REVIEW ARTICLE

Assessment of postcombustion carbon capture technologies for power generation

Mikel C. DUKE[1], Bradley LADEWIG[2], Simon SMART[3], Victor RUDOLPH[3], João C. Diniz da COSTA (✉)[3]

1 Institute for Sustainability and Innovation, Victoria University, Werribee Campus, PO Box 14428, Melbourne, Victoria 8001, Australia
2 Department of Chemical Engineering, Monash University, Clayton Vic 3182, Australia
3 School of Chemical Engineering, The University of Queensland, Brisbane Qld 4072, Australia

Abstract A significant proportion of power generation stems from coal-combustion processes and accordingly represents one of the largest point sources of CO_2 emissions worldwide. Coal power plants are major assets with large infrastructure and engineering units and an operating life span of up to 50 years. Hence, any process design modification to reduce greenhouse gas emissions may require significant investment. One of the best options to utilize existing infrastructure is to retrofit the power station fleet by adding a separation process to the flue gas, a practice known as postcombustion capture (PCC). This review examines the recent PCC development and provides a summary and assessment of the state of play in this area and its potential applicability to the power generation industry. The major players including the various institutes, government, and industry consortia are identified along with flue gas PCC demonstration scale plants. Of the PCC technologies reviewed, amine-based absorption is preeminent, being both the most mature and able to be adapted immediately, to the appropriate scale, for power station flue gas with minimal technical risk. Indeed, current commercial applications serve niches in the merchant CO_2 market, while a substantial number of smaller scale test facilities are reported in the literature with actual CO_2 capture motivated demonstrations now commencing. Hybrid membrane/absorption systems, also known as membrane contactors, offer the potential for the lowest energy requirements, possibly 10% of current direct scrubbers but are at an early stage of development. Other methods being actively pursued as R&D projects include solid absorbents, solid adsorbents, gas membrane separators, and cryogenic separation. The variety and different maturities of these competing technologies make technical comparison largely subjective, but useful insights could be gained through the development and application of econometric techniques such as 'real options' within this context. Despite these limitations, it is clear from this review that amine scrubbing is likely to be adapted first into the existing power station fleet, while less mature technologies will grow and become integrated with the development of future power stations.

Keywords post-carbon capture, amine absorption, adsorption, membranes, technology assessment

1 Introduction

1.1 Major drivers for climate change research

The topic of CO_2 capture is raised by many countries looking toward reducing their emissions after the Kyoto Protocol. Consequently, organizations have been established to advise governments on the significance of this issue and strategies for addressing it. The Intergovernmental Panel on Climate Change (IPCC) was set up in 1988 by the World Meteorological Organization and the United Nations Environment Programme to scientifically assess the risk of human induced climate change, its impacts and viable options for adaptation and mitigation. The International Energy Agency (IEA) greenhouse gas (GHG) R&D programme (www.ieagreen.org.uk) was later established in 1991 to undertake technical and economic evaluations of options to mitigate GHG emissions. Various countries interests are combined with corporate sponsorship from ALSTOM, BP, Chevron, ENI Technologies, EPRI, ExxonMobil, RWE, Shell, Total Fina Elf, Rio Tinto, BHP Billiton, and Schellemberger, among many other oil and coal resource companies and interests around the world.

The Carbon Sequestration Leadership Forum (CSLF),

established by the US State Department and US Department of Energy (DoE), is an international climate change initiative focussing on the development of technologies for capture and storage of CO_2 (www.cslforum.org). The charter, signed in June 2003, now involves 20 countries and will stay in effect for 10 years to enable cooperation in providing cost effective and secure means to capture and store CO_2. The CSLF does not actually conduct research but has endorsed 10 international projects in this field.

1.2 International collaborations

The effort to reduce GHG emissions spans across the world, with major efforts from the European Commission, United States, Canada, Norway, Australia, and Japan.

1.2.1 European Commission

The European Commission (EC) has announced it will reduce GHG emissions by 30% by 2020 [1]. The organization of such projects appears to be one of the greatest in the world. Major projects for CO_2 capture have included the Alstrom partnered Advanced Zero Emissions Power Plant (AZEP) for advanced membranes and the BP partnered Grangemouth Advanced CO_2 Capture Project (GRACE) for capture in process. These were funded by both industry and Framework Programme 5 (FP5) at €9.3M and €3.2M, respectively [2].

CO_2 from Capture to Storage (CASTOR) is a European initiative, consisting of 30 partners from industry, research institutes, and universit ies (www.co2castor.com). The project has been accepted for funding for four years from 2004 by the European Commission within the Sixth European Framework Programme, having a total budget of €16M. The aims of the project are to apply the mature absorption processes, specifically achieving

● absorption liquids with energy consumption at 2.0 GJ/tonne CO_2 at 90% recovery;
● cost of CO_2 avoided to not exceed 30€/tonne; and
● carry out demonstration process.

1.2.2 United States

The United States has not ratified the Kyoto protocol but has proposed an initiative that, in 2015, will cap the GHG emissions at the 2010 baseline. Major US government funding from DoE has been committed to CO_2 sequestration. Primary objectives of the US DoE are to reduce the cost of capturing CO_2, which is recognized as being the most significant cost in the overall capture and storage process. The Office of Fossil Energy is responsible for many initiatives specifically aimed at clean coal technologies with a funding of US $2 billion, mostly aimed at hydrogen production. The key programme under the DoE for CO_2 capture is the Carbon Sequestration Core Program,

which has subdivisions for capture and advanced technologies such as membranes. Since 2000, many projects with collaborations between industry and academia have been initiated. Funding is aimed at expediting the development of emerging technologies such as advanced absorbents, solid adsorbents, and membranes. From 2000 to 2003, US $25M from both government and industry has been allocated to the projects. The US DoE continues to fund projects in this field either via the National Energy Technology Laboratory (NETL), which is interested in the advanced technologies, or other research facilities.

1.2.3 Canada

Canada has proposed to reduce annual greenhouse gas emissions by 6% in 2008–2012, relative to the 1990 level. The Canadian CO_2 Capture and Storage Technology Network (CCSTN) was established under the Canadian Government's Natural Resources Canada, to coordinate activities undertaken by various groups working on R&D and demonstration of national capture and storage initiatives. CANMET is a key research arm of the CCSTN, and the CANMET Energy Technology Centre collaborates with industry, government, and academia to develop and deploy various technologies for the capture of CO_2. Funding sources are generally a combination of the Canadian government and industry. For instance, in 2005, Natural Resources Canada announced CA $15M for two years to Canadian industry as an incentive to develop CO_2 capture and storage systems.

