimation” technology is employed.

Although, the cost of CO₂ capture from natural gas processing is lower than for post-combustion capture (Table 8-1), it is higher than for pre-combustion capture from IGCC power plants (Table 8-3). This is the case even though both streams are at high pressure. Firstly, the CO₂ concentration of the synthesis gas from IGCC power plants is higher (40% compared to 15% or less in natural gas streams), thereby reducing the unit cost for the separation equipment. Secondly, for IGCC, the estimated operating cost does not include the added cost of the loss of hydrocarbon (natural gas) such as in the analysis for natural gas processing.

8.7 Iron and steel production

BlueScope Steel (Bluescopesteel, 2005), the largest manufacturers of iron and steel in Australia, emitted 14.5 million tonnes of CO₂ from their processing plants in 2004 and 2005,. The total amount of CO₂ emitted from iron and steel production in 2004 in Australia was 14.7 million tonnes. Approximately 11 million tonnes were emitted from the BlueScope Steel facility at Port Kembla. The potential of capturing CO₂ from this large single point source suggests that CCS for such a facility may have benefits of economies of scale.

Steel production is a highly energy intensive process. Steel making generates CO₂ both directly from the manufacture of iron and steel, and indirectly through the use of electricity and gas as an energy source. CO₂ is directly emitted in two key processes. These are 1) the blast furnace where coal and coke are used as a chemical reductant to extract pig iron from iron ore, and 2) the basic-oxygen furnace where the pig iron is converted into crude steel.

The flue gas from both the conventional blast furnace and basic-oxygen furnace comprises of a mixture of H₂, N₂, CO, as well as CO₂. Approximately 70% of the total carbon input is emitted in the conventional blast furnace, and it is more likely that CO₂ would be captured from this flue gas stream than from the basic-oxygen blast furnace. There are two opportunities for capturing CO₂ from blast furnace gas. First, the CO₂ can be recovered directly. Second, the CO in the blast furnace flue gas can be converted into CO₂ and H₂ in a water-shift reaction (Figure 8-6). The advantages of the CO conversion include capturing the CO₂ from a high pressure stream similar to that in IGCC power plants, and the possibility of using the hydrogen enriched stream for power generation. Both options are considered in this thesis.

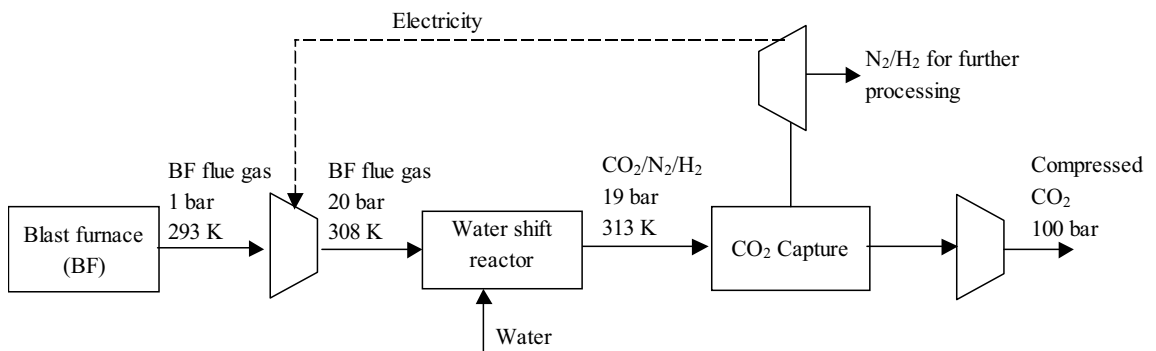


Figure 8-6 Process flow diagram of CO₂ capture by converting a conventional blast furnace with a water shift reaction

Iron and steel in Australia is generally produced using conventional air blown blast furnace technology. However, internationally there is an increase in the development of new iron production technologies. These technologies use pure oxygen instead of air to reduce the iron ore into pig iron. The resulting flue gas is a mixture has a similar composition to the synthesis gas of an IGCC process. By using oxygen, the CO₂ content

of the flue gas increases from less than 20% in conventional blast furnaces to over 30% (Lampert and Ziebig, 2006). In this study, the cost of capturing CO₂ from the flue gas of the advanced Corex process is also investigated. The Corex process was chosen, as it is a commercially proven technology (Wingrove et al., 1999). The Corex process achieves the blast-furnace function in two separate reactors. In the first reactor iron ore is reduced to a sponge-iron, and the production of reducing gases and the melting of the sponge iron is carried out in a smelting gasifier. The main difference between the Corex and the traditional blast furnace flue gas is that the N₂ concentration in Corex is significantly less, and the CO₂ concentration is higher.

An alternative to the Corex process or blast furnace technology is the Direct Reduced Iron (DRI) process. In DRI, iron ore comes into contact with a hot stream of H₂ and CO, reducing it to iron, H₂O and CO₂. The CO₂ from DRI facilities can easily be separated, and the cost for CCS would only entail the costs for compression and storage. Thus, CO₂ capture from DRI is not considered in this study.

Conventional blast furnace

The cost of capturing CO₂ from a conventional blast furnace ranges from A\$17 to A\$38 per tonne CO₂ avoided as shown in Table 8-6. The lowest cost is for the low temperature anti-sublimation technology, with higher cost estimates for CO₂ capture using absorption, adsorption and membrane technology. Assuming cost reductions can be achieved by improved technology, the capture cost reduces to A\$20/tonne CO₂ avoided for the chemical absorption, to less than A\$35/tonne CO₂ avoided using membranes, and to A\$26/tonne CO₂ avoided using VSA with a new adsorbent.

Table 8-6 Capture costs for iron production blast furnace flue gas

	Farla et al. (1995)	Absorption		Membrane		Adsorption		Low temperature
Process description		Current	New	Current	New	Current	New	New
CCS energy penalty (kJ/kg captured CO ₂)	~1150	1610	780	1660	1350	1115	1016	650
Capital cost (\$/tonne capture CO ₂ /year)	US\$133	A\$100 US\$75	A\$71 US\$52	A\$65 US\$50	A\$71 US\$56	A\$77 US\$65	A\$70 US\$60	A\$52 US\$38
A\$/tonne CO ₂ avoided	--	38	20	34	33	29	26	17
US\$/tonne CO ₂ avoided	35	33	17	31	29	26	24	15

Farla et al. (1995) estimate a similar cost of capture from conventional blast furnaces based on MDEA solvent (and capital costs for MEA absorption systems) of US\$35/tonne CO₂ avoided. This study estimates a similar cost of US\$33/tonne CO₂ avoided. The main differences between this study and Farla et al. (1995) is that our capital cost estimates are lower but the energy penalty is higher. The capital cost in this study is lower because it is assumed that only three absorption trains are required in order to capture approximately 3,000 tonne of CO₂ per day. In their study, Farla et al. (1995) assume eight absorption trains, which gives a higher capital cost. In addition, their analysis considered MDEA solvent for the absorption process, which gives a lower reported energy penalty. In contrast, this analysis assumes MEA solvent was used.

Shift conversion

The capture of CO₂ from conventional blast furnaces may be improved by converting the CO in the blast furnace into CO₂. This can be accomplished with the water-shift reaction where steam is reacted with the blast furnace flue gas under high temperature and high pressure. To achieve this, the conventional blast furnace flue gas must first be pressurised. The CO₂ capture process that follows the water-shift conversion is similar to that from other high pressure streams such as synthesis gas from IGCC processes.

The process flow diagram for converting the blast furnace flue gas is shown in Figure 8-6.

This thesis assumes that the flue gas is pressurised to 20 bar for the water- shift reaction and the incoming blast furnace flue gas is heated by the exiting hot synthesis gas. This is because the water-shift reaction is exothermic, producing 40.6 KJ of heat per mol of CO₂ generated. The economic evaluation includes the capital costs for the flue gas compressor, the water-shift reactor as well as the CO₂ capture and compression system.

In the initial analysis for the converted blast furnace flue gas, an estimate of the capture cost is made excluding the cost for hydrogen electricity production and the electricity gain. This allows a comparison of the different CO₂ capture technologies available. In a second analysis, the benefit of producing hydrogen electricity, as a by-product of the waste gas is included. This allows us to evaluate the advantages and disadvantages of the different approaches selectively. In the second analysis, the hydrogen electricity from the waste gas is assumed to offset 0.28 GJ/tonne of CO₂ avoided. The electricity production price is also assumed to be A\$15/MWh and US\$15/MWh as outlined in Gielen (2003). This is a high estimate of benefits. The results are shown in Table 8-7.

Table 8-7 CO₂ capture costs for the converted synthesis gas of a blast furnace

	Gielen (2003)	Absorption	Membrane	Adsorption	Low temperature	New membrane reactor or SERP
Technology	Unknown	Current	Current	Current	Current	New
Capital cost (\$/tonne CO ₂ captured/yr)	--	A\$210 US\$150	A\$200 US\$146	A\$200 US\$150	A\$240 US\$175	< A\$100 <US\$100
No hydrogen electricity produced						
CCS energy penalty (kJe/kg captured CO ₂)	--	935	1160	1325	2110	< 1200
A\$/tonne CO ₂ avoided	--	46	48	50	84	< 30
US\$/tonne CO ₂ avoided	--	36	38	41	69	< 25
Hydrogen electricity produced						
CCS energy penalty (kJe/kg captured CO ₂)	620	650	885	1026	1770	<900
A\$/tonne CO ₂ avoided	--	36	35	43	53	<20
US\$/tonne CO ₂ avoided	18 - 19	27	27	34	41	<15

Neglecting the benefits of producing hydrogen electricity as a by-product, the cost of capturing CO₂ from the synthesis gas of a converted blast furnace ranges from A\$43 to A\$84 per tonne CO₂ avoided. This cost is significantly higher than the capture of CO₂ from the conventional blast furnace flue gas. The higher cost reflects the higher total capital cost, which is at least twice that as the cost for the conventional blast furnace. This is because the addition of the feed gas compressor and water-shift reactor increases the capital cost by approximately A\$110/kg captured CO₂. However, if it is possible to use a membrane or adsorption reactor for both the shift reaction and the separation (such as the sol-gel membrane or SERP), the capture cost could reduce possibly to below A\$30/tonne CO₂ avoided, based on the assumption that the membrane-shift-reactor costs is US\$500/m².

If the cost benefits of using hydrogen produced by the waste gas are included in the analysis, the capture cost reduces by 20%. The costs range from A\$36 to A\$53 per tonne CO₂ avoided using current technology. If the water-shift reactor could be combined with the membrane separator, the capture cost is less than A\$20 or US\$15 per tonne CO₂ avoided. In the study by Gielen (2003), the estimated CO₂ capture cost for a converted blast furnace using Selexol solvent is US\$18-19/tonne CO₂ avoided. The

lower cost in the study by Gielen (2003) is attributed to the assumption in his study that the water-shift reaction occurs in a membrane reactor with negligible cost compared to the CO₂ separation unit. If a similar assumption is adopted in this study, the capture cost would reduce to A\$27 and US\$20 per tonne CO₂ avoided.

Corex flue gas

Table 8-8 CO₂ capture costs for Corex iron production flue gas

	Gielen (2003)	Absorption	Absorption	Membrane	Adsorption	Low temperature
Technology	Selexol	Selexol	MEA	Current	Current	New
Capital cost (\$/tonne capture CO ₂ /year)	--	A\$104 US\$75	A\$88 US\$67	A\$134 US\$105	A\$81 US\$70	A\$41 US\$30
CCS energy penalty (kJ/kg captured CO ₂)	590	882	1433	1037	997	412
A\$/tonne CO ₂ avoided	---	27	33	42	27	13
US\$/tonne CO ₂ avoided	18.4	22	29	35	24	11

The cost of capturing CO₂ from the flue gas of an advanced iron production process such as the Corex process ranges from A\$13 to A\$42 per tonne CO₂ avoided (Table 8-8). The lowest cost has been estimated for low temperature “anti-sublimation”, while the highest cost is for membrane separation with vacuum permeate conditions. The low cost of CO₂ capture using anti-sublimation is a result of the moderately high CO₂ concentration. This is similar to capturing CO₂ from the flue gas of conventional blast furnaces. Note that if the flue gas of the Corex process is compressed, and CO₂ is recovered using physical absorption with Selexol solvent rather than through chemical absorption with MEA solvent, the capture cost reduces by 18%. The lower energy penalty of the physical absorption system outweighs the additional cost of the feed gas compressor. However, this was not observed for the conventional blast furnace where the CO₂ concentration is less.

The cost for CO₂ capture from Corex flue gas is estimated to be US\$18.4 by Gielen (2003). Using similar technologies and processing conditions as Gielen (2003), the cost is estimated to be US\$20/tonne CO₂ avoided. The differences in the results between this

study and that by Gielen (2003) arises because of the different economic assumptions used.

A summary of all the capture cost for the different options considered in this analysis is shown in Figure 8-7.

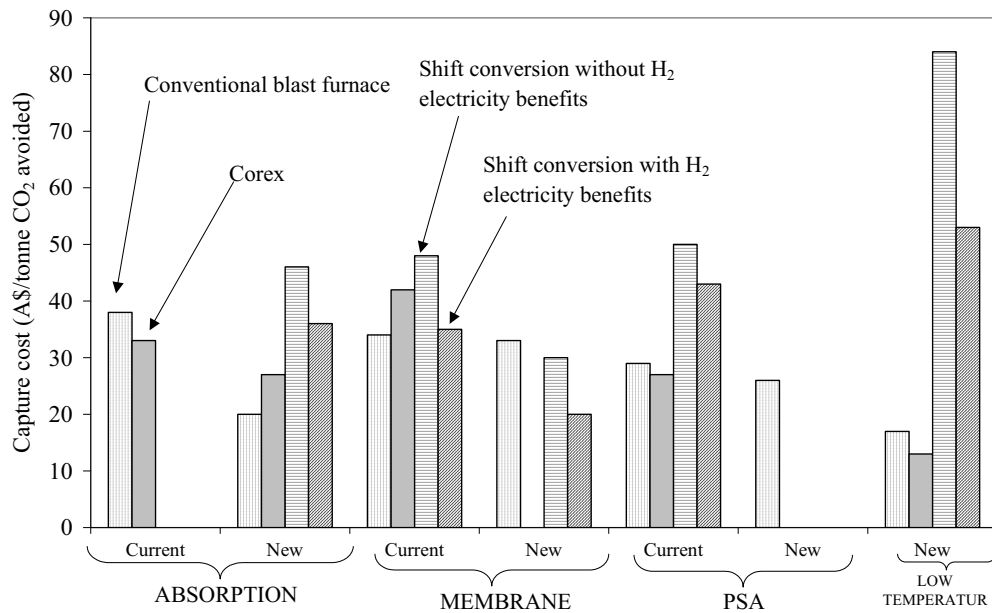


Figure 8-7 Comparison of different CO₂ capture costs and options for iron production

In summary, the incremental cost of capturing CO₂ from blast furnaces (either conventional or converted) and advanced flue gas such as from the Corex processes is lower than the cost of capture from other post-combustion processes such as pulverised coal plants. However, the cost is higher than for capture from pre-combustion technologies such as hydrogen production or from gases with high partial pressure CO₂ (natural gas processing). The analysis suggests that CO₂ capture from the advanced iron making process would be more advantageous than from the conventional process. The analysis also implies that converting CO into CO₂ in traditional blast furnaces without utilising the potential to generate electricity does not lead to economic benefits. This is because of the high cost of the additional processing equipment.

8.8 The petrochemicals industry

The CO₂ emitted from industrial facilities such as oil refineries and chemicals processing plants is primarily the result of the combustion in onsite gas-fired process heaters. The opportunity to capture CO₂ emissions from these facilities has been investigated by Farla et al. (1995), Slater et al. (Slater et al., 2002) and the IEA GHG (2000a) who report capture cost using MEA solvent in the range US\$33 to US\$74 per tonne CO₂ avoided. This study will also investigate the cost of retrofitting CO₂ capture based on Australian economic conditions. The results are shown in Table 8-9 and Figure 8-8.

The cost of capturing CO₂ from a chemical processing plant such as a typical oil refinery gas heater ranges from A\$36 to A\$79 per tonne CO₂ avoided. The lowest cost estimate is for chemical absorption with a new solvent and heat integration, or a vacuum swing adsorption with a new “ideal” adsorbent. In relation to using waste heat through integration, individual facilities will need to be examined to determine where the opportunities for heat integration exist. In this analysis it is assumed that half of the reboiler duty could be eliminated through heat integration with waste heat from the process. Additionally, this analysis assumes that retrofitting the CO₂ capture facility has no cost impact on the process plant. However for individual plants, the additional cost for land and shut-down may need to be considered. Thus the results presented in this analysis may be at the upper end of potential cost savings.

Table 8-9 Capture costs for CO₂ recovery from an oil refinery flue gas

	Slater (2002)	IEA GHG (2000a)	Farla (1995)	Absorption		Membrane		Adsorption		Low temp.
Status				Current	New	Current	New	Current	New	New
Capital cost (\$/tonne CO ₂ captured/yr)	-- US\$115	-- US\$145	-- US\$140	A\$130 US\$100	A\$100 US\$75	A\$140 US\$106	A\$80 US\$64	A\$120 US\$100	A\$90 US\$75	A\$85 US\$63
CCS energy penalty (kJe/kg CO ₂ captured)	--	2340	1420	1690	890	2750	1550	2385	1405	1510
A\$/t CO ₂ avoided	--	--	--	49	36	79	38	60	36	39
US\$/t CO ₂ avoided	40-45	27	46	43	32	70	33	55	33	32

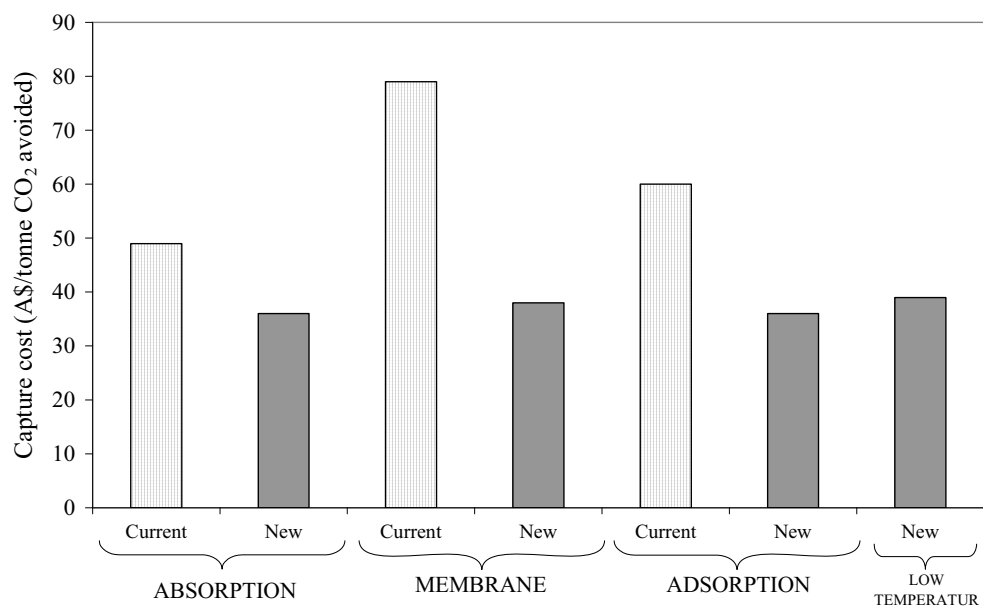


Figure 8-8 Comparison of capture costs for oil refineries

One of the key challenges in capturing CO₂ from a petrochemical plant is the complexity of the plant infrastructure in which CO₂ emissions are dispersed over a large area. The CO₂ flue gases could be treated individually at each source before being combined for transport. Alternatively, CO₂ could be processed in a centralised location, and thus yield economies of scale. This option is assumed in this thesis. According to Slater et al. (2002), this can reduce the total capital cost by 10%. However, the cost for ducting and pipe-work must also to be included. Based on the IEA GHG study (IEA-GHG, 2000a), 15% of the total capital cost is assumed for the pipe-work and ducting required.

The results in Table 8-9 indicate that the CO₂ capture cost using current technology from oil refineries is comparable to the cost of capturing CO₂ from subcritical pulverised coal power plants (Table 8-1). However, the cost reductions gain through technology developments is not as significant for oil refineries as for coal power plants flue gases because of the lower CO₂ concentration (9% compared to 13%).

8.9 Cement production

In 2004, cement production accounted for 3.5 million tonnes of CO₂ emitted in Australia. The CO₂ emissions from cement production come directly from the calcination of the limestone to produce the cement clinker and the combustion of fossil fuels for energy. Approximately half of the CO₂ originates from the combustion of the fossil fuels and half originates from conversion of the raw materials. CO₂ concentrations in the flue gas in cement stacks range from 14% to 33%.

The following section examines the economic feasibility of CO₂ capture from a typical flue gas from Portland cement production. Table 8-10 and Figure 8-9 shows the cost of capturing CO₂ from this cement facility.

Table 8-10 Capture costs for cement production flue gas

	Hassan (2005)	Absorption		Membrane		Adsorption		Low temperature
	Current	Current	New	Current	New	Current	New	New
Capital cost (\$/tonne CO ₂ captured/year)	-- US\$52	A\$102 US\$78	A\$96 US\$71	A\$74 US\$57	A\$86 US\$67	A\$90 US\$73	A\$77 US\$82	A\$67 US\$50
CCS energy penalty (KJ/kg captured CO ₂)	--	1601	750	1430	1178	1380	1080	665
Capture Cost								
A\$/t CO ₂ avoided	--	46	30	32	33	34	27	20
US\$/t CO ₂ avoided	49/tonne captured	41	26	29	28	31	23	17

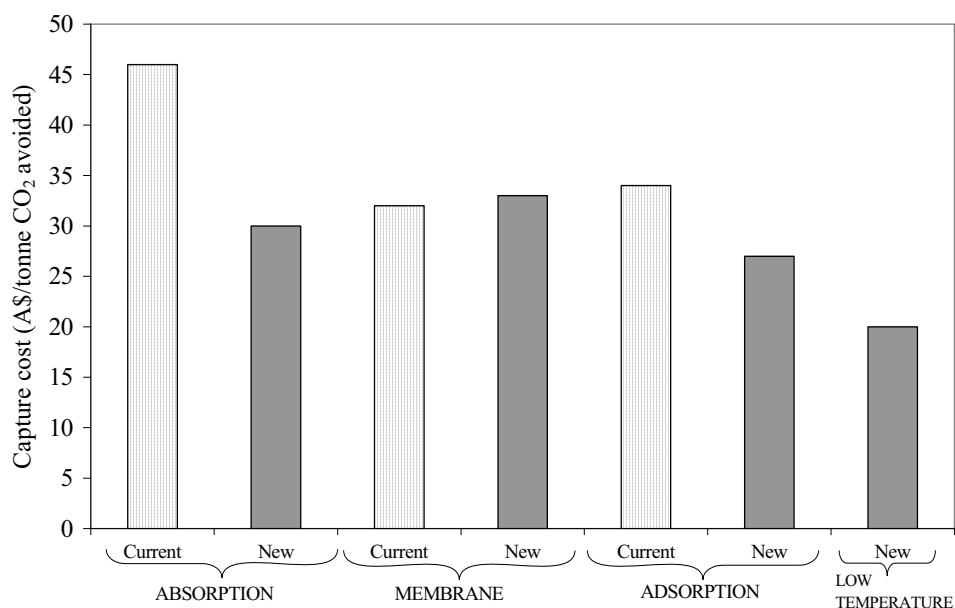


Figure 8-9 CO₂ capture costs for cement production flue gas

The cost of CO₂ capture from cement flue gas ranges from A\$20 to A\$46 per tonne CO₂ avoided. The lowest cost is for the anti-sublimation technology, with the highest cost estimated using current chemical absorption with MEA solvent. The costs for CO₂ capture using vacuum conditions in membrane and adsorption technology are approximately A\$32 to A\$34 per tonne CO₂ avoided using commercial membranes or adsorbents.

Hassan (2005) also estimated the cost for capturing CO₂ from Portland cement flue gas, with a reported cost of US\$49/tonne CO₂ captured, which is higher than is estimated in this study. This is because Hassan (2005) assumes that the source of auxiliary energy is a coal fired power plant with an electricity price of US\$60/MWh, whereas this study assumes an NGCC facility with an electricity price of A\$35 and US\$35 per MWh. If the conditions of the Hassan (2005) study are adopted, the capture cost becomes A\$80 and US\$74 per tonne CO₂ avoided (A\$49 and US\$45 per tonne CO₂ captured).

The cost of capturing CO₂ from cement flue gas is comparable with the cost of capture from pulverised coal power plants (Table 8-1). This is because both flue gases have a similar gas composition – N₂ (68% to 75%), O₂ (3%), H₂O (7%) and CO₂ (13% to 20%). Similarly, both flue gases are at atmospheric pressure and high temperature.

However, the slightly lower cost for cement flue gas reflects the higher CO₂ concentration.

8.10 Comparison of CO₂ capture technologies for different industries

The previous sections of this chapter show the economics of different CO₂ capture technologies for different Australian industries. The costs vary widely and are dependent not only on the capture technologies but also the CO₂ content of the waste gas. For R&D projects, it is important to understand which technology is better suited to which industry.

Figure 8-10 illustrates the lowest cost option estimated using absorption, adsorption, membrane and low temperature separation for each of the industrial sources.

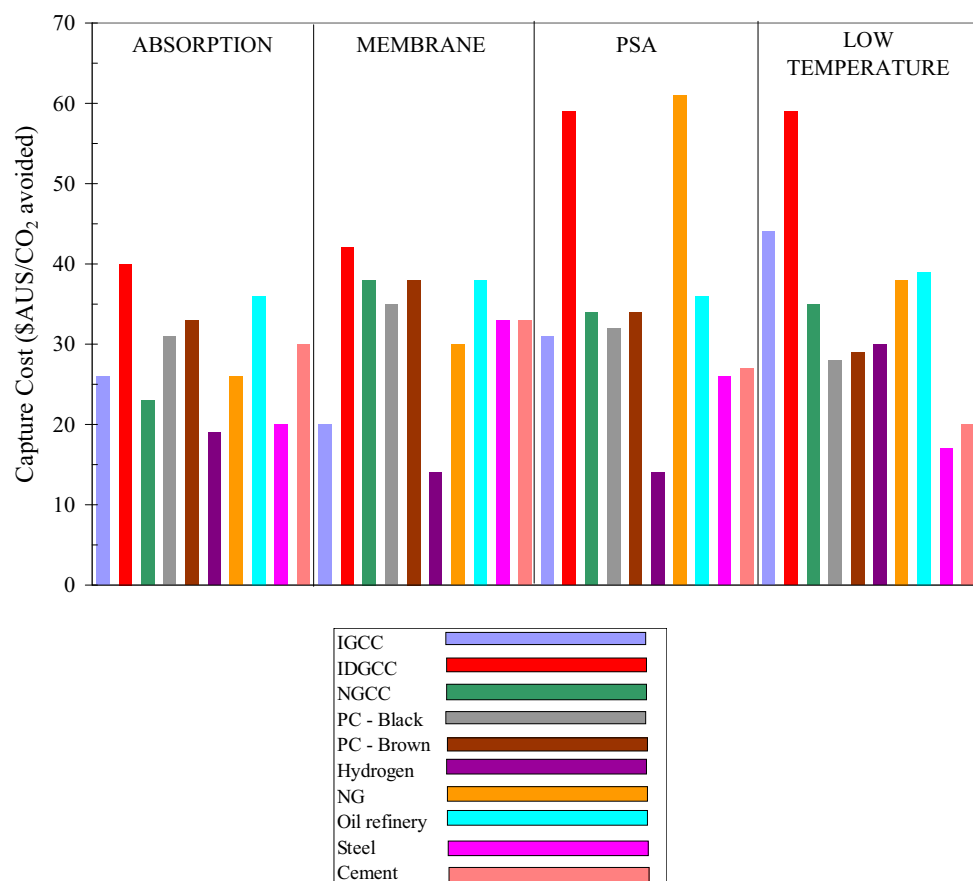


Figure 8-10 Lowest capture cost option for different Australian industrial sources

From Figure 8-10, absorption is the most widely favoured capture technique particularly in the low pressure, low CO₂ concentration regime such as obtained from pulverised coal, NGCC and IDGCC power plants, and oil refinery flue gas where chemical absorption achieves good results.