1.2.4 Norway

In 1997, the Norwegian National Technology Programme launched KLIMATEK for five years to promote technology to reduce GHG emissions. For carbon capture, KLIMATEK supports the CO_2 Capture Project to the level of NOK 29 M in Phase 1 (2001 to 2003). Long term research has also been funded to the level of NOK 10M for 3–4 years, which aims at developing more advanced technologies such as membranes and other systems such as novel adsorption/absorption systems.

1.2.5 Australia

The Australian Government, after initial opposition, ratified the Kyoto Protocol in 2008 and has committed funding for the R&D of GHG reducing systems with very strong partnerships with coal industries. Development of CO_2 technologies directly related for postcombustion capture are mostly managed by the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), a collaboration of government, industry, and academia including Geoscience Australia, CSIRO, several Australian universities, Chevron Texaco, Schlumberger, Shell,

BP, BHP Billiton, Xstrata Coal, Stanwell Corporation, Rio Tinto, ACARP, Woodside, and Department of Primary Industries, Victoria. In New Zealand, partners include Institute of Geological and Nuclear Sciences Ltd., Solid Energy Coals of New Zealand, and Genesis Energy. The CO2CRC commenced in July 2003 with a project budget over seven years of A$100M. CSIRO also has post combustion capture technology research programmes via its Energy Flagship.

1.2.6 Japan

Like EC, Japan has also committed to an 8% decrease in GHG emissions. Combined with government support, electric power research organisations such as the Centre Research Institute of Electric Power Industry (CRIEPI) and the Federation of Electric Power Companies of Japan are devoting R&D efforts to CO_2 capture technologies [3]. Such projects were funded mostly by power station interests and therefore focussed on close to market technologies, with options such as physical adsorption and chemical absorption trialled. While most trials have been terminated, Kansai Electric Power Company and Mitsubishi Heavy Industries are successfully conducting tests using patented chemical solvents. The Research Institute of Innovative Technology for the Earth (RITE) is interested in more advanced systems such as membranes and receives funding from industry and government via the Ministry of Economy, Trade, and Industry.

1.3 Global consortiums

1.3.1 The CO_2 capture project

The CO_2 capture project (CCP) is a joint project of eight major companies investing to reduce the cost of CO_2 capture and storage (www.co2captureproject.org). Phase 1 of this US $50M project, started in 2000, branches out to postcombustion capture, oxygen fired combustion, and precombustion decarbonization (i.e., gasification) research to facilitate new and efficient technologies for CO_2 capture and storage [4]. Companies collaborating on this project include BP (United Kingdom), Chevron Texaco (USA), ENI (Italy), Etop Esen (USA), Ricardo Branca (Brazil), Norsk Hydro ASA (Norway), EnCana, Shell (USA), and Statoil and Suncor Energy (Canada). Government organizations such as US DoE, European Commission, and the Research Council of Norway (KLIMATEK) are also involved in the collaboration. The project is now in Phase 2, which started in 2005. Reporting is in the early stages at this time, but latest news presented the intention to demonstrate amine-based systems by 2008–2010 using optimized designs determined in Phase 1. The only postcombustion capture project approved is CLIMIT (US $7M).

1.3.2 Electric power research institute

The Electric Power Research Institute (EPRI) was established in 1973 as a nonprofit center to conduct and sponsor independent research for energy and environment related to most aspects of power generation. EPRI research has been critically important for informing both electric energy company strategic divisions and climate policy-makers. Major locations are in California and North Carolina, USA. Members, scientists, engineers, and other leading experts from around the world represent 90% of the power generators in the USA. International participation represents 15% of EPRI's R&D programme. EPRI broadcasts its research to its members via the EPRI journal. Programme 165 in the 2006 portfolio is CO_2 Capture and Storage, which in the past has secured US $5.5M (2000–2005) with targeted funding in 2006–2008 of US $2M. Major deliverables relating to post combustion capture are studies of capture around the world and the development and pilot scale testing of an 'add-on' capture system.

1.3.3 Global carbon capture and storage institute

The Global Carbon Capture and Storage Institute (GCCSI) was established in 2009 by the Australian government, as an independent entity whose key mandate is to accelerate the deployment of commercial scale CCS solutions around the world. Still in its infancy, the GCCSI has over 80 foundation members including national governments, corporations, NGO's, trade organizations, and research institutes. The GCCSI will be hosted in Australia. The Australian government has pledged annual funding of up to $100 million, and its major contributions will be through accelerating CCS demonstration projects and working with NGOs to support and promote capture, transport, and storage projects in addition to raising community awareness.

2 PCC technology review

2.1 Introduction

Postcombustion capture (PCC) represents one approach to capture carbon from power generation. Other major options include oxygen fired combustion (oxyfuel) and precombustion capture; however, PCC represents the most intuitive retrofit option as the process can simply be added to the existing flue gas stream. This review will focus on the technologies available for this process.

2.2 Postcombustion capture of CO_2 from flue gas

When considering CO_2 capture from power station flue gas, the technologies which can target the removal of CO_2 from mixed streams are

- solvent scrubbing (chemical or physical);
- solid absorbents;
- adsorption;
- membranes; and
- cryogenic.

Cryogenic capture will not be considered as it is considered impractical for CO_2 capture from flue gases containing around 14 vol-% of CO_2. However, it should be noted that the CO2CRC in Curtin University published a project for hydrates and cryogenics [5]. Furthermore, since the CO_2 recovery in cryogenics for PCC requires high pressures [6], it may not be feasible under flue gas conditions. Biological fixation (e.g., algae) is sometimes considered for CO_2 capture, except size estimates for 500 MWe station are in the order of up to 100 km^2 and is considered too complex to manage [7]. Despite the loose ends identified with these alternatives, this report will focus on with the traditional forms being covered in great detail in the literature. It should be noted that industry is also tracking such processes for PCC of power station flue gas, for instance, ALSTOM in the United Kingdom, together with TNO in the Netherlands provided a report discussing options for PCC [8].

2.3 Chemical absorption using liquid solvents

Chemical absorption (scrubbing) is a conventional chemical engineering process based on well-defined mass transfer and thermodynamic theory. Amines have been developed and applied for H_2S and CO_2 removal from gas streams in the chemical and oil industries for over 60 years [9], and the technology is consequently mature. As applied to CO_2 scrubbing, the CO_2 in the gas phase is selectively taken into the amine solution by reversible reaction. Most commonly, mono-ethanolamine (MEA) in an aqueous solution of 15 wt-%–20 wt-% is used as the absorbent. The CO_2-rich liquor is treated in a stripper to release a CO_2 of very high purity and a regenerated amine sorbent ready for recycle. The process operates at approximately 40°C in the scrubbing tower and approximately 120°C in the regeneration column. Fig. 1 shows a process flow schematic of a MEA PCC operation. The status and relevance of amine scrubbing to PCC is summarized in Table 1. It can be clearly seen that amine scrubbing has a high potential for

PCC application in terms of scale and familiarity but has issues in terms of energy demand and solvent stability.
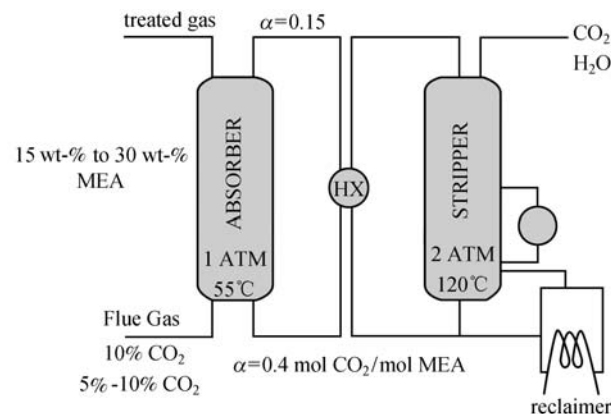

Fig. 1 Process flow diagram of a typical MEA CO_2 capture process [10]

Physical solvents are alternatives to amines and are mature in their use in industry. These are cold methanol (Rectisol process), dimethylether of polyethylene glycol (Selexol process), propylene carbonate (Fluor solvent process), and sulpholane for CO_2 absorption. Due to the low partial pressure of CO_2 in flue gas, they are not economically viable as they have low CO_2 absorption capacity and thus will require high operating pressures. Despite this, aqueous ammonia is being pursued to scrub power station flue gas at demonstration scales.

2.4 Chemical absorption using solid absorbents

Solid absorbents work in a similar way to amine scrubbing in that CO_2 is selectively taken out of the gas stream into another phase. The sorbent is then separated and regenerated, releasing relatively pure CO_2 and refreshed sorbent that can be reused. The main differentiating feature from amine scrubbing is that the sorbent is a solid instead of a liquid. Figure. 2 shows the PCC process flow diagram using solid absorbents, and the relevance to PCC is summarized in Table 2. A significant advantage lies in the high tolerance of many solid sorbents to sulphur and other contaminants in the flue gas. This process typically uses

Table 1 Summary of amine-based solvent chemical absorption for PCC

|	
technology status	Mature and widely used in petrochemical processing.
scalability	No technical hurdles to scale up. The largest, currently operating, scrubber in Trona California captures 800 t/day of CO_2 [11], cf ~6900 t/day, which would be required for a 350 MWe power station unit.
technology gaps	Solvents have been developed mainly for low temperature (< 100°C) and nonoxidizing petrochemical processes. Tailored solvents for PCC flue gas which are tolerant of SO_2, NO_x, and particulates are required.
solvent losses	Amine-based solvents suffer degradation caused by high temperature (> 120°C) in oxidizing environments and contaminants (SO_x and NO_x) generally need to be reduced to < 10ppmv to minimize loss.
energy penalties	Conventional MEA solvent: 4.2 MJ/kg-CO_2 [12]. New solvents eg KS-1: 3.3 MJ/kg-CO_2 [13].
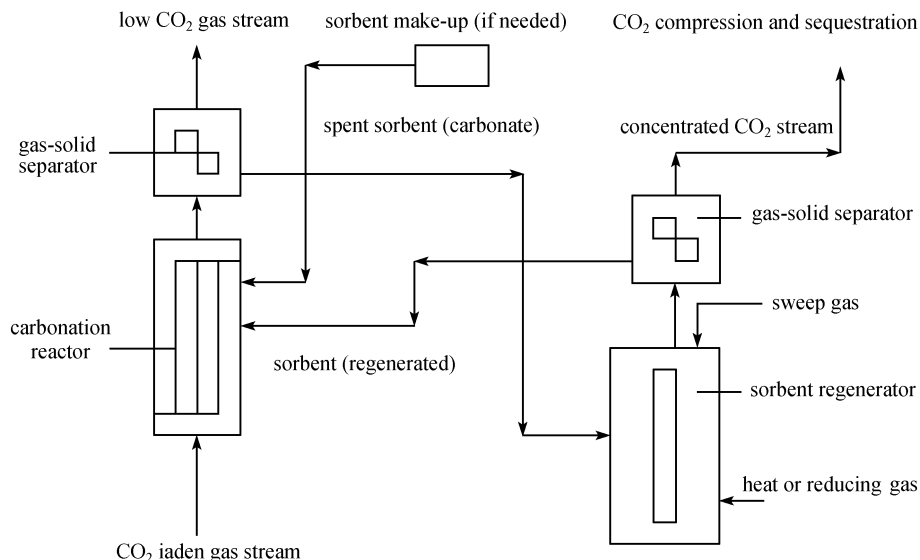
Fig. 2   Conceptual flow diagram of CO_2 PCC process [14]

Table 2   Summary of solid sorbent chemical absorption for PCC

technology status	Mature process in technological terms, but no pilot trials yet.
scalability	Relatively easy scale up but may require a large plant foot print.
technology gaps	Pilot trials at demonstration scale not available. New solid absorbents with high regeneration capacity (>1000 cycles) are needed. Similarly, an increased amount of CO_2 absorbed through the carbonation reactions is required.
common absorbents	CaO, Li_2ZrO_3, K_2O, and Na_2CO_3 [15].
absorbent regeneration	Not very effective at the moment, and make up (i.e., fresh absorbents) are required, making the process expensive.
carbonation reactions	The carbonation reactions are relatively slow and kinetic considerations dictate that the process be conducted at relatively high temperatures, typically 450°C–700°C, which is energy intensive.
in situ carbonation	In view of high temperatures, PCC can occur within the boiler. However, this may require boiler redesign and retrofitting.

well-known carbonation reactions through which the absorbent consumes CO_2 from a gas stream at around 450°C–700°C at near atmospheric pressure. The spent sorbent is then removed and may be regenerated by high-temperature calcination (>900°C) to release relatively pure CO_2 and regenerated sorbent. Spent sorbent may be sold as a mineral carbonate product.