Adsorption and low temperature processing may also find application in the low pressure regime as concentrations increase. The industrial sources that would be suited to this technology include flue gases from iron and steel furnaces and cement facilities which produce low pressure gas streams with higher relative CO₂ concentrations than other industrial sources. However, for low temperature anti-sublimation separation, because this is a relatively new technology, the capital cost estimates are highly uncertain and there is a possibility that the costs are underestimated.

For the higher pressure and higher concentration applications such as natural gas processing streams, the synthesis gas of IGCC power plants and hydrogen production, physical absorption, membrane and adsorption technology appear most favourable.

8.11 Application of technology learning and equipment cost reductions

As discussed in Chapter 2, many researchers and process developers are investigating opportunities to reduce the capture cost by improving or developing new technologies for CO₂ recovery.

Technology learning is a term used to describe the phenomenon where the unit cost of technologies decreases over time. As new technology is implemented over many years, the technology unit cost decreases by a fixed percentage. Major factors contribute to this including improvements in the technology design, materials, product standardisation, system integration, economies of scale and reduction in input prices. According to McDonald and Schrattenholzer (2001), the “technology learning curve” is a function of the rate of adoption of a technology. The higher the adoption rate, the higher the technology learning curve. In their study, McDonald and Schrattenholzer (2001) found that technology learning rates vary from 14% to 36%, with a median value of 16%.

These rates represent the average reduction in cost for each doubling of installed capacity.

A study by Carnegie Mellon University for the IEA GHG (IEA-GHG, 2006b), explores the cost trends for four power plant options with CO₂ capture. The study shows capital cost reductions of 10% to 18% after 100 GWe of capacity has been installed. For the base case assumptions, the lowest reduction is for pulverised coal power plants with CO₂ capture, with the capital cost expected to decrease by 9.1% from US\$1,962/kW to US\$1,783/kW. For NGCC and oxy-fuel combustion, the expected capital cost reductions are marginally higher at 10.8% and 9.0% respectively. Because power plants consist mainly of mature technology such as the boilers, the additional 100 GWe of capacity does not significantly impact the learning curve and thus cost reductions are low. In contrast, a much higher learning rate is expected for gasification technologies (IGCC), with capital cost expected to decrease by 17.8% from \$1,831/kW to US\$1,505/kW. Steep learning curves are expected for the novel core power generation sections (in particular the shift reactor). Reductions in the incremental capital cost of CO₂ capture are predicted to be 13% to 40%.

The IEA GHG report (IEA-GHG, 2003a) on gasification technologies estimates that by the year 2020 a 20% to 25% reduction in the predicted future electricity price for IGCC power plants with CCS can be achieved. This is accomplished through improvements in the gasification, oxygen production and combined cycle processes. This estimate is slightly higher than the estimate in the later study by Carnegie Mellon University, which predicted a reduction of 18% in the cost of electricity for IGCC power plants. The differences in results arise because of different assumptions used in the studies. The IEA GHG report (2003a) does not discuss technology development specifically for CO₂ capture technologies such as absorption or adsorption. Implementing gasification facilities such as IGCC and IDGCC for electricity are in themselves new concepts. The learning curve of these processes primarily focuses on the power plant rather than established CO₂ capture systems such as physical absorption.

In the study by Riahi et al. (2004), the CCS cost reductions expected for CO₂ capture using chemical absorption technologies were estimated. Their analysis is modelled on the learning curve experienced from implementing SO_x controlling technologies in power plants such as flue gas desulphurisation (FGD). FGD technology was chosen as a comparison as it employs similar principles of operation as chemical absorption capture systems. For FGD systems, investment costs declined by 13% for each doubling of capacity worldwide. A similar cost reduction was used as the reference value to quantify the “learning curve” for CO₂ capture technologies. The results of the study suggest that over a one hundred year period with 1000 GWe of CCS facilities installed, the total capture and storage costs for coal power plants with CCS reduces by 70% from US\$196 to less than US\$41 per tonne C avoided (or US\$53 reduced to US\$16 per tonne CO₂ avoided). If 100 GWe of capacity is installed, the cost reduction is estimated to be 50%.

In this chapter, technology improvements has been estimated to reduce the capture cost to less than A\$30/tonne CO₂ avoided. Assuming that CCS could be deployed at 80% of Australia’s stationary emission sources at this cost, the total capital cost for CCS deployment would be approximately A\$60 billion, of which capture contributes A\$35 billion. This corresponds to an annual capital investment cost of A\$5 billion and an annual operating cost of approximately A\$3 billion.

8.12 Conclusion

In this chapter, preliminary estimates of CO₂ capture costs are made for various Australian industries. The industries with the highest CO₂ emissions are power generators, natural gas processing plants, oil refineries, hydrogen production for ammonia, iron and steel production and cement manufacturers.

The cost of capture using post-combustion technologies ranges from A\$30 to A\$70 per tonne CO₂ avoided for pulverised coal power plants. For post-combustion capture of NGCC flue gas, this cost ranges from A\$30 to over A\$200 per tonne CO₂ avoided for current power plants, and A\$25 to A\$60 for advanced systems. The capture cost decreases for pre-combustion capture in IGCC power plants, with estimates of A\$25 to

A\$45 per tonne CO₂ avoided. The cost is higher for IDGCC power plants due to the added cost of drying and the larger flue gas flowrates and is estimated to be between A\$40 to A\$60 per tonne CO₂ avoided.

During hydrogen production and natural gas processing, CO₂ is and inherently part of the process. The capture cost for hydrogen production ranges from A\$15 to A\$30 per tonne CO₂ avoided. The capture cost for natural gas processing ranges from A\$30 to approximately A\$65 per tonne CO₂ avoided for the feed gas with a 15% CO₂ concentration.

In oil refineries, CO₂ can be captured from the flue gas of the process gas heaters. Capturing 0.8 million tonnes per year could cost from A\$39 using low temperature technology to A\$79 per tonne CO₂ avoided using gas separation membrane technology. CO₂ can also be recovered from iron and steel production blast furnaces. CO₂ capture from the flue gas of a conventional blast furnace is in the range of A\$17 to A\$38 per tonne CO₂ avoided. This flue gas can also be converted into a synthesis gas by the water-shift reaction with CO₂ capture to produce an enriched hydrogen stream. The resulting CO₂ capture cost is from A\$46 to A\$84 per tonne CO₂ avoided. The higher cost is associated with the additional equipment needed for the shift reaction. Part of this cost may be offset if electricity can be generated from the waste gas of the shift reaction. CO₂ capture from advanced iron production processes such as Corex have lower costs estimates of between A\$13 to A\$42 per tonne CO₂ avoided. The lower cost compared to conventional blast furnace flue gas reflects the higher CO₂ concentration in the flue gas.

The CO₂ emissions from cement plants can also be captured. The CO₂ capture cost range from A\$20 to A\$46 per tonne CO₂ avoided and could result in the capture of 2.8 million tonnes of CO₂ annually.

If the capture of CO₂ using the processes described in this chapter could be implemented across all of the industrial sources, Australia's total annual CO₂ emissions would reduce by more than 50%. However, the prospect of CCS deployment at each

facility would be influenced by factors such as the cost for capture, the likelihood of an emissions trading scheme emerging, the expected carbon price and proximity to geological storage facilities.

Based on the current carbon prices trading in the EU ETS in 2006 and the recommended carbon price by the Australian NETT (Chapter 1), hydrogen and natural gas processing plants are likely to be the first to see wide scale commercial deployment of CCS. The moderate cost of CO₂ capture from iron production facilities, and the likely economies of scale that may be obtained in Australia imply that this industry may also be deploy CCS at an early stage.

CCS at power generation (pulverised coal, NGCC, IGCC and IDGCC) and cement manufacturing is likely be implemented when technology improvements and confidence has been demonstrated at the pilot stage, and the costs have significantly been reduced.

The much higher capture costs for oil refineries and the complex nature of the facilities suggests that financial incentives or further technological improvements are required before CCS is applied.

Chapter 9. VARIABILITY AND UNCERTAINTIES IN CCS ECONOMICS

9.1 Overview

This chapter discusses the effect on capture costs by changing the conditions of the economic assumptions and the impact of uncertainties of the economic input data. The parameters evaluated include the reference point, the source and cost of energy supplying the capture facility, and methodological assumptions such as plant capacity factor, and the discount rate.

9.2 Introduction

The reported costs for CO₂ capture using one standard technology such as amine chemical absorption from a post-combustion power plant can range widely from a value as low as US\$30 (Gibbins and Crane, 2004b) to as high as US\$65 per tonne CO₂ avoided (Rao and Rubin, 2002). The discrepancies in the reported costs arise mainly because different authors use different methods and assumptions for their analysis.

Costs estimates vary because different authors adopt different estimating methods and/or assume different operating parameters for the capture process. These are predictable assumptions, but can differ from one study to another.

In contrast, uncertainties in costs arise because of the unpredictability of some assumptions. For example, the price of natural gas as a fuel source is a major uncertainty. The price changes over time and varies from country to country because of fluctuations in supply and demand. Uncertainties can also arise when operating parameters are unpredictable. For instance, gas compositions might in practice turn out to be different than expected.

9.3 The impact of methodological assumptions

Variations in methodologies have significant impact on the reported cost of CO₂ avoided. The following discusses the reference point, and the energy source for the CCS system.

9.3.1 The reference point

To determine the extent of the financial burden imposed by CCS, a reference point is required. The reference point chosen differs according to the objective of the comparison or study. The objectives could include:

1. Determining the incremental effect of CCS on the cost of the product.
2. Estimating the environmental impact of CCS implementation as a mitigation option versus another.
3. Determining the environmental benefit of using different power generators.
4. Determining the cost to the electricity sector of implementing CCS.
5. Providing a comparison of capture cost across different industrial processes.

In many studies, the researchers assume that the reference plant is the same the plant but without CCS. This assumption and method is valid if the objective is to determine the incremental cost of CCS to the business. However, it might not be valid if the objective is to estimate the economic and environmental impact of CCS compared to another mitigation option.

For example, new power plants such as integrated combined cycle gasification (IGCC) or natural gas-fired combined cycle (NGCC) systems have much lower CO₂ emission levels than current coal-fired pulverised (PC) plants. If the objective is to determine the environmental benefit of using an IGCC or NGCC power plant compared to a PC power plant, then the reference point would be the PC plant. The cost of CO₂ avoided is the difference in expenditure for building the IGCC or NGCC plant compared to a PC power plant, divided by the CO₂ emission reductions. This is shown in Table 9-1, in which reductions are achieved by fuel switching (that is using lower carbon fuels). The cost of reducing CO₂ emissions is A\$100/tonne CO₂ avoided for replacing a PC power

plant without capture with an IGCC power plant without capture, and A\$12/tonne CO₂ avoided for replacing the same PC power plant with an NGCC power plant without capture.

Table 9-1 Cost of CO₂ avoided for an IGCC compared to a PC and NGCC power plants

Reference plant		PC w/o capture	PC w/o capture
CO ₂ emission w/o capture	tonnes/MWh	0.9	0.9
COE w/o capture	A\$/MWh	30	30
Replacement plant		IGCC w/o capture	NGCC w/o capture
CO ₂ emission w/o capture	tonnes/MWh	0.75	0.4
COE w/o capture	A\$/MWh	45	36
Capture Cost	A\$/tonne CO ₂ avoided	100 = $\frac{45-30}{0.9-0.75}$	12 = $\frac{36-30}{0.9-0.4}$

Similarly in Table 9-2, the analysis demonstrates how the reported capture cost for an IGCC power plant with capture varies depending on the choice of the reference plant.