2.5   Adsorption

The main mechanism of separation within adsorption is the capture of a specific compound, like CO_2, within the porous structure of an adsorbent. CO_2 has an important feature compared with other gases in that it has a high adsorption capacity in many solids which have typically high surface areas, such as zeolites and activated carbon. Since these adsorbents are solid and continuous circulating systems like those used in amine scrubbing are much more difficult, so the process is usually performed in batch mode using either pressure swing adsorption (PSA) or temperature swing adsorption (TSA). Vacuum swing adsorption (VSA) is like PSA but utilizes vacuum

pressures for improving desorption capacity. The process is made up of a set of beds, as shown in Fig. 3, which are switched sequentially in the order 'adsorption', 'blow-down', 'purge', and 'pressurisation'. The amount of CO_2 kept within the adsorbent is dependant on temperature and pressure. In the case of PSA, CO_2 binds to the surface of the adsorbent at high pressure (adsorption). When this bed of solid sorbent is nearly saturated, the incoming flue gas flow is switched to another unit. The near-saturated unit pressure is then dropped, often to below atmospheric
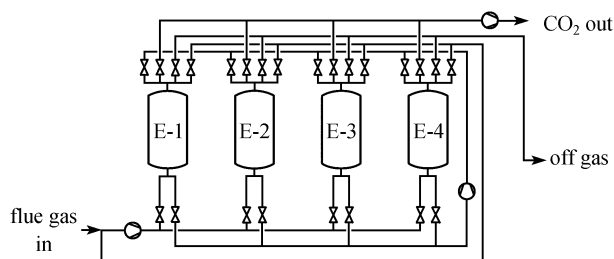

Fig. 3   Schematic of PSA process

pressure, which releases most of the contained CO_2, and the unit is ready again for sorption service. Temperature also strongly influences the capacity of sorbents. In TSA, adsorption is done at relatively low temperature, where the solids adsorb a large mass of CO_2, and regeneration/CO_2 release at a higher temperature. Other swinging conditions may also be used. Commercial systems exist for CO_2 removal from H_2, such as those from Air Products Inc. (USA) which use zeolites. The state of adsorption in PCC applications is summarized in Table 3.

2.6   Membranes

The term membrane refers to a barrier which only allows a chosen species to pass through. The conditions of separation vary greatly depending on the nature of the membrane and the diffusing species. In general though, the membrane is formed by making a thin film of the barrier material, and conditions on either side of the membrane are manipulated so that continuous separation takes place, usually by imposing a pressure difference. This can be done by compressing the feed or applying vacuum to the permeate side. The lack of moving parts, convenient start-up/shut down, and simple process requirements make membranes very promising for future separation applications. Simple versus two-stage configurations were modelled by Ho et al. [19] specifically for PCC of CO_2 from flue gas (Fig. 4). The simple configuration (Fig. 4(A)) requires a single membrane stage, while the two-stage configuration (B) involved two membrane stages, with recompression before the second membrane unit.

An interesting concept in membrane technology is combining the mature amine scrubbing process with membranes in what is know as a membrane contactor. In this process, the amine solution passes over one side of the membrane. The CO_2 diffuses through the membrane and is taken up into the solution, as shown in Fig. 5. The membrane acts as a barrier to undesired species which might otherwise react with the absorbent. Increased removal efficiency of membrane contactors translates to lower energy consumption compared to the standard scrubbing process.

Direct CO_2 separation membranes or membrane contactors represent the major approach to research in membranes for PCC. The status implications for PCC are summarized in Table 4. Membranes were found to be the least mature technology for PCC, as all trials are conducted at laboratory scale with a synthesized, and, hence, impurity free, flue gas.

3   PCC demonstrations

According to the IEA, there are several R&D projects across the world in PCC [23]. Until very recently, all of the working CO_2 capture plants are focussed on natural gas mining, enhanced oil recovery (EOR), or other applications, rather than GHG capture (e.g., Sleipner Field). These industrial scale systems, limited to those which take CO_2 out of flue gas (either coal or natural gas (NG) fired), are summarized in Table 5 and include plants currently shut down, working, or intended future demonstrations. The

Table 3   Summary of adsorption for PCC

| technology status	PSA and TSA are mature and well-established technology for H_2 and O_2 production and for CO_2 removal from natural gas. They have been developed extensively since the early 1950s [16]. VSA is considered the most effective route to CO_2 removal using zeolites [17].
scalability	Easy to scale up by using multiple units in parallel.
technological gap	Adsorbent materials capable of adsorbing CO_2 at high temperatures without adsorption losses are required.
adsorption losses	CO_2 adsorption capacity in zeolites is reduced for gas streams containing water, SO_x, and NO_x.
energy penalties	Require vacuum pumps for VSA resulting in high power consumption in excess of 2.52 MJ/kg-CO_2 [18].
major adsorbents	Zeolites, activated carbon, magnesium oxides, and Layered Double Hydroxides (LDHs).
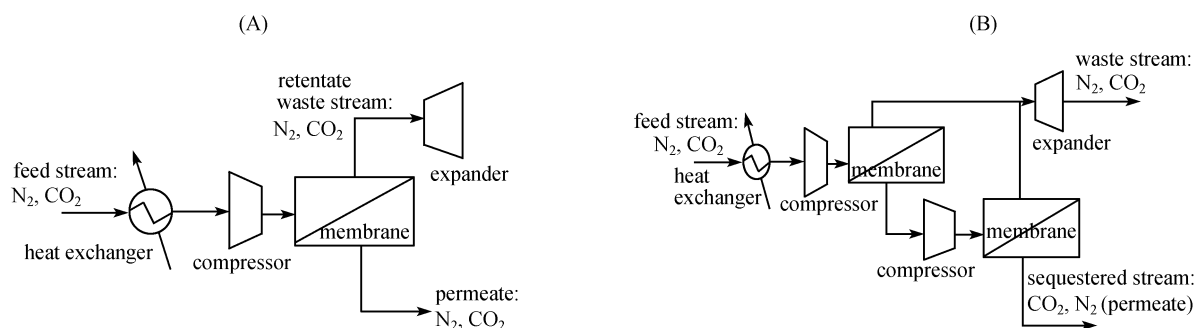
Fig. 4   Process configurations for modelling. Simple (A) and two stage (B) [19]
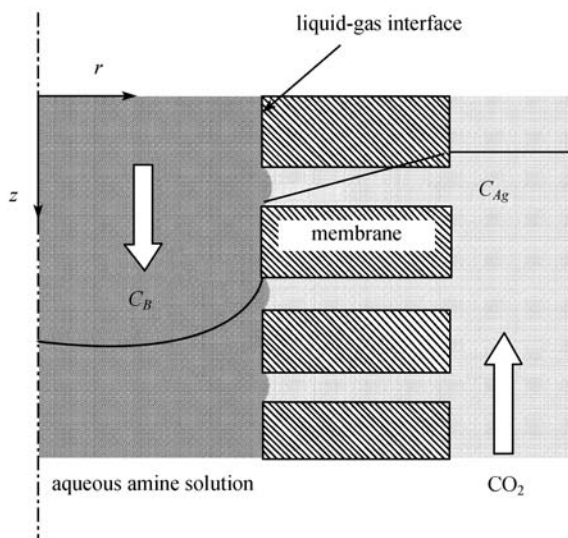
Fig. 5   Membrane contactor separation in nonwetted mode [20]

plants therefore demonstrate PCC technology for GHG capture purposes. Most of the power station plants generate food grade CO_2. The largest constructed CO_2 scrubber could handle 1200 t/day CO_2, being significantly less than the 6900 t/day CO_2 generated from a standard coal-fired 350 MWe power station unit. Two operating PCC demonstrations were found in this search, which is in Australia at the Loy Yang power station in Victoria, Australia, and HuaNeng Beijing Cogeneration Powerplant, China. Both use amine-based absorbers [24]. An aqueous ammonia plan is currently being commissioned at Lake Munmorah power station in NSW, Australia.

EOR = enhanced oil recovery

From this table, it is clear that the systems already built utilize amine scrubbers based on technology provided by Fluor, MHI, or ABB Lummus. The demonstrations planned for GHG capture provide an indication of which technologies are being actively advanced for PCC as potential competitors to chemical scrubbing and include membrane contactors, cold ammonia, and adsorption systems. EPRI has plans to develop a transportable 1 MWe unit based on solvents, which over the longer

term, will be based on membranes or adsorption technology [28]. Also noteworthy is the fact that the scale of the proposed demonstrations is no more than 200 t/day of CO_2 (excepting the Hammerfest project, which is considering increased pressures to optimistically handle full capture from the 100 MWe natural gas unit). This provides some insight into the maturity of the processes.

All the plants listed in the table are specifically for flue gas capture but not all are coal derived flue gases. The Lubbock, Trona, Sua Pan, Shady Point, Warrior Run, Chiba, and Esbjerg are the only coal-based power systems uncovered in this review.

4   PCC technology assessment

4.1   Activity assessment

This review provides some insight as to the direction of major industrial and research groups regarding the development of PCC systems. The number of active groups in each major process category is about the same (approximately 20). This may be interpreted as all categories getting approximately equal support and that there is no clear 'winner'. The range, specifically in terms of research activity, shows 26 independent groups actively working on membranes, to chemical absorption with 17 groups. The proportion of research activity for each technology is shown in Fig. 6. Table 6 lists the technologies in terms of their developmental stages, and the organizations which are supporting them.

Japanese industry provides the most corporate investment in prospective systems such as adsorption and novel absorption systems. As examples, Toshiba has been funding studies into lithium silica for solid absorption systems. Additionally, MHI already supplies amine scrubbers and clearly seeks a position as a supplier of new amines, such as the KS-1, specifically derived for PCC from power station flue gas. MHI is also investing in research of dual zeolite bed based PSA systems. Other systems, such as membranes, are primarily funded at the research level for PCC of power station flue gases, except for the membrane contactors due to the use of mature

Table 4   Summary of membranes for PCC

technology status	Embryonic technology apart from low temperature polymeric membranes.
scalability	Easy to scale up in modules. However, PCC may require a very large of membrane area depending on gas separation and fluxes.
technological gap	Membrane materials with high CO_2/N_2 separation at high temperature, while maintaining high fluxes are required.
selectivity and flux losses	Plasticisation of polymeric membranes and the reaction of membrane films with water and SO_x.
energy penalties for hybrid membrane contactors	An economic assessment by Sumitomo Electric Industries, Japan, [21,22] used a hollow fibre ultrafiltration membrane module with a mixed solution of diethanolamine and 2-(butylamino)ethanol. The energy requirement for such as system was estimated at 0.36 to 0.79 MJ/kg-CO_2.
membrane materials	Polymeric (polypropylene, polyphenyleneoxide, and polydmiethylsiloxane), ceramics, zeolites, carbon molecular sieves, molecular sieve silica, hybrids (polymer and zeolites)

Table 5 CO$_2$ capture plants around the world according to IEA [23], Grad [24], Bolland [25], and Herzog [26], as well as other sources if specified