Table 9-2 Capture cost for IGCC power plant with capture as a function of different reference points

Reference plant		IGCC	PC	NGCC	Generic source
CO ₂ emission w/o cap.	tonnes/MWh	0.75	0.9	0.4	0.8
COE w/o capture	A\$/MWh	45	30	36	35
Replacement plant		IGCC w/ capture	IGCC w/ capture	IGCC w/ capture	IGCC w/ capture
CO ₂ emission w/ cap.	tonnes/MWh	0.08	0.08	0.08	0.08
COE w/ capture	A\$/MWh	62	62	62	62
Capture Cost	A\$/tonne CO ₂ avoided	26	39	79	37

As shown in Table 9-2, if the reference plant is simply the same IGCC power plant without a CO₂ capture system, then the reported capture cost is A\$26/tonne CO₂ avoided (that is the incremental cost due to capture). However, if a pulverised coal or a NGCC power plant is selected as the reference point, then the cost is considerably higher at A\$39 to A\$79 per tonne CO₂ avoided. The reference point could also be generic. In Table 9-2, the generic cost of electricity (COE) is assumed to be A\$35/MWh and the generic CO₂ emission rate is 0.8 tonnes/MWh. The resulting cost of CO₂ avoided is A\$37. The higher capture cost of these reference points compared to the IGCC plant is attributed to the lower base COE for these other systems. Although the

cost of CO₂ avoided is much lower for an IGCC plant using the same plant as a reference, examining it in the context of other reference points allows a comprehensive evaluation. IGCC power plants may have a lower incremental CCS cost, but they cost more to build.

The choice of reference point depends on the characteristics of the industrial emission source and the objectives of the analysis. If the objective is to determine the economic impact of CCS on the electricity sector, then the incremental capture cost compared to a fixed electricity price may be of interest. For instance, the fixed electricity price could be determined as the average of national/state/regional electricity costs, or it could be a value set by industry.

Having a set value for the cost of electricity also has the benefit of allowing cost comparison across different sectors. The cost of implementing CCS for one industrial facility could then be compared to the relative cost of CCS at another facility. For instance, when comparing the impact of CCS for a power plant to CCS for an ammonia plant. In addition a comparison could be made with other mitigation options such as renewable energy. A set reference point also offers businesses a basis for trade in CO₂ credits.

9.3.2 Impact of different energy sources

In the analyses in the Chapters 4 to 7, it was assumed that the CO₂ capture facility was built as part of a new power plant. The capacity of the power plant is upgraded, such that the net output remains 500 MW regardless of the energy penalty for capture. However, there are alternative ways in which the energy can be supplied to the CO₂ capture facility. The different options for providing the energy include:

- A. The power consumed by the capture plant reduces the net output of the reference power plant (parasitic retrofit capture). The power loss is not compensated by an external energy source. This is shown schematically in Figure 9-1.

- B. Building a new power plant with additional power capacity to cater for the CCS facilities, and thus keeping the same net output as the original reference plant (Figure 9-1).
- C. The reference plant uses a supplementary energy source to supply energy to the CCS system. The supplementary sources are either by another new power plant onsite or the power is purchased from grid (Figure 9-2). The CO₂ emissions from supplementary energy may:
1. Be emitted into the atmosphere;
 2. Be capture by a separate CO₂ capture unit. This option is equivalent as purchasing energy for another power plant with CCS; or
 3. Be captured by the same CO₂ capture unit (assuming the supplementary source is in the same location).

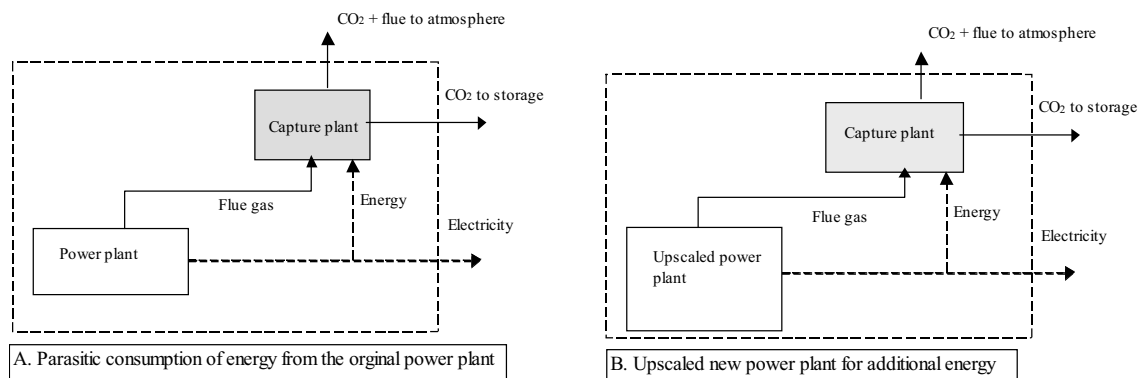


Figure 9-1 Schematic of options A and B for CO₂ capture from a power plant

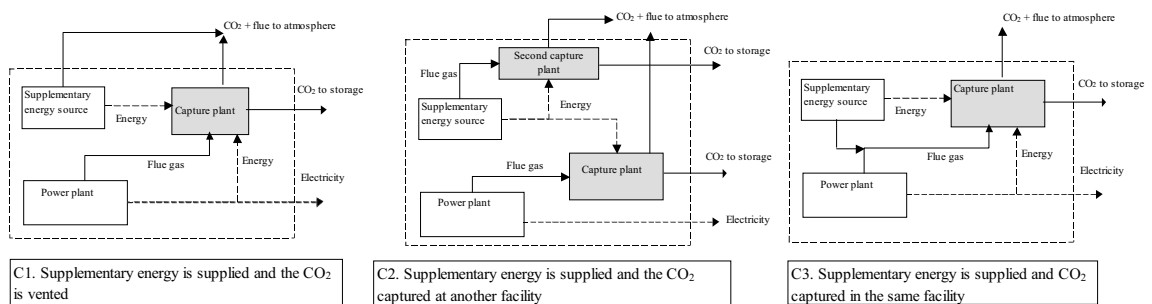


Figure 9-2 Schematic of options C1, C2 and C3 for CO₂ capture from a power plant

Retrofit or build a new power plant?

Using the same processing and economic assumptions and outputs for the baseline pulverised coal flue gas as outlined in section 3.5, the following analysis examines the effect of different sources of energy supplied for the CO₂ capture facility. The results are based on the base case scenario, and neglect cost reductions as a result of technology improvements. However, if these were considered, the trends reflected would remain the same.

For cases C1, C2 and C3, the supplementary power source is assumed to be another coal fired power plant. For C1 and C3, the emission rate for CO₂ is assumed to be 0.88 kg CO₂/kWh. While for C2, it is assumed that the external energy has CCS facilities with a CO₂ emission rate of 0.14 tonnes/MWh. For case C1, the external power is purchased at the same price as the reference cost of electricity and for case C2, the purchased cost of electricity is estimated to be A\$78/MWh. For case B, only the variable operational costs of labour and insurance are scaled up linearly. The capital costs and fixed operating costs are scaled up using a cost exponent of 0.7. The reference point is assumed to be the original pulverised coal power plant without CO₂ capture.

Table 9-3 shows key costs for the reference case, cases A, B, C1, C2 and C3.

Table 9-3 Key costs for cases A, B1, C, C2, C3 and reference power plant

	Reference	A	B	C1	C2	C3
Power plant capture option	No Capture	Retrofit	New plant	Retrofit	Retrofit	Retrofit
		Parasitic	Parasitic	External power emits	External power source with CCS	External power capture onsite
Original energy output (MW)	500	500	781	500	500	500
Total Energy penalty for capture facility (MW)	-	180	281	180	180	281
Net energy output w/ capture (MW)	-	320	500	500	500	500
Initial CO ₂ emissions (tonnes/MWh)	0.88	0.88	0.88	0.88	0.88	0.88
CO ₂ emitted with capture (tonnes/MWh)	--	0.14	0.14	0.40	0.14	0.14
Δ CO ₂ emissions due to capture (tonnes/MWh)	--	0.74	0.74	0.47	0.74	0.74
COE (A\$/MWh)	30	78	70	61	78	83
Change in COE (A\$/MWh)	--	48	40	31	48	53
Capture cost A\$/tonne CO ₂ avoided	--	66	54	66	66	72

From Table 9-3, the reference cost of electricity is assumed to be A\$30/MWh (NEMMCO, 2005). The capture costs for cases A, C1 and C2 are A\$66/tonne CO₂ avoided, while the cost for case B is lower at A\$54/tonne CO₂ avoided, and the cost for C3 is higher at A\$72/tonne CO₂ avoided.

The different capture costs for cases B and C3 compared with the others is because the capital costs and fixed operating costs for both the power plant and CO₂ capture plant have been scaled-up using an exponent of 0.7 rather than linearly. That is economies of scale have been assumed. The costs for the larger power plant, case B, are calculated using a fractional exponent reduces the total capital costs per MW. Conversely, for the smaller power plant in case C3, the capital cost per unit MW is larger. If a linear exponent were assumed, then the cost of capture for cases B and C3 would also be A\$66/tonne CO₂ avoided. However, rarely in process economics is a linear exponent applicable.

The capture cost for case C2 in the above results is the same as for cases A and C1. This is because of the assumption that the external power source with CCS was charging the

same cost of the electricity as the power plant with capture. However, if the purchased cost of electricity were higher than A\$78/MWh, for example A\$85/MWh, the capture cost would increase to A\$69.5/tonne CO₂ avoided. If the purchase cost of electricity were significantly lower, for example A\$60/MWh, the capture cost would be A\$57/tonne CO₂ avoided.

The results in Table 9-3 show that because of economies of scale, the financial penalty for implementing CCS is much less for a new power plant than to retrofit an existing one. Retrofits are approximately 20% more expensive in terms of costs of capture. The economies of scale gained can be a result of bulk equipment purchases and/or consolidated construction, labour and engineering costs. Additionally, there is the opportunity to reduce the cost by integrating the capture and power plant processes. Thus, there is an economic advantage in building a CCS system at the development stage rather than later. This analysis is based on current costs for retrofitting CCS systems and may change as new lower cost materials become available.

Varying the supplementary power for retrofitted plants

The choice of the source for the external supplementary power used to operate the CCS facilities will also have a significant impact on the value of the cost of CO₂ avoided. For the above case study (Table 9-3), the external supplementary power source is assumed to be another pulverised black coal (PC) power plant with the same CO₂ emissions. However, if the supplementary power system were another power source such as a NGCC power plant, the rate of CO₂ emissions for cases C1, C2 and C3 would be different.

Figure 9-3 compares the capture cost for the retrofitted PC power plant using four alternate sources of external supplementary energy under a case C1 scenario. These are:

1. PC power plant with CO₂ emission of 0.857 tonnes/MWh;
2. NGCC power plant with CO₂ emission of 0.4 tonnes/MWh;
3. IGCC power plant with CO₂ emission of 0.7 tonnes/MWh; and
4. Renewable energy source such as solar.

The changes in CO₂ emissions ($\Delta\text{CO}_2/\text{MWh}$) for the alternate energy sources are 0.65 tonnes/MWh for NGCC, 0.54 tonnes/MWh for IGCC and 0.79 tonnes/MWh for the renewable energy source.

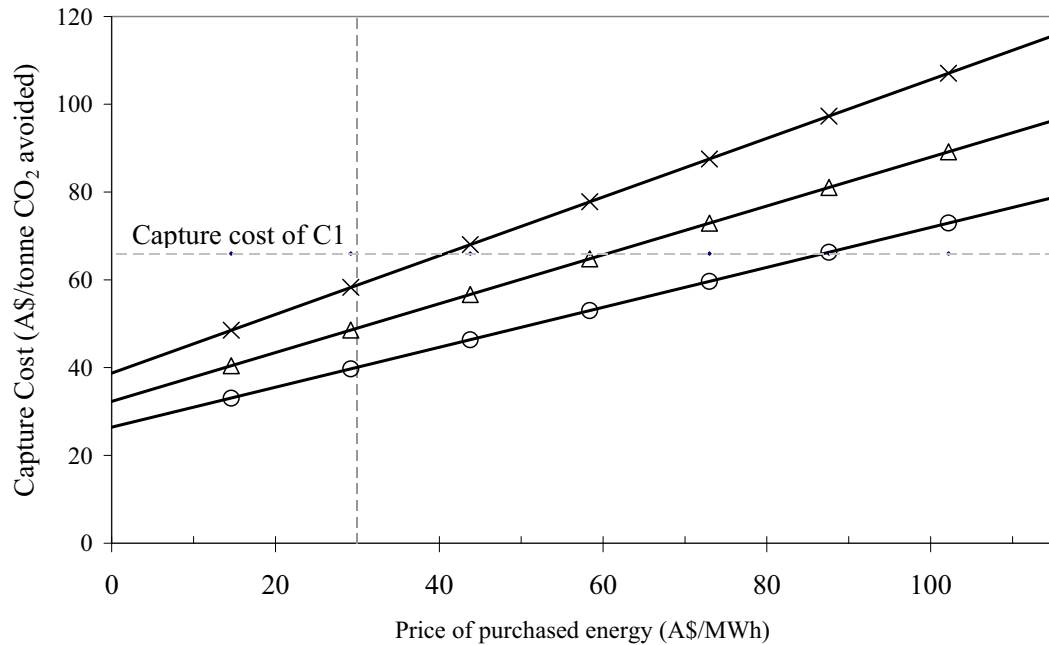


Figure 9-3 The capture cost for different power sources [renewable ($\circ$), NGCC (Δ) and IGCC ($\times$)] as a function of the purchased price of energy compared to case C1

If cost of purchased power is assumed to be the same from any external supplementary power sources (A\$30/MWh), the results from Figure 9-3 indicate that it would be economically beneficial to use the power of generators with a lower CO₂ emissions intensity. The lower emission intensity of the renewable energy source, NGCC and IGCC improves the capture cost by 40%, 25% and 15% respectively compared to the PC power plant.

However, the cost of electricity from alternative power sources is rarely equivalent in price to the generation cost of electricity from coal-fired power stations. In Australia, the cost of supplying power from natural gas can range from one to eight times the price of electricity produced by coal (NEMMCO, 2005, Origin, 2005).