technology	plant location	operator	scale	tech supplier	status	CO$_2$ use
solvent absorption (MEA)	lubbock, Texas, USA	carbon dioxide technology[b]	1200 t/day CO$_2$	Dow MEA	shut (1982–1984)	EOR
solvent absorption (mixed brines)	Trona, California, USA	IMC Global Inc[a]	800 t/day CO$_2$	Kerr-McGee/ABB Lummus	operating 1978–present	Soda ash production
solvent absorption (MEA)	Bridgeport, Texas, USA	Mitchell Energy[b]	493 t/day CO$_2$	Inhibited MEA	shut (1991–1999)	EOR
solvent absorption (MEA)	Bellingham, Massachusetts, USA	BOC[b]	350 t/day CO$_2$	Fluor	operating 1991–present	foods
solvent absorption (MEA)	Sua Pan, Botswana	Sua Pan[a]	300 t/day CO$_2$	Kerr-McGee/ABB Lummus	operating 1991–present	soda ash production
solvent absorption (MEA)	Shady Point, Oklahoma, USA	AES [a]	200 t/day CO$_2$	Kerr-McGee/ABB Lummus	operating 1991–present	foods
solvent absorption (MEA)	Warrior Run, USA	AES [a]	150 t/day CO$_2$	ABB Lummus	operating 2000–present	foods
solvent absorption (MEA)	Chiba, Japan	Sumitomo Chemicals [a]	165 t/day CO$_2$	Fluor and MHI	operating 1994	foods
solvent absorption (MEA)	Luzhou, China (fertiliser plant)	Luzhou Natural Gas Chemicals [c]	160 t/day CO$_2$	Fluor	operating 1998–present	urea production
solvent absorption (MEA)	Jagdishpur, India (fertiliser plant)	Indo Gulf Fertilizer Co. [c]	150 t/day CO$_2$	Fluor	operating 1988–present	ammonia production
solvent absorption (MEA and new solvents)	Petronas Fertilizer Co., Malaysia	Petronas Fertilizer Co.[c]	145 t/day CO$_2$	MHI	operating 1999–present	ammonia and urea production
solvent absorption (MEA)	Rio de Janeiro, Brazil	Prosint AGA [b]	90 t/day CO$_2$	Fluor	operating 1997–present	foods
solvent absorption (MEA)	Altona and Botany, Australia	Liquid Air	60 t/day CO$_2$ each	Fluor	operating 1985	
solvent absorption (MEA)	Loy Yang Power Station, Victoria Australia	CO2CRC, Loy Yang Power, CSIRO, International Power	12 t/day CO$_2$		operating March 2008	PCC demo
solvent absorption (MEA)	HuaNeng Beijing Cogeneration Powerplant, China	CSIRO, China Huaneng Group, Thermal Power Research Institute	8 t/day CO$_2$		operating June 2008	PCC demo
proposed projects						
adsorption (TSA and PSA)	Yokosuka, Japan	Tokyo Electric Power Company [a]	43 t/day CO$_2$		R&D Began 1997	capture demo
membrane contactor	Esbjerg, Denmark	CASTOR (major project, 30 partners) [a]	24 t/day CO$_2$		project began 2004-active	sequestration
solid sorbents	Hammerfest, Norway	Sargas, Hammerfest Energi, Siemens	100% capture of 100 MWe unit (~2000 t/day CO$_2$ [e])		project began 2005-active	sequestration
cold ammonia	TBA	EPRI [d]	50–100 MWe scale		project began (2006–2008)	sequestration
solvents then membranes and adsorption	Transportable	EPRI [d]	1 MWe scale		project starting 2006 (to 2010)	capture demo
aqueous ammonia	Lake Munmorah Power Station, NSW, Australia	Delta Electricity, CSIRO	11 t/day CO$_2$		pilot under commissioning. 270 t/day CO$_2$ scale by 2013	capture demo

a) Coal-fired power station demonstration (electricity also produced). b) Natural-gas-based flue gas. c) Sourced from flue gas of ammonia reformer. d) Sourced from EPRI under project 165 [27,28]. Flue gas type unspecified at this time. e) Calculated assuming 35% PS efficiency and HHV of NG 38 MJ·kg^{-1}
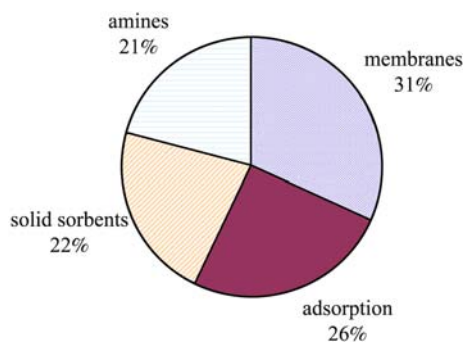
Fig. 6 Proportions of individual research activity given to each PCC option

membrane and amine technology. PCC research is receiving funding from governments in a variety of areas to encourage technological development.

As might be anticipated, demonstration projects are generally run by Industry; bench scale and semitechnical projects are funded through CASTOR, US DoE, and various governments; and laboratory scale work is most often conducted in research institutes, universities, and, to a lesser extent, corporate laboratories. R&D activities are concentrated in

● amine scrubbing process optimization;
● membrane contactors (optimisations and bench scale studies);
● solid sorbent materials;
● fixing amines in inorganic materials for adsorption;
● adsorption systems optimisation (PSA, VSA and TSA); and
● membrane materials for PCC.

The perceived technological risk and development profiles for implementation of the various technologies at industrial scale PCC are represented by the extent of

Table 6 Technology development and support showing activity band (A) for each

technology	A	interests
demonstration scale		
liquid amines	>9	CASTOR, industry (See Table 5) and CSIRO (proposed PCC demonstration)
blended amines	1–4	Canadian Government, Klimatek Programme
optimisation and cost studies		
liquid amines	>9	Sintef (Norway), USDoE (USA), TNO (Netherlands), Ontario Power Generation (Canada), Canadian Government, Spanish Government, European Commission, Korean Universities. CO_2 Capture Project, CO2CRC
solid CaO sorbents	1–4	European Commission and Canadian Government
adsorption	5–8	Mitsubishi Heavy Industries (Japan), Power Company (Japan), USDoE, CO2CRC (Australia), Korean Government
membrane systems	1–4	Norwegian Universities, CO2CRC (Australia), Canadian Government
membrane contactors	5–8	Singapore Government, TNO (Netherlands), CO2CRC (Australia), Japanese Government, Korean Government, China Government, CO_2 Capture Project (Kvaerner, Norway)
bench scale		
flue gas testing	1–4	Korean Government, Kansai Electric Power Company, Japan
aqueous ammonia	1–4	US DoE
aqueous piperazine/potassium carbonate	1–4	US DoE
solid sorbents *in situ*	1–4	Canadian Government
membrane contactor	1–4	CO_2 Capture Project (Norway), CASTOR (TNO-Netherlands)
laboratory scale		
ionic liquids	1–4	USDoE (NETL)
new solid sorbents	5–8	USDoE, US Universities, Japanese Government, Toshiba Japan, Korean Government, CO2CRC (Australia), Universities (UK)
solid CaO sorbent studies	5–8	European Commission, Ohio Government (USA), Canadian Universities. US DoE, Chuba Electric Power Company, Japan
electrical swing adsorption	1–4	CO2CRC (Australia)
combined membrane and PSA	1–4	Portuguese Government, Korean Universities
zeolite adsorption	1–4	Canadian Government
fixed amines (adsorption)	5–8	CO2CRC (Australia), Japanese Government, US DoE, Universities (UK and USA) and USA Space
PCC membrane materials	>9	CSIRO, Australian Universities, CO2CRC, Singapore Government, Universities (USA), Japanese Government, Korean Government, Canadian Government, US DoE, US Space

expenditure. Near term technologies, requiring demonstration, require the largest expenditures; the more prospective technologies require intermediate funding at small or semitechnical scales; and potential or promising methods require support at laboratory and research level.

Amine scrubbing has received the most attention by far, specifically for implementing it to PCC scales. Amine membrane contactors are seen as a promising technology to avoid some of the disadvantages with direct amine scrubbing. Despite the complexity of adsorption systems, attention is also being directed toward optimizing them for PCC. Generally, membranes and solid sorbent materials are seen as prospective but technologically unproven technologies, requiring additional development before any considered opinion may be made regarding their cost and risk profiles for large-scale industrial implementation.

4.2   Echnology 'Race' assessment

A simple methodology for comparison of competing technologies is to consider an implementation 'race'. For the purpose of this review, this describes the time expected to achieve full-scale operation of the process as applied to PCC from power station flue gases. Timing depends on an informed, but ultimately subjective, assessment which is informed by the technology maturity, research, and development activity and also funding support from industry and other sources. Our view of this assessment is shown in Fig. 7.
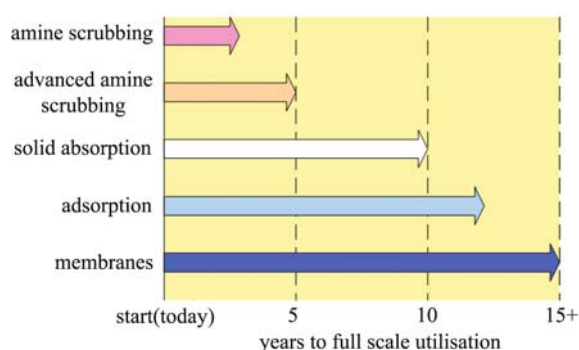

Fig. 7 Technology 'race' based on the technology review

Amine scrubbing systems are already developed in other applications and relatively easily adapted to PCC. Indeed, they are already being placed into demonstration systems for coal power plant flue gas. MHI is actively promoting its processes and sorbents specifically for PCC, and it may be predicted with reasonable assurance that more advanced systems, i.e., more energetically favourable processes, will become available within five years. With appropriate design, the benefits of advanced sorbents or process optimizations as advanced by Fluor could also be realized in plants using current best practice MEA absorbents.

Solid absorption is considered to be the next technology likely to be successfully applied, possibly within 10 years, based on significant research investment in this field funded by government and industry. The physical equipment requirements are well within current engineering capability.

Adsorption processes may feasibly be developed within 12 years. However, current adsorption systems are physically large, beyond current engineering capacity, and likely to be expensive. There is relatively little research being conducted on such systems with a view that it is not easily adapted to the very large scales necessary for power station applications.

Membranes systems are the most embryonic of all technologies and require significant research to improve performance and optimize process systems. Our assessment is that process development may take up to 15 years before membranes appear in PCC systems for power station flue gas. An exception may be combined membrane/absorption systems, if the theoretical energy advantages of these processes are demonstrated in practice. This could see significant investment and more rapid development of this technology. Considering this timeline, membranes may well be developed in parallel with power stations and become integrated into new designs as opposed to direct retrofitting.

The Electrical Power Research Institute (EPRI) reported the low likelihood of breakthroughs with more mature amine scrubbing technologies and placed them as a technology which should be implemented for 2013 with a view to change over to advanced technologies as they become available following demonstration around 2022. This is generally consistent with our assessment.

4.3   Echnology risk assessment

The progress of each option, showing maturity versus total investment, is displayed in Fig. 8. The maturity of each technology is categorized into 'Research', 'Development', 'Demonstration', 'Deployment', and 'Mature Technology'. At this stage, no technology has overcome the 'hump', and further interests are required to back their development toward deployment.

Technology development is driven by the promise of increased performance of a system, which reasonably balances benefits against costs. For early stage or novel technologies, there is a significant risk associated with the probability of a technology successfully maturing toward an operational state as a function of time. At early research stages, the activities are relatively inexpensive, but the risk is commensurately very high. The decision mechanisms and metrics being developed to value high risk R&D portfolios at different stages of development are the 'real options' analysis-based methods. However, there are no examples that we are aware of where this method has been used in the current context. The economic valuations of the
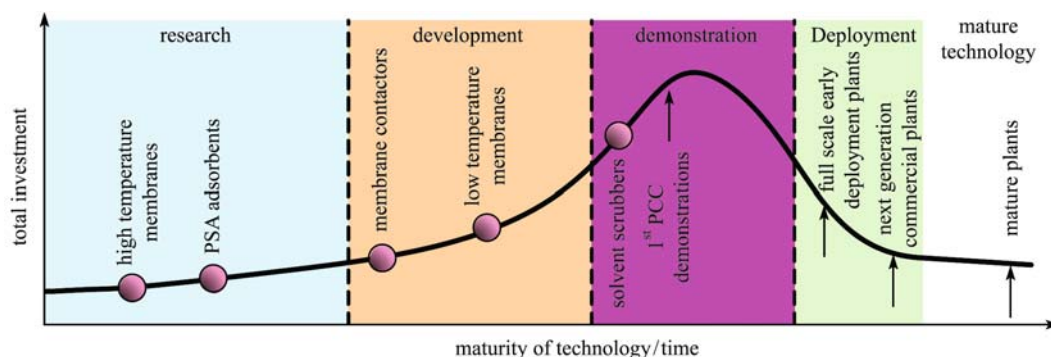
Fig. 8　Maturity versus total investment for PCC technologies

alternative technologies using this methodology would be informative and provide a quantitative insight concerning their relative merits.