Figure 9-3 also shows that in choosing to retrofit an existing coal-fired power plant using energy from a supplementary source, an important factor is the cost of that power and the CO₂ emission intensity.

If an IGCC power plant provided the external energy for CCS, then the price of electricity needs to be less than A\$40/MWh before it becomes more profitable to use a retrofitted coal-fired power plant with capture. For the NGCC power plant, the price threshold is close to twice (A\$60/MWh). Using renewable energy sources with a zero CO₂ emission rate, the cost of electricity would have to be three times more expensive than coal-fired power plants. If the cost of any of the alternate energy sources is greater than A\$90/MWh, then it would be more economical to build another PC power plant with capture.

In reality the price of electricity alone would not be the sole consideration. Other factors such as the capacity for the supplementary source to provide sufficient energy, the availability of the fuel, the variability in the costs of the fuel source, and environmental policies/regulations would play a significant role.

9.3.3 Other methodological parameters

While many factors contribute to the variation in the reported cost of capture, according to Rubin and Rao (2002), the parameters that have the most significant impact include the power plant efficiency, plant capacity factor and the fixed charge or discount rate. Another study by Palfreyman et al. (2004) showed in their sensitivity analysis that the cost of CO₂ avoided was greatly affected by the cost of energy, the operating capacity and the uncertainties in the cost of capital.

For a business assessing the feasibility of a CCS scheme as a possible mitigation option, it is worthwhile and meaningful to be able to report the cost of CO₂ avoided as a range where the variability and uncertainties of the costs involved in the project have been taken into account. The following section investigates the economic variables that have the most bearing on CO₂ capture costs.

Variations in baseline assumptions

The following analysis re-examines the baseline cost for CO₂ capture using MEA chemical absorption as detailed in Chapter 4. The baseline assumptions and preliminary data range are listed in Table 9-4.

Table 9-4 Baseline economic assumptions

Processing	Nominal value	Range
Plant operating capacity factor	85% (7446 hours)	80-90
Energy price	A\$30/MWh US\$32/MWh	20 - 40
Discount rate	7% real	5-15
Project life	25 years	20-30
Confidence in capital costing	100	± 20%

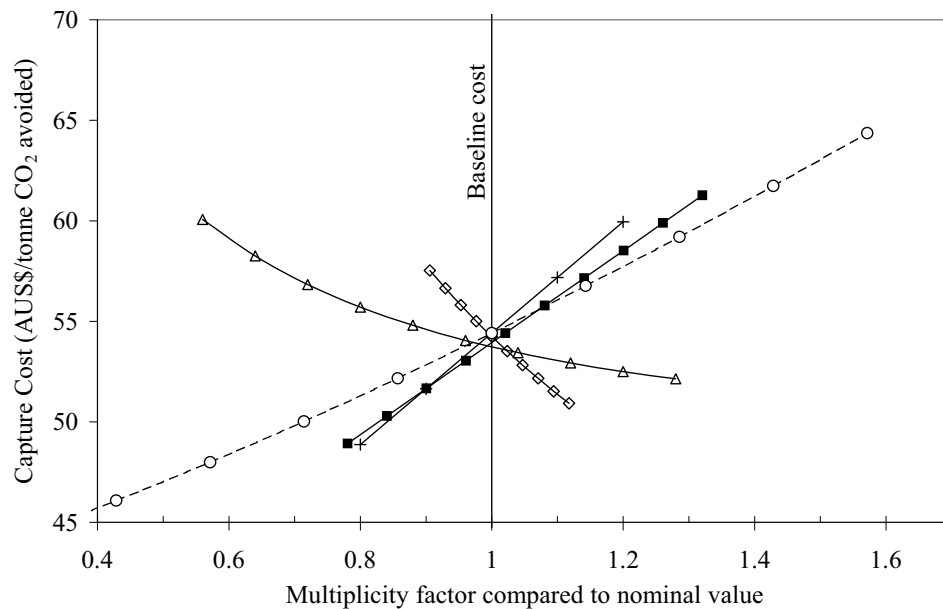


Figure 9-4 Sensitivity of capture cost due to processing and economic assumptions; discount rate (○), energy cost (■), plant operating capacity factor (◇), capital cost (+) and project life (Δ)

Figure 9-4 illustrates that uncertainties in the capital costing has a significant effect on the capture cost. If the capital cost is 20% lower than the base case, then the capture cost decreases from an original estimate of A\$54 to A\$48 per tonne CO₂ avoided, a difference of approximately 10%. The other parameters that significantly affect the capture cost include the cost of energy, the project life, the plant operating capacity and the discount rate. Increasing the cost of energy or the discount rate by 20% increases the capture cost by 8% and 7% respectively. Although the length of the expected project

life and plant capacity factor do impact the capture cost, they only have a large effect if the project life is less than 80% of the nominal value (or less than 20 years) and if the plant capacity is operating at or near maximum capacity (100%).

9.3.4 Economic variability

A detailed analysis of the effects of capital costs, energy cost as a result of fuel prices, and discount rate is discussed below. The data ranges for the economic parameters have also been refined to reflect current Australian economic conditions.

Discount rates

The discount rate is a parameter used to determine the net present value of a project. The discount rate can be defined as the return that could be obtained on an alternative investment with a similar risk to the project being evaluated.

The default nominal discount rate for this analysis is assumed to be 10% nominal based on the sum of 5.5% cash rate plus a risk premium of 4.5% for industrial equity risks (Damodaran, 2006). Assuming an inflation rate of 3% based on the Reserve Bank of Australia's upper limit on inflation based on the consumer price index, the default real discount rate is therefore 7%. Variations in the real discount rate from 3% to 15% are assumed for the sensitivity analysis.

Capital costing

There are significant uncertainties in estimating capital costs. Variations in equipment prices can arise due to changes in commodity prices, differences in vendor costs and fluctuations in exchange rates. Table 9-5 outlines the nominal values of equipment costs, a breakdown of the capital costing procedure used in the cost model and the assumed distribution. The table shows the low, middle and high points of the ranges assumed for all equipment unit costs. Cost estimated in Australian dollars supplied by local vendors are used where possible. However, for some equipment costs, costs are obtained only in US dollars and then translated into Australian costs using an exchange rate of US\$0.75 for A\$1.

Table 9-5 Cost model parameter, nominal values and data range

	Capital cost elements	Nominal value for 2005	Data range
	FGD	18 (US\$/kg of flue gas/hr) 24(A\$/kg of flue gas/hr)	(15, 18, 21) (20, 24, 28)
	Absorber	11 (US\$/train) 12 (A\$/train)	(8,11,14) (10,12,16)
	Regenerators	155 (US\$/kg of CO ₂ produced/hr) 160 (A\$/kg of CO ₂ produced/hr)	(145, 155, 165) (190, 205, 220)
	Heat Exchangers	5.5 (US\$/kW) 5.5 (A\$/kW)	(2.5, 5.5, 8.5) (2.5, 5.5, 8.5)
	Compressors	530 (US\$/MW) 800 (A\$/MW)	(450, 530,650) (750, 800,1050)
	Drying equipment	1890 (US\$/kg CO ₂ produced/hr) 2520 (A\$/kg CO ₂ produced/hr)	(1500, 1890, 2200) (2000, 2520, 2930)
A	Process Equipment Cost (PEC)	Sum of all process equipment	
B	General facilities	10% PEC	(5,10,20)
	Total Equipment Cost (TEC)	A+B	
C	Instrumentation	10%TEC	(5,10,20)
D	Piping	10% TEC	(5,10,20)
E	Electrical	5 % TEC	(3,5,10)
F	Total Installed Cost (TIC)	A + B + C+ D +E	
G	Start-up costs	1% BPC	(0.5,1,2)
H	Engineering	5% BPC	(1, 5,10)
I	Project Contingency	10% BPC	(5,10,15)
J	Owner's cost	0 % BPC	(0, 5)
	Total Capital Cost	F+G+H+I+J	

Energy and fossil fuel prices

The energy price, which is dependent on the type and cost of fossil fuel, constitutes another important variable in reported costs for CO₂ avoided. As illustrated in Figure 9-4, a 40% variance in energy prices has an effect on the reported cost of capture by approximately 10%.

According to the Australian Bureau of Agricultural and Resource Economics (ABARE, 2005), the nominal market price of exported thermal coal increased from A\$1.3/GJ to A\$1.9/GJ from 2001 to 2005. The price is forecast to fall back to \$1.3/GJ by 2010 in real terms. However, this variability in exported coal prices does not reflect the complexities of domestic coal prices in Australia, which varies based on agreed market pricing between the supplier and the purchaser. According to the Electricity Supply Association of Australia, the domestic price of coal has ranged between A\$0.8 to A\$1.1/GJ during 2002 to 2005. If the price of coal varies from A\$0.2/GJ to A\$2.0/GJ,

then the corresponding electricity generation cost for a pulverised coal-fired power plant ranges from A\$23/MWh to A\$39/MWh.

Results of economic variability analysis

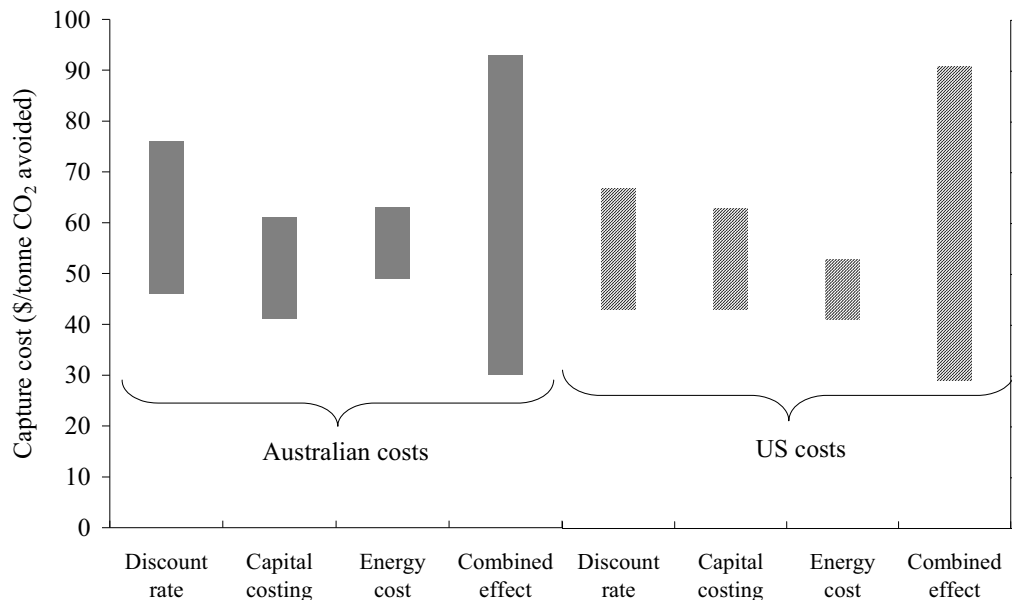


Figure 9-5 Range cost uncertainties for the baseline MEA case study

Figure 9-5 shows the range in CO₂ capture cost with variation in the discount rate, capital costing, energy cost and the combined effect of all three parameters for the baseline MEA case study. The results are reported for both Australian and US conditions. Keeping all baseline line costs fixed, the CO₂ capture cost ranges from A\$46 to A\$76 per tonne CO₂ avoided when the discount rate varies from 3% to 15%. The capture cost varies from a low of A\$41 to A\$61 per tonne CO₂ avoided based on high and low assumed equipment costs. The effect of varying the energy price from A\$23 to A\$39 per MWh changes the capture cost from A\$49 to A\$63 per tonne CO₂ avoided. If the upper and lower limits of the three parameters are examined together, the capture cost ranges from A\$30 to A\$93 per tonne CO₂ avoided. This is a decrease of 45% or increase of 70% compared to the baseline cost estimate of A\$54/tonne CO₂ avoided.

This impact is more pronounced for the Australian costs than for the US based costs. This is because in translating the uncertainties of the capital costing from US to

Australian dollars, the data distribution for the equipment cost is wider than those nominated in Table 9-5.

The analysis in this chapter shows that capture cost is sensitive to changes in the input parameters, particular the capital costs. However, it ignores the probability that an input may be a given value and is very restrictive and cumbersome in analysing the effect of combined uncertainties in the inputs. This limitation can be overcome by Monte Carlo analysis, a technique that takes into account (a) the probability that an input has a particular value and (b) the effect of combined uncertainties in the inputs. The result is a probability distribution of capture costs. If a probability analysis is applied to the results in Figure 9-5, the extreme estimates would have a very low probability of occurring (Rubin and Rao, 2002). A Monte Carlo simulation is outside the scope of this thesis. However, a more comprehensive evaluation of CCS economics including Monte Carlo simulation is recommended.

9.4 Conclusion

The cost of CO₂ avoided is a useful and easy economic tool to use for the comparison of different CO₂ mitigation options. However, there is inherent variability and uncertainty in the cost estimates. In addition, the cost of CO₂ avoided can also be misleading if its basis is not clearly defined. In particular the definition of the reference plant is important, different options cannot be accurately compared if the cost per tonne CO₂ avoided is based on different reference plants.

The results from this analysis show that variabilities such as the choice of retrofitting or building a new power plant, the fossil fuel source of energy, the uncertainties in costs and different reference conditions all contribute to a range of cost of CO₂ avoided being reported. The analysis has been undertaken for a pulverised coal-fired power plant, but the analysis can be applicable to any CCS system.

Chapter 10. CONCLUSION

More frequent and extreme weather events with serious economic repercussions have been occurring because of increasing CO₂ and greenhouse gas emissions, and global warming (AGO, 2005). A number of options for greenhouse gas mitigation have been proposed. One option, capturing the CO₂ at stationary emission sources and storing it in geological locations, otherwise referred to as carbon dioxide capture and storage (CCS), offers a medium-term mitigation strategy. In evaluating CCS as a possible mitigation option, it is important to understand the costs of establishing capture and storage infrastructure at existing or new CO₂ emissions sources. Numerous economic assessments have been carried out. The most recent assessments are collated in the IPCC Special Report on Carbon Dioxide Capture and Storage (IPCC, 2005). To date, almost all of the assessments for CO₂ capture are studies for either North American or European conditions. Only one previous study by Dave et al (Dave et al., 2000) has been reported in the open literature for an Australian CO₂ emission source. If CCS is to be deployed in Australia, an economic evaluation of CO₂ capture costs based on Australian conditions is necessary.

An additional gap in the existing literature is that much of it has focused on evaluating capture costs using commercially available chemical or physical absorption technology. Very few economic analyses have assessed the potential of emerging capture technologies, such as adsorption, membrane and low temperature separation.

In this thesis, a preliminary estimate of CO₂ capture cost was undertaken for a range of Australian industries. These include power generation, natural gas processing, oil refinery, hydrogen production, iron and steel production, and cement manufacturing. A new techno-economic model has been developed to estimate the capital, operating and avoidance cost of CO₂ capture at these facilities.

Four CO₂ capture technologies were evaluated; solvent absorption, pressure swing adsorption, gas separation membranes and low temperature separation. The cost of capturing CO₂ using the four technology options has been compared for different industrial sources. It is the first analysis under Australian conditions for membrane, pressure swing adsorption and low temperature separation technology. Because these technologies have their inherent advantages and disadvantages, the application of a specific technology option was shown to be better suited to one particular industrial source more than another.

The results of the study suggest that absorption technology is the most promising technology for low concentration CO₂ flue gas such as is obtained from pulverised coal, NGCC and IDGCC power plants, and oil refinery flue gas. For gas streams with a high CO₂ concentration such as natural gas processing streams, the synthesis gas of IGCC power plants and hydrogen production, membrane and adsorption technology appear to provide the most opportunities for low cost capture. Low temperature separation using “anti-sublimation” technology is a relatively low cost option when the CO₂ concentration is moderate and the feed gas pressure is low. The industrial sources that could possibly benefit from this technology include exhaust flue gases from iron and steel furnaces and cement facilities.

The cost of CO₂ capture using current technology can range from A\$15 to over A\$100 per tonne CO₂ avoided. The costs are highly dependent on the capture technology option selected and the characteristics of the waste gas from the emission source. The lowest capture cost was estimated for capturing CO₂ from hydrogen synthesis gas, while the highest cost estimate is for NGCC flue gas. In both cases the capture option was membrane technology.

Low cost estimates of less than A\$30/tonne CO₂ avoided were generally observed for gas streams with high partial pressure CO₂ as are encountered in processes such as hydrogen production, IGCC power plants and natural gas processing. Higher costs of A\$40 to over A\$80 were estimated for low partial pressure CO₂ flue gas streams (pulverised coal and NGCC power plants, and combustion of fuel in oil refineries and

cement facilities) and, for IDGCC synthesis gas which contains very high levels of moisture. CO₂ capture from iron production blast furnace flue gases results in moderate costs of A\$30 to A\$40 per tonne CO₂ avoided.

At the time of writing (2006), the European Union had completed the first phase of its Emissions Trading Scheme (EU ETS) with carbon prices in 2005 and early 2006 ranging from A\$30 to A\$45 per tonne CO₂ avoided (Capoor and Ambrosi, 2006, BBC_News, 2005). A report released by the Australian National Emissions Trading Taskforce (NETT) set up by the Australian State and Territories Governments has recommended that an emissions trading scheme also be established in Australia by 2010. It is anticipated that industrial facilities with CCS will participate in the scheme by at least 2020 at a carbon price between A\$30 to A\$35 per tonne CO₂ avoided for CCS (NETT, 2006). In addition, the Australian Federal Government has announced a federal task force to investigate the role Australia might play in any global emissions trading system (Howard, 2006). Therefore, it is possible that in the near future an emissions trading scheme will be established in Australia and CCS deployed to enable participation in this scheme.

Based on the cost estimates for capture and the current carbon price it is expected that wide scale commercial implementation of CCS will most likely be first undertaken at hydrogen and natural gas processing facilities. CO₂ capture is already an inherent part of these processes and CCS would require only the addition of compressors and the identification of suitable storage locations. In this thesis, the capture costs for industries that produced a pure stream of CO₂ in their processes, such as the production of aluminium and ethanol from biomass, were not evaluated. However, it would be straightforward and cost effective to adapt these processes for CCS, and early implementation at these facilities. In future work, it would be worthwhile exploring the CCS potential of these industries.

The moderate cost of CO₂ capture from iron production facilities suggests that this industry may also be keen to deploy CCS in the near future. Of the CO₂ emitted from iron and steel production in Australia in 2004, 75% came from a single point source at

the BlueScope Steel facility in Port Kembla. Capturing and transporting a large quantity of CO₂ from a single source may have transport and storage cost benefits, and further economic evaluation is merited.

If wide-scale CCS could be deployed in industries such as power generation, Australia's total CO₂ emissions could decrease by up to one third. However, the current costs of capturing CO₂ from combustion power plants (over A\$40 to A\$50 per tonne CO₂ avoided) using current technology is likely to be prohibitive. The Australian NETT has suggested that future increases to the capacity of coal power plants in Australia take the form of IGCC with CCS rather than converted pulverised coal power plants (NETT, 2006). This is because the CO₂ capture cost is much lower for these facilities (less than A\$30/tonne CO₂ avoided). Nevertheless, if CCS is to make a significant impact on reducing CO₂ emissions, it is imperative that the existing pulverised coal and NGCC power plants be included in the matrix. Thus the cost of capture needs to reduce significantly. Improvements in technology and process design are expected to provide such reductions.

A set of sensitivity analyses has been undertaken exploring the opportunities to reduce costs and highlight the direction of future R&D development. The effect of varying process parameters on the cost of the four capture options was examined. Although the analysis was for the flue gas from a black coal pulverised power plant, the results and conclusions are applicable for any industrial emissions source with a low partial pressure CO₂ waste gas.

The high cost of CO₂ capture using chemical absorption technology is due to two key factors. These are the high thermal energy input needed for solvent regeneration and the high capital cost of the equipment. The results of Chapter 4 show that future R&D focus should include the development of new solvents that are resistant to degradation, are non-corrosive and possess high absorption rates but require low regeneration energy. Secondly, examining the opportunities for utilising waste heat from the absorption process with the industrial process plant would be beneficial. Thirdly, opportunities to

reduce the cost for absorption and regeneration vessels by designing “fit-for-purpose” equipment should be investigated.

The high cost of capture using membrane technology is dominated by the capital and operating expenses for the flue gas and post-capture compressors (Chapter 5). Operating the permeate stream under vacuum conditions may reduce costs significantly. Improvements in membrane CO₂ permeability, increased CO₂ selectivity and lower membrane costs are also needed to achieve further costs reductions.

As with membrane technology, the capture costs for pressure swing adsorption technology are dominated by the costs for the flue gas and post-capture compressors (Chapter 6). Use of vacuum swing adsorption significantly reduces the costs. Further costs reductions are achievable by using new adsorbents with higher adsorption capacity for CO₂, and higher CO₂ selectivity.

For membrane and adsorption systems, developing water and impurity tolerant membranes/adsorbents to eliminate the need for a feed gas drying will be of enormous value. Additionally, developing solvents, membranes or adsorbents that can tolerate high temperatures, will eliminate the need for pre-treatment cooling. Furthermore, capture costs can be reduced significantly by developing low cost, high efficiency compressors that can tolerate low levels of moisture to eliminate the need for pre-compression drying.

As discussed in Chapter 7, low temperature separation using “anti-sublimation” is an emerging alternative CO₂ capture option for low partial pressure CO₂ waste gas streams. Future R&D efforts for low temperature separation should focus on developing low cost equipment and integrating capture with processes such as gasifying LNG plants to utilise the waste heat from the gasification process.

Applying the cost reductions due to technology and process improvements, the capture cost from low partial pressure CO₂ streams such as in the flue gas of pulverised coal and NGCC power plants reduces to less than A\$30/tonne CO₂ avoided. If CCS could be

deployed at 80% of Australia's stationary emission sources at this cost, the total capital cost for CCS deployment would be approximately A\$60 billion, of which capture contributes A\$35 billion. This corresponds to an annual capital investment cost of A\$5 billion (over an assumed plant life of 25 years and a discount rate of 7% per annum) and an annual operating cost of approximately A\$3 billion. Although this cost remains high in absolute terms, comparatively, the cost of not addressing global warming may result in even higher economic costs. For comparison:

- The cost of Hurricane Katrina in 2005 was over US\$135 billion, including US\$45 billion for insured losses (ABRCC, 2006);
- The cost of the 2002-03 Australian drought was A\$13 billion (Adams et al., 2002), with similar costs expected for the current 2006-07 Australian drought and a further A\$8 billion loss in export earnings due to reduced pastures (Allen_Consulting_Group, 2006);
- The Australian Greenhouse Office predicts that the potential agricultural losses due to adverse weather could be in the order of A\$12 billion annually, neglecting impacts of droughts (AGO, 2005);
- Natural disasters cost the Australian insurance industry over A\$1.14 billion annually (AGO, 2005);
- The cost for the 1997 Sydney hailstorm was A\$1.7 billion (AGO, 2005); and
- The cost for Cyclone Larry in 2006 is in excess of A\$350 million (Johnston, 2007).

Thus, if CCS could be deployed to mitigate some of the adverse economic repercussions, an annual CCS cost of A\$8 billion appears comparable to the annual predicted agricultural losses of A\$12 billion

Variations in methodological assumptions have a significant impact on the reported cost of CO₂ avoided. The methodological assumptions used are based on the economic conditions in 2006 in Australia. The results will change if the analysis is undertaken for a different cost year and/or for a different national economy. However, given the tools developed for this study, such reviews and sensitivities can be screened quickly. It has been shown that the economic parameters that significantly affect the capture cost include capital costs, discount rate and the cost of energy for CCS. If the capital is under

or over- estimated by 20%, the estimated capture cost increases or decreases by 10%. Decreasing the discount rate from the nominal value of 7% to 3%, the estimated capture cost decreases by 15%. Likewise, if the discount rate increases to 15%, the capture cost increases by 40%. Variations in energy cost have similar effects. If the upper and lower limits of the three parameters are examined together, the baseline estimate of the capture cost can be affected by as much as 70%. Additionally, the cost of CO₂ avoided is influenced by variabilities and uncertainties in the economic analysis such as:

- whether to retrofit the CO₂ capture facility to an existing industrial plant or to incorporate it as part of a new plant;
- the type of fossil fuel used for the CCS energy; and
- the choice of the reference condition.

The pre-feasibility scoping analysis in this thesis estimates costs on a pre-tax basis. The impact of income tax, energy and resource tax, resource rent royalties, R&D tax concessions and financial subsidies offered for the use of natural resources are neglected (NIEIR, 1996). If an emissions trading scheme is implemented, variables such as emissions caps, the offsets allowable, and the value and number of permits offered will undoubtedly influence the cost of CCS. In any future evaluation of the economic costs of capture and/or storage, these parameters must be included.

The analysis in this thesis considered only simple variations in costs and did not include a probability analysis. It is recommended that a more extensive evaluation of CCS economics using Monte Carlo analyses be considered so that the full effect of uncertainty is incorporated.

The capture costs have been evaluated for CO₂ emission sources from a single process facility and are indicative of the cost of separating and compressing the CO₂ to a “transport ready” state. To fully evaluate the potential of CCS as a greenhouse gas mitigation option, the analysis must also consider the costs of transport and storage. Furthermore, the analysis must evaluate and compare the costs of different potential geological storage sites. Considerations of the technical feasibility and physical

constraints in understanding the optimum source-to-sink combination are also warranted.

Many of the industrial emission sources in Australia are concentrated in regional pockets, and thus there is the opportunity to establish hub networks. Evaluating the economic potential of CCS hubs is suggested for future work. It would also be valuable to assess the individual characteristics of each industrial emission source to provide a more accurate estimate of the CCS price for specific cases.

The four CO₂ capture systems of absorption, adsorption, membrane and low temperature separation have been considered in this thesis. This is because they show the most promise in delivering wide-scale short and medium term CO₂ reduction goals. Novel CO₂ capture applications such as hydrate formation or chemical looping have not been evaluated. However, there may be cases where the application of these novel capture options may be technically and economic advantageous and further investigation of these possibilities is recommended.

Despite these limitations, this research presents an indication of the potential costs of capturing Australian CO₂ emission. It also provides insights into the cost opportunities of emerging technologies such as vacuum adsorption and membrane separation, and demonstrated that CO₂ can be economically captured using improvements in technology.