As the evolution of PCC technologies progresses, the requirements for larger demonstrations call for large investment, where the cost and risk are often partly offset by partnering and sharing resources. The establishment of PCC consortia around the world, with significant funding from industrial interests and governments, seems to be developing strongly in carbon capture and storage.

5　Conclusions and recommendations

All of the processes described, though at very different stages of development, are being actively pursued and consequently deemed possible 'winners' by their supporters. However, in the short term, (five years) absorption systems (i.e., solvent scrubbing) seem likely to be deployed as industrial scale demonstration projects with a view to 'learning-by-doing' and providing opportunities for evolutionary process improvement. Process contractors like MHI and Fluor could provide systems off the shelf with guaranteed performance. In addition, the process could be designed with a sufficient degree of flexibility to take advantage of potential developments in amine technology. Plant integration issues seem relatively straightforward, although there may be opportunity for improved process designs and some innovation, e.g., managing cold plumes from the scrubber. The main hurdle to immediate deployment is cost. In this sense, the absorption process provides a logical benchmark against which alternatives can be evaluated. The variety and different maturities of the competing technologies make comparisons, assessments, and risk-reward analyses largely subjective. Useful insights could be gained through the development and application of econometric techniques such as 'real options' within this context.

References

1. Pine R. CO_2: Parliament launches action plan to reduce its carbon footprint. In: European Parliament Press release, 20090220IPR50134, 2009, 1

2. EC. European CO_2 capture and storage projects. In: European Commission EUR 21240, Brussels, Belgium, 2004, 3

3. Yokoyama T. Japanese R&D on large scale CO_2 capture. In: Separations Technology VI: New perspectives on very large-scale operations, ECI Symposium Series, 2004, RP3: 1–12

4. Simmonds M, Hurst P, Wilkinson M B, Watt C, Roberts C A. A study of very large scale post combustion CO_2 capture at a refining & petrochemical complex. In: Greenhouse gas control technologies. Kidlington UK: Elsevier Science, 2003, 2: 39–44

5. CO2CRC. Project 2.5 hydrate formation & cryogenic distillation systems. In: Capturing CO_2—research program overview, cooperative research centre for greenhouse gas technologies. Canberra, Australia, 2005, 5

6. White V. Purification of CO_2 from oxy-fuel combustion. In: Proceedings of the 2nd workshop of the oxy-fuel combustion network, international energy agency greenhouse R&D program and Alstom Power, 2007, 1–13

7. IEA. Solutions for the 21st century—zero emissions technologies for fossil fuels: technology status report. In: International energy agency, committee on energy research and technology, working party on fossil fuels, 2002, 12

8. Bailey D W, Feron P H M. Post-combustion decarbonisation processes. Oil and Gas Science and Technology, 2005, 60: 461–474

9. DTI. Review of the feasibility of carbon dioxide capture and storage in the UK. In: UK— Department of Trade and Industry, Report DTI/ Pub URN 03/1261, 2003, 1–33

10. Goff G S, Rochelle T. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Ind Eng Chem Res, 2004, 43: 6400–6408

11. IEA. ERM—Carbon dioxide capture and storage in the clean development mechanism. In: International energy agency greenhouse gas R&D programme 2007/TR2, Cheltenham UK, 2007, A10

12. Chapel D, Ernst J, Mariz C. Recovery of CO_2 from flue gases: commercial trends. In: Canadian Society of Chemical Engineers annual meeting, 1999, 1–16

13. Iijima M. Flue gas CO_2 capture (CO_2 capture technology of KS-1). In: Global Climate & Energy Project, Stanford USA, 2004, 1–28

14. Fauth D J, Frommell E A, Hoffman J S, Reasbeck R P, Pennline H W. Eutectic salt promoted lithium zirconate: Novel high temperature sorbent for CO_2 capture. Fuel Proc Tech, 2005, 86: 1503–1521

15. Abanades J C, Rubin E S, Anthony E J. Sorbent cost and performance in CO_2 capture systems. Ind Eng Chem Res, 2004, 43: 3462–3466

16. Ding Y, Alpay E. Equilibria and kinetics of CO_2 adsorption on hydrotalcite adsorbent. Chem Eng Sci, 2000, 55: 3461–3474

17. Chou C T, Chen C Y. Carbon dioxide recovery by vacuum swing adsorption. Separ Pur Tech, 2004, 39: 51–65

18. Cho S H, Park J H, Beum H T, Han S S, Kim J N. A 2-stage PSA process for the recovery of CO_2 from flue gas and its power consumption. Studies in Surface Science and Catalysis, 2004, 153: 405–410

19. Ho M T, Leamon G, Allinson G W, Wiley D E. Economics of CO_2 and mixed gas geosequestration of flue gas using gas separation membranes. Ind Eng Chem Res, 2005, 45: 2546–2552

20. Wang R, Li D F, Liang D T. Modeling of CO_2 capture by three typical amine solutions in hollow fiber membrane contactors. Chem Eng Proc, 2004, 43: 849–856

21. Matsumiya N, Teramoto M, Kitada S, Matsuyama H. Evaluation of energy consumption for separation of CO_2 in flue gas by hollow fiber facilitated transport membrane module with permeation of amine solution. Separ Pur Tech, 2005, 46: 26–32

22. Matsumiya N, Teramoto M, Kitada S, Haraya K, Matsuyama H. Cost evaluation of CO_2 separation from flue gas by membrane-gas absorption hybrid system using a hollow fiber membrane module. Kagaku Kogaku Ronbunshu, 2005, 31: 325–330

23. IEA. CO_2 Capture and storage—R&D projects database. In: International energy agency greenhouse gas R&D programme, Cheltenham UK, 2005

24. Grad P. Trials of carbon capture. Engineers Australia, 2009, 81: 45–47

25. Bolland O. CO_2 capture technologies—an overview. In: Proceedings of the second trondheim conference on CO_2 capture, transport and storage, 2004, 1–29

26. Herzog H. An introduction to CO_2 separation and capture technologies. In: MIT Energy Laboratory, 1999, 1–8

27. EPRI. 2006 Program 165 CO_2 capture and storage. Electric Power Research Institute, 1013048, 2005, 1–2.

28. EPRI. CO_2 Capture and Storage Test Centers: First transportable CO_2 capture pilot. Electric Power Research Institute, 2007, 1–9