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APPENDICES

Appendix A “Economic and processing assumptions of literature studies”

Appendix B “Physical absorption model”

Appendix C “Parameters and costs of the different solvents, membranes and adsorbents used in this thesis”

Appendix D “Detailed results of Chapter 8 case studies”

Appendix A

A. ECONOMIC AND PROCESSING ASSUMPTIONS OF LITERATURE STUDIES

Table A-1 Economic and processing assumptions of power plant CCS literature studies (used for comparison in Chapters 4 to 7)

	Absorption				Membrane			PSA	Low temperature		
Study	Dave	Rubin	Parsons	Gibbins (2004)	Gibbins (2004)	Roberts (2004)	Hendriks (1994)	Feron (1992)	Moneco (1992)	Brockmeir (1994)	Hendriks (1994)
Power plant cycle										Unknown	
Thermal efficiency LHV (%)	37	41	45	44	44	44	40	40	40		40
Net output before capture (MWe)	500	524	506	831	831	831	600	500	500		600
CO₂ Capture										Unknown	
Material	MEA	MEA	MEA	MEA	MEA	FG Plus	Ube polyimide membrane	PPO membrane	Molecular seive		
CO ₂ capture efficiency (%)	90	90	90	90	90	90	90	80	95		90
CO ₂ compression (bar)	80	139	84	100	100	100	80	1	100		80
Economics										Unknown	
Project life (years)	25	30	20	25	25	25	25	20	35		25
Discount rate (%)	9	10	Unknown	10	10	10	5	10	10		5
Currency	Aus	US	US	US	US	US	US	US	US	US	US
Cost year	2000	2002	2000	2000	2000	2003	1990	1992	1992		1990
Plant operating capacity (%)	90	75	65	85	85	85	68	85	85		68
External power cost (\$/MWh)	15								-		
Reference COE (\$/MWh)	-	46	44	43	44	43	37	53	53.4		37

Table A-2 Economic and processing assumptions of industrial plants with CCS literature studies (used for comparison in Chapter 8)

Industrial source	Hydrogen	Hydrogen	Iron & Steel	Iron & Steel	Petrochemicals	Cement
Study	NRC	Farla (1995)	Farla (1995)	Gielen (2003)	Slater (2002)	Farla (1995) Hassan (2005)
CO ₂ Capture	Unknown	Unknown				
Material			MDEA/MEA solvent	Membrane reactor	MEA solvent	MEA solvent
CO ₂ capture efficiency (%)			90	90	90	90
CO ₂ compression (bar)		110	110	Unknown	100	1
Economics						
Project life (years)		25	25	25	25	20
Discount rate (%)		5	5	12	10	7
Currency		US	US	US	US	US
Cost year		1990	1990	2001	1999	2005
Plant operating capacity (%)		Unknown	Unknown	Unknown	90	90
External power cost (\$/MWh)		50	50	15	50	60

Appendix B

B. PHYSICAL ABSORPTION MODEL (SELEXOL)

B.1 Process configuration

Physical solvents are selected for CO₂ recovery in systems where the partial pressure of CO₂ in the flue gas is greater than 3.45atm (345kPa). The main physical solvent of interest is Selexol.

The exact process diagram for physical absorption systems depends on the type of solvent used. Figure B-1 shows a very simplified version of a physical absorption system. Like the chemical absorption system, feed gas enters the absorber where the CO₂ and/or H₂S are selectively absorbed into the lean solvent. Using pressure reduction in a flash unit or temperature flash regenerates the rich loading solvent. The physical absorption process that utilises the solvent Rectisol operates under 0°C and requires refrigeration.

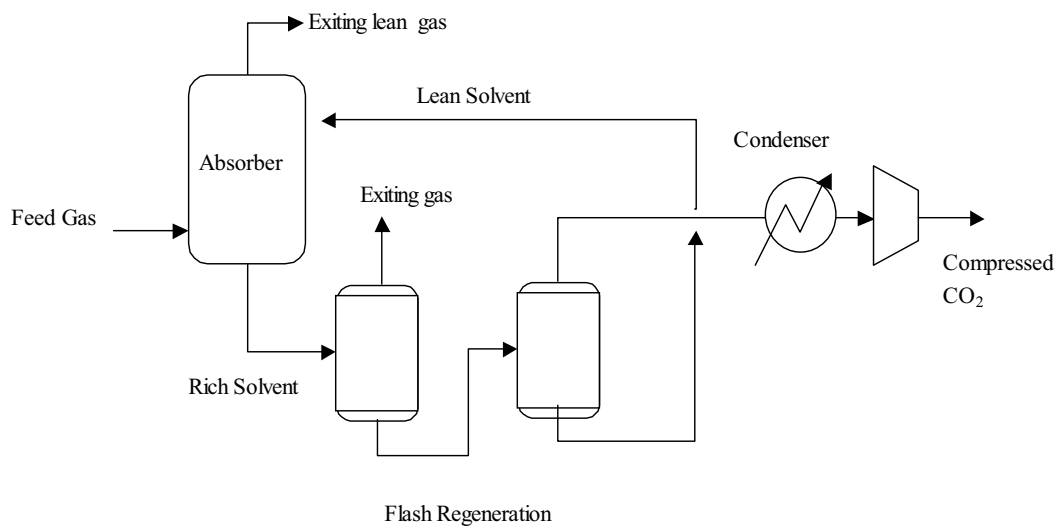


Figure B-1 Simplified flow diagram of a physical absorption system

B.2 Processing equations

The solvent flowrate L (m³/hr) is estimated as:

$$L = \frac{n(\text{CO}_2)}{\text{CO}_{2\text{solubility}} * \text{Conversion}} \quad (\text{B.3})$$

where:

$n(\text{CO}_2)$ = amount of CO_2 to be removed (kmol/hr)

CO_2 solubility = solubility of CO_2 in solvent (kmol/m³)

Conversion = rate of CO_2 absorption into solvent (fraction)

The diameter and height of the absorber can be calculated as the same for chemical absorption systems.

For high-pressure absorption systems, the CO_2 is regenerated using flash units rather than a stripper. The total power loss for regeneration can be estimated as [13]:

$$W_{\text{regeneration}} = L \times \frac{(P_{\text{abs}} - P_{\text{flash}} + P_{\text{loss}})}{\eta_{\text{pump_eff}}} \quad (\text{B.4})$$

where:

$W_{\text{regeneration}}$ = work for pumping solvent to flash units (MW)

L = solvent flowrate (m³/s)

P_{abs} = pressure of the absorber (Pa)

P_{flash} = pressure the CO_2 is flashed to (Pa)

P_{loss} = any losses along the absorber (Pa)

$\eta_{\text{pump_eff}}$ = pump efficiency (fraction)

Appendix C

C. PARAMETERS AND COSTS OF THE DIFFERENT SOLVENTS, MEMBRANES AND ADSORBENTS USED IN THIS THESIS

Table C-1 Solvent properties and cost

	MEA	KS1	Econami ne FG Plus	MDEA	Ideal	Selexol
A\$/kg	1.5	3.0	1.5	3.0	5.0	3.5
US\$/kg	1.5	3.0	1.5	3.0	5.0	5.0
Solvent concentration (%)	30	--	--	50	35	
Rich solvent loading (mol CO ₂ /mol solvent)	0.45	> MEA	> MEA	0.5	0.75	
Lean solvent loading at reboiler temp. 125°C (mol CO ₂ /mol solvent)	0.23	--	--	0.15	0.23	
Latent heat of vaporisation (kJ/kg)	826	--	--	550	<826	
Heat of reaction (kJ/mole of CO ₂)	85	< MEA	--	53.2	<85	
Reaction rate constant (mol/L.s)	7600	--	> MEA	9.2	~7600	
Solvent degradation rate (kg/tonne CO ₂)	1.6	0.35	1.6	1.6	0.5	
CO ₂ conversion rate (%)						65
CO ₂ solubility (Ncm ² /g.bar at 25oC)						0.82

Table C-2 Membrane properties and cost

Manufacturer/ Brand name/ Researcher	UBE PI_A	UBE PI_B	GKSS	Delair	Bondar et al (2000)	Diniz Da Costa et al (2002)	Yampol skii et al (2006)	
Material	Poly- imide	Poly- imide	Poly- dimethy l- siloxane (PDS)	Poly- phenyle n-oxide (PPO)	Copoly mer PEO	Sol gel membra ne		Ideal
A\$/kg	65	65	65	65	65	65	65	65
US\$/kg	50	50	50	50	50	50	50	50
CO ₂ Permeability (Barrer)	20	20	430	72	120	5.5	210	500
Selectivity								
CO ₂ /N ₂	17	43	11.4	19	52		42	40
CO ₂ /O ₂	3.4	3.7	5.2	4	10		9.5	8
CO ₂ /CH ₄	25.5	27.5		12			14	
CO ₂ /H ₂	1/10.8	1/ 4.5	1/5		9.8	1/26	2.67	
CO ₂ /CO	8.5	12.3	7.7	5.2	1.47		10	40

Table C-3 Adsorbent properties and cost

Material	Zeolite 13X	Zeolite 5A	Zeolite NaY	Ideal
A\$/kg	5	5	5	5
US\$/kg	5	5	5	5
Bulk bed density (kg/m ³)	750	795	700	750
Bed porosity (fraction)	0.348	0.36	0.364	0.35
Parameters for Langmuir isotherm				
q _m (CO ₂) = A/B (mol/kg)	4.65	4.31	6.19	10
A(CO ₂) (mol/kg)	40.78	2.35	13.78	100
B(CO ₂) (1/bar)	8.76	0.54	2.23	10
q _m (N ₂) = A/B (mol/kg)	0.95			0.95
A(N ₂) (mol/kg)	0.76			0.76
B(N ₂) (1/bar)	0.8			0.8
q _m (CH ₄) = A/B (mol/kg)	1.5	2.75	2.16	
A(CH ₄) (mol/kg)	1.5	0.70	0.35	
B(CH ₄) (1/bar)	1	0.25	0.16	
q _m (H ₂) = A/B (mol/kg)		0.54		
A(H ₂) (mol/kg)		0.02		
B(H ₂) (1/bar)		0.04		

Note:

Henry's constant = A

Langmuir constant = B

Absorbent capacity = q_m

Appendix D

D. DETAILED RESULTS OF CHAPTER 8 CASE STUDIES

Table D-1 Capture cost for existing subcritical pulverised coal power plants using different CO₂ capture technologies

	Absorption		Gas separation membranes			Adsorption		Cryogenic
	2006	2006	2006	2006	2006	2006	2006	
Cost year	2006	2006	2006	2006	2006	2006	2006	2006
Status of technology	Baseline commercial	State-of-the-art commercial	Improved technology	Emerging	Emerging	Emerging	Emerging	Emerging
Process description	Multiple trains with no heat integration	Stripper designed with 50% heat utilisation	Stripper designed with 50% heat utilisation	Vacuum permeate membrane (TCSM-RR)	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	VSA	Refrigeration at ambient pressure
Separation material	MEA solvent	KS1 solvent	Ideal solvent	GKSS membrane	Research TIPS membrane	Zeolite 13X	Ideal sorbent	CO ₂ anti-sublimation
CO ₂ recovery (%)	90	90	90	90	90	82	88	90
CO ₂ % in recovered stream	> 95	> 95	> 95	75	95	77	88	> 95
Brown PC subcritical								
Energy penalty (%)	45	27	20	48	36	28	28	24
Capital cost A\$/kW	1530	1000	875	1135	1065	925	930	860
ΔCOE (A\$/MW/h)	59	36	30	48	41	31	31	21
A\$/t CO ₂ avoided	66	37	33	56	46	38	34	28
US\$/t CO ₂ avoided	62	33	29	54	42	35	31	23

Continued Table D-1

	Absorption			Gas separation membranes				Adsorption			Cryogenic
	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006	
Cost year	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006
Status of technology	Baseline commercial	State-of-the-art commercial	Improved technology	Emerging	Emerging	Emerging	Emerging	Emerging	Emerging	Emerging	Emerging
Process description	Multiple trains with no heat integration	Stripper designed with 50% heat utilisation	Stripper designed with 50% heat utilisation	Vacuum permeate membrane (TCSM-RR)	Vacuum permeate membrane (TCSM-RR)	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	VSA	Refrigeration at ambient pressure		
Separation material	MEA solvent	KS1 solvent	Ideal solvent	GKSS membrane	Research TIPS membrane	Ideal membrane	Zeolite 13X	Ideal sorbent	CO ₂ anti-sublimation		
Black PC – subcritical											
Energy penalty (%)	36	20	17	42	30	30	24	24	22		
Capital cost A\$/kW	1100	750	680	930	800	640	700	680	700		
ΔCOE (A\$/MWh)	42	27	24	36	32	25	24	23	24		
A\$/t CO ₂ avoided	56	34	31	52	44	35	36	32	28		
US\$/t CO ₂ avoided	52	31	28	49	39	32	33	29	20		
Black PC – supercritical											
Energy penalty (%)	34	20	16	41	28	29	22	22	19		
Capital cost A\$/kW	1000	750	640	840	775	640	660	660	680		
ΔCOE (A\$/MWh)	40	25	22	34	31	25	26	23	21		
A\$/t CO ₂ avoided	54	34	30	50	42	34	35	31	28		
US\$/t CO ₂ avoided	49	31	27	48	37	31	32	28	24		

Table D-2 Capture cost for NGCC power plants using different CO₂ capture technologies

Cost year	IEA GHG (2004)	Absorption			Gas separation membranes			Adsorption		Low temperature
		2006	Baseline commercial	2006	State-of-the-art	2006	Improved technology	2006	Emerging	
Status of technology	Baseline commercial	Baseline commercial	Baseline commercial	2006	State-of-the-art	2006	Improved technology	2006	Emerging	2006
Process description	Multiple trains with no heat integration	Multiple trains with no heat integration	Multiple trains with no heat integration	2006	Stripper design with 50% heat integration	2006	Stripper design with 50% heat integration	2006	Vacuum permeate membrane (TCSM-RR)	Refrigeration at ambient pressure
Separation material	MEA solvent	MEA solvent	MEA solvent	2006	KS1 solvent	2006	KS1 solvent	2006	Vacuum permeate membrane (TCSM-RR)	CO ₂ sublimation
Current NGCC										
CO ₂ recovery (%)	85	90	90	2006	90	2006	90	2006	90	90
CO ₂ % in recovered stream	> 95	> 95	> 95	2006	> 95	2006	> 95	2006	46	> 95
Energy penalty (%)	16	17.5	17.5	2006	9	2006	8	2006	34	28
Capital cost A\$/kW	--	568	568	2006	350	2006	296	2006	640	430
ΔCOE (A\$/MWh)	--	19	19	2006	11	2006	10	2006	36	24
A\$/t CO ₂ avoided*	--	57	57	2006	33	2006	31	2006	110	73
US\$/t CO ₂ avoided	41	45	45	2006	26	2006	24	2006	85	55
Advanced NGCC										
CO ₂ recovery (%)	85	90	90	2006	90	2006	90	2006	90	90
CO ₂ % in recovered stream	> 95	> 95	> 95	2006	> 95	2006	> 95	2006	86	> 95
Energy penalty (%)	15	16	16	2006	10	2006	8	2006	16	14
Capital cost A\$/kW	--	345	345	2006	255	2006	220	2006	211	240
ΔCOE (A\$/MWh)	--	13.5	13.5	2006	9	2006	7.5	2006	12.5	11.5
A\$/t CO ₂ avoided	--	41	41	2006	27	2006	23	2006	38	35
US\$/t CO ₂ avoided	30	32	32	2006	21	2006	18	2006	30	26

Table D-3 CO₂ capture cost: new IGCC and new IDGCC power plants.

	Rubin (2004)	IEA (2003a)	Absorption	Membrane	Membrane	Adsorption	Low temperature
Cost year	2004	2002	2006	2006	2006	2006	2006
Status of technology	Commercial	Commercial	Commercial	Commercial	Emerging (New)	Commercial	Commercial
Process description			Multiple trains with no heat integration	High pressure feed (SMS)	High pressure feed (SMS)	High pressure swing adsorption	Liquefaction
Separation material	Selexol solvent	Selexol solvent	Selexol solvent	Commercial UBE PI-A membrane	Sol-gel membrane	Zeolite 5A	Liquefaction
IGCC							
CO ₂ recovery (%)	90	85	90	90	90	90	90
CO ₂ % in recovered stream	>95	>95	> 95	65	83	81	> 95
Energy penalty (%)	14	12	11	17	20	21	25
Capital cost A\$/kW	--	--	970	1022	1057	1154	1396
ΔCOE (A\$/MWh)			19.5	21	21	23	33
A\$/tonne CO ₂ avoided	--	--	26	28	28	31	44
US\$/tonne CO ₂ avoided	20	16	20	23	23	27	37
IDGCC							
Separation material	Selexol solvent	Selexol solvent	Selexol solvent	Commercial UBE PI-A membrane	Research PEO membrane	Zeolite 5A	Liquefaction
CO ₂ recovery (%)	--	--	90	90	90	90	90
CO ₂ % in recovered stream	--	--	> 95	28	80	65	> 95
Energy penalty (%)	--	--	8	18	18	28	22
Capital cost A\$/kW	--	--	1611	2150	1800	2212	2042
ΔCOE (A\$/MWh)			23	32	25	34	34
A\$/tonne CO ₂ avoided	--	--	40	54	42	59	59
US\$/tonne CO ₂ avoided	--	--	31	44	35	51	49

Table D-4 Capture cost for hydrogen production

	NRC (2004)	Farla (1995)	Absorption	Membrane	Membrane	Membrane	Membrane	Adsorption	Low temperature
Status	Unknown	Commercial	Current	Current	New	New	New	Current	Current
Cost year	2000	1990	Commercial 2006	Commercial 2006	Emerging 2006	Emerging 2006	Emerging 2006	Commercial 2006	Commercial 2006
Process description	Unknown	Compression only	Multiple trains with no heat integration	High pressure feed (SMS)	High pressure feed (SMS)	High pressure feed (SMS)	High pressure feed (SMS)	High pressure swing adsorption	Liquefaction
Separation material	Unknown	--	Selexol solvent	Commercial UBE PI-A membrane	Research co-polymer PEO membrane [34]	Research Sol-gel membrane [14]	Research Sol-gel membrane [14]	Zeolite 5A	Liquefaction
CO ₂ recovery (%)	92	--	90	90	90	90	90	96	90
CO ₂ captured (MtCO ₂ /yr)	6.385	0.7	1.5	1.5	1.5	1.5	1.5	1.6	1.5
CO ₂ % in recovered stream	>95	--	> 95	60	85	81	81	57	>95
% H ₂ enriched stream	>90	--	>90	90	91	93	93	95	>95
Capital cost for capture facility (\$/tonne CO ₂ captured)	--- US\$4.10	--	A\$70 US\$51	A\$51 US\$39	A\$45 US\$34	A\$43 US\$33	A\$43 US\$33	A\$66 US\$52	A\$69 US\$51
CCS energy penalty (KJ/kg CO ₂ captured)	785	322	681	510	1000	640	640	795	1090
A\$/t CO ₂ avoided *	--	--	19	14	18	14	14	20	30
US\$/t CO ₂ avoided	4.4	8	16	12	16	12	12	17	26

Table D-5 CO₂ capture cost for natural gas processing for low, medium and high CO₂ concentration feed gases

CO ₂ concentration in feed gas (%)	Absorption			Membrane			Adsorption			Low temperature		
	5	10	15	5	10	15	5	10	15	5	10	15
Cost year	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006	2006
Process description	Chemical absorption in multiple absorption trains with no heat integration			High pressure feed membrane systems (TCMS-RR)			High pressure swing adsorption with cascade			Liquefaction		
Separation material	MEA solvent	MDEA solvent		Commercial membrane	UBE	PI-BH	Commercial zeolite NaY			Liquefaction		
CO ₂ recovery (%)	90	90	90	90	90	90	80	80	80	90	90	90
CO ₂ captured (MtCO ₂ /yr)	0.5	1.01	1.51	0.5	1.01	1.51	0.45	0.9	1.33	0.5	1.01	1.51
CO ₂ % in recovered stream	>95	>95	>95	64	88	92	40	72	89	>95	>95	>95
Fraction of methane recovered	0.99	0.99	0.99	0.97	0.99	0.99	0.55	0.50	0.45	0.99	0.99	0.99
Methane loss (\$/Million/year)	A\$6 US\$5	A\$6 US\$5	A\$6 US\$5	A\$21 US\$18	A\$10 US\$8	A\$9 US\$8	A\$47 US\$40	A\$34 US\$29	A\$18.5 US\$16	A\$6 US\$5	A\$6 US\$5	A\$6 US\$5
Separation cost (A\$/MMSCF)	A\$0.11	A\$0.16	A\$0.19	\$0.25	\$0.20	A\$0.23	A\$0.38	A\$0.36	A\$0.33	A\$0.15	A\$0.18	A\$0.27
Capital cost for capture facility (\$/tonne CO ₂ captured)	A\$102 A\$81	A\$105 US\$85	A\$85 US\$68	A\$140 US\$114	A\$81 US\$64	A\$66 US\$50	A\$115 US\$98	A\$100 US\$65	A\$70 US\$56	A\$100 US\$70	A\$90 US\$65	A\$79 US\$60
CCS energy penalty (KJe/kg CO ₂ captured)	1330	740	738	66	42	37	140	95	80	60	52	42
A\$/t CO ₂ avoided *	49	32	26	107	41	30	270	105	61	63	47	38
US\$/t CO ₂ avoided	43	27	23	92	35	26	240	95	55	53	40	32

Table D-6 Capture cost for CO₂ recovery from the flue gases of an oil refinery

	Slater (2002)	IEA GHG (2002)	Farla (1995)	Absorption	Membrane	Adsorption	Low tempera-ture
Status				Commercial	Emerging	Emerging	Emerging
Cost year	2001	1999	1990	2006	2006	2006	2006
Process description				Multiple trains with no heat integration	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	Refrigeration at ambient pressure
Separation material	MEA	MEA	MEA	MEA	GKSS membrane	Zeolite 13X	Anti-sublimation
CO ₂ recovery (%)	90	90	90	90	90	85	90
CO ₂ % in recovered stream	>95	>95	>95	>95	51	42	>95
CO ₂ captured (MtCO ₂ /yr)	1.26	1	1.8	0.8	0.8	0.75	0.8
Capital cost for capture facility (\$/tonne CO ₂ captured)	US\$115	US\$145	US\$140	A\$130 US\$100	A\$140 US\$106	A\$120 US\$100	A\$85 US\$63
CCS energy penalty (KJt/kg CO ₂ captured)	--	2340	1420	1690	2750	2385	1510
A\$/t CO ₂ avoided*	--	--	--	49	79	60	39
US\$/t CO ₂ avoided	40-45	27	46	43	70	55	32

Table D-7 Evaluation of CO₂ capture cost from conventional blast furnace iron production

	Farla et al (1995)	Absorption	Absorption	Membrane	Membrane	Adsorption	Adsorption	Low temperature
		Current	New	Current	New	Current	New	New
Cost year	1990	2006	2006	2006	2006	2006	2006	2006
Status		Commercial	Improved technology	Commercial	Emerging	Commercial	Emerging	Emerging
Process description		Multiple trains with no heat integration	Stripper design with 50% heat integration	Vacuum permeate membrane (TCSM-RR)	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	VSA	Refrigeration at ambient pressure
Separation material	MDEA/MEA solvent	MEA solvent	Ideal solvent	GKSS membrane	Ideal membrane	Zeolite 13X	New sorbent	CO ₂ sublimation
CO ₂ recovery (%)	90	90	90	93	93	90	93	90
CO ₂ % in recovered stream	>95	> 95	> 95	66	83	78	93	>95
CO ₂ captured (MtCO ₂ /yr)	2.8	2.75	2.75	2.84	2.83	2.71	2.82	2.75
CCS energy penalty (KJc/kg captured CO ₂)	--	1610	780	1660	1350	1115	1016	650
Capital cost (\$/tonne captured CO ₂)	US\$133	A\$100 US\$75	A\$71 US\$52	A\$65 US\$50	A\$71 US\$56	A\$77 US\$65	A\$70 US\$60	A\$52 US\$38
A\$/tonne CO ₂ avoided	--	38	20	34	33	29	26	17
US\$/tonne CO ₂ avoided	35	33	17	31	29	26	24	15

Table D-8 Evaluation of CO₂ capture cost from the converted synthesis gas of a blast furnace

	Gielen (2003)	Absorption	Membrane	PSA	Low temperature
Cost year	2001	2006	2006	2006	2006
Process description	Multiple trains with no heat integration	Multiple trains with no heat integration	High pressure feed (TCMS-RR)	High pressure swing adsorption	Liquefaction
Separation material	Selexol	Selexol	Commercial UBE PI-A membrane \$50/m ²	Zeolite 5A \$5.0/kg	Liquefaction
CO ₂ recovery (%)	90	90	90	90	90
CO ₂ % in recovered stream	> 95	> 95	57	84	> 95
CO ₂ captured (MtCO ₂ /yr)	4	5.65	6.18	5.4	5.65
CCS energy penalty (KJc/kg captured CO ₂)	620	935	1180	1325	2110
Capital cost (\$/tonne captured CO ₂)	--	A\$210 US\$150	A\$195 US\$145	A\$200 US\$150	A\$240 US\$175
A\$/tonne CO ₂ avoided	--	46	48	50	84
US\$/tonne CO ₂ avoided	18 - 19	36	39	41	69

Table D-9CO₂ capture cost of Corex iron production flue gas

Cost year	Gielen (2003) 2001	Absorption 2006	Absorption 2006	Membrane 2006	Adsorption 2006	Low temperature 2006
Process description	Multiple trains with no heat integration	Multiple trains with no heat integration, includes feed gas compressor to 20 bar	Multiple trains with no heat integration	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	Refrigeration at ambient pressure
Separation material	Selexol	Selexol	MEA	Commercial PI-A membrane \$50/m ²	Zeolite 5A	CO ₂ sublimation
CO ₂ recovery (%)	90	90	90	90	95	90
CO ₂ % in recovered stream	>99	>99	>99	42	91	>99
CCS energy penalty (kJe/kg captured CO ₂)	590	882	1433	1037	997	412
Capital cost (\$/tonne captured CO ₂ /year)	--	A\$104 US\$75	A\$88 US\$67	A\$134 US\$105	A\$81 US\$70	A\$41 US\$30
A\$/tonne CO ₂ avoided	---	27	33	42	27	13
US\$/tonne CO ₂ avoided	18.4	22	29	35	24	11

Table D-10 Evaluation of CO₂ capture cost from cement production flue gases

Cost year	Hassan (2005) 2005	Absorption 2006	Membrane 2006	Adsorption 2006	Low temperature 2006
Process description	Multiple trains with no heat integration	Multiple trains with no heat integration	Vacuum permeate membrane (TCSM-RR)	Vacuum Swing Adsorption (VSA)	Refrigeration at ambient pressure
Separation material	MEA	MEA	GKSS membrane	Zeolite 13X	Anti-sublimation
CO ₂ recovery (%)	90	90	90	85	90
CO ₂ % in recovered stream	>95	>95	81	67	>95
CO ₂ captured (MtCO ₂ /yr)	0.66	0.65	0.67	0.65	0.65
Capital cost for capture facility (\$/tonne CO ₂ captured)	-- US\$52	A\$102 US\$78	A\$74 US\$57	A\$90 US\$3	A\$67 US\$50
CCS energy penalty (KJc/kg captured CO ₂)	--	1601	1430	1380	665
Capture Cost					
A\$/t CO ₂ avoided	--	46	32	34	20
US\$/t CO ₂ avoided	49/tonne captured	41	29	31	17